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Glasgow

Peeling a Better Future: Development of
Microporous Activated Carbons Derived from
Citrus Waste for Carbon Dioxide Capture

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Aidan Docherty Harvey

01/04/2026

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Abstract

As worldwide reliance on fossil fuels refuses to subside, the importance of developing Carbon Capture and Storage (CCS) technologies grows. Within this field, there is a growing interest in reusable solid adsorbent materials that can be derived from sustainable sources. This study investigates the production of microporous nitrogen-doped biochars and hydrochars from surplus citrus peels, contributing to a circular economy through valorisation of waste streams, for use in carbon dioxide (CO₂) capture systems.

A robust Design of Experiments process was carried out for both biochar and hydrochar synthesis routes to identify influential process parameters, and statistical optimisation models were produced, after being informed by material characterisation results. These models aimed to optimise the porosity and elemental characteristics of the materials to enhance their applicability to carbon capture technologies. The samples with the highest response metrics, from both synthesis routes, were then tested for their CO₂ adsorption performance and regenerative ability, under conditions analogous to industrial flue gas.

Nitrogen doping, through inclusion of urea in the synthesis process, was found to successfully increase nitrogen content within carbonaceous chars, and activation of the chars using CO₂ was found to develop highly microporous materials. The highest performing sample in terms of CO₂ adsorption, BC Control Mandarin, exhibited CO₂ capacities of 0.61 mmol/g (0.1 bar) and 0.78 mmol/g (0.2 bar), at 60 °C. Meanwhile, the most effective nitrogen-doped char was found to be an optimised material, OPB Micropore Orange, with CO₂ capacities of 0.48 mmol/g (0.1 bar) and 0.70 mmol/g (0.2 bar), at 60 °C. Microporosity, particularly ultramicroporosity, of the materials was found to be key to adsorption at low pressure (< 1 bar), while overall pore volume determined adsorption capacity at higher pressure (5 – 19.5 bar). Meanwhile, increasing the nitrogen content of the samples was not seen to

increase CO₂ adsorption in any meaningful way, contrasting with literature findings. All samples tested for their cyclic adsorption characteristics showed minimal loss in capacity, indicating high levels of regenerative ability.

This study has provided a detailed and extensive comparison between two synthesis routes for carbonaceous char sorbents, using two similar but distinct biological waste peel feedstocks of orange and mandarin, which both descend from the *Rutaceae* family. Through elemental and textural characterisation, it aims to provide an overview and assessment of the advantages and disadvantages of both char synthesis methods, and reaffirms the ability of CO₂ to be used as an activating agent to promote micropore formation. By considering the properties and adsorption performance of the carbonaceous char materials, it has been established that *Rutaceae* peel-derived chars are sustainable and viable solid adsorbents for post-combustion carbon capture applications. The Design of Experiment work in this study also provides a base level to progress from for further process optimisation of chars produced from such feedstocks.

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List of Abbreviations

ANOVA	Analysis of Variance	IUPAC	International Union of Pure and Applied Chemistry
AT	Activation Temperature	k_1	Double Exponential Fast Rate Constant
ATR	Attenuated Total Reflectance	k_2	Double Exponential Slow Rate Constant
BC	Biochar	K_2CO_3	Potassium Carbonate
BET	Brunauer–Emmett–Teller	$K_2C_2O_4$	Potassium Oxalate
BJH	Barrett-Joyner-Halenda	K_2O	Potassium Oxide
CCC	Circumscribed	KOH	Potassium Hydroxide
CCS	Carbon Capture and Storage	MOF	Metal Organic Framework
CCUS	Carbon Capture, Utilisation and Storage	N_2	Nitrogen
CHNS	Carbon, Hydrogen, Nitrogen, Sulphur (Analysis)	NaOH	Sodium Hydroxide
CO	Carbon Monoxide	NH_3	Ammonia
CO_2	Carbon Dioxide	OBC	Optimised Biochar
DoE	Design of Experiments	OHC	Optimised Hydrochar
DR	Dubinin-Radushkevich	OPB	Optimal Biochar
DSL	Dual-Site Langmuir	OPH	Optimal Hydrochar
FTIR	Fourier Transform Infrared (Spectroscopy)	P/P_0	Relative Pressure
Ge ATR	Germanium Attenuated Total Reflectance	PIV	Pressure Isolation Valve
GHG	Greenhouse Gas	PTFE	Polytetrafluoroethylene
H_2	Hydrogen	SEM	Scanning Electron Microscopy
H_3PO_4	Phosphoric Acid	SSA	Specific Surface Area
HC	Hydrochar	t	Time
HMF	5-hydroxymethylfurfural	T	Temperature
HT	HTC Temperature	TGA	Thermogravimetric Analysis

HTC	Hydrothermal Carbonisation Temperature	VSA	Vacuum Swing Adsorption
IGA	Intelligent Gravimetric Analysis	XPS	X-ray Photoelectron Spectroscopy
IR	Infrared	ZnCl ₂	Zinc Chloride

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1 Introduction

1.1 Carbon Dioxide Emissions and Net Zero Goals

In an everchanging world, one of the largest threats to our modern society as a whole is posed by the prospect of irreversible global warming as a result of global carbon dioxide (CO₂) emissions. CO₂ is the most commonly released greenhouse gas (GHG) from anthropogenic activities on Earth, with global emissions reaching a new all-time high of 37.4 gigatonnes in 2023 [1], a year after the average CO₂ atmospheric concentration reached the all-time high of 417 ppm [2].

The process of global warming is simply the effect of the Earth's average temperature increasing due to the greenhouse effect. This greenhouse effect is a phenomenon that occurs in the Earth's atmosphere, and is caused by GHGs, such as CO₂, methane, nitrous oxide and other fluorinated gases [3]. These gases accumulate within the lower atmosphere layer and both absorb and emit thermal infrared radiation [4]. They allow the passage of solar radiation from the sun, which provides heat to the planet, but they also absorb heat that is emitted in the opposite direction from the Earth. This is the primary issue, as small changes to the relative concentrations of GHGs can have large effects on the radiation absorbed by them, leading to an increase in global temperature due to the accumulation of heat.

This global warming effect is likely to accelerate the journey to worldwide tipping points; a point of no return, where unavoidable natural disaster events will be triggered which will take, at a minimum, multiple generations to recover from. Examples of this are thought to be scenarios where loss of the West Antarctic ice sheet causes significant rises in sea level, causing cities to be submerged, or Arctic permafrost thaw which will release vast levels of GHGs into the atmosphere and destroy ecosystems [5], [6]. Similarly, the risk of more

frequent extreme weather events such as wildfires, flooding, storms and hurricanes is strongly linked with increasing global warming [7], [8].

The landmark Paris Agreement signed at the UN Climate Change Conference (COP21) in Paris, 2015, was designed with a view to prevent the rise in global temperature to a maximum of 2 °C above pre-industrial levels, and more pertinently, to limit this rise in temperature to 1.5 °C above pre-industrial levels [9]. It was agreed upon by 195 parties (governments), and in order to meet the 1.5 °C goal it was required that GHG emissions must have peaked by 2025. However, current emission predictions envisage this peak occurring at the end of the 2020 decade [10]. As of 2019, global emissions were required to decrease by 43 % by 2030, and become net zero by 2050 to achieve a maximum rise of 1.5 °C [11]. Based on current legislation and actions this seems more and more unachievable.

Scotland as a nation has set a closer target of 2045 to achieve Net Zero [12]. Barriers to the success of this strategy do nonetheless remain, as there are doubts over the ability of current energy providing infrastructure to cope with future demands, and sustained retrofitting of homes will be required to provide scope for use of heat pumps and hydrogen energy sources [13], [14]. In terms of fuel, concentrated focus is required on the petroleum and gaseous fuel sector as CO₂ emissions are still sizeable in this sector. For gaseous fuels in particular, the CO₂ emissions from this source was found to have risen from 1990 to 2019 [15]. Over the same period, petroleum CO₂ emissions decreased slightly, but further effort is required to deliver the reductions required.

CO₂ is one of the main contributors to global warming. Production as a result of fossil fuel use is a significant source of emissions [16], and whilst this will decrease with the transition to greener energy sources, remediation methods must be employed to bridge the gap between current energy production methods and the idealised future where renewable

sources become the primary source. Carbon capture, utilisation and storage (CCUS) technologies present an opportunity to realise this solution. These can be applied to industrial plants where there are large scale CO₂ emissions, to attempt to prevent CO₂ from entering the atmosphere. After capture of the gas, it can either be utilised in onward process applications, or transported to, and stored in, underwater geological formations such as depleted oil wells [17].

1.2 Methods of Carbon Capture from Industrial Emission Sources

There are currently three main methods for carbon capture that are utilised in industry, all at different scales. These are: post-combustion capture, pre-combustion capture and oxy-fuel combustion.

1.2.1 Post-Combustion CO₂ Capture

Carbon Capture and Storage (CCS) carried out through post-combustion methods involves the utilisation of technologies to remove CO₂ from output streams of industrial processes. This generally consists of CO₂ being removed from exhaust flue gases, preventing its release to the environment after the combustion of fossil fuels. This is the most widely adopted method of carbon capture in use currently, due to being the easiest to retrofit to existing plant installations. It has been demonstrated to perform well when applied in industrial settings, and can be applied universally with no restriction on the fuel type used [18]. Nonetheless, it has high energy requirements, and the solvents used in current post-combustion plants degrade over time, resulting in reduced efficiency of the process.

Typically, industrial plants with CO₂ emissions carry out post-combustion capture through absorption processes which deploy amine solutions to remove CO₂ from flue gas streams. A simplified diagram of this is shown in Figure 1.1. At standard conditions of 1 atm and 40 °C,

liquid absorbents provide adequate capacities for CO₂ removal; diethanolamine displays a CO₂ capacity of 0.95 mmol/g, while monoethanolamine can absorb 4.09 mmol/g [19].

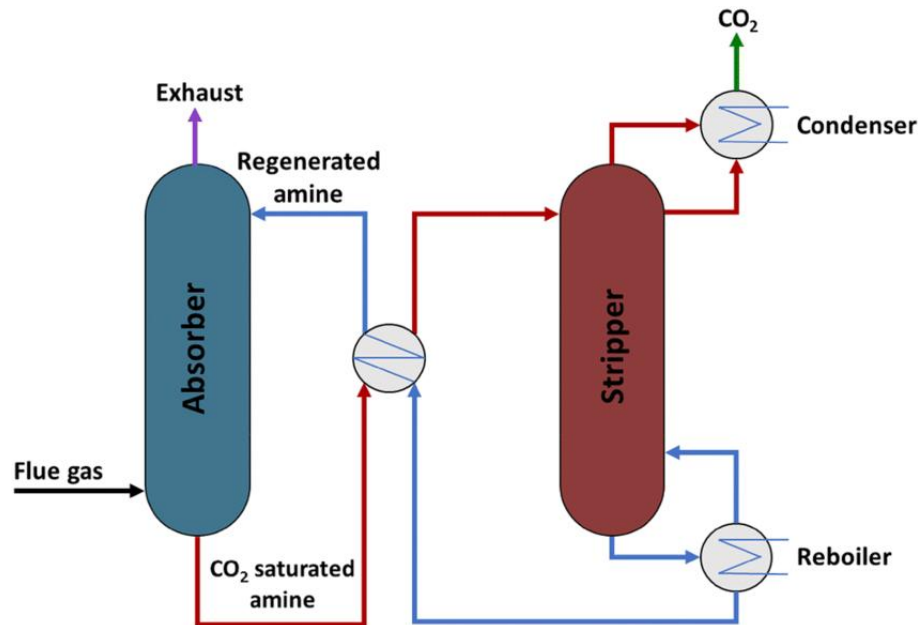


Figure 1.1: Example of CO₂ Absorption in Industrial Setting Using Amine Solution Configuration [20]

Although they provide effective CO₂ removal, high temperatures of approximately 125 °C are required to regenerate the amine solution and release the CO₂ in order for it to be compressed and stored [21]. Due to the presence of impurities in the mixture at the point of regeneration, amine degradation commonly occurs which both reduces performance and increases the risk of equipment corrosion and fouling. Due to this, there is a desire to find new types of sorbents for CO₂ capture that could be implemented in post-combustion systems.

1.2.2 Pre-Combustion CO₂ Capture

This method is used to remove CO₂ before combustion of the relevant fuel has been conducted. A two-step method of steam reforming and water-gas shift reactions are used to convert fossil fuel into a mixture of CO₂ and hydrogen (H₂), which can then be separated; CO₂

can then be utilised in other processes or transported and stored appropriately, and H_2 can be used as a clean fuel [17].

Steam reforming is the process of reacting the fuel, usually a hydrocarbon, with air or oxygen and water (H_2O) to produce carbon monoxide (CO) and H_2 , a mixture commonly referred to as syngas. Note that for solid fuels such as coal this initial stage is usually gasification, while steam reforming is applied to liquid and gaseous forms of fuel such as natural gas. This resulting syngas can then be subjected to a water-gas shift reaction, where CO reacts with H_2O to produce H_2 and CO_2 . While this process can provide high CO_2 capture efficiency, it too requires significantly high energy input which can impact on the efficiencies of the plants it is fitted to, and H_2 production within the process brings additional storage, handling and safety challenges [18].

1.2.3 Oxy-Fuel Combustion

Oxy-fuel combustion is the process of burning the chosen fuel in an oxygen-rich atmosphere, which ensures that the resultant flue gas is a mixture of primarily CO_2 and H_2O , making the final separation process more efficient and streamlined. Instead of air, a mixture of 95 mol% pure oxygen (O_2) and 5 mol% recycled flue gas provides the atmosphere within the reactor for combustion [22].

This method requires an air separation unit to remove nitrogen (N_2) and any other trace gases from the incoming air, which typically necessitates cryogenic level temperatures as the individual gases are separated based on their boiling points. The purified O_2 can then be used for combustion of the chosen fuel. The resulting flue gas would be expected to contain mainly CO_2 and H_2O , allowing CO_2 capture to occur by condensing the H_2O from the stream [22]. The use of highly pure O_2 also results in lower NO_x emissions from the final flue gas.

The main drawback from this form of carbon capture technology is the energy demands resulting from the need for both an air separation unit (pre-combustion) and a CO₂ capture unit (post combustion), which can result in lower net efficiency for the technology when implemented on large scales [22]. There are examples of oxy-fuel plants on industrial scale, but they are limited in their power output compared to typical combustion plants.

1.2.4 Rising Potential of Solid Adsorbents for CO₂ Capture

In an effort to address the high energy consumption requirements incurred by using liquid absorbents in post-combustion CO₂ capture technologies, research has shifted focus to the potential of solid adsorbent materials. In contrast to conventional absorption technology, solid adsorbents present high CO₂ adsorption capacities, incur smaller energy demands for regeneration, and can be produced from renewable feedstocks [23]. Despite the promise shown there are still challenges to overcome, as selectivity towards CO₂ can be limited and the presence of impurities in flue gas streams can impact on performance of certain materials [19]. In addition, although advanced chemistry can be used to synthesise adsorbents specifically tailored to CO₂ removal (or indeed any pollutant or contaminant), the financial cost of production is a hinderance to the scalability of the materials. The kinetics of CO₂ adsorption on these materials and their long-term stability are often key to their suitability for use in carbon capture technology; faster kinetics allow for a more efficient process, while their stability indicates the reliability of the system and also determines the operating costs.

There are four main classifications of solid adsorbents that are actively being researched for industrial carbon capture applications: mesoporous silicas, zeolites, metal organic frameworks (MOFs), and carbonaceous materials. Note that this is not an exhaustive list, and many different variants of solid sorbent materials exist and are detailed further in literature.

Mesoporous silicas can provide high surface areas and material stability, but due to hydrophobic surface chemistry and neutral surface charge, their capacity for CO₂ is low [24]. Similarly, synthetic zeolites possess high surface area and fast CO₂ adsorption kinetics but their preference for adsorbing H₂O over CO₂ is problematic when considering applications where flue gas streams contain water vapour [25]. Additionally, they have low CO₂ selectivity over N₂ which is an issue for post-combustion scenarios [23]. In comparison, naturally occurring zeolites are widely available but do not display high CO₂ capacities. MOFs present possibly the largest CO₂ adsorption capacities and exhibit the highest levels of specificity of the four types of materials due to the fact they can be uniquely tailored towards target molecules [26]. Nonetheless, they can suffer stability issues when exposed to water vapour, particularly at high temperatures, and the associated expensive production methods limits their potential to be produced on the scale that is required for CO₂ remediation [27].

The development of carbonaceous materials for CO₂ adsorption is able to reconcile some of the drawbacks that are presented by other adsorbent materials. Within this classification of materials there are adsorbents such as graphene, carbon nanotubes and nanofibers, and activated carbons; this final category is where biochars and hydrochars fall into. The production of activated carbons can be carried out at low cost and at large scale due to the abundance of feedstock materials, as many of these materials are produced from waste biomass [19]. Additionally, the synthesis and activation processes can be tailored to develop high levels of porosity, and increased surface functionalisation can be carried out easily through doping with nitrogen- or oxygen-containing chemicals [28]. High CO₂ adsorption capacities have been reported in literature for both atmospheric conditions and high-pressure applications [29], [30], displaying the versatility of these materials. While their adsorption capacities may still be lower than those presented by MOF materials, the potential to scale activated carbon production is much greater, providing a solution to one

of the main challenges faced by MOFs. High selectivity for CO₂ over N₂ and enhanced cycling ability has also been reported for various carbon adsorbents [31]. The potential regeneration of activated carbons through temperature or pressure swing adsorption presents further flexibility in process integration.

The production of activated carbon typically involves taking a low-cost and readily available form of biomass and converting it through chemical and/or physical methods into the adsorbent material. In literature many different precursor materials have been used to produce biochars and hydrochars: sawdust and wood clipping, food waste such as olive stones or nut shells, brewery waste, and sewage sludge [32], [33], [34], [35], [36]. These are just a small selection of the numerous feedstocks that can be utilised in the synthesis of char adsorbents. An important consideration when choosing a precursor to use in this manner is both the availability but also the consistency of the material. This is why activated carbons are typically produced from wood or waste materials from a process stream, as they can be found to have generally homogenous consistencies and chemical formulations batch-to-batch. As a result, the uniformity of the produced carbons can be guaranteed to a certain extent; although with organic resources there will always be a certain degree of variation.

An interesting waste stream is that of citrus peels and pulp, especially orange peels. Oranges are an abundant citrus fruit worldwide with approximately 69 million tonnes produced annually [37], and are essential in different food and drink production process, such as fruit juice [38]. In this particular processing route, after the production of orange or associated juice there is a vast quantity of leftover waste, with 50 – 60 wt% of the original fruit being converted into orange peel waste [39]. Mandarins, of the same *Rutaceae* family as oranges, are also generated on a large scale globally with 48.6 million tonnes produced annually; when processed for juice production, the waste peels accounts for ~30 wt% of the original

mandarin [40]. Orange peel waste can be treated to remove valuable products such as essential oils, limonene and flavonoids [41], although most traditional disposal methods involved either landfilling or composting the material, which are not always environmentally friendly routes [42]. In order to avoid these routes, and provide a path for up-cycling the waste into a higher value product, there is scope to research the performance of orange and mandarin peel wastes as precursor materials for biochar and hydrochar production, for further use as CO₂ adsorbent materials.

1.3 Circular Economy and Sustainable Engineering

1.3.1 Circular Economy

Circular economy is a term used to describe a system which deviates from traditional linear systems of 'take-make-waste'; in a circular economy, waste materials are recycled and valorised to ensure that maximum value is extracted and minimal unusable waste is created. Figure 1.2 provides a visualisation of an ideal circular economy. Through consistent recycling and repurposing of resources, the lifecycle of many products can be elongated, and therefore the requirement for raw material input is lowered, reducing the dependence on non-replenishable materials. This can in turn remove volatility in supply chains and decrease the material consumption of individuals worldwide. Although an entire self-sustaining circular economy is unlikely to be achieved, it is important to strive through engineering to deliver a vision and future that is as close to it as possible, as this will inevitably aid in the journey to Net Zero.

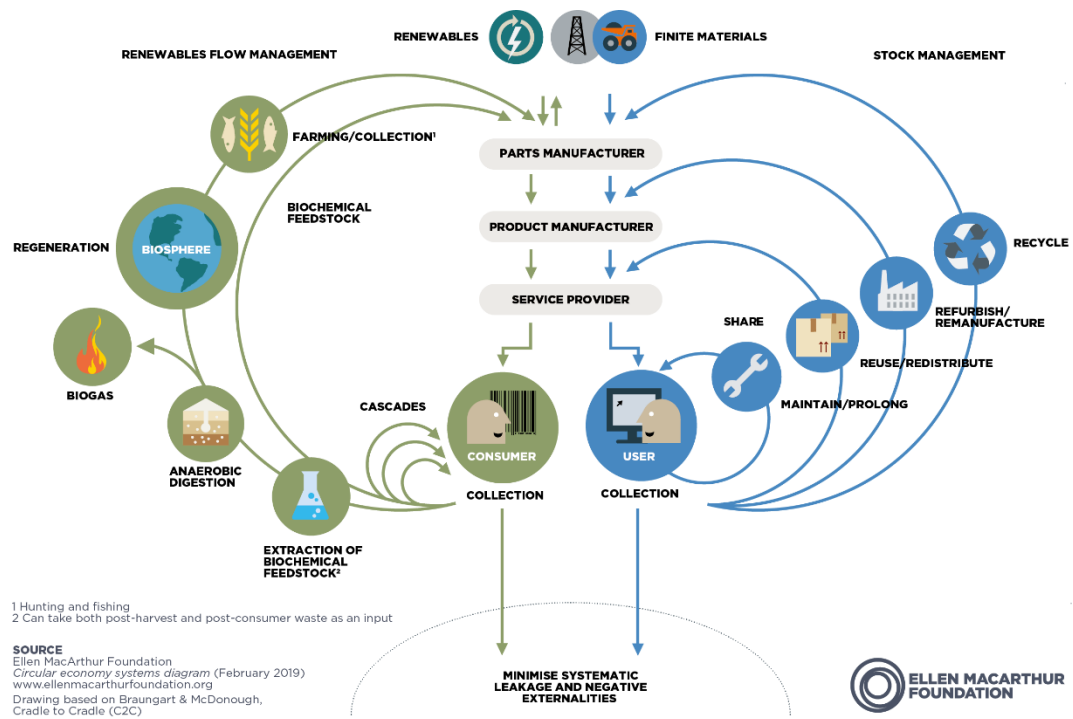


Figure 1.2: Visualisation of Circular Economy Principles [43]

Within this study, the main principle of circular economy that will be displayed is the process of valorising waste streams into materials which can be utilised for CO₂ remediation purposes. Waste biomass, such as food waste, agricultural residue and wood chippings can be converted through pyrolysis or hydrothermal carbonisation (HTC) processes into added-value products such as bioenergy fuel, or in the case that this thesis will examine, solid adsorbent materials [44], [45]. These materials can be utilised in adsorption applications, and tailored via their production methods to target specific pollutants. When used in this manner, the circular economy principles are met through both reducing material waste and removing the release of harmful contaminants and pollutants into the wider environment.

It must be noted that it is unlikely this idealised circular economy will be achieved, and thus, the materials produced in this study will have a defined lifetime as solid adsorbents; beyond this point, they will not be suitable for carbon capture applications. In order to maximise their use in this particular application, they can be regenerated through both temperature and

pressure methods; chars can be heated to approximately 100 °C to remove physisorbed CO₂, while exposing the materials to a vacuum will also lead to the removal of physisorbed CO₂. This follows Le Chatelier's principle; the process of physisorption is exothermic, meaning an increase in temperature will favour the desorption process, while increasing pressure creates a driving force for adsorption to occur. Thus, a decrease in pressure will consequently favour the desorption process.

This process would allow the chars to be reused, however, over time, other undesired contaminants will build up, leading to fouling of the material. Once the chars can no longer be regenerated, other applications must be considered. Chars have been found to be useful in soil remediation applications, with high surface area and the potential for chemical functionalisation being important factors in this sector [46]. In some environments they can improve water retention, leading to more available water for plants [47], and provide mechanisms for heavy metals removal in contaminated regions [48]. Incorporation into soil can also slow the degradation of biochar, which ensures that the carbon within the produced chars is sequestered and not released back into the atmosphere [49]. It would be vital to carry out a full chemical characterisation of the chars post-carbon capture application, if they were to be used in this field, to ensure they are both suitable and non-harmful to the chosen environment.

Alternatively, the char materials could be burned as a renewable energy source. Due to their character of being carbon-rich and produced from waste biomass, they are classified as a renewable energy source [50], which makes them a more attractive source than conventional fossil fuels. Characterisation of the materials, such as Higher Heating Value (HHV) experiments would be required to determine the applicability of the chars for this application. When combusted, the CO₂ released from these chars is considered to be

reabsorbed by plants as a feedstock, thus allowing these materials to be defined as carbon neutral fuels [50].

In both soil remediation and renewable energy applications, there is evidence that the solid char materials produced in this study would sit within a circular economy model. Without carrying out a full Life Cycle Assessment (LCA), it is difficult to provide a quantitative response to their level of environmental benefits, but the qualitative evidence shows they would be applicable in this scenario in some sense.

1.3.2 Green Chemistry

Green chemistry is a form of experimentation and engineering that aims to maximise sustainability and economic feasibility in the design of materials and processes. There are twelve key principles this field strives to implement, which can be utilised at different research and design stages [51]. This study aims to integrate the following principles from these practices:

- 3. Less hazardous chemical synthesis.
- 5. Safer solvents and auxiliaries.
- 6. Design for energy efficiency.
- 7. Use of renewable feedstocks.
- 10. Design for degradation.

Principles 3 and 5 were chosen in an attempt to reduce the chemical hazards that arise both directly and indirectly during the synthesis of adsorbent materials. During the production of char materials, doping agents such as tetraethylenepentamine, polyethylenimine and melamine are often used as nitrogen dopants [52], which are chemicals that present both handling hazards and environmental toxicity risks if released to the environment. Similarly, potassium hydroxide and sulphuric acid are examples of activating agents used to enhance

char characteristics through surface chemistry modification despite their own handling and environmental risks. To realise the design of 'greener' adsorbent materials, care should be taken to avoid use of environmentally harmful chemicals, and if chemicals are required, then those which pose the lowest harm should be utilised.

When settling on a synthesis process, Principles 3 and 6 are vital and the process conditions should be chosen in accordance. For char production, the temperature and length of time of the process will contribute largely towards the overall energy consumption, while also influencing the quality of final product. Care should be taken to minimise the energy usage and associated input materials, while also attempting to reduce the formation of waste by-products, chemical or otherwise. In addition, extra processing steps that incorporate unnecessary chemicals should be avoided, such as acid-washing of produced materials.

Using food waste as a feedstock for the char production process brings compliance with Principle 7, as the chosen feedstock for this research work -originates from agricultural waste products, thus can be categorically defined as a renewable feedstock.

Finally, Principle 10 is key, as to meet circular economy ethos it is important that the produced materials can be fed back into the environment without any pollution effects or additional treatments. Char, while not biodegradable, can be utilised for other purposes after its use as an adsorbent is exhausted: it can be spread on fields to increase soil quality and release nutrients, or burned as a renewable energy source.

1.4 Thesis Outline and Structure

The introduction to this thesis, Chapter 1, has attempted to set the scene for this research project, and hinted at what is to follow. The overall aim is to produce solid adsorbent materials for use in carbon capture adsorption technology, using waste citrus peels as a feedstock. Chapter 2 provides a detailed description of the materials that will be produced,

biochars and hydrochars, their synthesis routes and the characteristics that are shaped by these processes. Examples of related materials from literature are presented, alongside their experimental results in relation to CO₂ adsorption. The identified literature gap that this project intends to fill is then discussed, and the detailed aims set out.

The fundamental knowledge and scientific principles that will be employed throughout the thesis are discussed in Chapter 3. Chapter 4 details the methodologies followed, describing the process of experimental design, synthesis routes and characterisation methods employed.

The results of the thesis are then split across three chapters. Chapter 5 provides the characterisation of all biochars produced in the study, and addresses the optimisation of these materials. The next chapter, Chapter 6, is a mirror chapter which presents the same information, but in this case, for the hydrochars produced in the study. The third results chapter, Chapter 7, moves the focus to the CO₂ adsorption ability of the best performing chars produced throughout the study. This compiles CO₂ adsorption capacities measured under both laboratory conditions and under conditions analogous to industrial flue gases, along with thermodynamic data and cyclability testing.

Finally, Chapter 8 lays out the conclusions from the research project and proposes future work that could be carried out for either these materials, or comparable carbonaceous chars.

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2 Literature Review

2.1 Introduction

This chapter consists of a review of the available literature surrounding carbon-based adsorbents, namely biochar and hydrochar materials, and their applicability to carbon capture scenarios. The fundamental properties and production methods of both char types are discussed, along with the impact that different process parameters can have on their characteristics, behaviour and performance as adsorbents. The activation and doping methods available to enhance their properties are then assessed, before examples of their use in CO₂ adsorption situations are presented in a comprehensive manner; this is in tandem with an assessment of the current research into chars produced from the chosen feedstock of citrus peels. Finally, key research gaps are highlighted, aims for the project are stated and the novelty of the project contextualised within the framework of the scientific field.

2.2 Carbonaceous Materials

2.2.1 Biochar

Biochar is a carbon-rich material that is derived from waste biomass through the process of pyrolysis. This process is used to remove volatile materials from the biomass and carbonise it, giving a solid form that can then be used and tested in a range of applications, including as an adsorbent. Typically, biochar production involves a two-step procedure of carbonisation and activation – where the properties of the material are enhanced by physical or chemical means; however, some production processes combine these steps into a single operation.

In the case of a two-step process, the initial stage is termed pyrolysis. During this part of the process carbonisation of the biomass can take place at temperatures ranging from 300 °C to

600 °C, under an inert, oxygen-free atmosphere to facilitate the removal of non-carbon components of the biomass [1]. After this, the product will be a form of biochar that will be carbon-rich, but which may not have the desired level of porosity or chemical characteristics to make it effective for use in adsorption applications [2]. Therefore, it is common practice for biochar to be activated by using either chemical or physical methods to further tailor the characteristics of the biochar to enhance its adsorption potential for targeted species. This second stage is usually carried out at temperatures of 600 – 900 °C [3]. Conversely, it is possible to produce activated biochar through a single-step process [4]; the biomass precursor is typically impregnated with selected chemicals before being pyrolysed to produce an activated carbon, at temperatures ranging from 500 – 900 °C [5], [6], [7]. This can increase variability in the final product, but in terms of energy efficiency, it may be a preferable process [8]. Note that this single-step process is also commonly referred to as pyrolysis, therefore it is important to differentiate whether biochar production is carried out in a single- or two-step process.

Biomass is primarily composed of three main polymers: cellulose, hemicellulose and lignin [9]. During the pyrolysis process, the heat encourages the breakdown of these lignocellulosic structural components of the biomass, which in turn helps to create a porous structure and the removal of volatile non-carbonaceous components. Hemicellulose is the first component to degrade, occurring around 250 – 350 °C [1], with cellulose beginning to break down once the temperature reaches 325 °C. There are various reports on the degradation temperature of lignin, and different temperature ranges are reported for its decomposition; it is the most complex of the three components, and degradation initiates around 300 °C, however, some reports suggest onset at temperatures as low as 170 °C. Nonetheless, it may then require temperatures of up to 900 °C to fully remove all lignin from the material [10], [11], [12].

For all three structural components, a variety of reactions take place during pyrolysis. Initially, depolymerisation and dehydration take place before molecular rearrangement occurs within the material as intermediates are produced. This then allows further polymerisation and aromatisation to occur, giving rise to the graphitic biochar structure that is commonly found [13]. The pyrolysis process can also be split into three stages from a carbonisation perspective; firstly, in the range of 250 – 450 °C, aromatic rings begin to form, after any residual water is evaporated and volatiles begin to be removed. Beyond this, between 450 – 750 °C, polycondensation occurs, which leads to further aromatisation and a two-dimensional structure begins to form, as oxygen-containing functional groups are removed. Above 750 °C, structured layers begin to form and porosity within the material develops [14].

Prior to any heat treatment, carbons can be classified as graphitic or non-graphitic, based on their naturally occurring structure [15]. Graphitic carbons exhibit an ordered three-dimensional structure, while non-graphitic carbons only possess ordering in a maximum of two-dimensions, consisting of planar sheets. The non-graphitic carbon can further be categorised into graphitisable or non-graphitisable carbon based on its ability to form graphitic carbon upon heating to 3000 °C and beyond, as defined by Franklin [16], [17]. Graphitisable carbons are typically found to be soft and dense materials, in stark comparison to low density, harder non-graphitisable carbons, see Figure 2.1. Notably, non-graphitisable carbons are found to contain pores in the microporous range, as small as nanometres; it is this classification into which biochars, and hydrochars, fall. A graphitisable carbon will pass through a liquid phase upon heating, before forming an ordered three-dimensional structure [18], as described above, while this will not be achievable for non-graphitisable carbons under the same conditions.

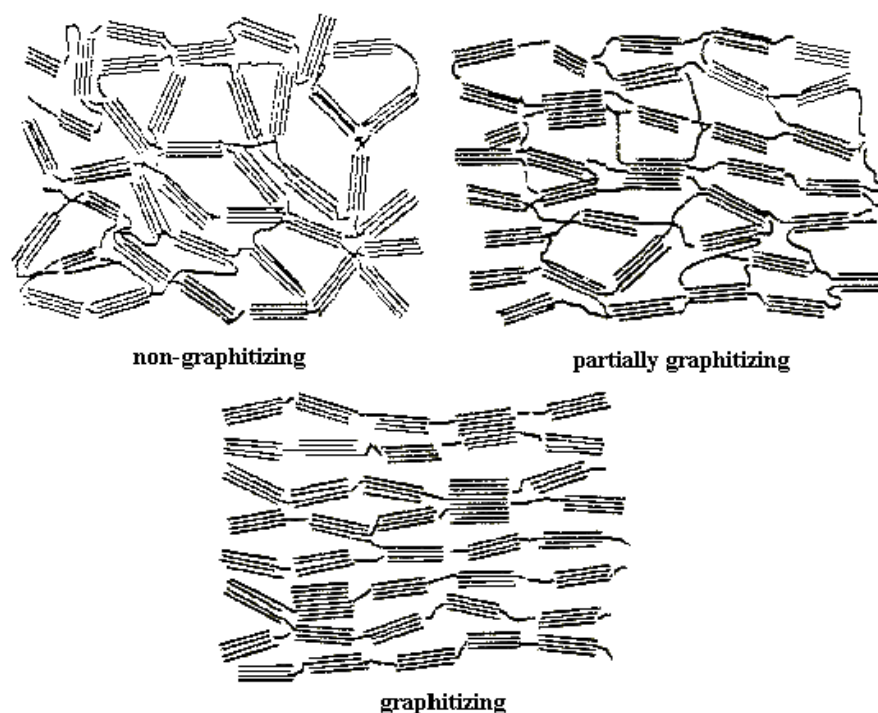


Figure 2.1: Franklin's Models of Carbon Structures [19]

Examining these non-graphitisable carbons in more depth, they are seen to be isotropic in nature, see Figure 2.2. Thus, chars are seen to consist of unique, random internal carbon layers that never form a fully ordered three-dimensional structure. The process of carbonisation and/or pyrolysis is crucial in increasing the (two-dimensional) order of these carbon materials, even if they are not graphitisable materials [20]. As these carbons do not pass through a liquid stage when undergoing heat treatment, they do not achieve a graphitic crystalline structure, and instead possess a porous network of varying sizes, but primarily in the microporous region [21]. The small layer regions seen in both Figure 2.1 and Figure 2.2 can be termed 'crystallites', which are joined to each other by cross-links; these crystallites struggle to join together due to the nature of the cross links, meaning a full graphitic crystalline structure cannot be achieved in these non-graphitisable carbons, instead resulting in small collections of turbostratic layer-structures [19]. However, it is due to this that the

aforementioned pores, and, therefore, internal surface area, are produced in chars, and thus, provides the characteristics in these materials that make them favourable for adsorption processes. Within the isotropic lamellae structures exist heteroatoms, atom vacancies, and defects [22], and it is these points, along with the edge of the carbon layers, with which gasifying agents can interact, in order to further increase the porosity, and, subsequently, the surface area of the materials. For example, gasification can be carried out using CO_2 , where carbon and CO_2 react via the Boudouard reaction, to produce carbon monoxide, and create enhanced microporosity within carbon materials [23].

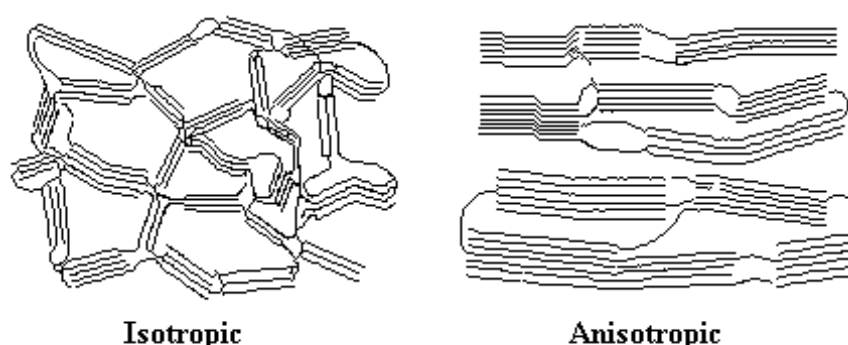


Figure 2.2: Isotropic and Anisotropic Carbon Lamellae Structure [15]

It should be noted that the definitions of biochar and hydrochar can be conflated within surrounding literature. In the main, it is very common for articles to refer to any solid material produced through either pyrolysis, torrefaction, hydrothermal carbonisation (HTC) or gasification, as biochar [24]. In contrast, other authors will use the term hydrochar exclusively to describe the product of the HTC process [25]. This work will differentiate between the two materials, titling those materials produced through pyrolysis as biochar, and those produced through HTC as hydrochar.

2.2.2 Hydrochar

Hydrochar is the name given to the solid product recovered after HTC of a wet biomass mixture; two other products are commonly formed in this process, namely bio-oil (biofuel/effluent) and biogas [26]. The hydrochar material produced is found to be carbon-rich, and has the potential to be used in different processes such as adsorption of pollutants, soil remediation and amendment, or directly as a renewable energy source [27]. HTC has recently been viewed as an attractive alternative to pyrolysis, torrefaction or gasification of biomass, as it can be carried out using wet feedstock [28]. It is particularly interesting for the valorisation of food waste materials, as it can be utilised in a much shorter time scale than anaerobic digestion technology [29].

The process is carried out in a wet environment, with water commonly used as the reaction medium, where the biomass is heated in a sealed vessel to temperatures generally ranging from 180 – 250 °C, and beyond [30]. Similarly, residence times within the vessel can range from a few minutes up to 24 – 48 h [28]. Chemical doping can also be implemented by including the desired chemical in the reaction mixture before HTC takes place [31], [32]. The hydrochar product present after HTC is commonly found to have low levels of porosity; a significant issue if the intended application of the material is within adsorption processes, such as carbon capture. Consequently, further activation of the hydrochar is undertaken to increase its usability, quite analogous to the process of biochar production. These processes follow similar methods too; either chemical or physical activation can be carried out.

During HTC, a variety of reactions occur within the vessel between the biomass feedstock and the process solution, typically water. These reactions are crucial for the breakdown of the structural components of biomass such as lignin, hemicellulose, and cellulose. As the process is carried out in a sealed vessel, the water solution exists within its subcritical region;

this is where water remains in its liquid state at temperatures above 100 °C. This is possible because the pressure within the vessel exceeds the saturation pressure of water at the elevated temperatures, thereby maintaining it in a liquid phase. When water is present in subcritical form, its fundamental properties change; for example, its dielectric constant decreases, which in turn reduces its polarity, allowing non-polar components from the biomass to dissolve more freely [29]. Concurrently, the hydrogen bonding within the water molecules weakens, which leads to more H^+ ions being present in the mixture, further assisting any acid-catalysed reactions that occur.

Overall, there is a wide range of reactions occurring in the HTC process, with many different pathways available to components. Generally, polymer hydrolysis is the first step, with carbohydrates and the lignocellulosic materials being broken down into monosaccharides, monomers and oligomers [26]. Acids are also generated early in the process, assisting further in hydrolysis, as well as the next stage of dehydration and latterly decarboxylation reactions [33]. From this stage, a selection of reactions, such as condensation, polymerisation, and aromatization, can occur, all leading to the formation of the final desired product of hydrochar, and by-products of bio-oil and gas [34]. A simplified diagram illustrating this process is shown in Figure 2.3.

Looking at the structural components, it is notable that hemicellulose and cellulose begin to degrade at temperatures commonly seen in HTC, around 180 °C and 230 °C, respectively, while lignin does not decompose until temperatures above 260 °C [35]. This mirrors observations from biochar production, in that lignin is more resistant to degradation attempts. Therefore, although it will break down to some extent, lignin may still be present within the final carbonised material, as it is not as common to see temperatures of above 250 °C used in HTC processes, due to safety considerations [36].

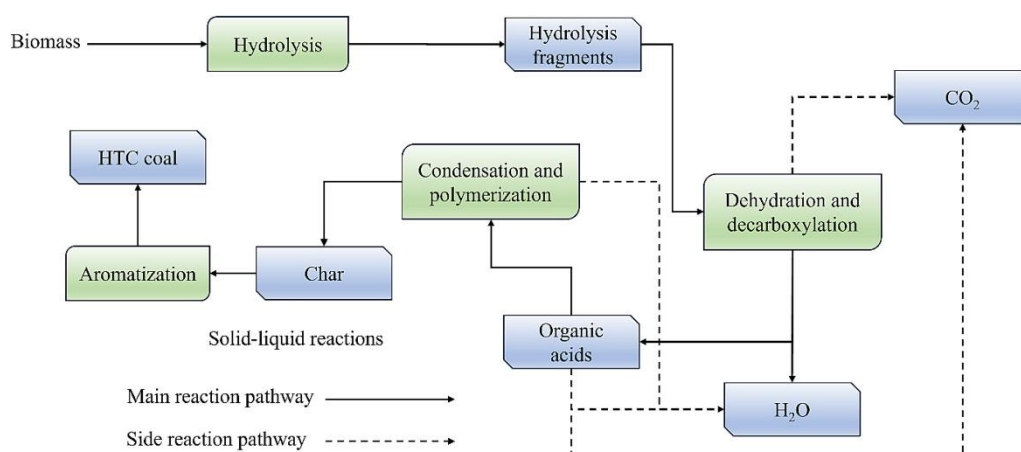


Figure 2.3: Simplified Breakdown of Reactions Occurring During HTC of Biomass [35]

2.2.3 Pyrolysis and Associated Nomenclature

Pyrolysis has been discussed in Section 2.2.1, but it is important to contextualise the use of this term within this study and in the wider literature. Pyrolysis is defined as the chemical reaction processes that occurs when biomass material is heated in an oxygen-free atmosphere [37]. Under the umbrella of this term lies the method of carbonisation, which is the process of creating carbon-rich materials through heating organic precursors in the absence of oxygen to remove volatile components. This is typically carried out under an inert atmosphere of N_2 or argon gas. This is the common method of biochar production. Hydrochars are produced through HTC, as described in Section 2.2.2, which is also classified as carbonisation.

After the chars are produced through either route, they are typically subjected to an activation process. Activation can be carried out in either a chemical manner or a physical manner. Chemical activation involves the addition of chemical activation agents, such as bases (potassium hydroxide, sodium hydroxide) or acids (hydrochloric acid, nitric acid), to the char before further thermal treatment is undertaken [38]; the addition of the chemicals to the process facilitates reactions with the char, and can lead to increases in porosity in the

material, introducing surface functionalities that can aid adsorption. Alternatively, physical activation can be carried out, which involves heating the char to temperatures of 700 °C and beyond in the presence of CO₂, steam or air; this promotes pore development due to the oxidative environment provided [39].

Focusing on physical activation using CO₂, this process can be specifically termed char gasification, as it takes place via the Boudouard reaction, Equation 2.1. This reaction involves the CO₂ gas reacting with the carbon in the char material to produce carbon monoxide, and in turn creating porosity within the char material, as the carbon is etched away during the process. In the literature, there are numerous examples of the process being termed gasification [40], [41], [42] or physical activation [43], [44], [45], and both are deemed to be appropriate; gasification is the process of heating biomass in order to produce gaseous fuel [46] (in this case carbon monoxide), while physical activation is defined as the process of heating char material in the presence CO₂ or steam to increase the porosity of the material [47].



In the context of this work, the biochar materials created, using the methods outlined in the experimental section, are produced through a single-step process, which consists of heating the biomass under a N₂ atmosphere, before it is exposed to CO₂ gas in order to attempt to increase its porous characteristics. This is a one-step synthesis route, and can be described in different terms, such as a combined carbonisation-gasification process [48], or alternatively a one-step physical activation process [49], [50], [51], [52]. Both terms are used within the literature in the field, and, thus, are used interchangeably throughout this thesis, but the process they are describing is consistently the same with regards to the experiments

carried out here. Nitrogen doping is also carried out, through soaking the precursor material in urea prior to heat treatment, which matches with the 'one-step' aspect of the process.

The hydrochar material created, however, is produced through a two-step process of carbonisation (through HTC) followed by gasification (or activation) using CO₂ to promote the formation of micropores. Again, the above caveats around gasification and activation apply to the terminology for description of this process through the thesis.

2.2.4 Important Properties and Characteristics of Carbonaceous Materials

2.2.4.1 *Surface Area*

When considering potential materials for their capability in adsorption applications, surface area is a key characteristic to prioritise. This is because target molecules will, ideally, adsorb to sites on the surface of the adsorbent material through physicochemical bonding; thus, theoretically, a higher surface area material offers a higher adsorption capacity than a material with a lower surface area [53]. By generating a high surface area, this means samples have more active sites for adsorption and therefore, increase the likelihood of adsorption occurring.

CO₂ adsorption on char-based materials occurs mainly through physisorption mechanisms, and furthermore, higher surface areas correlate with increased CO₂ adsorption [54], [55], [56], meaning creating a material with a large surface area is key to the success of this study. Surface area can further be classified in terms of its type: either microporous or mesoporous surface area. As CO₂ molecules are small with a kinetic diameter of 0.33 nm, which falls within the microporous range (see Section 2.2.4.2), it is preferable to create this type of surface area to maximise adsorption potential [57].

2.2.4.2 Porosity

Porosity can be seen as a more general way of expressing surface area, pore volumes, sizes and the general networked structure within porous materials. When either of pyrolysis or HTC are carried out, the degradation of lignocellulosic material occurs through reaction pathways, creating void spaces within the structure of the char. These reactions also release gases, such as CO, CO₂ and volatile matter, creating pathways throughout the material as the gases 'push' their way through the biomass to be released [58]. This creates a porous network, which can be utilised for transportation and adsorption of pollutant molecules.

Pore volume is analogous to surface area in that an increased pore volume should hypothetically lead to increased adsorption capacity for a given char material. And, as pore filling is another important mechanism in adsorption processes for porous materials, it is often crucial to create large pore volumes in adsorbent materials [59]. However, each individual adsorption scenario requires consideration of the balance of each type of pore volume, such as micropores or mesopores. The focus of this project is the production of materials for use in CO₂ adsorption applications; to achieve effective CO₂ adsorption at low pressures, micropore volume is the important factor to maximise, whereas for high pressure CO₂ adsorption, mesopores and their associated volume are more important [60].

The size of pores within chars can be of vital importance when targeting a specific contaminant molecule. It has been reported that to maximise adsorption, materials with pores of between 1-2 times the size of the target molecule should be used [57]. Based on the kinetic diameter of CO₂ (0.33 nm), pores of around 0.4 – 0.6 nm should be the optimal aim for this study, which is the ultramicropore size region. Again however, at higher pressures (approx. 10 – 20 bar) larger micropores and mesopores become more dominant for CO₂ capture [61].

Finally, the overall pore structure can be key to enhancing adsorption processes. A well-balanced network of macro-, meso- and micropores is useful, as it can provide navigable pathways for molecules to travel through. It has been demonstrated that mesoporous activated chars exhibit lower intraparticle diffusion resistance in their carbon frameworks than microporous samples [26]; thus, CO₂ molecules are able to move more easily through pores.

A trade-off between microporosity and pore volume can sometimes occur, dependent on the conditions of use for the char – higher pressure applications are favoured by materials with greater pore volumes, while lower pressure applications benefit from the use of microporous materials.

2.2.4.3 Functional Groups

As the adsorption of CO₂ occurs in physicochemical terms, the surface functionalities of the chars play an essential role in adsorbing the gas. Both nitrogen- (N) and oxygen- (O) containing functional groups are important for adsorption, owing to the active sites they provide. This is due to the unpaired electrons offered by both groups, which can cause Lewis acid-base interactions with other polar species, such as CO₂ [39]. Oxygen groups such as carbonyls and hydroxyls can also encourage interactions with CO₂ molecules through hydrogen bonding [62].

Typically, these functional groups can be incorporated into chars in different ways. The choice of feedstock can impact the functional groups that remain after pyrolysis and HTC processes, as, despite carbonisation taking place, some groups will remain on the surface of the char. For example, using biomass with an initial high level of nitrogen can lead to the production of nitrogen-rich chars [63]. Nonetheless, including a doping agent in either the preliminary carbonisation (pyrolysis or HTC) or activation stage is more common to increase

the level of surface functionalities and influence surface chemistry. The use of different activating chemicals or gases can lead to the creation of favourable sites for chemisorption of target molecules.

Typically, nitrogen doping chemicals such as urea, melamine and variations of ammonium salts are included in char production steps to increase nitrogen content [64]; meanwhile, air can be used to incorporate more oxygen-containing functional groups on char [65]. Doping of phosphorous and metals is also seen in literature [66]. It is known that different types of configurations of nitrogen bonds are formed with the carbon structure during nitrogen doping processes, such as pyrrolic nitrogen (pyrrolic-N), pyridinic nitrogen (pyridinic-N) and graphitic nitrogen (graphitic-N) [67]. These nitrogen moieties have a basic nature, which allows them to attract CO₂ into the chars' micropores and diffuse to appropriate adsorption sites. High pyrrolic-N content has been observed to enhance adsorption by creating Lewis base sites for CO₂ to bond with and promoting hydrogen bonding between CO₂ and surface functional groups [68]. In the same research, oxygen-containing functional groups were found to contribute to the high adsorption of CO₂, due to their hydrophilic nature.

2.2.5 Biochar Process Parameters

2.2.5.1 *Pyrolysis Temperature*

Pyrolysis temperature is often regarded as the most influential parameter during a pyrolysis process. It is key not only for carbonisation of the material, but for the development of porous structures and the makeup of surface functional groups, which are both essential for the facilitation of adsorption [69].

Increased temperature reduces overall yield of biochar, as it encourages more volatile components to be removed from the biomass material, and also results in higher ash content of the final product [70]. Therefore, while resulting in lower yields, the degree of

carbonisation of the material is increased, meaning the biochar produced at these elevated temperatures shows high levels of elemental carbon [71]. Unsurprisingly, this higher temperature does therefore impact the number of functional groups present on the samples; the increase in carbonisation causes more oxygen-, hydrogen- and nitrogen-containing functionalities to be removed, as the aromaticity of the sample increases [72]. The number of oxygen-containing functional groups has been seen to decrease when pyrolysis temperature increases beyond 500 °C [73], with similar results seen in literature for nitrogen-containing functional groups when pyrolysis temperature increased from 400 °C to 700 °C [71].

In terms of surface area, higher temperatures generally have a positive influence on porosity development within the biochar. Below 400 °C, devolatilisation of compounds within the char does not proceed to completion, meaning pores are not widely generated. At between 400 – 500 °C, this process begins to create a porous structure in the material, as more volatiles are released, creating fractures and voids in the carbon structure, which initiates pore development [74]. Increasing the temperature beyond 500 – 600 °C can then lead to two scenarios: either, a further increase in surface area due to increased pore development, or a reduction in surface area. This inflexion point can be seen at different temperatures for different materials; pine nut biochars were shown to have their highest surface area at 600 °C [75], for rice husk biochars this occurred at 700 °C [76], and the optimum temperature for bagasse-based biochar was found to be 900 °C [77]. The reductions in surface area after a certain temperature could be attributed to pore blocking due to increased ash content, or the amalgamation of smaller pores into larger ones, thus reducing the overall surface area. On the other hand, in the case of bagasse, increasing temperature may continue to enhance the release of volatile material from the precursor material, in turn, giving a well-developed pore network including micro-, meso- and macropores. This proves that there is no

‘optimum’ temperature for general biomass pyrolysis with regards to creating a superior surface area. Instead, different temperatures must be tested for each given material to establish the most favourable conditions. It should be noted from the above, and also the table compiled from available literature, seen in Section 2.3.5, that acceptable pyrolysis temperatures can vary from 300 – 900 °C.

Note, however, that activation methods, either chemical or physical, can be considered as an alternative to overcome low biochar surface area and counteract the effect of blocked and/or under developed pores [78]. This will be discussed in Section 2.3.

2.2.5.2 Pyrolysis Residence Time

Residence time is an important factor to balance in the production of biochar; it is essential that biomass is pyrolysed for a long enough period to ensure that carbonisation occurs, but if the period becomes too long then detrimental effects can be witnessed.

With respect to biochar yield, the effect of residence time is complicated and often hard to define. In one study, using straw as biomass, residence time has been shown to have little to no effect on any properties of the resulting biochar, over a range of 1 – 4 h [79], while another study using sewage sludge and cotton stalks showed a decrease in yield as residence time increased from 0.5 h to 1.5 h, but no further decrease from 1.5 h to 2.5 h [80]. A slight negative trend of residence time with yield was also seen with rapeseed biochar, but the differences in yield are sufficiently small that the results may fall within the same error region, thus raising the question of whether the trend is significant [81].

It could be argued that increased residence time gives more time and opportunity for volatile materials to be driven off from the biochar, thus giving a carbon-rich biochar product [82]. As a result however, reduced levels of oxygen- and hydrogen-containing functionalities can

also occur, as the extended time the biomass experiences harsh conditions may cause the loss of many other functional groups, while increasing the degree of carbonisation [83].

Regarding surface area, residence time has been seen to exhibit an inflection point, due to longer times resulting in increased detrimental degradation. [84]. However, in another study, residence time was shown to positively influence surface area, as the longer periods gave more time for porosity to develop [85].

Coupled with higher temperatures, long residence times can be detrimental to the overall biochar product, as exposure to higher temperatures for long periods of time will result in break-down of the carbon framework of the material.

2.2.5.3 Heating Rate

There are four main types of pyrolysis: slow, fast, intermediate, and flash pyrolysis. Slow pyrolysis is the typical route used to produce biochar, as it operates around the magnitude of 1 – 10 °C/min, and thus is favourable for the production of solid products from biomass [53]. In contrast, fast pyrolysis implements heating rates of over 100 °C/min and very short residence times to enhance the production of bio-oil rather than biochar [59], with flash pyrolysis operating at even higher heating rates, 500 – 1000 °C/min. Meanwhile intermediate uses heating rates similar to fast pyrolysis but longer residence times, from seconds up to approximately 10 minutes. A study looking at poplar wood produced at heating rates of between 10 – 50 °C/min, found that higher heating rates reduced biochar yield at temperatures of 400 °C, but this effect became minimal at higher temperatures of 600 °C [86]. High heating rates, around 30 – 50 °C/min, have also been seen to cause a decrease in yield when tested using safflower seeds, and this also correlated with increasing temperature [87]. Production of rapeseed stem biochar at different heating rates in the range of 1 – 20 °C/min showed the optimum rate in this study was 5 °C/min, but also noted from their

literature search that heating rate was not statistically significant for the parameter of biochar yield [81]. Another study using rapeseed feedstock assessed a large range of heating rates (5 – 50 °C/min), and found that increasing the rate of heating led to an increase in the burn off rate of the material.

In terms of pore development, a study investigating rice straw derived biochar showed that lower heating rates are more conducive to pore development [88]. This concurs with literature examining moso bamboo derived biochar; chars produced at 10 °C/min in the study displayed superior textural properties compared to chars produced at 20 °C/min [89]. This observation was ascribed to the kinetic limitations that may have occurred when using the higher heating rate, as there was not sufficient time for gradual volatile removal to take place, and thus pore development was limited.

A previous study carried out in the research group examined pyrolysis heating rate, and found it to be non-statistically significant at low heating rates (5 – 20 °C/min) [90]. This study will focus on slow pyrolysis, as it is the route which is most appropriate for biochar production.

2.2.5.4 Inert Gas Flowrate

During the pyrolysis process, a flowing gas is passed through the furnace and over the biomass sample to provide an inert environment, which prevents combustion of the sample. The most commonly used gas is N₂, due to its widespread availability [91], but there are instances of argon also being used [92].

Biochars produced from date pips under different levels of N₂ showed that the amount of gas flowed over the samples can impact on the final porosity; a range of flows from 50 – 400 mL/min were tested, with 150 mL/min being found as the optimum level to use to maximise biochar yield [93]. This effect is due to the fact increased gas flowrate leads to

increased removal efficiency of volatile components. However, increasing the rate beyond a certain value results in cooling of the biochar, which negatively impacts the volatile removal process and inhibits pore development. Studies with oil-palm-shells report a similar occurrence of an inflection point when testing flowrates of 50 – 300 mL/min N₂ [94].

In the case of a study of peanut shells, increased gas flowrate was also found to slow down secondary reactions during pyrolysis, further reducing volatile removal, which impacted on both porosity and carbon content of the biochar product, and gave rise to lower yields at higher flowrates [95]. Noticeably, increasing flowrate, from 20 mL/min to 200 mL/min of N₂, gave a consistent increase in surface area for each sample; it should be noted that these surface areas were very similar, so may be within error ranges.

2.2.6 Hydrochar Process Parameters

2.2.6.1 *HTC Temperature*

Temperature of the HTC process is generally seen as the most important factor in the process, due to the fact that it provides the energy to initiate a range of reactions in the mixture, and also provides the conditions for the maintained subcritical water phenomena [96]. As a result, it follows that the higher the temperature used, the lower the yield of hydrochar recovered; at elevated temperatures, there is more driving force for reactions to occur, which break down the initial biomass [33]. Once the temperature exceeds 200 °C, hydrothermal liquefaction becomes more prominent, which also acts to increase the bio-oil yield at the expense of solid product [97]. Decrease in yield with increasing temperature has been observed experimentally, for example, with hydrochars produced from grape pomace [34]. In the same study, it was reported that elemental carbon content increased with increasing temperature. This matches with other literature, in that higher temperature correlates with higher levels of carbonisation [98], as more of the volatile materials are removed.

In terms of surface area, it can be said that increasing temperature results in higher values, but for unactivated hydrochars this can be misleading; in general, hydrochars are low to non-porous materials, meaning HTC alone is not enough to create a material suitable for carbon capture applications. Nevertheless, increases in surface area were observed when temperature was increased from 200 °C to 250 °C, in a study examining maize straw hydrochar formation [99]. Further increases, beyond 250 °C, were then seen to cause a decrease in surface area; it is expected that HTC below this temperature allows for degradation of hemicellulose and cellulose, creating gases in the process which can penetrate and create a porous network, but beyond 250 °C this network then collapses, causing the observed reduction in surface area and general porosity.

The process parameters used in HTC have, in the main, comparable effects on the final hydrochar yield as they do for biochar. When assessing HTC reaction temperatures, lower temperatures result in higher yields of solid hydrochar produced but at the expense of a lower conversion of biomass material to carbon. This creates a product with more oxygen- and hydrogen-containing functional groups than for a conventional 'char'. Thus, higher temperature HTC process can be seen as an effective carbonisation route for waste materials, but may need to be supplemented by a subsequent activation stage to create a product with high fixed carbon content that is suitable for use in gas adsorption processes.

2.2.6.2 HTC Residence Time

HTC residence time produces similar results to its associated parameter in biochar production, in so much as biomass must undergo HTC for a long enough period to give sufficient removal of volatile components and produce a carbon rich product. That said, a vast range of residence times are reported in literature, from 0 h experiments to anything up to several days. Silver fir sawdust hydrochar was produced using times of 0 – 2 h, loblolly pine

was treated for 0.5 h, and tree leaves were subject to HTC for 5 h [100], [101], [102]. At the other end of the scale, sugarcane bagasse was tested at HTC times of 12, 24, 36 and 48 h [103]. A range of examples with a variation of residence times can be seen in the literature table, Section 2.3.5.

Conflicting information is, however, found with regards to the effect of HTC residence time within the literature. A surface response methodology used to produce hydrochars from food waste reported a clear link between increased residence time (from 2 h to 6 h) and a decrease in product yield [104]. This study also found that temperature had the same effect on yield. In other papers, it has been stated that residence time does not have the same effect on yield as temperature, as increasing the time for HTC of fir wood was seen to cause no significant change to the final yield [105]. A similar result in terms of no change in yield was noted in the HTC of soybean hulls, where times of 0.5 – 6 h were tested [106]; nonetheless, a minimal increase in elemental carbon content was registered. It also reported a decrease in porosity and associated surface area with increased experiment time. The same trend for surface area was found in bamboo hydrochars, and is ascribed to the reaction pathways that HTC follows [107]. It is thought that once the hydrolysis of biomass constituents has occurred and started to develop porosity, carbonisation commences and can cause a breakdown of this pore network. Conversely, another surface response study examining residence time of 2 – 8 h for hydrochar production using microalgae showed a consistent increase in surface area with thermal residence time; therefore, it is possible that both factors are intrinsically linked [108]. The statistical analysis results from this last study suggests temperature is the dominant factor, but that residence time remains important, although with less impact on carbonisation.

Most evidence points towards increased HTC residence time resulting in an increase in carbon content of hydrochar, as seen by the above papers and again in the case of HTC of municipal waste materials; a change in the quantity of oxygen-containing functional groups is not observed here though [109]. Therefore, it can be said that, generally, longer HTC residence times should result in a carbon rich product, but the degree of porosity achieved may vary depending on the chosen feedstock.

2.2.6.3 HTC Heating Rate

It may be expected that heating rate remains an important factor in HTC, similar to the role it plays in pyrolysis of biochars. Yet, despite frequent references to this in the literature [110], [111], it is an under-investigated parameter of the process. Naturally it would be thought to have an effect on the carbonisation aspect, as it directly influences the time of the process and the heat transfer that can take place. One study showed that increased heating rate of a hydrothermal process involving corn stover led to a decrease in hydrochar yield and increase in bio-oil yield [112]. Although not examined in terms of the hydrochar porous properties, heating rate of HTC processes was found to have minimal to no effect on the adsorbent potential of pineapple waste based hydrochars when tested in a fixed-bed column [113]. Beyond these studies, most literature and research use a set heating rate usually in the range of 5 – 10 °C/min for HTC [102], [114], [115].

The main issue with using a high heating rate is that this can result in a limitation to both mass and heat transfer within the mixture, and also reduce the time available for secondary reactions to take place during HTC [116]. The combination of these issues would be expected to result in incomplete carbonisation of the biomass, and subsequently a poorly developed pore network, both of which are detrimental to adsorption.

2.3 Activation and Doping Methods

It is commonly found, after the preliminary processes of pyrolysis and HTC, that the chars produced in each case are of high carbon content, but do not always possess a well-developed porous structure, high surface areas, or multiple surface functionalities. Therefore, methods of improving these characteristics are usually implemented to make the materials more suitable for adsorption of target components [117]. Chemical and/or physical activation can be carried out, which normally enhances the textural properties, while doping of desired chemical components can be carried out separately or alongside this to increase the content of different elements.

2.3.1 Chemical Nitrogen Doping

Chemical doping can be carried out to increase the number of functional groups or atoms of a desired element onto the surface of chars to help target certain contaminants for adsorption [66]. Typically, in applications targeting CO₂, it is nitrogen- and oxygen-containing surface functionalities that are most desired to assist with adsorption, as discussed in Section 2.2.4.3. Thus, nitrogen doping onto char samples can be an effective way of increasing CO₂ adsorption capacity. It can be carried out via various methods: doping of biomass precursor prior to any processing, doping during initial pyrolysis/HTC process, or during the activation process after initial char production [118]. An alternative route is to use biomass rich in elemental nitrogen to produce nitrogen-doped chars without any additional agents [119].

While nitrogen can be generally introduced via doping, the specific forms of nitrogen present after pyrolysis and/or activation are dependent on the temperatures utilised in these processes. The three typical forms of nitrogen functionalities found in chars (doped and non-doped) are: pyrrolic (N-5), pyridinic (N-6) and quaternary (N-Q) [120], and these can be seen in Figure 2.4. An additional form, called pyridone nitrogen, is also classified under N-5. Upon

heating the biomass or char material to 600 °C, N-5 is seen to remain stable while N-6 slowly begins to undergo condensation reactions to initiate the formation of N-Q [120], [121]. Upon increasing the temperature to 800 °C, N-5 content is typically seen to decrease, as it is converted to N-6 [122]. Finally, as temperatures increase to 1000 °C, N-5 forms of nitrogen disappear from the material, leaving N-6 and N-Q, along with some forms of oxidised nitrogen (N-X).

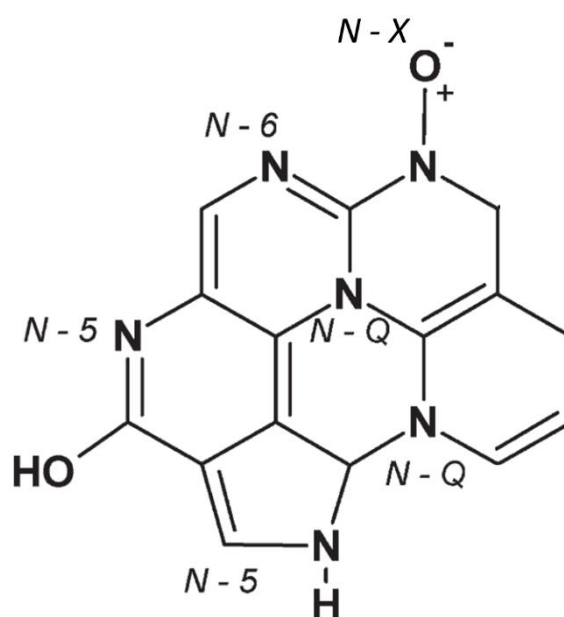


Figure 2.4: Nitrogen-Containing Surface Functional Bonding Groups [123]

N-5 represents nitrogen that exists in five-membered aromatic rings, while N-6 exists in six-membered rings, and N-Q can be seen as a modified version of six-membered rings. These N-5 and N-6 forms are thus seen to be present on the edge of the carbon layers within the char material, while N-Q exists as the most stable form of nitrogen within the graphene-like layers that have formed during pyrolysis [124]. As the temperature increases in the range of 800 – 1000 °C, the five-membered rings break open, leading to ring expansion, resulting in an increase in six-membered rings, such as N-6 and N-Q [120]. Additionally, N-Q formation

occurs as the nitrogen atoms in either N-5 or N-6 rings position themselves within the aforementioned layers, replacing carbon atoms. This, in turn, affects the potential for nitrogen functionalities to interact during adsorption, as the N-5 and N-6 forms are more accessible to CO₂ molecules as they move through the char structure, while the N-Q form, which is embedded within the carbon layer structure, cannot be accessed as easily.

While nitrogen doping is reported to increase CO₂ adsorption capacity, it may not always be an effective step in the synthesis process, as, if the doping is carried out post-carbonisation then, it can result in pore blocking, which reduces the accessible surface area available for adsorbate molecules [125]. Furthermore, the use of nitrogen doping agents post-carbonisation may also cause the degradation of pores during the activation stage; melamine was seen to destroy the pore structure of soybean derived biochars when used as an activator, leading to a reduction in overall surface area [126]. In another case, urea doping, combined with KOH activation, was shown to cause a decrease in the porous properties of biochar due to reactions between KOH and nitrogen-containing functional groups, leading to the breakdown of pore walls, once again reducing the surface area [127]. Alternatively, when incorporated in the initial carbonisation stage, the nitrogen doping agents can take part in reactions during pyrolysis, such as dehydration, condensation and polymerisation reactions, which help to integrate nitrogen-containing functionalities into the developed carbon framework [128]; note that this may still cause pore blocking in the resultant product.

In the literature, melamine and urea are frequently seen as useful nitrogen sources for in-situ doping of the biomass or char, whereas flowing ammonia (NH₃) over produced char samples can prove to be effective at nitrogen doping during activation processes. Black locust tree derived biochar has previously been activated with potassium hydroxide (KOH) and then NH₃ to produce highly porous materials [129]. The use of NH₃ was observed to result in

significant increase in surface area of the sample, and an increase in elemental nitrogen content; the combination of these two factors was later seen to enhance CO₂ adsorption capacities.

It has been observed that melamine-doped orange peel hydrochars, activated with potassium oxalate (K₂C₂O₄), were found to have superior surface and pore characteristics, and enhanced CO₂ adsorption uptakes, compared to non-melamine doped samples [130]. During the activation process, K₂C₂O₄ was seen to decompose to potassium carbonate (K₂CO₃), which subsequently reacted with the nitrogen-containing moieties on the sample surface and the melamine to produce NH₃. This led to an increase in porosity of the samples, likely due to NH₃ permeating into the carbon network of the char, as the nitrogen content decreased and gave more favourable features for CO₂ adsorption. Thus, despite nitrogen content decreasing after activation, the overall process had still incorporated nitrogen on to the surface of the chars, while also assisting in increasing porosity.

Another study using hydrochar produced from potato starch, cellulose and sawdust saw chars further activated using KOH and melamine as a doping agent; the results showed highly microporous and micromesoporous carbons were produced, with increased nitrogen-containing functionalities [60]. The inclusion of melamine was thought to both incorporate nitrogen atoms within the structure and enlarge pore sizes, due to the gases released during its decomposition, as seen above. Impressive results were found for CO₂ adsorption with these materials (2.8 mmol/g at 25 °C) but the samples without melamine doping demonstrated marginally better performances than those including it; this indicates that, while functional groups can play a part in CO₂ adsorption, the development of a porous network is of greater importance.

This concurs with doping that was carried out with KOH activated cucumber biochars, where melamine was again used as nitrogen doping agent [68]. While a sufficient level of CO₂ adsorption was observed for the nitrogen-doped activated chars, the non-doped chars adsorbed slightly more gas, further indicating microporosity is the dominant factor for adsorption in this case. High concentration of oxygen molecules, likely carbonyl groups, were seen to be another factor that influenced adsorption on the non-doped samples, as their electrical quadrupole moment attracted CO₂ molecules and enhanced adsorption. Considering these melamine-doped chars, their activation at 900 °C caused the nitrogen doping to significantly widen the pores within the material and led to breakdown of the microporous network, impacting their adsorption ability. Therefore, it seems apparent that a middle ground must be found to allow for sufficient nitrogen-containing groups to exist on the chars and improve their porosity, but using conditions that do not adversely affect other characteristics.

Urea has been used, though normally along with other activators, for nitrogen doping in both biochars and hydrochars. D-glucose derived hydrochars were doped with urea before undergoing activation with K₂CO₃ and tested for CO₂ adsorption [131]. The doping process showed increased nitrogen content on the hydrochar samples, which then decreased after activation due to the reactions with K₂CO₃; this was, however, coupled with an increase in surface area, likely due to gaseous products causing pore development. Results for CO₂ adsorption were positive in comparison to other studies, but no direct correlation between CO₂ capacity and microporosity, or nitrogen content, was found. Nonetheless, on an individual sample basis, the reference sample produced with no urea doping was outperformed by a sample made at the same condition with urea, suggesting that doping had a positive influence.

In terms of biochars, urea impregnation has been coupled with KOH activation to produce nitrogen-doped bagasse derived biochars [132]. The addition of nitrogen-containing functionalities was found to increase both surface area and CO₂ adsorption, up to a certain level of doping; beyond that point, higher levels of doping brought no further improvements.

It is clear, based on the literature, that nitrogen doping can be deemed important in not only providing new nitrogen sites for adsorption to occur, but also in helping to form an appropriate pore network suitable for adsorption. While ammonia and melamine have been shown to be used to good effect for enhancing CO₂ adsorption, they are both unpleasant chemicals to work with. Melamine is classified as a health hazard and carcinogen [133], and ammonia has many hazards such as being toxic, corrosive to skin, flammable and a general danger to the environment if released [134]. Alternatively, urea does not possess any of these dangers and is classified as a non-hazardous substance; subsequently, it would be appealing to use this more widely for nitrogen doping in future.

2.3.2 Chemical Activation

One of the most commonly used chemical activators is KOH, as it can produce materials with large surface areas of over 2000 m²/g [135]. It is also especially useful for developing more micropores in the materials [136], essential in this case for CO₂ adsorption. Typically used as an activator at 600 – 800 °C, the KOH can initiate the formation of other potassium-based compounds, such as potassium oxide (K₂O) and K₂CO₃, and together all three diffuse into the carbon structure of the chars, causing pore widening and formation [24]. Meanwhile, gaseous products from these reactions can further etch into the network and increase textural properties [137]. As well as being used as an activator after char production, KOH can be used in a one-step method where carbonisation and activation are carried out

together; both methods are shown to increase overall Brunauer–Emmett–Teller (BET) surface area [138], [139].

Zinc chloride (ZnCl_2) is another chemical used for char activation; it works in a similar manner where it reacts with the carbon structure, and the gaseous products formed etch micropores into the material structure [140]. A study of biochar derived from pine sawdust saw both KOH and ZnCl_2 activation give an increase in overall surface area and micropore volume of the samples [141].

Phosphoric acid (H_3PO_4) can be used as a dehydration agent for activation, and has been used for production of sunflower seed husk derived biochars, resulting in enhanced surface areas compared to a purely pyrolysis process [142]. Sodium hydroxide (NaOH) also works in the same way as KOH, and greatly improved the porous structures of spent coffee ground biochars when applied as an activator [143]. However, it has been seen to cause pore blocking in some instances [144].

Nevertheless, all of these chemicals can present problems in their own way. KOH is classified as a corrosive and irritant substance, which can cause severe burns and skin damage [145]. ZnCl_2 shares these classifications, while also being an environmental hazard, which raises issues both in handling and cross-contamination if the activated chars were to be used in sensitive industries [146]. H_3PO_4 and NaOH both fall under corrosive hazards, again posing a potential risk of burns and skin damage. While all four are proven to be effective activators, they do present risks during their use; either through exposure in the production process or in the final application of the chars. As such, it would be preferable to use methods of activation that are less harmful and more environmentally friendly.

2.3.3 Physical Activation

The main alternative to chemical methods of activation is physical activation, using gases such as CO₂, steam or air. The process of activation remains comparable; it is commonly carried out after initial carbonisation, but sometimes, in the case of biochars, a one-step process of carbonisation-activation is employed [6], [147]. This method allows the chosen gaseous agent to diffuse into and react with the carbon network of the char; thus, creating new porous structures and widening existing pores [39]. It is carried out at elevated temperatures of 700 °C and above, with some examples reaching 1000 °C [148]. While this can be energy intensive, the oxidative environment created can provide the final activated chars with increased quantities of oxygen-containing functional groups to provide adsorption active sites.

Air is generally the least common of the three activators, as it obviously heightens the risk of the carbon-based char undergoing oxidation and burn-off, thus, it is important that the oxidising environment is well controlled. The oxidation process causes the production of CO and CO₂, along with intermediates, which react to produce oxygen-containing functionalities on the char surface. When carried out correctly new pores are formed, but over-activation is common and can cause complete pore collapse [149]. There is evidence that this method increases surface area properties; wood derived biochar was activated under a mixed atmosphere of N₂/air to increase the BET surface area from 389 m²/g to 586 m²/g when temperature increased from 600 °C to 800 °C [150]. Despite this, air activation is not useful for increasing microporosity at lower temperatures (300 – 600 °C) and can further reduce the micropore volume by pore blocking through newly created oxygen-containing functional groups [39].

Steam activation is driven by chemisorption of the water molecules onto char surfaces, followed by water shift and gasification reactions, with the reaction sequence well documented in the literature [39]. It is a useful agent, as it can react with leftover volatile functional groups from pyrolysis, creating both fresh mesopores and micropores, and has been shown to give higher total pore volumes than CO₂ activation [151]. However, downsides to this activation can occur, as, at high temperatures and residence times, steam will cause the porous structure to collapse and reduce the overall char surface area, and bring about higher ash content [152].

For the activation stage, when using CO₂ as an activator, the main reaction mechanism follows the Boudouard reaction, see Equation 2.1 in Section 2.2.3, where carbon reacts in a gasification reaction with CO₂ to give CO [153]. As the Boudouard reaction is highly endothermic at 25 °C (~ 172 kJ/mol), this gasification process becomes thermodynamically favourable at temperatures of 700 °C or above [39]. Notably, this method of activation is known to create activated chars with greater microporous structures, and higher surface areas than those activated using steam [74]. This can be related to both the different reaction mechanism of steam and also the fact that steam molecules are smaller; thus, they can diffuse faster than CO₂, and have a greater tendency to increase the size of micropores to mesopores, rather than just creating fresh micropores which is what CO₂ does [154]. CO₂ activation has also been known to produce biochar with greater levels of aromaticity, and the final materials are of a high carbon purity, meaning that no post-activation washing stage is required (as may sometimes be needed after chemical activation) [151]. Research using barley straw biochar has confirmed these characteristics, as CO₂ activation gave an approximate 40 % increase in surface area and micropore volume compared to steam activation [155]. Further to this, CO₂ activated cotton-stalk biochar was found to have increased CO₂ adsorption compared to unmodified biochar [156]. In addition to this, using

CO₂ instead of N₂ as pyrolysis gas can lead to increased oxygen and nitrogen content in the produced char [39]; this is a desired trait as discussed in Section 2.2.4.3, as these types of functional groups can improve CO₂ adsorption.

In literature, a Life Cycle Assessment (LCA) was found that focused on CO₂ activated hydrochar derived from municipal solid waste for use in the plaster industry [157]. In this case, activation with CO₂ was found to be the most impactful stage of the process, mainly due to the high temperatures required for the process, but the thermal energy category of the study found significant energy recovery was present during syngas combustion. Overall, the process was seen to prove that net environmental gains in terms of climate change were achievable through the combined HTC-activation process, when compared to typically waste management practices. Similarly, a study examining physical activation of cellulose derived chars via CO₂, H₂O and combined CO₂-H₂O methods carried out an LCA that found CO₂ activation to be the most environmentally beneficial method of the three tested [158]. Again, the activation stage was the most impactful stage of the process, which is understandable, due to the temperatures required and the use and release of unreacted CO₂ during it. A study of coconut shell biochar included a qualitative LCA, and compared chemical and physical activation of the same feedstock; while no numerical values are presented, the chemical activation route is seen to include an additional stage for washing and neutralisation compared to the physical activation route [159]. This extra stage could possibly require additional energy or water input, which, in turn, increases the negative environmental impact of the chemical synthesis route in comparison to the physical route.

A further study, which conducted an LCA on chemically and physically activated carbons found that steam activation was a more viable route for mitigating the environmental impact of the process compared to activation with H₂SO₄ and H₃PO₄ [160]. While not identical to CO₂

activation, this provides further backing to the notion of physical activation meeting circular economy principles. Note that the literature does acknowledge that this is not always the case, as a H_3PO_4 microwave activated carbon was seen to have a lower environmental impact than an equivalent CO_2 activated carbon in an alternative study [161]. Thus, without carrying out an in depth LCA on each individual synthesis route for a given material, it is difficult to quantify the full impact of each process, meaning each method must be assessed on a case by case basis. It can be suggested, however, that, in the case of this project, by incorporating CO_2 activation in the synthesis method and then utilising the final material in CO_2 capture applications, there is scope for a net positive environmental impact to be achieved; this would require a full and detailed LCA to be carried out to validate these suggestions.

2.3.4 Biochars and Hydrochars Used for CO_2 Capture

Table 2.1 shows data obtained for a variety of biomass-based char materials produced through either pyrolysis or HTC for use as CO_2 adsorbents. From surveying literature, it is abundantly clear that KOH is the most commonly favoured material for chemical activation [11]; this is understandable, based on the positive results it consistently gives in terms of porosity creation. Meanwhile, CO_2 activation seems to be the most commonly used physical method.

The adsorption data in Table 2.1 has been selected to give a view of the varying range of CO_2 adsorption capacities observed in other literature. A larger and more comprehensive table is included later in the thesis in Chapter 7, alongside further observations on individual studies. Briefly, the main characteristics that influence CO_2 adsorption are the quantity of narrow micropores [31], otherwise known as ultramicropores (pore width < 0.7 nm), and the abundance of functional groups on the surface of the chars, such as nitrogen- or oxygen-containing functionalities [162] [163].

Table 2.1: CO₂ Adsorption Capacities of Various Biochar and Hydrochar Materials Produced in Literature

Biomass Material	Biochar or Hydrochar	Activation	CO ₂ Adsorption Capacity (mmol/g)		Ref.
			0 °C, 1 bar	25 °C, 1 bar	
Orange Peel	Hydrochar	Chemical (K ₂ C ₂ O ₄)	6.67	3.97	[130]
Jujun Grass	Hydrochar	Chemical (KOH)	-	4.9	[164]
<i>Cemellia japonica</i>	Hydrochar	Chemical (KOH)	-	5.0	[164]
Garlic Peel	Hydrochar	Chemical (KOH)	6.25	4.22	[31]
Cellulose Fibres	Biochar	Physical (steam)	-	2.33	[165]
Lignin	Hydrochar	Chemical (KOH)	6.0	-	[166]
Camphor Leaves	Biochar	Chemical (KOH)	5.86	3.74	[167]
Celtuce Leaves	Biochar	Chemical (KOH)	6.04	4.36	[168]
Cucumber Peels	Biochar	Chemical (KOH and melamine)	7.35	4.30	[68]
Pine Nut Shells	Biochar	Chemical (KOH)	6.05	3.96	[169]
Black Locust Tree	Biochar	Chemical (KOH)	7.19	5.05	[129]
Potato Starch	Hydrochar	Chemical (KOH)	-	2.8	[60]
Sugarcane Bagasse	Biochar	Chemical (KOH and urea)	-	4.80	[132]
Cotton Stalk	Biochar	Physical (CO ₂ and NH ₃)	-	2.25 (20 °C)	[156]
Orange Peel	Biochar	Chemical (KOH)	1.01	-	[170]
Bamboo	Biochar	Chemical (KOH)	0.63	-	[170]
Orange Peel	Hydrochar	Chemical (KOH)	-	3.05	[171]
Starch	Biochar	Physical (CO ₂)	-	2.1 (approx.)	[148]
Vine Shoot	Biochar	Physical (CO ₂)	4.07	1.58	[172]
Pomegranate Peels	Biochar	Chemical (KOH)	6.03	4.11	[173]
Soybean Straws	Biochar	Physical (CO ₂ and NH ₃)	-	2.02 (30 °C)	[174]
Sawdust	Biochar	Chemical (Urea phosphate)	-	1.34 (30 °C)	[175]
Avocado Seeds	Biochar	Chemical (H ₃ PO ₄)	-	3.30	[176]
Olive Stones	Hydrochar	Chemical (ZnCl ₂)	2.78	-	[30]
Microcrystalline Cellulose	Hydrochar	Chemical (NaOH)	-	5.49	[177]
Date Seeds	Biochar	Physical (CO ₂)	-	2.94	[178]
Coconut Shell	Biochar	Chemical (Urea and K ₂ CO ₃)	6.0	4.0	[179]

2.3.5 Identification of Char Production Process Parameters for Investigation

Table 2.2: Previous Literature Studies That Have Used Citrus Peels or Waste for Biochar Production and Characterisation

Feedstock	Synthesis Conditions			Further Activation	Surface Area (m ² /g)	Application	Ref.
	Temperature (°C)	Time (h)	Other Factors				
Orange Peels + Blended Biomass	650	1	50:50 w/w blends 5 – 10 °C/min N ₂ inert gas	No	No measurements	Characterisation	[180]
Orange Peel	337 (peak)	2 (approx.)	A variable reactor was used	ZnCl ₂	104.4 – 132.6	Characterisation	[181]
Pomelo Peel	800	4	Mixture of H ₂ SO ₄ , KOH and nickel acetate	Chemical – KOH	798 – 1615	Supercapacitor	[182]
Orange Peel	300 – 700	1		No	67.5	Phenol adsorption	[183]
Orange Peel	150 – 700	6		No	7.75 – 201	Naphthalene and 1-naphthol adsorption	[73]
Orange Peel (post limonene and fatty acid extraction)	550	1	10 °C/min N ₂ inert gas	Physical – CO ₂ and N ₂ (800 °C, 10 °C/min, 1 h)	40 – 326	Characterisation	[184]
Orange Peel	700	2	N ₂ inert gas One-step process	Chemical – KOH (pre-pyrolysis)	592.5	Water remediation	[185]
Orange Peel	450 – 550		N ₂ inert gas One-step process	Chemical – H ₃ PO ₄ and ZnCl ₂ (pre-pyrolysis)	611.4 – 1450.6	Methylene blue adsorption	[186]
Orange + Lemon Peels	600	3	Equal mix of orange and lemon peels	Chemical – H ₃ PO ₄ (pre-pyrolysis)	168.3	Methylene blue adsorption	[187]
Orange Peel	700		N ₂ inert gas	Chemical – K ₂ CO ₃ (carried out in microwave stage post-pyrolysis)	6.9 – 1104.5	Methylene blue adsorption	[188]
Orange Peel	500	2		Chemical – H ₃ PO ₄ (pre-pyrolysis) and CTAB (posy-pyrolysis)	618.4 – 697.1	Congo red dye adsorption	[189]
Orange Peels	400	3	N ₂ inert gas	Chemical – KOH (900 °C, 3 h, N ₂ inert gas)	23.6 – 1998	Chromium removal from water	[190]

Feedstock	Synthesis Conditions			Further Activation	Surface Area (m ² /g)	Application	Ref.
	Temperature (°C)	Time (h)	Other Factors				
Orange Peels + Various Kitchen Waste	400	1	25 % mix of orange peel, with the balance made up of potato and banana peels and coffee residue	No	4.8	Methylene blue and methyl orange adsorption	[191]
Orange Peels	250 – 600	1		No	46.2	Characterisation	[192]
Orange Peel	550	0.5		Chemical – ZnCl ₂ (pre-pyrolysis)	1079	Methylene blue	[193]
Orange Peels	500	1	10 °C/min	Chemical – KOH (pre-pyrolysis)	51.6	CO ₂ adsorption	[170]
Orange Peels	700	2	5 °C/min N ₂ inert gas	Chemical – H ₃ BO ₄ Also doped with MOF material	172.5 – 674.3	Ammonia adsorption	[194]
Orange Peels and Orange Albedo	300	2		No	352.5 – 356.3	Characterisation	[195]
Orange Peel	500 – 700	1	5 °C/min N ₂ inert gas	Ball-milled post-pyrolysis	296	Wastewater remediation	[196]
Orange Peel	400	1	8 °C/min	Chemical – KOH (pre-pyrolysis)	403.1	Aminophenol adsorption	[197]
Mandarin Peel	700	6	5 °C/min N ₂ inert gas	Chemical – NH ₄ Cl and ZnCl ₂ (both pre-pyrolysis)	8.5 – 1085.0	Methyl orange and fast green FCF adsorption	[198]
Orange Peel	550	1	10 °C/min N ₂ inert gas	Chemical – H ₃ PO ₄ (pre-pyrolysis)	29 – 675	Demetallisation adsorbent	[199]
Orange Peel	300 – 800	1	8 °C/min N ₂ inert gas	Chemical – KOH (pre-pyrolysis). One and two-step process tested	965 – 1404	Phenol Adsorption	[200]
Orange Peels	300 – 600	1	N ₂ inert gas	No	0.8 – 2.2	Lead adsorption	[201]
Orange Peels		0.25	Microwave pyrolysis – 900 W	Chemical – H ₃ PO ₄ (pre-microwave)	67.4	Chromium adsorption	[202]
Orange Peels	800	3		No	1049 – 1074	Methylene blue	[203]
Orange and Mandarin Peels	900	0.25	5 °C/min N ₂ inert gas	Physical – CO ₂ and H ₂ O	166 – 399	Cu (II) adsorption	[204]

Feedstock	Synthesis Conditions			Further Activation	Surface Area (m ² /g)	Application	Ref.
	Temperature (°C)	Time (h)	Other Factors				
Tangerine Peels	400	2	2.5 °C/min N ₂ inert gas	Chemical – KOH (post-pyrolysis)	8 – 1047	Methylene blue, tetracycline, fluorescein sodium	[205]
Orange Peel	800	1	8 °C/min N ₂ inert gas	Chemical – KOH (pre-activation) Physical – pre-carbonisation was also tested	965 – 1404	Phenol	[200]
Orange Peels	600	1.5	N ₂ inert gas	Chemical – H ₃ PO ₄ (pre-activation) Then washed with KOH post-activation	497	No adsorption	[206]
Orange Peels	400	0.75	5 °C/min N ₂ inert gas Microwave prepared sample produced	Physical – CO ₂ (800 °C, 0.75 h)	263 – 266	Herbicides	[207]
Orange Peels	400	2	10 °C/min N ₂ inert gas	Chemical – melamine (pre-pyrolysis) and KOH (post-pyrolysis, 800 °C, 2 h)	1681 – 2350	Water deionisation	[208]
Orange Peels	400	2	5 °C/min N ₂ inert gas	Chemical – MgO (post-pyrolysis, 600 °C, 2 h)	270 – 460	Ammonium adsorption	[209]
Mandarin Peels	500	1		No	8	Methylene blue	[210]
Tangerine Peels	800	1	N ₂ inert gas	Chemical – CaCl ₂ and FeCl ₃ (pre-pyrolysis)	9 – 559	Phosphate ions	[211]
Orange Peel	400	2	N ₂ inert gas	Chemical – potassium citrate and magnesium citrate (post-pyrolysis, 750 °C, 2 h)	309 – 1768	CO ₂ adsorption	[117]

Table 2.3: Previous Literature Studies That Have Used Citrus Peels or Waste for Hydrochar Production and Characterisation

Feedstock	Synthesis Conditions			Further Activation	Surface Area (m ² /g)	Application	Ref.
	Temperature (°C)	Time (h)	Other Factors				
Orange Peels	190	24	15 g feed: 110 mL water 8 °C/min	Oxidised with HNO ₃	20 – 34	Methylene blue adsorption	[212]
Orange Peels	200	20	10g feed: 100 mL water	Physical – CO ₂ , N ₂ and Air Chemical – H ₃ PO ₄	0.4 – 618	Pharmaceuticals adsorption	[213]
Orange Peel	180 – 220	3	4 g feed: 60mL water	Chemical – KOH (700 °C, 2 h)	50.60 – 457.22	CO ₂ adsorption	[171]
Orange Peel	210	2	15 g feed: 120 mL urea solution	Physical – Ar Chemical – KOH	7.6 – 3053	Toluene and iodine adsorption	[214]
Orange Peel	200	2 – 24	Peel solution of 60 % moisture	No	7.1	Soil amendment	[215]
Orange Peel	240 700 – 900 activation	4 (2 for activation)	6 g feed: 6 g melamine: 60 mL water	Chemical – K ₂ C ₂ O ₄	530 – 2130	CO ₂ adsorption	[130]
Orange Peels	150	3	5 g feed: 50 mL H ₃ PO ₄	Chemical – K ₂ CO ₃ (impregnated, no heating)	2.4 – 21.2	Biodiesel	[216]
Orange Peels	210	2	15 g feed: 120 mL urea solution	Chemical – KOH (800 °C, 2 h)	1643 – 2934	Volatile organic compound (VOC) adsorption	[32]
Orange Peels	175	12	2 g feed: 75 mL water and 100 mL copper solutions	Chemical – CuSO ₄ (pre-HTC)	27 – 31	Reduction of methylene blue	[217]
Orange Pulp and Bagasse	100 – 200	8 – 14	6.25 g: 50 mL water	Chemical – H ₃ PO ₄ , NaOH (post-HTC) Then thermally activated at 300 °C	0	Fe and Mn removal from water	[218]
Orange Juice	180	6	30 mL of juice	Chemical – KOH (800 °C, 0.5 h)	1724	No adsorption	[219]

Feedstock	Synthesis Conditions			Further Activation	Surface Area (m ² /g)	Application	Ref.
	Temperature (°C)	Time (h)	Other Factors				
Orange Peel	160	12	3 g feed: 30 mL water	Chemical – HCl and H ₂ O ₂ (post-HTC) Some activated at 600 °C under N ₂	7 – 312	Pharmaceutical pollutants	[220]
Orange Peel	180 – 250	1	1 g feed: 5 g water		46 – 64	Cationic dye	[221]
Orange Peel	150 – 200	2 – 24	20 g orange peel paste	Chemical – magnetite deposition	6 – 73	Brilliant Black food colouring	[222]
Orange Peel	240	2	1 g feed: 8 mL water	No	7 – 27	No adsorption	[223]
Orange Peel	190	24	20 g feed: 120 mL water	No	7 – 15	Methylene green	[224]
Tangerine Peel	200	3	2.5 g feed: 20 mL FeCl ₃ solution	Chemical – FeCl ₃ (pre-HTC) Physical – N ₂ (post-HTC, 800 °C, 4h)	7 – 287	Ni(ii) adsorption	[225]

Table 2.2 and Table 2.3 present an overview of literature studies that have used orange or other citrus peels for biochar and hydrochar production respectively, and the process parameters that were used. It is clear that high pyrolysis temperatures are a key contributor to producing high surface area materials, with residence time and doping methods also influencing the process. Over the studies presented, there is a wide range of conditions for both temperature and residence time, although no definitive set of conditions are presented as 'optimal', as most works only vary one of these parameters. This raises the opportunity for research to be conducted into this area of the process, and attempt to determine the influence that each process parameter has on the final produced char. For this project, it was decided to choose a selection of the most commonly tested parameters from these literature studies, and study the effect of varying them through a Design of Experiment (DoE) methodology. The use of this method would allow for quantification of both the impact of each process parameter, but also the interactions between the parameters. Presented in Appendix A are two tables showing further examples of biochars and hydrochars produced in literature, and the range of conditions used for synthesis; factors such as pyrolysis temperature, residence time and gas flow rate are presented, along with the various type of activators employed in different studies. These tables provide the basis for the following discussion on the range of values to be tested for each factor.

In terms of pyrolysis temperature of biochars in general, there is a wide range of values seen in different studies, ranging from low temperatures of 300 – 400 °C up to 800 – 900 °C. It is commonly known that porosity does not begin to significantly develop until temperatures have increased beyond 500 °C [74], therefore, it was decided to use this as the lower bound for this project (note that this was later altered in the optimisation stage of the biochar experiments). Conversely, excessively high temperature can be damaging to the char and lead to high rates of burn off and pore coalescence. With regards to the Boudouard reaction,

typically temperatures of 700 °C or higher are required for the reaction to become thermodynamically favourable [226]. Therefore, an upper limit of temperature was chosen to be 800 °C, in order to allow the Boudouard reaction to proceed, but limit the degradation of the char samples. The use of a lower temperature bound of 500 °C was also in line with the sustainability goals of the study. An estimate of thermal energy cost required to heat the tube furnace and crucible to the target pyrolysis temperatures of 500 °C and 800 °C was carried out using Equation 2.2, using an average heat transfer coefficient for alumina [227], which is the material of manufacture for the tube furnace used in this study.

$$Q = c m \Delta T \quad \text{Equation 2.2}$$

Where:

Q = thermal energy required (J)

c = specific heat capacity of alumina (J/kg K) $\approx$ 850 J/kg K

m = mass of alumina furnace tube and crucible (kg) $\approx$ 0.95 kg

ΔT = change in temperature, from room temperature to pyrolysis target

temperature (K) = 475 K for 500 °C target, and 775 K for 800 °C target

Using the above values, the Q values are found to be 384 kJ and 626 kJ for the 500 °C and 800 °C target temperatures respectively. Note that this is an approximation, and further detailed calculations would be required to provide a comprehensive energy cost for the process at both temperatures. Nonetheless, this estimate demonstrates that if chars could be produced at 500 °C that possess positive characteristics in relation to CO₂ adsorption, the use of this lower temperature would present energy saving benefits, and therefore, a more sustainable synthesis route for solid adsorbents.

When assessing appropriate residence times, it is clear from the data presented in Table 2.2 and Appendix A that porosity is achievable in relatively short times, e.g. 0.5 – 1 h, and that, in some cases, longer times lead to higher values of surface area being achieved in biochar materials. As such, a lower limit of 0.5 h was chosen with a view to minimising heating time in order to conserve energy. The upper limit of 3 h was selected in order to determine if the benefits of a longer time period, and subsequent energy cost, would be worth the trade-off compared to the 0.5 h experiments.

In terms of ramp rate, the 15 °C/min used in the experimental stage of this project is higher than the commonly used values of 5-10 °C/min (see Appendix A, Appendix Table A.1), but was required due to time restraints related to cooling of the biochars and laboratory policy on operation of gas cylinders outwith the hours of 9 am and 5 pm. Note however, that there are even higher values of ramp rates reported in literature for biochar production, up to 25 °C/min [228], [229], indicating that the chosen rate of 15 °C/min is still an acceptable value. A range of gas flow rates, of either N₂ or CO₂, was chosen to be 100 and 400 mL/min based on the literature values presented in Appendix A; 400 mL/min was a typical value seen in other studies, while the use of the lower flowrate 100 mL/min was again an attempt to minimise gas usage, in line with green chemistry principles.

For the hydrochar studies, the influence of the initial HTC factors is difficult to contextualise, as when subsequent activation is carried out, this masks the initial characteristics of the materials. For example, two studies into hydrochars derived from orange peels used similar conditions, 190 °C and 24 h vs 200 °C and 20 h [212], [213], yet the char activated with HNO₃ displayed a surface area of 34 m²/g, compared to a surface area of 618 m²/g for the sample activated using H₃PO₄. Similar examples of this effect can be seen in Appendix A, further emphasising the importance of activation of hydrochar materials. If activation is not

employed, then hydrochar materials typically present a low porosity no matter the temperature and residence time utilised during HTC; orange peel hydrochar produced at 240 °C for 2 h displayed a surface area of 21 m²/g [223], while a similar study also using orange peel precursor produced a hydrochar with surface area of 15 m²/g after undergoing HTC at 190 °C for 24 h [224]. 180 °C is commonly seen in literature to be the lower limit of temperature used in hydrochar studies, see Appendix A, Appendix Table A.2, as temperatures below this tend to result in lower levels of carbonisation and poor char characteristics in general [98]; thus, this was chosen as the lower limit to be followed in this project. The upper temperature limit of the equipment being used in this study was 250 °C, as above this it was possible that issues relating to overpressure would occur. In order to work below this inherent limit, a maximum of 220 °C for HTC temperature was chosen for the initial experiments.

The choice of residence time was also limited, due to the fact that experiments had to be run overnight; thus, the experiment had to be started at 4:45pm, and to have completed and cooled to room temperature by 9 am the next day. As a result, 12 h was deemed the upper limit of time that would allow the process to run in line with laboratory policy. A lower limit of 2.5 h was set, to allow an appropriate time for carbonisation to occur, but also a short enough period to fit with the aim of lower energy consumption.

The activation temperature range for the hydrochar materials was chosen to be 750 – 800 °C, partly due to the limitation of the Boudouard reaction below 700 °C, and partly due to the success of these temperatures in the biochar phase of the project. Use of higher temperatures in the biochar section of the work, such as 831 °C, had led to large relative reductions in yield of final char, so it was decided to keep the upper limit of hydrochar

activation around 800 °C. A ramp rate of 15 °C/min and a gas flow rate of 400 mL/min CO₂ were chosen to maintain consistency between the biochar and hydrochar syntheses.

In terms of activation, the chemical route appears to give slightly better properties within the resulting activated chars. For example, KOH activation biochars produced from pomelo peels [182], and orange peels [200], are seen to give surface area values in the range of 1400 – 1600 m²/g, while hydrochar derived from orange peel and activated with KOH was shown to exhibit a surface area of approximately 2900 m²/g [32]. Other chemicals, such as H₃PO₄ and ZnCl₂, used with orange peel biochar gave surface areas in the range 610 – 1450 m²/g [186]. But, as previously discussed, there is a desire to avoid chemical activation in this project in order to meet green chemistry principles. Therefore, for this study the use of physical activation was selected, in order to try and minimise the environmental damage that could occur through the synthesis process. The decision to choose CO₂ as the physical activation agent was primarily due to evidence from the literature that shows its usefulness in creating micropores, which are essential for CO₂ capture, as highlighted in Section 2.3.3; while the data presented in Table 2.2, shows that surface areas in the range of 260 – 400 m²/g have been produced for other orange peel related studies using CO₂ [184], [204], [207]. It should also be noted that the experimental configuration available in the laboratory was also deemed unsuitable for use with steam at the high temperatures required in this study.

Something that has not been discussed within literature so far is a comprehensive comparison between the two processes used to produce chars – namely pyrolysis and HTC. To do this for a specific feedstock would be significant as it would allow a review of the different properties each process brings to the respective products, and possibly showcase which route is ‘better’ to follow. Thus, a feedstock was selected to carry out such a comparison; and thorough research into the physicochemical makeup of different biomass

found in the literature allowed orange and mandarin peels to be selected. This was mainly due to their apparent high cellulose content in the range of 22 – 40 wt% [230], [231], [232], [233], and their vast abundance as a waste material, in both the food and drink industry [234], with approximately 32 million tonnes of orange peel waste generated per year [235]. Additionally, the use of these two feedstocks allowed for comparisons between similar yet distinct feedstocks, as both peel types originate from the same genus, the *Rutaceae* family.

A DoE response surface methodology was used for the duration of the process, to allow for statistical analysis of results and, eventually, an optimisation process to take place, which would hopefully produce ‘optimal’ chars for targeted adsorption of CO₂.

2.4 Research Gap, Novelties and Project Aims

2.4.1 Research Gap

A large amount of work has been carried out researching the production of both biochars and hydrochars from citrus related biomass, as portrayed in Section 2.3.5. Within these studies, a small selection have tested the produced chars for CO₂ adsorption capacities. The following research gaps were identified during the literature search:

- Biochars have been produced for carbon capture applications through physical activation using CO₂, and have also been produced using urea in the process as a nitrogen doping agent. However, no biochar has been produced by incorporating urea and CO₂ activation together within the production process. The same can be said for hydrochar produced for carbon capture processes.
- Sustainable engineering or circular economy is often attributed to methods of production of biochar and hydrochar, despite hazardous activating and doping agents being used such as KOH or ZnCl₂. Similarly, an excessive number of pre-treatment steps, some of which are energy intensive, are often carried out in the

process of producing these chars, meaning there is doubt over the net environmental benefit that the final product provides. This presents a gap to explore the use of non-hazardous doping agents in these char production processes, and similarly, the opportunity to reduce the pre-treatment of any material.

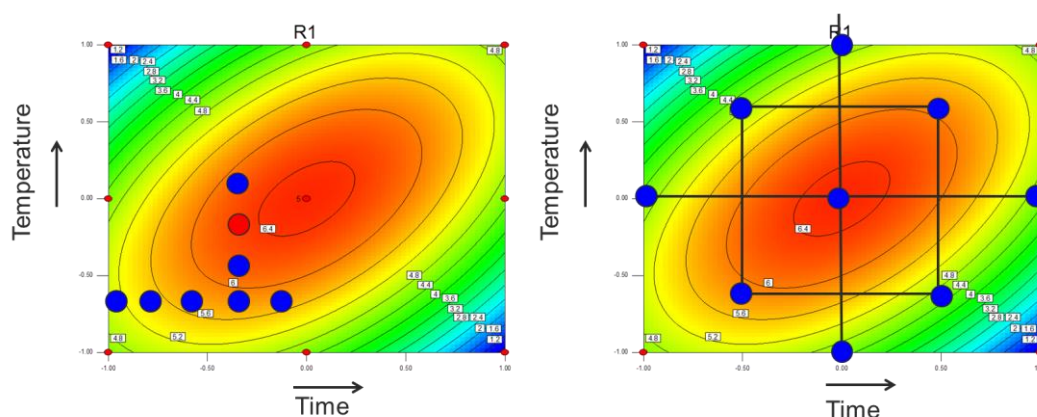


Figure 2.5: Example of Traditional Method of Varying One Process Parameter at a Time (left) v Varying Both Parameters Simultaneously Using a Design of Experiment Methodology (right) [236]

- Studies are often found to vary one process parameter such as pyrolysis/HTC temperature or residence time, with all other parameters maintained at a constant value. This is not the most effective method of assessing parameter influence on a process, as optimal points or areas can be missed, see Figure 2.5. As such, this raises a research gap which could be explored by using a DoE methodology in an aim to optimise multiple process parameters towards production of a material with optimal adsorption performance. This type of experimental design has not been utilised within any previous studies on citrus peel derived biochar.
- The majority of studies which use citrus fruits focus on waste orange peels, with little distinction between the types of oranges available: sweet oranges, mandarins, bitter oranges etc. Therefore, there is scope for investigation into the effect that the peel precursor has on char properties and adsorption performance.

- No study has compared the two different char production methods (pyrolysis for biochars, and HTC followed by activation for hydrochars) for the same feedstock. This presents an opportunity to develop a comparative study into production methods of biochar and hydrochar, for orange and mandarin peel feedstocks.
- The use of biochars and hydrochars in post-combustion CO₂ remediation technologies is often discussed and reported, but the results presented in studies are often at temperature levels not comparable to flue gas that would typically be treated by post-combustion methods (flue gas temperature is > 60 °C, studies often test at 0 °C or 25 °C). Thus, there is scope to carry out adsorption studies at industrially applicable conditions, with specific attention to flue gas composition and temperatures.

2.4.2 Research Aims and Objectives

To address the research gaps highlighted in Section 2.4.1, the following aims were set for the work in this thesis:

- Nitrogen-doped biochars will be produced through a single-stage pyrolysis-activation process, and nitrogen-doped hydrochars produced through a two-stage HTC and activation process. The nitrogen doping will be carried out using urea as a doping agent and activation by using CO₂ as an activating agent.
- A Design of Experiments methodology will be used to examine four different process parameters in both the biochar and hydrochar production processes. This will take the form of a screening and then optimisation design for each of the chars. From these designs, optimisation models will be used to produce ‘optimal’ samples of both char types to attempt to maximise their performance as CO₂ sorbents.

- Material characterisation will be carried out on each type of char produced, to determine their textural and elemental properties and yield insights into how process parameters influence the make-up and porosity of the chars.
- A comparison will be made between the chars produced from each feedstock, orange peels and mandarin peels, to determine which is more suitable for sorbent material production. Similarly, a comparison will be made between the two different char production routes for each feedstock.
- The chars which show characteristics most suitable for CO₂ adsorption will be tested for their CO₂ capacity under a range of conditions (temperature and pressure), and under conditions analogous to those found in flue gas streams.

2.4.3 Research Novelties

Following on from the aims set out in Section 2.4.2, this study will look to realise the following research novelties:

- Investigate two char production routes which adhere to green chemistry and sustainable engineering principles, alongside circular economy goals. This will be achieved by carrying out minimal pre-treatment to the feedstocks, and through the use of urea as a doping agent. The use of CO₂ as an activating agent as well as the target adsorption molecule fulfils the circular economy aspect, as does the valorisation process of turning waste orange and mandarin peels into higher value products.
- The use of Design of Experiments will facilitate the comparison between using two different but related feedstock materials for char production, and the comparison between the two different char production routes for each feedstock.

- The use of Design of Experiments will also allow for the simultaneous optimisation of process parameters in the production of citrus peel derived biochars and hydrochars. This will aim to produce nitrogen-doped chars tailored towards the adsorption of CO₂.
- The adsorption performance of the chars most suited to CO₂ adsorption will be tested under both conventional laboratory conditions, and under conditions analogous to those found in flue gas streams. The testing carried out under flue gas stream conditions allows a more realistic judgement of the suitability of materials for application in industrial CO₂ capture processes.

2.5 References

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3 Fundamental Adsorption Theory Chapter

This chapter outlines the fundamental background theory which underpins the science and engineering that is demonstrated in this thesis. The basis of adsorption is discussed, and various isotherm models are presented. Adsorption thermodynamics and kinetic theories are then defined, along with methods used to define textural characteristics of porous materials, and their associated uncertainties.

3.1 Adsorption Fundamentals

Adsorption is the process whereby molecules adhere to and/or accumulate on a surface, but do not permeate through the surface [1]. The material onto which a species is adsorbed is called the '*adsorbent*' and the species that becomes adsorbed onto that surface is called the '*adsorbate*' (note that prior to adsorption occurring the adsorbate is called the '*adsorptive*' as it has not undergone the adsorption process yet). The process of sorption is reversible: adsorption is the forward part of the process, and desorption is the reverse in which an adsorbate will desorb and remove itself from the adsorbent. The desorbed molecule may differ from the initial molecule adsorbed.

Adsorption can occur through two mechanisms, either physisorption or chemisorption. Physisorption is governed by weak intermolecular interactions such as van der Waals forces and electrostatic interactions, while chemisorption involves the process of a chemical bond forming between the adsorbent and the adsorbate [2]. The surface of the adsorbent comprises an array of adsorption sites which can be either energetically homogenous or heterogenous, depending on their enthalpy of adsorption. These sites provide the area onto which adsorbate molecules may adsorb. When all adsorption sites on the adsorbent are full, this is considered complete monolayer coverage.

Chemisorption may only occur to the extent of monolayer formation on the adsorbent, as each molecule needs to form a chemical bond with a specific adsorption site on the adsorbent surface. Conversely, physisorption can exist in either monolayer or multilayer formations; the physisorbed molecules can either bond to the adsorbent sites through weak interactions, or they can adsorb onto molecules that have already chemi- or physisorbed onto the surface. This allows for multiple layers of adsorbed molecules to exist. An example of this can be seen in Figure 3.1.

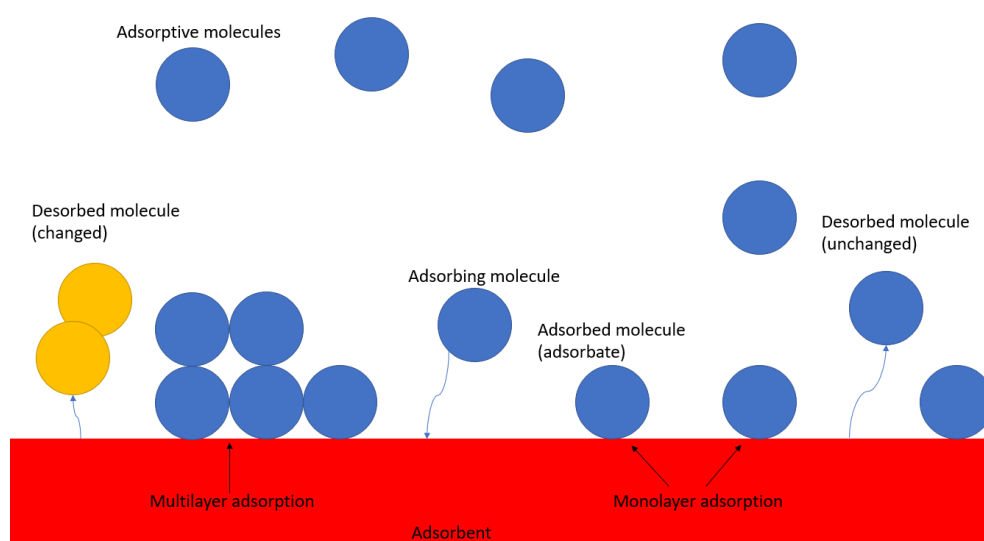


Figure 3.1: Visual of Adsorption and Desorption Process

As stated above, both chemisorption and physisorption are reversible processes, however, due to the nature of the stronger interactions involved, chemisorbed molecules require a higher energy input to remove them from the adsorbent. The principle characteristics of physisorption and chemisorption can be seen in Table 3.1. In terms of gaseous adsorption, physisorption is highly dependent on the porosity of the adsorbent material, whereas chemisorption will primarily depend on the different functionalities that exist on the adsorbent surface.

Table 3.1: General Characteristics of Physisorption and Chemisorption, adapted from [3]

	Physisorption	Chemisorption
Heat of Adsorption range (kJ/mol)	20 – 40	> 80
Rate of adsorption at 0 °C	Fast	Slow
Temperature dependence of uptake with increasing temperature	Decreases	Increases
Desorption	Easy – reduce pressure or increase temperature	Difficult – high temperatures required to break bonds
Desorbed species	Adsorbate is unchanged	May be different to original adsorptive
Specificity	Non-specific	Very specific
Monolayer coverage	Mono- or multilayer coverage can occur	Only monolayer coverage

The activated case of chemisorption is shown in Figure 3.2; this illustrates that in the activated case there is a potential barrier that must be overcome to allow the molecules to fall into the chemisorption potential well, in order to chemisorb to the surface [4]. Meanwhile, the non-activated case is shown in Figure 3.3, where the chemisorption and physisorption curves cross below the 0 value of potential energy and, as a result, there is no potential barrier to overcome, meaning that the adsorption process occurs spontaneously. Note that, while the physisorption well is further from the surface, compared to the chemisorption well, it has a shallower well, which results in physisorption bonds being weaker than chemisorption bonds (which have deeper wells).

Similarly, the depth of the wells has an influence on the temperature dependence of adsorption. As temperature increases, the kinetic energy of the physisorbed molecules increases, which means they are able to escape the physisorption well, thus, the degree of physisorption observed decreases. Upon increasing the temperature, a point will be reached where the molecules that have escaped the physisorption well will have enough energy to overcome the potential barrier to chemisorption, and will then drop into the chemisorption

well; meaning the degree of chemisorption observed can increase with increased temperature. In a related manner, this concept also explains why the rate of physisorption at 0 °C is higher than the rate of chemisorption at the same temperature; at 0 °C, many molecules will not have sufficient energy to overcome the potential barrier for chemisorption but will have adequate energy to reach the physisorption potential well. Additionally, once adsorbed onto the surface, it is harder for chemisorbed molecules to desorb, as they require significantly more energy to escape the chemisorption well, than if they were in the physisorption well; thus, higher temperatures are required to facilitate this desorption process.

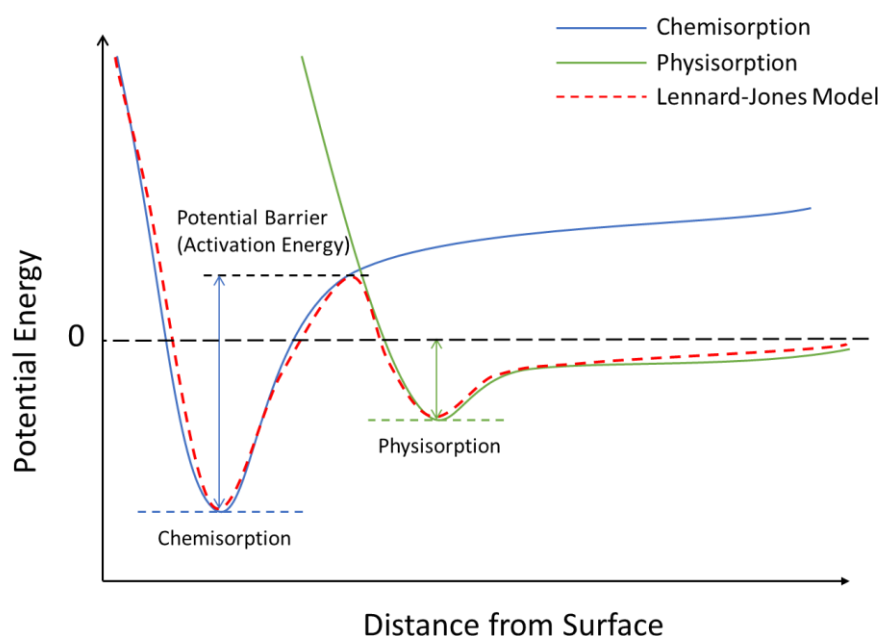


Figure 3.2: Lennard-Jones Potential Diagram for Activated Chemisorption

The gap in the average heat of adsorption values, stated in Table 3.1, namely the 40 – 80 kJ/mol range, is again due to the difference in the potential wells between the two forms of adsorption. As seen in Figure 3.2 and Figure 3.3, the physisorption well is consistently shallower than the chemisorption well, so smaller quantities of energy are released when

molecules fall into this well, and the difference in depth between the two wells represents this gap.

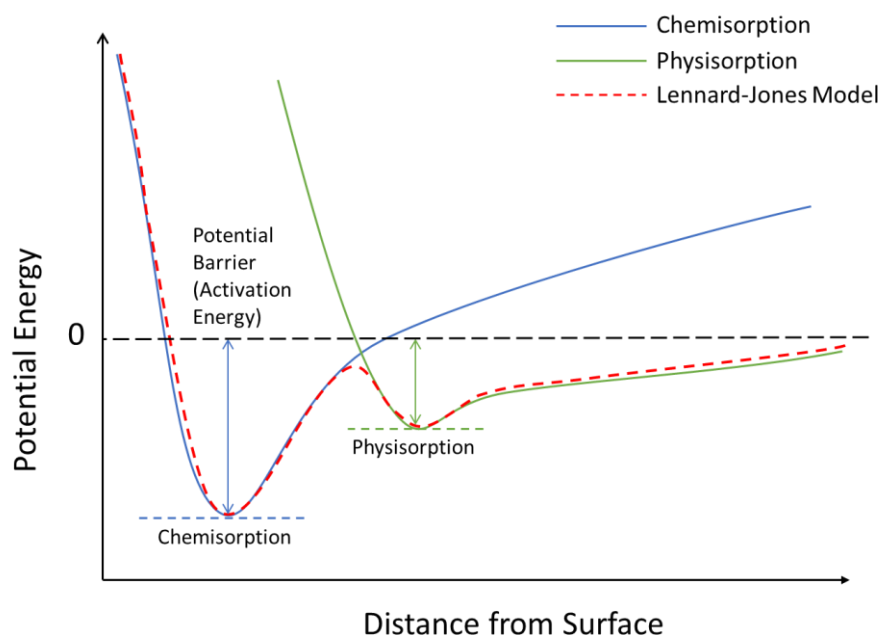


Figure 3.3: Lennard-Jones Potential Diagram for Non-Activated Chemisorption

3.2 Porosity

Adsorbent materials are commonly classified based on the size of their pores. The generally accepted classification of pores, from the International Union of Pure and Applied Chemistry (IUPAC) [5], is shown in Table 3.2, with the subdivision of micropores also included. As adsorption capacity of materials is proportional to surface area, and surface area is generally proportional to the porosity, it follows that enhancing porosity is a key factor in producing materials that can be useful in adsorption applications.

Table 3.2: Pore Size Definitions [5]

Type of Pores		Size of Pores
Macropores		Greater than 50 nm
Mesopores		Between 2 – 50 nm
Micropores	Supermicropores	Between 1.4 – 2 nm
	Micropores	Between 0.7 – 1.4 nm
	Ultramicropores	Less than 0.7 nm

A visual example of the different pore types can be seen in Figure 3.4. It is important, especially in the case of CO₂ adsorption, that the adsorbent material has a well-developed pore network, as this aids in the transport of target adsorbate molecules to the smaller micropores and also provides potential for capillary condensation to occur in mesopores.

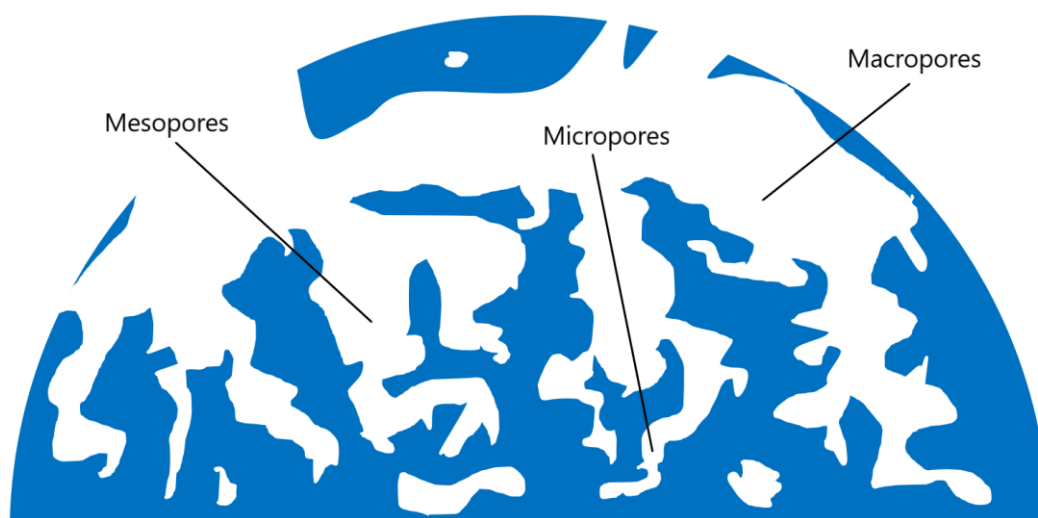


Figure 3.4: Visual Example of Different Pore Types

3.3 Isotherms

Isotherms are the most common method of recording adsorption data; in the case of gaseous systems, this involves measuring the change in quantity of adsorbed material by varying pressure, for a given temperature. For liquid systems, the change in quantity adsorbed is measured as a function of the concentration of adsorptive in the system. Isotherm plots can be vital in providing an understanding of the type of adsorption taking place on a chosen adsorbent material, and also the characteristics of the adsorbent.

As an example, the shape of isotherms can indicate the type of pore structure of the adsorbent, and combining a series of isotherms for a given material can enable calculations of heat of adsorption data that indicates either chemisorption or physisorption behaviour. Isotherm data can also be fitted to standard models such as Langmuir, Freundlich, Temkin etc., which offer information on the interactions between the adsorbate and adsorbent.

3.3.1 Typical Isotherms

Isotherms for physisorption process can be classified into six main types, with Type I and Type IV isotherms having two different possible forms [5]. The shape of an isotherm can give key information on the properties of the adsorbent material. Examples of each isotherm type can be seen in Figure 3.5.

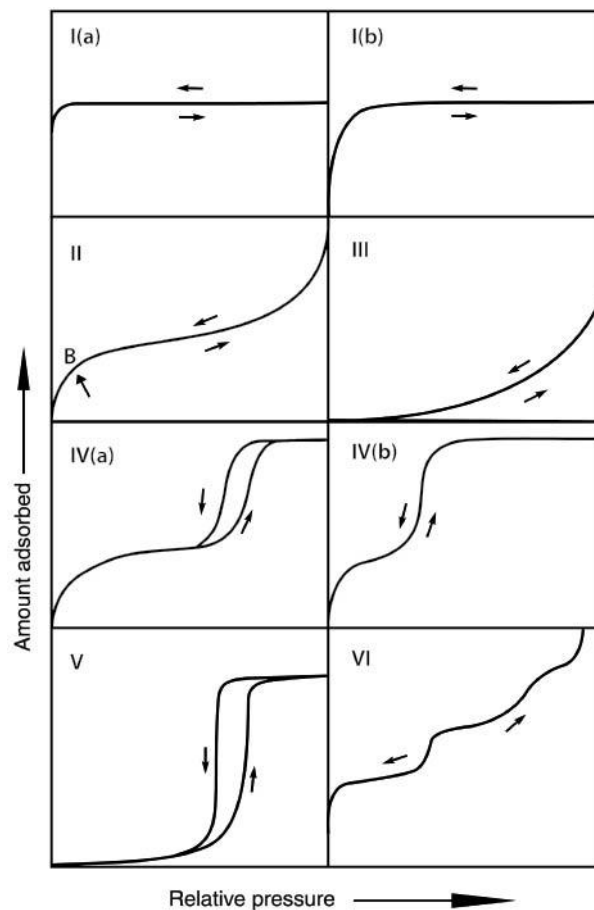


Figure 3.5: IUPAC Classification of Adsorption Isotherms [5]

Type I isotherms are characteristic of microporous materials that exhibit low external surface area values, with internal pore volume providing the basis for the adsorption capacity [5]. The strength of adsorbate-adsorbent interactions in narrow micropores leads to the rapid filling observed at low relative pressure $\left(\frac{P}{P_0}\right)$, meaning maximum adsorbent capacity is reached at relatively low pressures. Type I(a) isotherms indicate a material comprising predominantly micropores < 1 nm in size, whereas Type I(b) indicates a more varied pore size distribution and the presence of small mesopores (< 2.5 nm).

Type II isotherms present an initial similar behaviour of micropore filling at low $\frac{P}{P_0}$, but adsorption then continues, indicating multilayer formation occurs unrestricted and potentially the presence of larger pores [6]. The Type III isotherms are indicative of poor interactions between adsorbent and adsorbate; this leads to accumulation of adsorbed molecules at the most favourable adsorption sites on the adsorbent surface, before a steep increase in uptake at higher pressures, dominated by adsorbate-adsorbate interactions resulting in multilayer adsorption. Both Type II and III isotherm shapes are evidence of macro- or non-porous materials.

In contrast, Type IV isotherms are examples of mesoporous materials, and present similar behaviour to Type II; there is initial pore filling, and then multilayer adsorption, but pore condensation then follows. This is where gas condenses to a liquid form within the pores despite being at a pressure lower than its saturation pressure. After this phenomenon is complete, saturation of the adsorbent is observed, as proven by the plateau in the graph. The presence of wider mesopores gives rise to Type IV(a) isotherms, which exhibit hysteresis, and, in contrast, smaller mesopores lead to the observation of Type IV(b) isotherms.

Type V isotherms are comparable to Type III, and are typical of non-porous materials. Initially the weak adsorbent-adsorbate interactions cause accumulation of molecules at favourable

sites, before pore filling occurs leading to higher uptake. Type VI show repeated multilayer adsorption occurring on a non-porous surface, with the intensity of each layer determined by its capacity for further adsorption and the general thermodynamics of the system.

Hysteresis loops are a phenomenon witnessed in cases of multilayer formation and can be attributed to capillary condensation effects. The different forms of hysteresis loops can be seen in Figure 3.6.

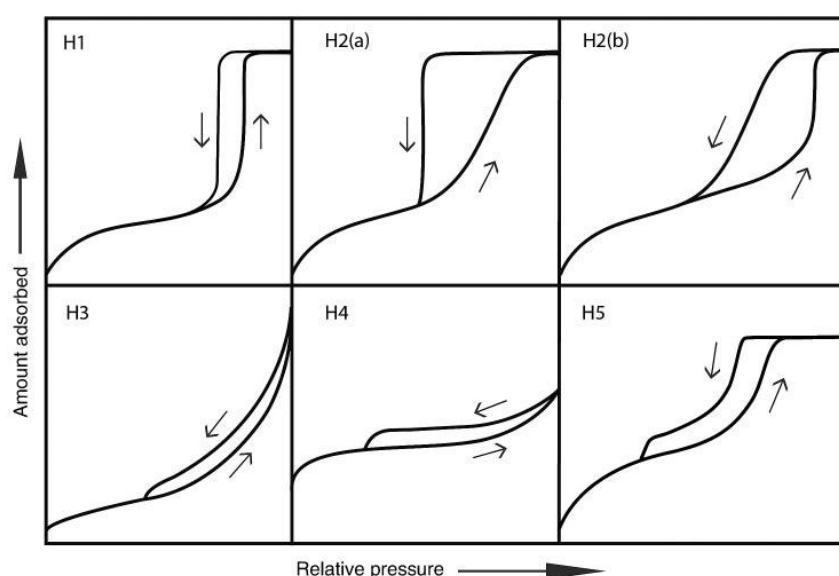


Figure 3.6: IUPAC Classification of Hysteresis Loops [5]

Type H1 loops are exhibited by mesoporous materials typically composed of ink bottle shaped pores, and where pore network effects are negligible [5]. In contrast, Type H2(a) and H2(b) loops are commonly seen in materials with convoluted pore networks, where pore blocking can play a significant role in the sorption processes; H2(a) are generally obtained for materials with narrower pore necks than H2(b) materials [7].

Type H3 follows a characteristic Type II isotherm, and is produced by materials containing macropores that are only partially filled when capillary condensation occurs in the pores, or loosely layered materials [8]. These are relatable to Type H4, with the only difference coming

from the Type I/II isotherm nature of H4 loops. Meanwhile, Type H5 is seen in instances of mesoporous materials that contain a mixture of blocked and open pores

The shape of isotherm obtained can often provide insight into the interactions between the adsorbent and adsorbate, and several isotherm models have been developed to aid interpretation of this data.

3.3.2 Langmuir Isotherm Model

The Langmuir isotherm model was proposed by Irving Langmuir to describe the adsorption of a gas onto a surface at constant temperature, and is based on three main assumptions [9]:

- The adsorbent surface is composed of a two-dimensional array of adsorption sites, which are energetically homogenous (sites are energetically equivalent).
- Only one molecule can adsorb onto each site, and when each site is filled the saturation limit of the adsorbent has been reached, providing monolayer coverage.
- There are no interactions between any of the adsorbed molecules.

Therefore, by defining the total number of sites, and splitting them into occupied and unoccupied sites, the fraction of occupied sites can be defined as follows:

N_m = total number of surface sites

$N_s = N_{ads}$ = number of occupied sites

N_o = number of unoccupied sites

$$\theta = \frac{N_s}{N_m} = \text{fraction of occupied sites} \quad \text{Equation 3.1}$$

In the case of a specific adsorbent, where temperature is constant, then N_m is constant but N_s varies with pressure (or concentration in the case of liquid systems). The rate of adsorption

can be described by the chance that a molecule collides with an unoccupied site, and the rate of desorption by the number of occupied sites. Thus:

Rate of adsorption = collision rate x chance of unoccupied site

k_{ads} = rate constant of adsorption (bar^{-1})

P = pressure (bar)

Rate of adsorption = $k_{ads} * P(1 - \theta)$

And:

Rate of desorption = $k_{des} * \theta$

k_{des} = rate constant of desorption (unitless)

When the system is at equilibrium, the rate of adsorption and desorption is equal, therefore:

$$k_{ads} * P(1 - \theta) = k_{des} * \theta \quad \text{Equation 3.2}$$

$$k_{ads} * P - k_{ads} * P * \theta = k_{des} * \theta$$

Allowing the equilibrium constant for the system to be defined and substituted in:

$$\text{Equilibrium constant} = K = \frac{k_{ads}}{k_{des}} \text{ (bar}^{-1}\text{)} \quad \text{Equation 3.3}$$

$$K * P = \theta(K * P + 1)$$

$$\theta = \frac{K * P}{K * P + 1} \quad \text{Equation 3.4}$$

Recalling Equation 3.1, the fractional coverage can also be defined as:

$$\theta = \frac{n_s}{n_m} \quad \text{Equation 3.5}$$

Where:

n_s = moles of gas adsorbed onto the surface at pressure P (mmol/g)

n_m = monolayer adsorption capacity of the adsorbent (mmol/g)

$$n_s = \frac{n_m * K * P}{K * P + 1} \quad \text{Equation 3.6}$$

Equation 3.6 is the conventional form of the Langmuir equation, and can be applied to both gaseous and liquid phase systems; for liquid systems, pressure terms would be replaced for concentration terms.

3.3.3 Brunauer-Emmett-Teller Isotherm Model

The Brunauer-Emmett-Teller (BET) isotherm arises from an extension of the Langmuir isotherm to adjust for when it fails in reality; namely, when there is high surface coverage the model does not match with collected experimental results, and it does not consider situations when the adsorbed material acts as a surface for further adsorption [10]. The new developed theory therefore accounts for both these situations through the following assumptions:

- The adsorbent surface is composed of an array of adsorption sites equal in energy – there is constant adsorption enthalpy in this layer regardless of surface coverage, equal to ΔH_A .
- Adsorption in the monolayer only occurs on these sites.
- Adsorbed molecules do not interact with any neighbouring molecules.
- Multilayer adsorption can occur.
- Adsorption enthalpy in the second and any subsequent layers is equal to the heat of liquefaction, ΔH_L .
- Adsorption and desorption can only occur from or on to exposed adsorption sites.

The full BET equation is shown in Equation 3.7:

$$\frac{P}{n(P_0 - P)} = \frac{1}{n_m} + \left[\frac{(c - 1)}{n_m * c} * \frac{P}{P_0} \right] \quad \text{Equation 3.7}$$

Where:

P = pressure (bar)

P_0 = saturation vapour pressure (bar)

n = moles of gas adsorbed at pressure P (mmol/g)

n_m = monolayer adsorption capacity of the adsorbent (mmol/g)

c = dimensionless constant, related to adsorption energy

$$c = \exp\left(\frac{|\Delta H_A| - |\Delta H_L|}{RT}\right) \quad \text{Equation 3.8}$$

Where:

ΔH_A = heat of adsorption of the first adsorbed layer (J/mol)

ΔH_L = heat of adsorption of second and any subsequent multilayers (J/mol)

The BET model is useful for predictions of surface area of microporous materials, which is discussed further in Section 3.6. It is subject to failing at both high (over-estimation) and low (under-estimation) pressures, therefore when being used for evaluation the appropriate pressure range to use is $0.05 < \frac{P}{P_0} < 0.3$ [5].

3.3.4 Freundlich Isotherm Model

The Freundlich isotherm model was developed empirically by Herbert Freundlich in order to account for heterogeneity of adsorbent surfaces, based on the assumption that the enthalpy of adsorption varies exponentially with surface coverage [11]. The surface heterogeneity may be caused by different chemical moieties existing on the surface of the adsorbent, interactions between the adsorbate and the adsorbent, and/or adsorbate-adsorbate interactions.

The model is based on the following six assumptions:

- The adsorbent surface is composed of an array of adsorption sites that are heterogenous in energy.
- Adsorption in the monolayer only occurs on these sites.
- Adsorbed molecules have the potential to interact with any neighbouring molecules.
- Multilayer adsorption can occur on molecules in the monolayer.
- Adsorption enthalpy changes logarithmically with increase in pressure.
- Adsorption and desorption can only occur from or on to exposed adsorption sites.

The Freundlich equation can be seen in Equation 3.9:

$$q_e = K_F * P^{\frac{1}{n_F}} \quad \text{Equation 3.9}$$

Where:

q_e = moles of gas adsorbed at pressure P (mmol/g)

P = pressure (bar)

K_F = Freundlich isotherm constant (mmol/g bar^{-1/n_F})

$\frac{1}{n_F}$ = heterogeneity factor (dimensionless)

The Freundlich constant is related to the magnitude of the driving force for adsorption; thus, the higher the driving force, the higher the constant. The heterogeneity factor is representative of the affinity for adsorption between the adsorbent and the adsorbate molecules [12]. The smaller the factor, the more heterogeneity of the adsorption sites on the adsorbent. Numerically, the values for $\frac{1}{n_F}$ can be described as follows:

- < 1 indicates poor adsorption characteristics and lack of affinity.
- 1 – 2 indicates moderate affinity.

- 2 – 10 indicates good affinity and thus good adsorption characteristics.

This model has limitations due to the fact it fails at low pressures by not obeying Henry's Law, and fails at high pressures as it does not reach a theoretical adsorption maximum.

3.3.5 Temkin Isotherm Model

Similar to the Freundlich isotherm model, the Temkin isotherm model is an empirically developed model proposed by Mikhail Temkin, which attempts to account for heterogeneity on the surface of adsorbents. It differs from Freundlich's model as it assumes there is a linear distribution of adsorption site energies. It too accounts for indirect adsorbate-adsorbate interactions [12].

It operates on the following six assumptions:

- The adsorbent surface is composed of an array of adsorption sites that are heterogenous in energy.
- Adsorption in the monolayer only occurs on these sites.
- Adsorbed molecules have the potential to interact with any neighbouring molecules.
- Multilayer adsorption can occur on molecules in the monolayer.
- Adsorption enthalpy changes linearly with increase in pressure.
- Adsorption and desorption can only occur from or on to exposed adsorption sites.

The Temkin equation can be seen in Equation 3.10:

$$q = n_T * \ln(K_T * P) \quad \text{Equation 3.10}$$

Where:

q = moles of gas adsorbed at pressure P (mmol/g)

P = pressure (bar)

K_T = Temkin isotherm equilibrium binding constant (bar^{-1})

$$n_T = \text{constant (mmol/g)}, \text{ defined as } n_T = \frac{R \cdot T}{b}$$

Where:

R = universal gas constant (8.3145 J/(mol K))

T = temperature (K)

b = Temkin constant (J/mol * g/mmol)

The Temkin isotherm equilibrium binding constant relates to the binding energy of the molecules. This model also fails at high pressures due to the fact it cannot account for an adsorption maximum.

3.3.6 Dual-Site Langmuir Isotherm Model

The Dual-Site Langmuir isotherm model was developed to address the heterogeneity of surface adsorption sites that occurs in reality and causes limitations in the applicability of the original Langmuir isotherm. The simplest example of this model describes the situation where an adsorbent is composed of two different types of adsorption sites, with one type of site having a different enthalpy of adsorption to the other. Thus, when adsorption occurs, the more favourable sites are filled first, then the less favourable sites filled afterwards [13], [14]. The model uses the following assumptions:

- The adsorbent's surface is composed of a two-dimensional array of two different types of adsorption sites which are energetically heterogeneous (one type of site has a different energy to the other type).
- Only one molecule can adsorb onto each site, and when each site is filled the saturation limit of the adsorption has been reached, providing monolayer coverage.
- There are no interactions between any of the adsorbed molecules.

The Dual-Site Langmuir equation can be seen in Equation 3.11:

$$n_s = n_m * \left[(1 - \alpha) * \frac{K_1 * P}{1 + K_1 * P} + \alpha * \frac{K_2 * P}{1 + K_2 * P} \right] \quad \text{Equation 3.11}$$

Where:

n_s = moles of gas adsorbed onto the surface at pressure P (mmol/g)

n_m = monolayer adsorption capacity of the adsorbent (mmol/g)

α = weighting coefficient ($0 < \alpha < 1$)

P = pressure (bar)

$K_1 = \frac{k_{ads,1}}{k_{des,1}}$ = equilibrium constant for site '1' (bar^{-1})

$K_2 = \frac{k_{ads,2}}{k_{des,2}}$ = equilibrium constant for site '2' (bar^{-1})

In reality there will likely be more than two discrete types of adsorption sites, but this model has been found to be effective at describing adsorption in this manner [14]. It will however fail beyond monolayer adsorption, as the conventional Langmuir model does.

3.4 Thermodynamic Theory

3.4.1 Gibbs Free Energy

The Gibbs free energy equation is shown in Equation 3.12, and is a measure of the potential energy in a system that is available to do work. It can be used to determine if a process will occur spontaneously, indicated by $\Delta G < 0$.

$$\Delta G = \Delta H - T\Delta S \quad \text{Equation 3.12}$$

Where:

ΔG = Change in Gibbs free energy of the system, (J/mol)

ΔH = Change in enthalpy of the system, (J/mol)

ΔS = Change in entropy of the system, (J/ (K mol))

T = Temperature of the system (K)

The different combinations of ΔH and ΔS values are portrayed in Figure 3.7. In sorption terms, for adsorption to occur spontaneously then ΔG must be negative. In the case of physisorption, molecules from the bulk phase are seen to adsorb onto the adsorbent surface, which represents an increase in order of the system. This results in ΔS taking a negative value; by convention ΔH must also be negative for the process to occur spontaneously, meaning all physisorption processes are exothermic.

	$\Delta H < 0$	$\Delta H > 0$
$\Delta S > 0$	$\Delta G < 0$ System is spontaneous at all temperatures	System is spontaneous at high temperatures, when $T\Delta S$ is large
$\Delta S < 0$	System is spontaneous at low temperatures, when $T\Delta S$ is small	$\Delta G > 0$ System is non spontaneous at all temperatures

Figure 3.7: Scenarios That Determine the Spontaneity of a Reaction [15]

In the case of chemisorption, ΔH can be positive or negative, depending on the type of bond formation occurring. Exothermic chemisorption can occur when the adsorbate molecule forms a chemical bond with the adsorbent surface, the system becomes more ordered, and heat is released. Conversely, if pre-existing bonds on the surface of the adsorbent need to be broken first before the adsorbate can form a chemical bond, this requires energy to be input into the system; in this case, the system can become more disordered and results in endothermic chemisorption [16].

When the temperature of the system is increased, this causes a decrease in physisorption as per Le Chatelier's principle, and equilibrium moves towards the desorbed state. In contrast, chemisorption can increase or decrease when temperature increases depending on the specific species and reactants involved in the system.

3.4.2 Enthalpy of Adsorption – Van't Hoff Isochore

The enthalpy of adsorption for adsorption onto porous materials can be measured by utilising the adapted van't Hoff equation [17], [18], see Equation 3.13, derived from the Clausius-Clapeyron equation [19]. By plotting multiple isotherms, collected at different temperatures, on the same graph, an isochore can be produced; this is a line which represents the constant surface coverage as temperature and pressure vary. An example of this type of plot is shown in Figure 3.8.

$$\ln P = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad \text{Equation 3.13}$$

Where:

ΔH° = isosteric enthalpy of adsorption (J/mol)

ΔS° = isosteric entropy of adsorption (J/ (K mol))

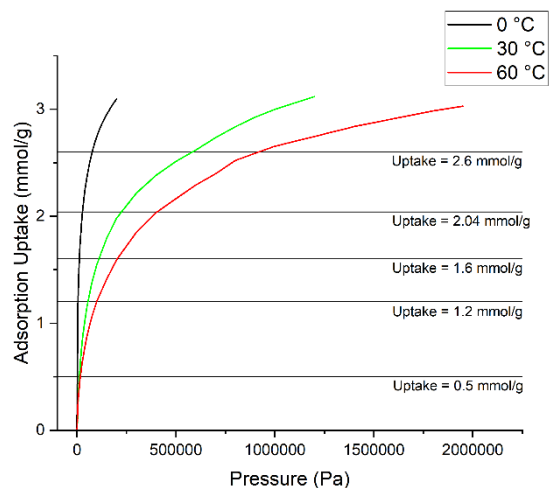


Figure 3.8: Example of van't Hoff Isochores Produced in This Study

In this study for CO₂ adsorption, isotherms were collected at three temperatures (0 °C, 30 °C and 60 °C) which were used to produce isochores. The data collected from each isochore can be used to plot $\ln(P)$ vs $\frac{1}{T}$, an isostere, which then allows a linear regression fit to be applied. From this fit, the gradient can be used to calculate the enthalpy of adsorption and the intercept to find the entropy of adsorption. An example of this plot can be seen in Figure 3.9.

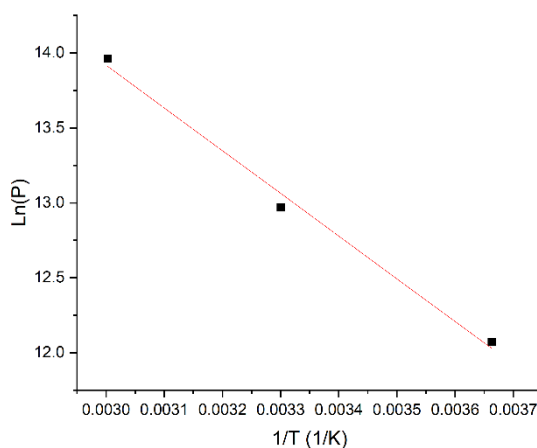


Figure 3.9: Example Isostere Plot of $\ln(P)$ vs $1/T$ Used in This Study

Equation 3.14 and Equation 3.15 are used for the calculation of both enthalpy and entropy of adsorption respectively. Calculating these values for each isochore allows the comparison of enthalpy of adsorption with changing surface coverage.

$$\Delta_{ad}H^{\circ} = -gradient * R \quad \text{Equation 3.14}$$

$$\Delta_{ad}S^{\circ} = -intercept * R \quad \text{Equation 3.15}$$

Where:

$$R = \text{universal gas constant} = 8.3145 \text{ J/(mol K)}$$

3.5 Adsorption Kinetics

Kinetic models can be fitted to data collected at individual pressure points within isotherms to describe the rate at which adsorption occurs at that pressure, and also determine the maximum uptake potential. In this study, two kinetic models were tested: the stretched exponential model and the double exponential model.

3.5.1 Stretched Exponential Model

The stretched exponential model is used to assess adsorption kinetics, using a parameter of β to describe the distributions of relaxation times in the process [20]. The rate constant, k , describes adsorption that has a single rate-limiting step associated with the process, such as pore diffusion [21]. The model can be seen in Equation 3.16 [22]:

$$\frac{M_t}{M_e} = 1 - e^{-(k*t)^{\beta}} \quad \text{Equation 3.16}$$

Where:

$$M_t = \text{mass uptake at time } t \text{ (mg)}$$

$$M_e = \text{mass uptake at equilibrium (mg)}$$

$$t = \text{time (s)}$$

k = rate constant of adsorption process (s^{-1})

β = exponential parameter of adsorption process (unitless), $0 < \beta < 1$

3.5.2 Double Exponential Model

The double exponential model can be applied when it is suspected that there are two modes of diffusion in the adsorption process [23]; in gas adsorption cases this could be a mixture of pore filling coupled with adsorption onto surface functional groups. Similarly, the rate constants, k_1 and k_2 , describe the two rate-determining steps within the process. This model is described by Equation 3.17:

$$\frac{M_t}{M_e} = A_1(1 - \exp(-k_1 * t)) + A_2(1 - \exp(-k_2 * t)) \quad \text{Equation 3.17}$$

Where:

M_t = mass uptake at time t (mg)

M_e = mass uptake at equilibrium (mg)

t = time (s)

k_1 = rate constant of kinetic process 1 (s^{-1})

k_2 = rate constant of kinetic process 2 (s^{-1})

A_1 and A_2 are two unitless weighting components based on the contributions from each of the two kinetic processes, where $A_1 + A_2 = 1$ and $0 < A_1, A_2 < 1$

3.6 Textural Properties Theory

3.6.1 BET Surface Area Method and Rouquerol Correction

The BET model is commonly used to determine the surface area of porous materials, based on N_2 isotherms carried out at -196°C .

Recalling the BET equation:

$$\frac{P}{n(P_0 - P)} = \frac{1}{n_m} + \left[\frac{(c - 1)}{n_m * c} * \frac{P}{P_0} \right] \quad \text{Equation 3.18}$$

By plotting a graph of $\frac{P}{n(P_0 - P)}$ vs $\left(\frac{P}{P_0}\right)$, and applying a linear fit, a gradient and intercept can be found which can in turn be used to calculate c and n_m . The surface area of the sample can then be calculated using Equation 3.19:

$$SSA = n_m * N_A * area_{N_2} \quad \text{Equation 3.19}$$

Where:

SSA = specific surface area calculated via BET method (m^2/g)

n_m = amount of gas adsorbed in monolayer (mol/g)

N_A = number of molecules per mol (6.023×10^{23} molecules/mol)

$area_{N_2}$ = cross sectional area of nitrogen molecule ($1.62 \times 10^{-19} \text{ m}^2/\text{molecule}$)

As discussed in Section 3.3.3, the typical range used for the linearisation of the model is $0.05 < \frac{P}{P_0} < 0.3$; however, it has been reported that this can give erroneous results when used to characterise microporous materials, and produces values for c that are not sensible in reality [24]. To counter this, a microporous correction can be applied, named the Rouquerol correction, which identifies the appropriate pressure range to use for BET analysis for each individual sample, as opposed to using all points lying in the range mentioned above. The Rouquerol function is shown in Equation 3.20:

$$\text{Rouquerol function} = n * \left(1 - \frac{P}{P_0} \right) \quad \text{Equation 3.20}$$

The Rouquerol function can be plotted against $\frac{P}{P_0}$. The following criteria are then used to identify the appropriate points to use for surface area analysis [24]:

- The plot of Rouquerol function vs $\frac{P}{P_0}$ should continuously increase.
- The corresponding BET plot produced from the points identified should be linear, and give a meaningful value of c i.e., should be positive.
- The $\frac{P}{P_0}$ value for the calculated n_m should be found in the range that has been selected for the BET analysis.
- If the third statement of the above criteria is not met, then the value for $\frac{P}{P_0}$ should be able to be recalculated from c using the BET equation and setting $n = n_m$.

An example of the test Rouquerol plot is shown in Figure 3.10, with a vertical line shown corresponding to the last point where the gradient is increasing.

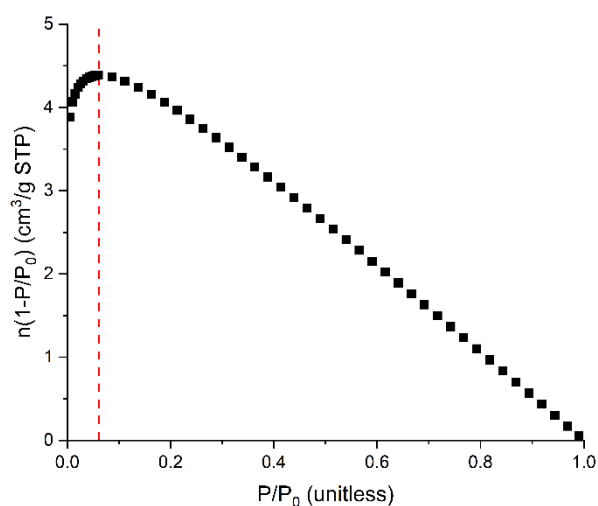


Figure 3.10: Example of a Rouquerol Plot Used in This Study

The corresponding points which should be used for BET analysis based on this method are shown in Figure 3.11, and the points that would conventionally be used for BET analysis are shown in Figure 3.12 for comparison. A linear fit has been applied to both sets of points; it is

clear to see that the points selected from the finding of the Rouquerol correction give a better fit, and thus, justify the use of the Rouquerol correction in this study.

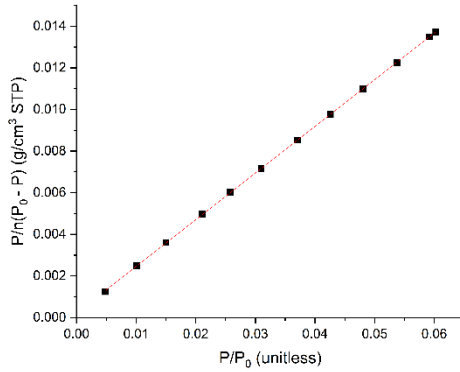


Figure 3.11: Points used for BET Analysis Based on Rouquerol Correction

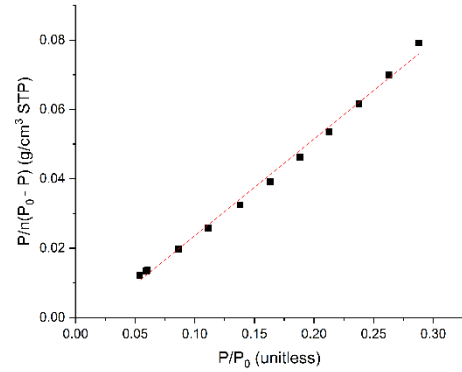


Figure 3.12: Points That Would Typically Be Used for BET Analysis

3.6.2 The t-plot Method

The t-plot method was developed by De Boer and Lippens and can be used to assess the microporosity of a material [25]. The method relates the amount of gas adsorbed to the average thickness of the layer of gas adsorbed on the sample, allowing a curve called the t-plot to be created [26]. Note that to create a t-plot curve, an isotherm from a non-porous reference material that is similar in character to the sample is required; for chars it is common practice to use the carbon black STSA reference curve, from standard ASTM D6556 [27]. The equation for carbon black thickness layer is shown by Equation 3.21:

$$t = 0.88 \left(\frac{P}{P_0} \right)^2 + 6.45 \left(\frac{P}{P_0} \right) + 2.98 \quad \text{Equation 3.21}$$

Where:

t = statistical layer thickness of N_2 on carbon black (Å)

P = pressure (bar)

P_0 = saturation vapour pressure (bar)

The volume of gas adsorbed for each $\frac{P}{P_0}$ can be plotted against the corresponding calculated thickness to give the t-plot curve. An example of this is shown in Figure 3.13. The range of thickness values used for carbon black is 3.5 – 5 Å, highlighted by the red lines [28].

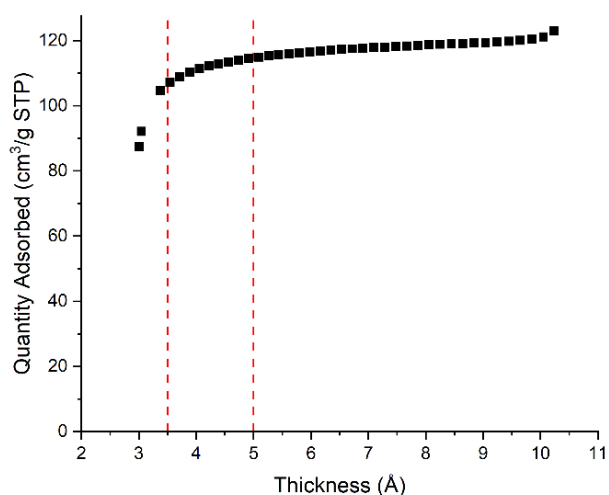


Figure 3.13: Example of t-plot Curve Used in This Study

In the case of a non-porous material, this curve would be a straight line through the origin. For mesoporous materials the curve would be seen to deviate from a straight line through the origin in the vertical direction, and for microporous materials it would deviate in the horizontal direction; examples of this are shown in Figure 3.14, and subsequently it can be said that Figure 3.13 is example of the microporous deviation.

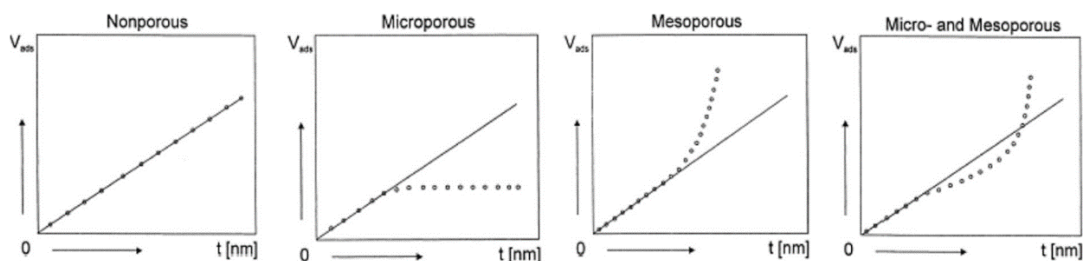


Figure 3.14: Example t-plots of Different Porous Materials [29]

The points lying in the range of 3.5 - 5 Å can be used to fit a linear plot, shown in Figure 3.15, of which the gradient (units of cm³/(g Å) STP) can be used to find the external surface area of the sample, shown in Equation 3.22.

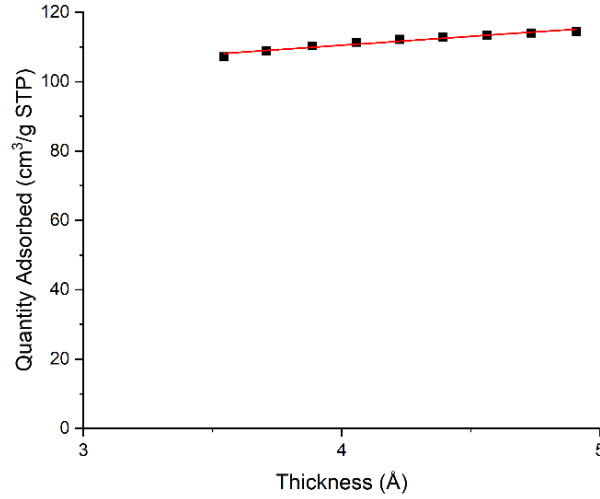


Figure 3.15: Example of a Linear Fit to t-plot Range for Microporous Carbon Sample

$$EXSA = gradient * \frac{1 \text{ Å}}{1 * 10^{10} m} * \frac{1 m^3}{100^3 cm^3} * \frac{\rho_G}{\rho_L} \quad \text{Equation 3.22}$$

Where the conversion for Å to m, and cm³ to m³ are included and:

$$EXSA = \text{external surface area (m}^2\text{/g)}$$

$$\rho_G = \text{density of the gas adsorbed} = 0.00125 \text{ g/cm}^3 \text{ for nitrogen}$$

$$\rho_L = \text{density of the liquid adsorbent} = 0.808 \text{ g/cm}^3 \text{ for nitrogen}$$

The micropore surface area (MSA_{t-plot} (m²/g)) can then be calculated using $EXSA$ and the Rouquerol corrected surface area by Equation 3.23:

$$MSA_{t-plot} = SSA - EXSA \quad \text{Equation 3.23}$$

The micropore volume of the sample (V_{t-plot} (cm³/g)) can likewise be calculated from the intercept of this linear fit, shown in Equation 3.24:

$$V_{t-plot} = intercept * \frac{\rho_G}{\rho_L} \quad \text{Equation 3.24}$$

3.6.3 Polanyi Adsorption Potential

When considering CO₂ adsorption, ultramicroporosity is one of the key characteristics that must be possessed by adsorbent materials. This has been seen in previous studies assessing CO₂ adsorption on char materials [30], [31], [32], and can be attributed to the overlapping electric potential fields arising from pore walls [33]. In turn, this can be explained through examination of Polanyi adsorption potential theory. This was developed by Michael Polanyi to describe multilayer adsorption on non-porous materials [34], but has, in time, been adapted to describe adsorption on microporous solids. This model assumes that adsorbed molecules exist in a potential energy gradient, so in the space above the adsorbent surface there exists a number of equipotential surfaces, which each contain a finite adsorption volume, n_i . For the phenomenon of adsorption to occur, these adsorption volumes must be filled with potential energy of E_i until $E_i = 0$, which, in turn, leads to the adsorption volume being filled. At this point, n_i is equal to its maximum value of n_o . As such, the adsorption energy is related to adsorption volume. The adsorption potential is then defined as the work required for the adsorbed molecule to move from the gas phase to the adsorbed phase.

In terms of CO₂ adsorption, as ultramicropores are of a similar size to the CO₂ molecules, this results in the electric potential fields from opposing walls coalescing and enhancing the depth of the potential wells which increases the attraction of CO₂ towards these pores. This has also been seen for N₂ and CH₄ adsorption in narrow slit-shaped pores, where the narrowing of the pores causes potential wells to interact and, thus, increase the adsorption potential in these smaller pores [35]; the example of this for N₂ molecules can be seen in Figure 3.16. This

results in Type I isotherms (discussed in Section 3.3.1) being collected during adsorption measurements of these materials.

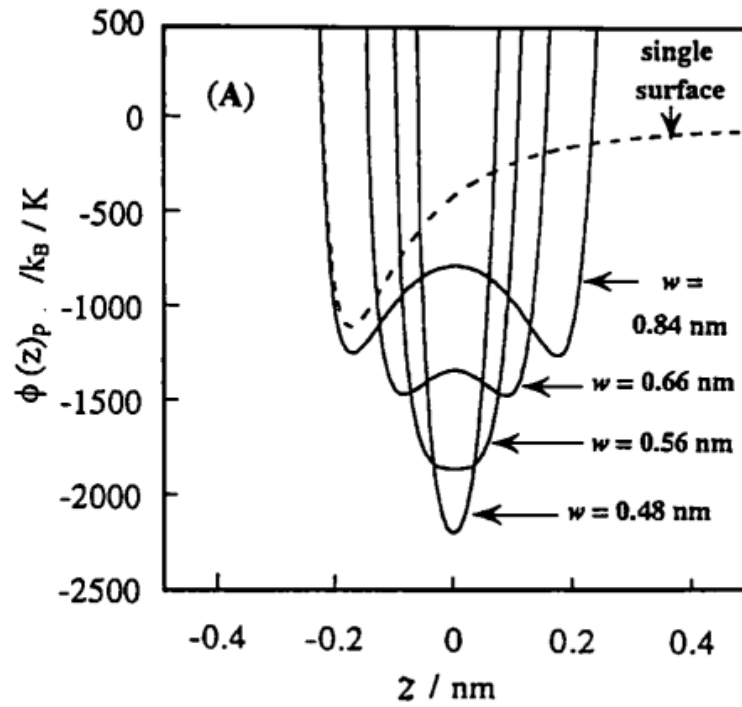


Figure 3.16: Interaction Potential Profile of N_2 Within A Graphitic Slit Pore as A Function of Pore Width (w) [35]

Polanyi theory also gives rise to the pore filling mechanism that is typically applied to microporous materials, and is described in the following section.

3.6.4 Dubinin-Radushkevich Method

The Dubinin-Radushkevich (DR) method was developed to describe adsorption in microporous materials [36]; it proposes that adsorption occurs in micropores by pore filling instead of layer upon layer adsorption that is assumed in other models such as BET [37]. In order to consider this, the extent of micropore filling must be defined.

$$\theta = \frac{w}{w_o} \quad \text{Equation 3.25}$$

Where:

w = micropore volume filled

w_o = total micropore volume

As ΔG can be stated as a function of the adsorbed amount:

$$-\Delta G = f(\theta) \quad \text{Equation 3.26}$$

$$\theta = \phi\left(-\frac{\Delta G}{\beta}\right) \quad \text{Equation 3.27}$$

Upon the assumption of a Gaussian pore size distribution, Dubinin and Radushkevich proposed that the micropore filling could be described by Equation 3.28.

$$\theta = \exp\left(-\frac{k}{\beta^2} (-\Delta G)^2\right) \quad \text{Equation 3.28}$$

Where:

k = an indication of the breadth of the Gaussian distribution

By combining Equation 3.25, Equation 3.27 and Equation 3.28, the micropore volume filled can be described by Equation 3.29.

$$w = w_o * \exp\left(-k \left(\frac{A}{\beta}\right)^2\right) \quad \text{Equation 3.29}$$

Where:

A = Polanyi Adsorption Potential, related to ΔG

k = Pore Size Distribution Characteristic Parameter

β = Adsorbate Affinity Coefficient, which enables comparison of characteristic curves of θ vs ΔG for various adsorbates with a standard reference (for which Dubinin chose benzene).

Combining Polanyi Adsorption Potential, Equation 3.30, with Equation 3.29, gives Equation 3.31.

$$A = RT * \ln \left(\frac{P_0}{P} \right) \quad \text{Equation 3.30}$$

$$w = w_o * \exp \left(-k \left(\frac{RT}{\beta} \right)^2 \left(\ln \frac{P_0}{P} \right)^2 \right) \quad \text{Equation 3.31}$$

Equation 3.31 can be simplified to Equation 3.32.

$$\frac{w}{w_o} = \exp \left(-B \left(\frac{T}{\beta} \right)^2 \left(\log \frac{P_0}{P} \right)^2 \right) \quad \text{Equation 3.32}$$

Where:

$$B = (2.3026R)^2 * k$$

Applying a linearisation transformation to Equation 3.32 yields Equation 3.33.

$$\log w = \log w_o - D * \log^2 \left(\frac{P_0}{P} \right) \quad \text{Equation 3.33}$$

Where:

$$D = B \left(\frac{T}{\beta} \right)^2$$

The adsorbed volume can be related to the adsorbed amount through Equation 3.34, which can be used to give the common form of the DR equation shown in Equation 3.35.

$$w = \frac{n}{\rho_a} \quad \text{Equation 3.34}$$

Where:

ρ_a = density of the adsorbed phase

$$\log(n) = \log(n_0) - D_{DR} * \log^2 \left(\frac{P_0}{P} \right) \quad \text{Equation 3.35}$$

Where:

n = amount of gas adsorbed in micropores at pressure P (mmol/g)

n_0 = total capacity for gas to adsorb in micropores (limiting micropore capacity)
(mmol/g)

D_{DR} = constant of D-R equation (log(mmol/g))

P = pressure (bar)

P_0 = saturation vapour pressure (bar)

The D_{DR} constant is related to the pore size distribution of the adsorbent, which is assumed to follow a Gaussian distribution.

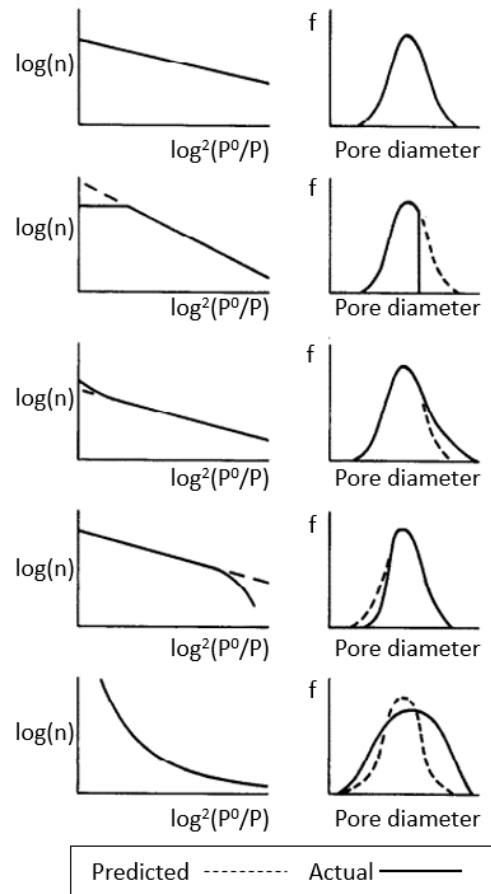


Figure 3.17: Variations of the DR Plot (left), and the Associated Difference in Pore Size Distributions (right) [38]

By plotting experimental data of $\log(n)$ vs $\log^2\left(\frac{P_0}{P}\right)$, a linear plot can be fitted which allows the calculation of total micropore volume (n_0) [39]. If the produced plot deviates from a straight line, this allows for further analysis as it can indicate differences in pore size

distribution of the material, see Figure 3.17. As discussed in Section 3.6.3, as ultramicropores are expected to be one of the defining factors that will influence the adsorption of CO₂ in the materials produced in this study, the micropore analysis provided through the DR method will be vital in the characterisation of these materials. As such, there is a large focus on this data throughout the project.

An example of the DR plot used in this study is shown in Figure 3.18. As can be seen from the high-pressure region of the graph (low $\frac{P_0}{P}$), the DR fit deviates from a straight line and curves in the vertical direction; this implies that the sample contains more larger micropores than would be predicted by the normal distribution [38].

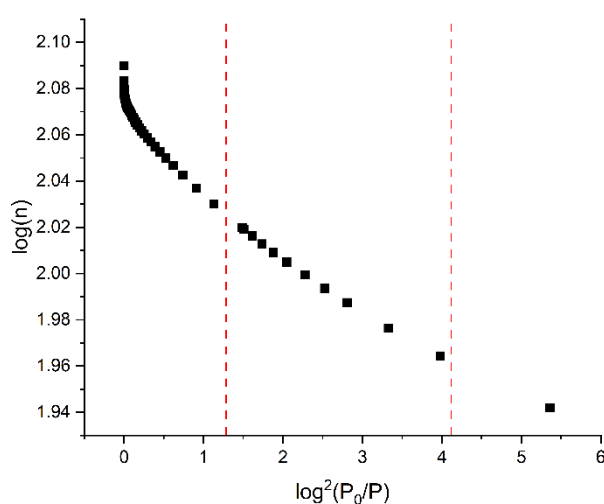


Figure 3.18: Example of DR Plot Used in This Study

Fitting a linear regression to the selected points will give a plot, see Figure 3.19, where the intercept can be used to find the limiting micropore capacity, and in turn this can be used to calculate the micropore volume, using Equation 3.36, Equation 3.37 and Equation 3.38. (Note that limiting micropore capacity can be converted from cm³/g STP to mol/g using the information that 1 mole of an ideal gas occupies 22,400 cm³ at STP).

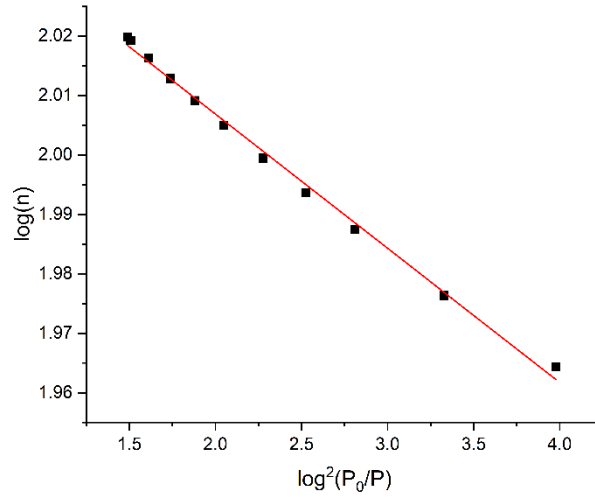


Figure 3.19: Example of a Linear Fit to DR Range used in This Study

$$n_0 = 10^{\text{Intercept}} \quad \text{Equation 3.36}$$

$$n_0 \left(\frac{\text{mol}}{\text{g}} \right) = n_0 \left(\frac{\text{cm}^3}{\text{g}} \text{STP} \right) * \frac{1 \text{ mol}}{22400 \text{ cm}^3} \quad \text{Equation 3.37}$$

$$V_{DR} = \frac{n_0}{\rho_M} \quad \text{Equation 3.38}$$

Where:

n_0 = total capacity for gas to adsorb in micropores (/limiting micropore capacity)
(cm³/g or mol/g)

V_{DR} = micropore volume calculated via DR method (cm³/g)

ρ_M = molar density (mol/cm³) (0.0289 mol/cm³ for N₂ and 0.0232 mol/cm³ for CO₂)

The equivalent micropore area can also be calculated from the limiting micropore capacity using Equation 3.39. Throughout this thesis, the DR equivalent micropore surface area is commonly referred to as the 'DR surface area'.

$$SSA_{DR} = n_0 * N_A * \text{area}_M \quad \text{Equation 3.39}$$

Where:

SSA_{DR} = equivalent micropore area calculated via DR method (m²/g)

n_0 = limiting micropore capacity (mol/g)

N_A = number of molecules per mol (6.023x10²³ molecules/mol)

$area_M$ = cross-sectional area of adsorbate molecule (m²/molecule)

Note that $area_M$ is 1.62 x10⁻¹⁹ m²/molecule for N₂ and 1.7x10⁻¹⁹ m²/molecule for CO₂.

The average micropore width can also be calculated from the characteristic energy, E_0 , which itself is derived from the DR linear regression, using Equation 3.40 [40].

$$L = \frac{10.8}{E_0 - 11.4} \quad \text{Equation 3.40}$$

Where:

L = average micropore width (nm)

E_0 = characteristic energy of the carbon material (kJ/mol)

It should be noted that the DR method has been found to overestimate adsorption capacity at low relative pressures ($< 0.0015 \frac{P}{P^0}$) [41], and also when there is significant skewing of the DR plot away from linearity [42].

3.7 Uncertainty Calculations

The uncertainties in the presented textural properties, such as surface area and pore volume, were calculated through propagation of the uncertainties associated with the linear regression, for each individual property. The error in N₂ BET surface area calculations were found using Equation 3.41 [28]. This same type of method was used for t-plot microporous surface area, microporous volume and DR microporous volume calculations, with the equation altered depending on whether the gradient value, intercept value, or both, were used in the calculations. These can be seen in Equation 3.42 to Equation 3.47 [28].

$$\sigma_{SSA} = \frac{SSA * \sqrt{V_{gg} + V_{ii} + 2V_{gi}}}{gradient + intercept} \quad \text{Equation 3.41}$$

Where:

σ_{SSA} = propagated uncertainty in the specific surface area (m²/g)

SSA = specific surface area (m²/g)

V_{gg} = variance in the gradient of the straight line fit (g/cm³ STP)²

V_{ii} = variance in the intercept of the straight line fit (g/cm³ STP)²

V_{gi} = covariance between the fitted gradient and intercept (g/cm³ STP)²

$gradient$ = gradient of the straight line fit (g/cm³ STP)

$intercept$ = intercept of the straight line fit (g/cm³ STP)

Note that any surface area value below 10 m²/g was reported as 0 m²/g due to the intrinsic error in the equipment, and similarly any pore volume below 0.001 cm³/g was reported as 0 cm³/g for the same reason.

$$\sigma_{t-plot\ XSA} = \frac{t - plot_{XSA} * \sqrt{\sigma_g^2}}{gradient} \quad \text{Equation 3.42}$$

$$\sigma_{t-plot\ MSA} = \sqrt{\sigma_{t-plot\ XSA}^2 + \sigma_{SSA}^2} \quad \text{Equation 3.43}$$

Where:

σ_g = standard error of the gradient from the straight line fit (g/cm³ STP)

$\sigma_{t-plot\ XSA}$ = propagated standard uncertainty in the t-plot external surface area (m²/g)

$t - plot_{XSA}$ = t-plot external surface area (m²/g)

$\sigma_{t-plot\ MSA}$ = uncertainty in the t-plot microporous surface area (m²/g)

$$\sigma_{t-plot\ V} = \frac{V_{t-plot} * \sqrt{\sigma_i^2}}{intercept} \quad \text{Equation 3.44}$$

Where:

σ_i = standard error of the intercept from the straight line fit (g/cm³ STP)

$\sigma_{t-plot\ V}$ = uncertainty in the t-plot micropore volume (cm³/g)

V_{t-plot} = t-plot micropore volume (cm³/g)

$$\sigma_{n_0} = n_0 * (\ln 10) * \sigma_i \quad \text{Equation 3.45}$$

$$\sigma_{V\ DR} = \frac{\sigma_{n_0}}{\rho_M} \quad \text{Equation 3.46}$$

$$\sigma_{SSA\ DR} = \sigma_{n_0} * N_A * area_M \quad \text{Equation 3.47}$$

Where:

σ_{n_0} = propagated standard uncertainty in limiting micropore capacity (mmol/g)

n_0 = limiting micropore capacity (mmol/g)

$\sigma_{V\ DR}$ = propagated standard uncertainty in DR micropore volume (cm³/g)

ρ_M = molar density (mol/cm³)

$\sigma_{SSA\ DR}$ = propagated standard uncertainty in DR equivalent microporous surface area (m²/g)

N_A = number of molecules per mol (6.023x10²³ molecules/mol)

$area_M$ = cross-sectional area of adsorbate molecule (m²/molecule)

3.8 References

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4 Experimental Methodology Chapter

This chapter details the synthesis methods used to produce nitrogen-doped and non-doped biochars and hydrochars, and the characterisation methods applied to them. The biochars were produced through a single-stage pyrolysis-activation process using a furnace, while the hydrochars underwent hydrothermal carbonisation (HTC) in a sealed autoclave, and subsequent activation through pyrolysis using a furnace. The conditions used within each production process were instructed from assessment of literature on the subject. The range of experiments conducted were chosen using Design of Experiments (DoE) based rationale, and a DoE methodology followed in order to optimise the selected responses.

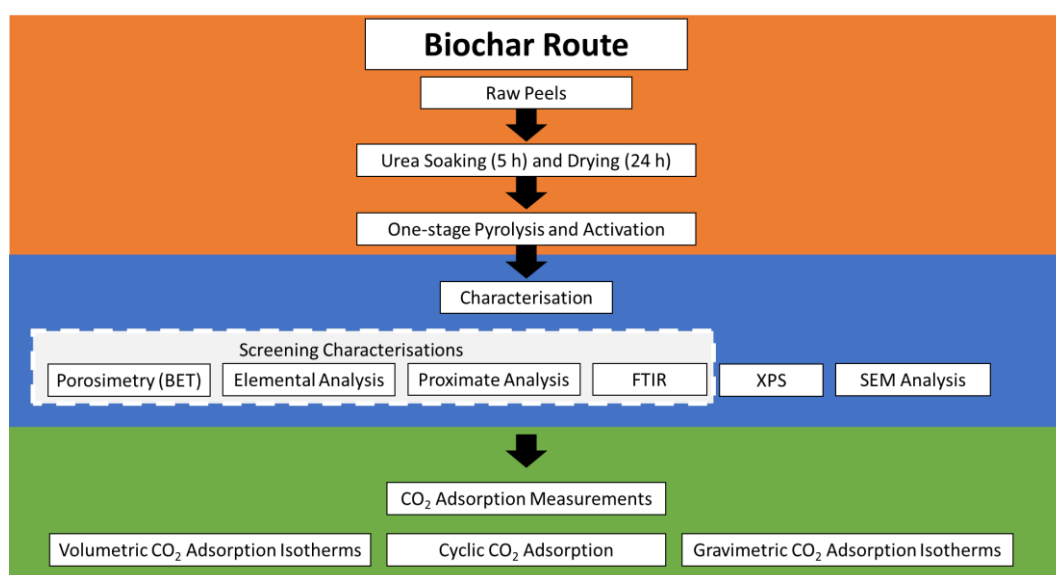


Figure 4.1: Visualisation of Experimental Production and Characterisation of Biochars Produced in this Study

Figure 4.1 and Figure 4.2 show the full process of production and characterisation of the biochars and hydrochars respectively. For both materials, the samples produced in the screening DoE were characterised for specific properties that were used to inform the DoE statistical analysis. Next, the samples produced in the optimisation stage were subject to full characterisation. The results from these tests were then used to determine the most

promising samples for further analysis. This allowed the CO₂ adsorption capacity of a selection of both biochars and hydrochars to be measured using more specialised techniques.

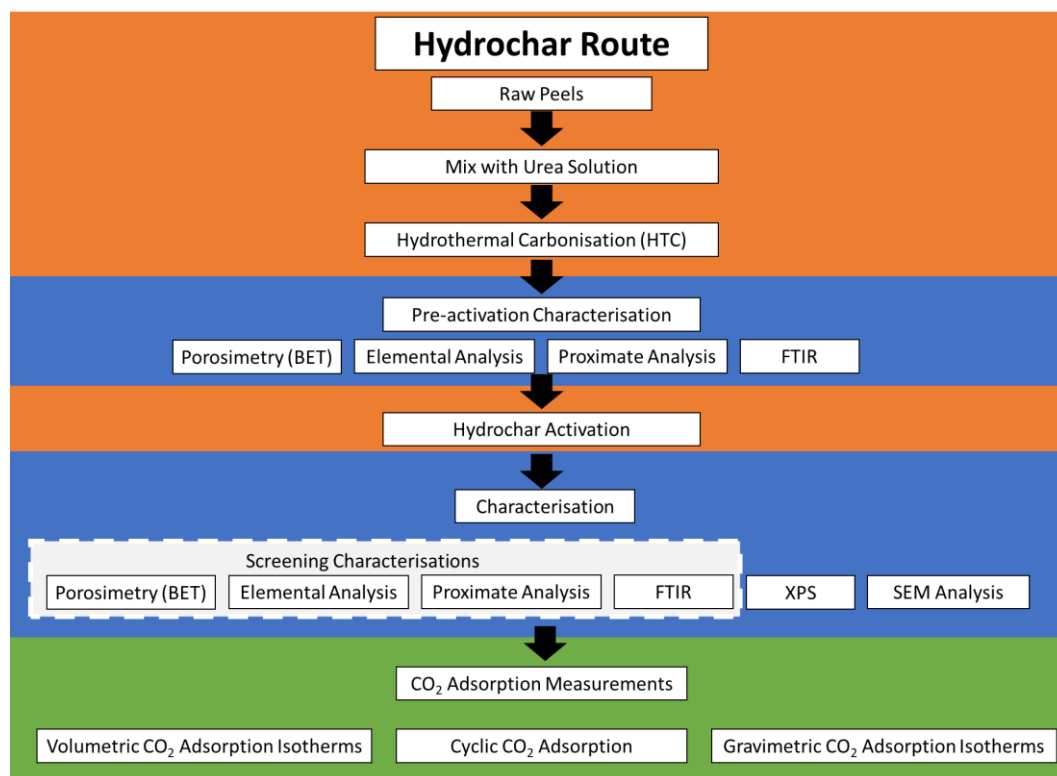


Figure 4.2: Visualisation of Experimental Production and Characterisation of Hydrochars Produced in this Study

4.1 Design of Experiment Methodology

4.1.1 Design of Experiments Explained

DoE is a statistical method used to test the response of a system to a selection of process parameters. It reduces the number of experiments required, as multiple parameters are varied at a time, compared with traditional methods of varying one factor at a time; see Figure 2.5, Chapter 2 for a visual representation of this. DoE can also be used to quantify both the impact that each parameter, and the interactions between parameters, have on the system's response [1]. This study uses DoE for both the screening and optimisation stages,

with the optimisation results used to create surface response models. These are statistical models that use the experimental results to predict maximum and minimum points within a defined range. In this case, they can be used to find the process parameters that can be used to create a char that is optimal for a chosen response i.e., to create a char with the highest surface area.

There are three important terminologies for DoE: factors, levels and responses. Factors are the process parameters that can be changed, and are being tested to determine if they are influential. Factors can be defined as continuous, in which they can be any value from within a chosen range i.e., temperature, or discrete, where they are limited to specific set values i.e., colour. Levels are the different values of each factor; for example, temperature could be a factor in a DoE, and tested at two levels of 100 °C and 200 °C. Finally, there is response, which is the parameter being measured and assessed, such as the yield or performance of a product.

Full factorial designs were used for each stage: screening and design. This was undertaken to ensure there was no confounding seen between main factor effects and two-factor interaction effects. To ensure a manageable number of experiments were planned, the factors chosen to be investigated were tested at two levels in the screening stage, rising to five levels in the optimisation stage.

An initial screening stage was used to test different process parameters in the production of biochar and how they affected the system responses, i.e., the characteristics of the biochar. Analysis of results from this stage then led to an optimisation stage being carried out, which varied the significant factors, as determined in the screening stage, to find optimal conditions to give the 'best' char based on the chosen responses.

The Minitab Statistical Software 22 programme was used to assist in the analysis of DoE. This allowed for Analysis of Variance (ANOVA) and regression equations to be produced, which in turn allowed for the assessment of each model that was produced for the system responses. The use of regression equations allowed for one optimal char to be produced for each response.

4.1.2 Screening Designs

When producing the biochars, four factors were identified for testing in the screening stage. These were: pyrolysis temperature, pyrolysis residence time, peel type, and CO₂ gas flowrate. These were tested at two levels in this stage; the numerical values for each level and the rationale behind choosing them are discussed in Chapter 5. This led to 16 experiments being carried out, as per no. of experiments = no. of levels^{no. of factors} = 2⁴ = 16.

For hydrochar production, again four factors were chosen for testing at two levels during the screening stage: HTC temperature, HTC residence time, peel type, and activation temperature. Levels and experiment details are described in Chapter 6, with an identical number of 16 experiments carried out.

4.1.3 Optimisation Designs

Analysis of biochar screening results reduced the factors to three: pyrolysis temperature, pyrolysis residence time, and peel type. A circumscribed (CCC) design was chosen and the two continuous factors, temperature and time, were tested at five levels within this, while peel type remained the same (orange and mandarin). This led to 18 experiments being carried out. As there is a discrete factor, i.e. peel type; the experiments for each peel type are, therefore, used to create two different models. Thus, the optimisation DoE can be used to assess the influence of the three factors being tested at this stage, and also to create individual biochar optimisation models for each peel type. The levels of the two continuous

factors used in this stage are determined by the alpha value of the design, which is calculated as follows: DoE alpha = [no. of initial levels tested^{no. of continuous factors}]^{1/4}.

Note that this alpha is different to the alpha related to ANOVA calculations; therefore, the alpha discussed in this section will be referred to as the DoE alpha [2]. As there are two continuous factors being tested, and they were tested at two levels in the initial screening design, this means the DoE alpha is found to be: DoE alpha = $(2^2)^{1/4} = 4^{1/4} = 1.414$.

For the hydrochar optimisation stage a similar outcome was reached; the screening stage determined that the three factors of HTC temperature, peel type and activation temperature were influential, while HTC residence time was not. As a result, another CCC design was created, with both temperatures (the continuous factors) tested at five levels and peel type remaining as orange and mandarin. Again, 18 experiments were carried out from this, and due to there being two continuous factors found to be significant from the screening design, the DoE alpha for this design was also calculated to be 1.414.

4.1.4 Final Optimisation Process

After the optimisation biochars were characterised, and their response results input into the Minitab software, this allowed a full surface response model to be created for each of the three chosen responses. By utilising this, it was then possible to create six 'optimal' biochars, one made from each peel type for each response. In theory, the biochar for each response should give the highest or best possible result i.e., the orange-derived biochar produced using the micropore area response model should give the highest micropore area from all the orange-derived biochars tested.

This same method was followed for the production of six 'optimal' hydrochars.

4.2 Biochar Synthesis

Biochars were produced from two types of feedstocks: orange peels (*Navel Fukumoto*) and mandarin peels (*Tang Gold Spain* and *Nardcott*). This allowed for a comparison of two similar feedstocks, which are from the same family of plants, the *Rutaceae* family [3]. Nitrogen doping was carried out on the relevant samples using prepared urea solutions. A variety of pyrolysis conditions were used, as determined by the DoE methodology, allowing estimation of optimal conditions for tailored production of biochar for CO₂ adsorption. As it was not possible to measure CO₂ adsorption isotherms for each biochar produced, N₂ sorption isotherms were instead run and used as proxies for CO₂ adsorption. This meant that microporous surface area calculated from the N₂ isotherm data were designated as a measure of how effective the biochars would be for CO₂ adsorption, as microporous surface area is well referenced in literature as being key to achieving high CO₂ capacity.

4.2.1 Biomass Preparation

Solutions of 3 M urea were prepared by dissolving 180.18 g of solid urea (98+ %, Thermo Scientific Chemicals) in 1 L of deionised water. These solutions, if not being used instantly, were stored in a dark cupboard to prevent urea degradation, for a maximum of three days.

The relevant species of oranges and mandarins were bought from Tesco Supermarkets in Falkirk, and the peels collected from the fruits. The peels were initially blended using a food blender into small pieces of approximately 1 mm x 0.5 mm, before being washed in deionised water to remove any debris and potential chemical residues from transport or previous processing.

For peel being used for production of non-doped biochar, after washing, the peels were drained of water before being dried in an oven at 80 °C for 24 h. If the peels were for production of nitrogen-doped biochars, the washed peels were transferred to a beaker and

mixed with urea solution. The volume of urea solution was always determined on a 1:1 mass basis with respect to the mass of peels (recorded before washing). For example, for a mass of 90 g of peels, this would equate to 90 g of urea, and based on a 3 M urea solution would equate to 0.5 L of solution.

1 g raw peel: 1 g urea in solution

$$n_{Urea} = \frac{M}{GFM} = \frac{90}{60.06} = 1.50 \text{ mol (3 sig. fig.)}$$

$$V_{Urea \text{ solution}} = \frac{n}{c} = \frac{1.50}{3} = 0.5 \text{ L}$$

The mixture of peel and urea solution was stirred for 5 h at room temperature in a sealed container, before the peels were drained and dried in an oven at 80 °C for 24 h.

4.2.2 Pyrolysis Process

The biochars were produced by the process of pyrolysis using a Lenton tube furnace, model 12/38/500. The ceramic tube used in the furnace had dimensions of 750 mm length and 25 mm inner diameter. Pyrolysis was carried out using the pre-determined conditions, and the produced biochar was collected at the end of each run, after cooling.

For the screening stage, the four variables investigated at two levels each were: pyrolysis temperature (500 and 800 °C), pyrolysis time (0.5 and 3 h), peel type (orange and mandarin) and CO₂ gas flowrate (100 and 400 mL/min). These were determined based on a review of literature, as discussed in Chapter 2. This resulted in the production of 16 biochars. A ramp rate of 15 °C/min was used for each experiment.

From the analysis of the screening results obtained, CO₂ gas flowrate was deemed not significant in the study and was set at 400 mL/min for any future experiments. This was based on reports in the literature [4], that increased gas flow resulted in increased volatilisation, to

a point, and the increased gas flow should also facilitate removal of gaseous volatiles and provide cooling of the sample. Of the three remaining variables, the two continuous factors were tested at a wider range of levels based on the circumscribed DoE selected, see Table 4.1. The lower level of pyrolysis temperature was increased, as it was clear that 500 °C produced no discernible porosity within the samples, as the Boudouard reaction was not active at this temperature. This gave a total of 18 new biochars produced. The ramp rate of 15 °C/min remained unchanged from the screening stage.

Incorporating these initial levels, of 650 – 800 °C and 0.5 – 3 h, with the DoE alpha calculated in Section 4.1.2, the other three levels to be tested were calculated, shown in Table 4.1 and Figure 4.3. These are calculated based on the normalisation of the two continuous factor ranges, with respect to the DoE alpha, and were tested for both peel types. The distance from the centre point of the DoE design to the upper and lower level points of the optimisation design should be equal to 1.412 alpha (see both Figure 4.3 and Figure 4.4). Also note, the lower initial level of the design used here is higher (650 °C instead of 500 °C, due to the reasons discussed above). A traditional normalised figure showing the spread of alpha points in a CCC design is shown in Figure 4.4 to help illustrate how the calculated points in this study map onto the design.

Table 4.1: DoE Levels for Continuous Factors Used in Optimisation Biochar Production in this Study

Variable	Level to Test (normalised based on DoE α)				
	-1.412 α	1 α	0	1 α	1.412 α
Pyrolysis Temperature (°C)	619	650	725	800	831
Pyrolysis Time (h)	0	0.5	1.75	3	3.52

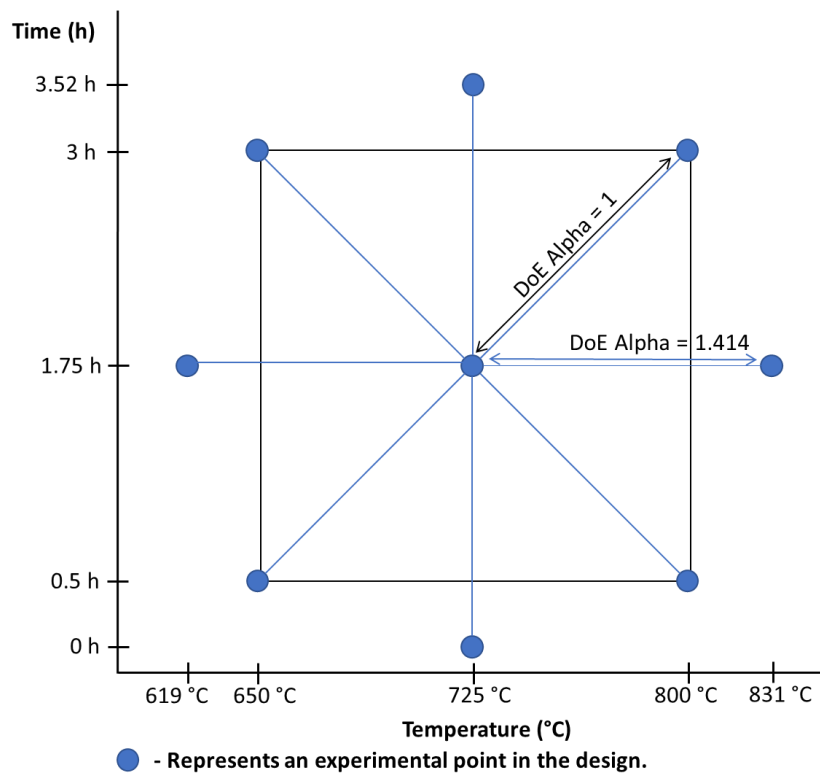


Figure 4.3: Example of the Experimental Points and Conditions for One Peel Type in the Biochar DoE Optimisation Process

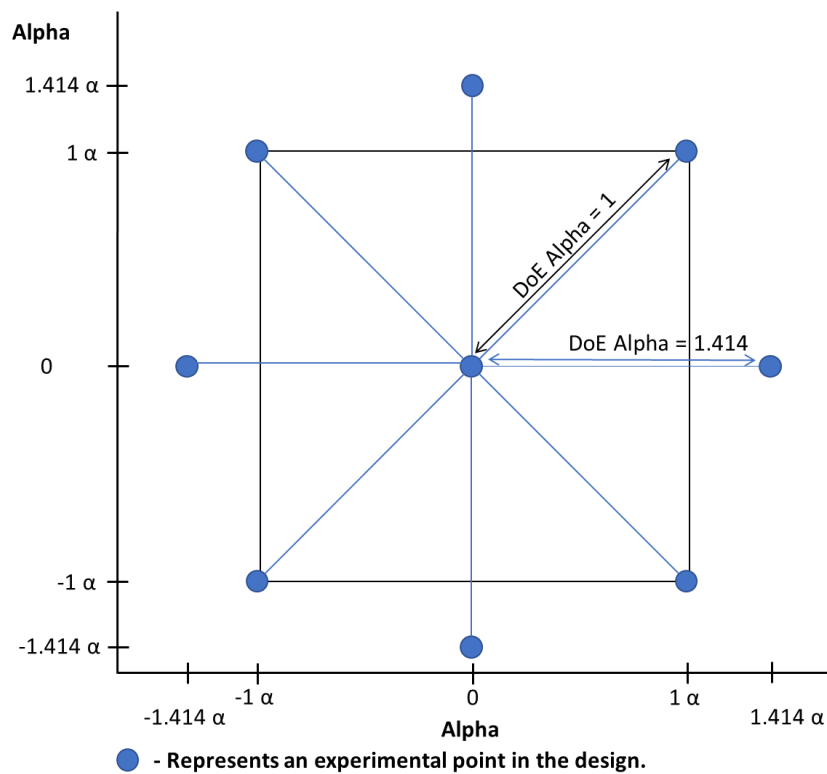


Figure 4.4: Example of Traditional Normalised Values of DoE Alpha in DoE Optimisation CCC Design

Dried peel samples were loaded into two alumina crucibles, with dimensions of 90 mm × 17 mm × 11.5 mm (L × W × H), and both crucibles were subsequently placed in the centre of the ceramic tube (end-to-end) which was slid into the furnace. Each crucible held around 5 g of the dried peel (with exact masses recorded prior to pyrolysis). N₂ gas (BOC, 99.998 % purity) was flowed through the setup as an inert atmosphere (400 mL/min) and furnace heating was initiated under N₂. The setup can be seen in Figure 4.5, Figure 4.7 and Figure 4.8.

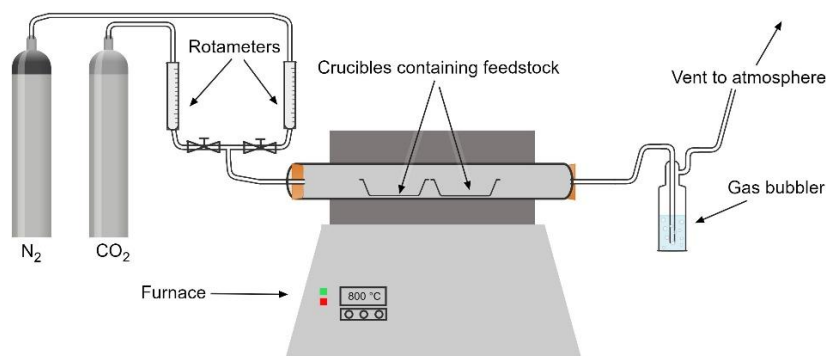


Figure 4.5: Schematic of Furnace Setup

Once at the target temperature, the gas was changed from N₂ to CO₂ (BOC, 99.8 % purity), and set at the desired flowrate for the pre-determined dwell time, after which the system was left to cool [5]. The gas was not changed at the end of the dwell time; thus, the material was left to cool under a CO₂ atmosphere (at the same specific flowrate that was applied during each individual experiment); this was done in order to maximise contact time between the gas and the material in the crucible. As a result of this, it is likely that, in the case of experiments carried out at 700 °C or higher, activation may have continued after the stated dwell time was complete. This must be acknowledged, as, if these reactions did continue then, the yield and porosity of the final char may have been influenced by the additional exposure to CO₂. There is also a possibility that the reverse Boudouard reaction may have occurred, due to it becoming thermodynamically favourable at the lower temperature encountered during cooling (300 – 400 °) [6]. While this was not desired, there is the potential

that it may have occurred, and as such, it may have had an unquantifiable effect on the final biochar yield and surface chemistry, as carbon monoxide still present in the furnace atmosphere may have been deposited back onto the surface of the material in the form of carbon.

Due to safety policy in the lab, the furnace and gas could not be left to run overnight. As the autoignition of carbon black is approximately 350 – 400 °C [7], it was, therefore, necessary to turn off the gas and remove the connection to the scrubber from the water trap to ensure no backflow of water into the gas tubing, approximately 15 min before the lab shut each day, to avoid sample degradation. The temperature was found, on the vast majority of occasions, to be below 300 °C by this stage, and always below 350 °C. Unfortunately, this would result in the chars being exposed to oxygen in the ambient air, which, in turn, may have led to surface oxidation of the chars occurring; while this was in no way desired, it was also unavoidable due to the laboratory safety policy. In turn, the errors that could arise from this process must be considered, and while they are unquantifiable, they should be acknowledged in the appropriate sections. For example, if oxidation did occur this would lead to larger values of oxygen-containing functional groups in chemical surface analysis, than would be expected if the cooling procedure was allowed to take place until the sample reached room temperature. Similarly, oxygen-containing peaks may be detected during Fourier Transform Infrared Spectroscopy that would otherwise not have been present. Figure 4.6 presents a temperature profile of a typical biochar experimental run with the flowing gas shown for each stage (run conditions are: temperature of 800 °C, time of 3 h and ramp rate of 15 °C/min).

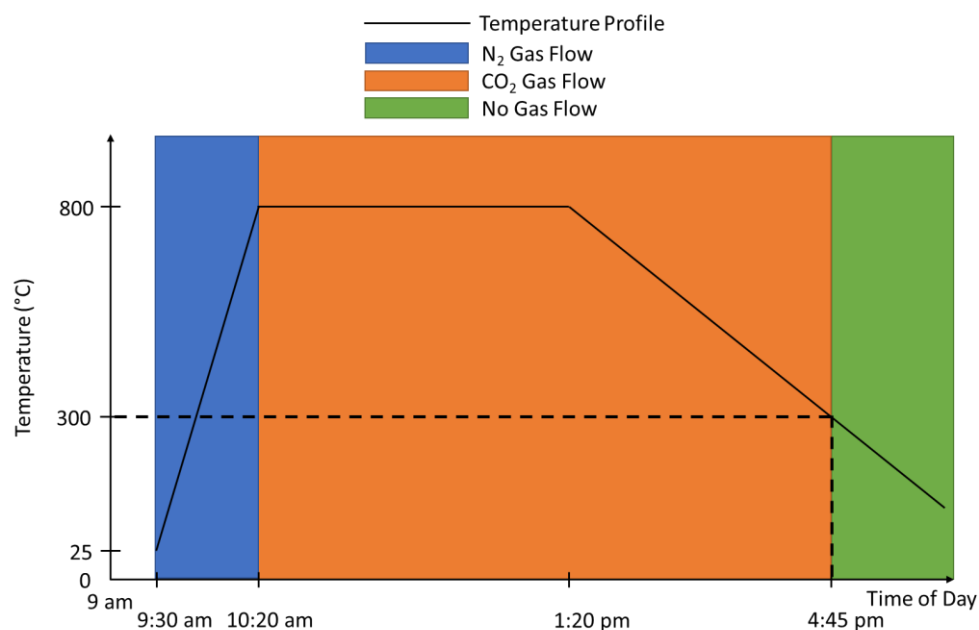


Figure 4.6: Temperature Profile of Typical Biochar Experimental Run, Including Flowing Gas for Each Stage

The crucibles were removed from the furnace the next day, and the produced biochar collected and its weight recorded. The yield of biochar produced was calculated using Equation 4.1.

$$\text{Yield (\%)} = \frac{\text{Mass of biochar produced (g)}}{\text{Mass of feedstock used (g)}} * 100 \quad \text{Equation 4.1}$$



Figure 4.7: Lenton Tube Furnace



Figure 4.8: Gas Cylinder Setup Connected to Lenton Furnace

The use of a horizontal tube furnace may have also impacted upon the diffusion of the activating gas, CO₂, into the samples during the gasification process. In this setup, the inlet gas flows over the biomass sample in the crucible meaning that diffusion occurs over the boundary layer on top of the sample, whereas in a vertical furnace setup the gas would flow and diffuse through the sample, with the vertical method likely resulting in more effective mass transfer and better contact with the sample. The horizontal setup employed in this study does allow for CO₂ gasification to take place, but it must be acknowledged that this may have implications on the degree of activation achieved when compared to a vertical configuration, and similarly, on the relationship that gas flow rate has with the char responses tested in this study. Note that a higher flowrate of 400 mL/min of CO₂ was used in the optimisation experiments; this theoretically should result in a larger concentration gradient between the bulk gas flow and the surface of the sample in the crucible, in turn possibly increasing the level of mass transfer [8].

4.2.3 Sample Storage

Samples, once removed from the furnace, were stored in 50 mL sample bottles, labelled based on their production conditions and retained in a cupboard in the lab at room temperature. The same procedure was followed for all biochars produced. An example of the produced biochar material can be seen in Figure 4.9.



Figure 4.9: Example of Biochar Material Produced in This Study

4.3 Hydrochar Synthesis

The same species of orange and mandarin peels used to produce biochars were also used to produce the hydrochars in this study.

4.3.1 Biomass Preparation

Similar to the biochar route, the relevant species of orange and mandarins were bought from Tesco Supermarkets in Falkirk, their peel removed and blended into small pieces of around 1 mm x 0.5 mm. They were washed in deionised water, before being dried at 80 °C for 24 h in the oven. After drying, the peels were stored in labelled airtight bags in a drawer in the lab until they were used in experiments.

4.3.2 Hydrothermal Carbonisation Process

Hydrochars were produced using a 125 mL Parr 4748 Acid Digestion Vessel, Figure 4.11, and a Memmert UF55 Plus Oven, Figure 4.13 and Figure 4.14. HTC was carried out using the pre-determined conditions based on the generated DoE.

For the screening stage, the four variables investigated at two levels each were: HTC temperature (180 and 220 °C), HTC residence time (2.5 and 12 h), peel type (orange and mandarin) and activation temperature (750 and 800 °C). Again, the values for these parameters were informed from the literature review. This resulted in the production of 16 hydrochars. A ramp rate of 5 °C/min was used for each experiment.

From the analysis of the screening results obtained, HTC residence time was deemed not significant in the study and was set at 2.5 h for any future experiments. This was based on the fact that a lower residence time would result in lower energy consumption of the process, and would also reduce the associated safety risks arising from the process. Of the three remaining variables, the two continuous factors were tested at a wider range of levels based on the circumscribed DoE selected, see Table 4.2. This was calculated in the same manner as in Section 4.1.2. See Figure 4.10 for a visualisation of the design points, for a single peel type. This gave a total of 18 new hydrochars produced. The ramp rate of 5 °C/min was once again utilised.

Table 4.2: DoE Levels for Continuous Factors Used in Optimisation Hydrochar Production in this Study

Variable	Level to Test (normalised based on DoE α)				
	-1.412 α	1 α	0	1 α	1.412 α
HTC Temperature (°C)	172	180	200	220	228
Activation Temperature (°C)	740	750	775	800	810

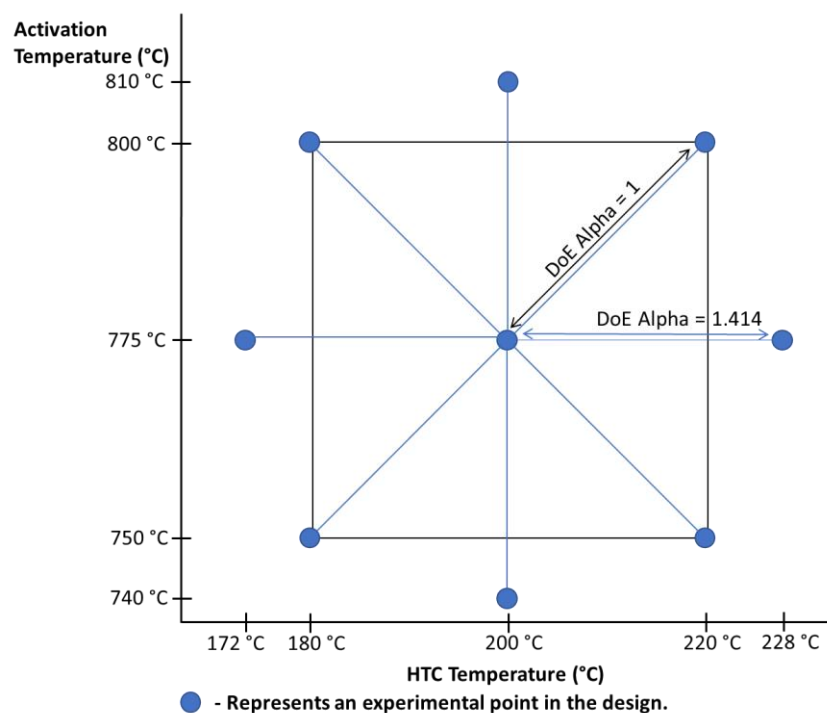


Figure 4.10: Example of the Experimental Points and Conditions for One Peel Type in the Hydrochar DoE Optimisation Process

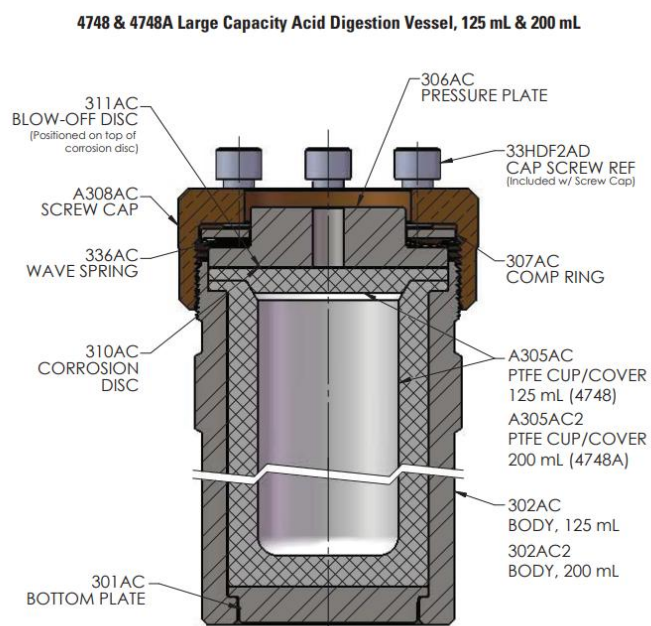


Figure 4.11: Schematic of 4748 Acid Digestion Vessel 125 mL, Used to Produce Hydrochars In This Study [9]

For each sample, 2.50 g of either orange or mandarin peel was weighed out and added to a 125 mL PTFE liner. To meet filling level regulations for the equipment, 31 mL of urea solution was the maximum volume possible to use in experiments. As such, it was calculated that, working from a ratio of 2.5 g of peel to 2.5 g of urea, and with the volume restriction of 31 mL, a solution of 1.34 mol/L urea was required. Solutions matching this concentration were made up in 500 mL batches, as and when required.

Thus, 31 mL of the urea solution was added to the PTFE liner with the prepared peel and the lid placed on the liner, which was subsequently placed inside the stainless-steel autoclave. The autoclave was sealed, using its cap screws and placed inside the Memmert oven. For samples produced without nitrogen doping, the process followed was identical to that described above but with urea eliminated from the process, meaning only a mixture of peel and deionised water was placed in the PTFE liner.

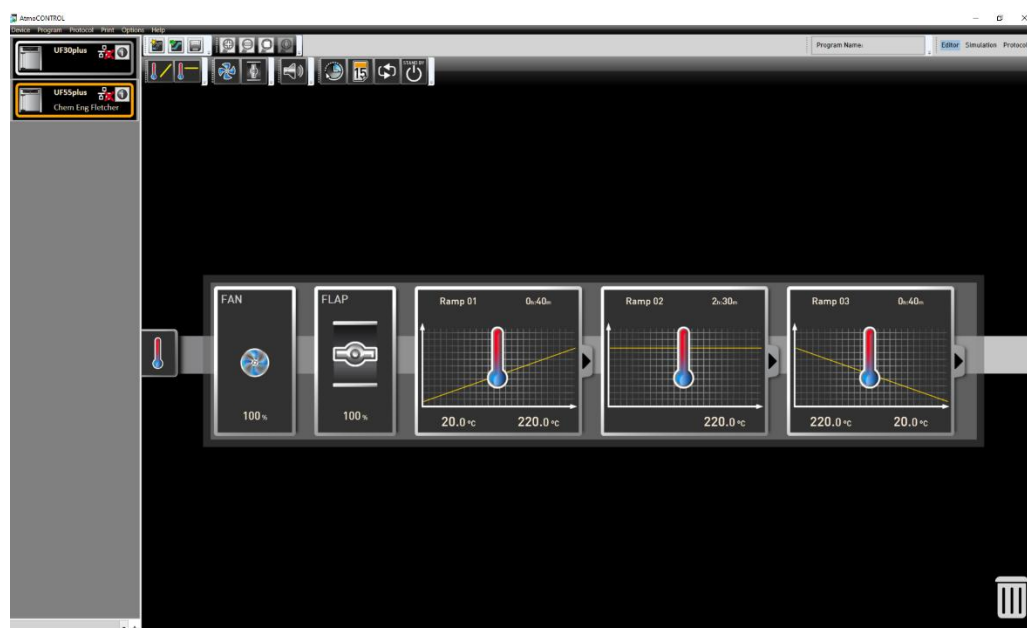


Figure 4.12: AtmoCONTROL Software Used to Programme the Memmert UF55 Plus Oven

Using the Memmert software AtmoControl, Figure 4.12, a programme was created for the oven to follow for each run; this allowed for the ramp rate, HTC temperature and HTC

residence time to be set. Once the autoclave was in the oven, the programme of operation was started and left for the required time for the experiment to complete. Due to safety concerns around urea degradation reactions that could occur during the HTC process, the experiments were carried out overnight when the lab was empty, to minimise safety risks to other researchers and staff. Therefore, experiments were prepared and started at 4:30 pm each day before lab closure. The experimental runs would then complete during the night, and the autoclave would cool to room temperature by 9 am the next day to coincide with the lab re-opening.



Figure 4.13: Memmert Oven UF55 Plus



Figure 4.14: Autoclave Inside Memmert UF55 Plus Oven

The next day, the autoclave would be opened and the PTFE liner, containing the hydrochar, removed. The liner was placed in a fume hood, where the lid was removed and left to stand for 30 min; this allowed for any gases produced during the process to be removed by the ventilation system. After this time had passed, the mixture of liquids and solids was vacuum

filtered through standard Fisherbrand filter paper using a Buchner funnel system. The liquid was then disposed of and the solids were rinsed with water before being dried in an oven for 24 h at 80 °C.

The yield of hydrochar was calculated using Equation 4.2, based on the dried mass of peel used in the specific experiment.

$$\text{Hydrochar HTC yield (\%)} = \frac{\text{Mass of dried hydrochar produced (g)}}{\text{Mass of dried peel used in process (g)}} * 100 \quad \text{Equation 4.2}$$

4.3.3 Physical Activation Process

After the produced hydrochar was dried, it was analysed for porosity and the functional groups present on the material surface, using Brunauer-Emmett-Teller (BET) porosimetry, volumetric CO₂ adsorption and Fourier Transform Infrared (FTIR) spectroscopy techniques respectively. This was carried out at this stage to determine their initial adsorption capacity, as the purpose of activating the samples was to increase their porosity with a view to creating characteristics that would be advantageous for carbon capture; thus, it was deemed important to show the 'before' and 'after' of hydrochar activation in order to provide evidence of the impact of activating the samples.

For activation of the produced hydrochar, the same set up as described in Section 4.2.2 was utilised. A recorded mass of hydrochar was weighed out into a single crucible and placed in the centre of the ceramic tube, which was slid into the Lenton tube furnace. CO₂ gas flow was set at a rate of 400 mL/min to provide an activating atmosphere inside the furnace, and after this the heating programme was initiated. A residence time of 0.5 h was chosen, based on experience gained from the biochar production studies, and the activation temperature was varied based on the DoE specifications. A ramp rate of 15 °C/min was used to mirror the

biochar production. Once the dwell time was complete, heating of the sample stopped and the material was left to cool under the same CO₂ atmosphere, at a rate of 400 mL/min. At the end of the day, as had been required during biochar production, the CO₂ gas flow was turned off and the connection to the scrubber lifted from the water trap to ensure no backflow of water into the gas tubing. Once again, this unfortunately exposed the samples to oxygen in the ambient air, and may have led to oxidation of the char surface. This raises the same uncertainties regarding the analysis of chemical surface data discussed in Section 4.2.2, however, it was unavoidable due to laboratory safety policy. Figure 4.15 presents a temperature profile of a typical biochar experimental run with the flowing gas shown for each stage (run conditions are: temperature of 800 °C, time of 0.5 h and ramp rate of 15 °C/min).

The crucible was removed the following day, the activated hydrochar collected and weighed, and the overall yield of hydrochar calculated, using Equation 4.3.

$$\begin{aligned} & \text{Overall hydrochar yield (\%)} \\ &= \frac{\text{Mass of activated hydrochar produced (g)}}{\text{Mass of dried peel used in process (g)}} * 100 \end{aligned} \quad \text{Equation 4.3}$$

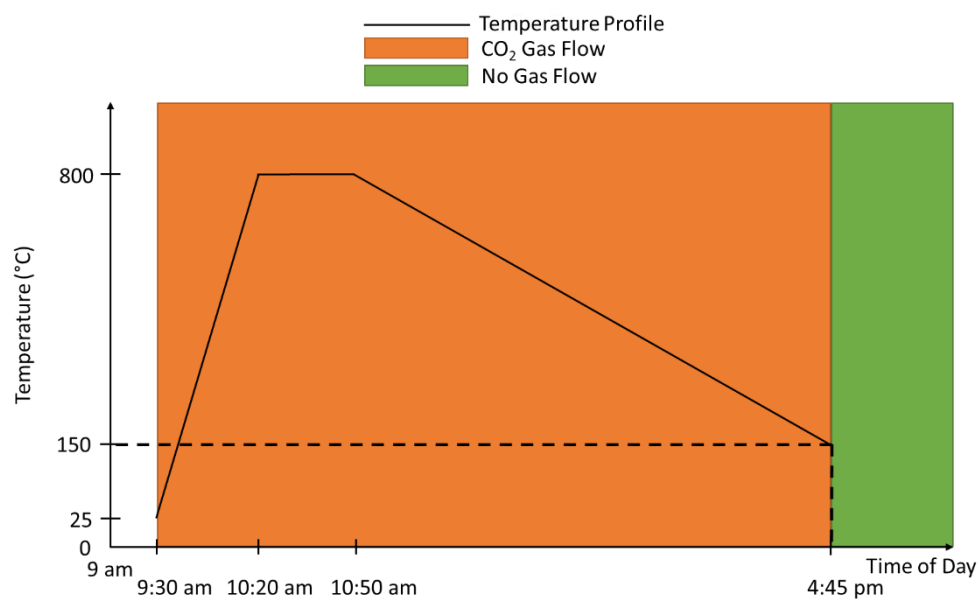


Figure 4.15: Temperature Profile of Typical Hydrochar Experimental Run, Including Flowing Gas for Each Stage

4.3.4 Sample Storage

The hydrochar and activated hydrochar samples were stored identically to the biochar samples, as described in Section 4.2.3. An example of the hydrochar material produced in this study is shown in Figure 4.16.



Figure 4.16: Example of Hydrochar Material Produced in This Study

4.4 Sample Nomenclature

4.4.1 Biochar Nomenclature

Biochars produced in the screening stage of the process were labelled as 'BC WW-XX-YY-ZZ', where BC stands for biochar, WW represents the pyrolysis temperature (°C), XX the pyrolysis residence time (h), YY the type of peel (O for orange or M for mandarin) and ZZ the flowrate of CO₂ gas over the sample (mL/min). For example, a sample produced at 800 °C, with a residence time of 3 h, using orange peel and a CO₂ flowrate of 400 mL/min would be labelled 'BC 800-0.5-O-400'.

For the biochars produced in the optimisation stage, the same style of nomenclature was used but without the CO₂ flowrate term, as this factor was held at a constant value for these experiments. Thus, these samples were labelled as 'OBC WW-XX-YY', where OBC stands for optimised biochar, and WW, XX and YY represent the same factors as described above.

Finally, for the biochars produced from the optimised DoE equations, samples were named 'OPB AA YY', where OPB stands for optimal biochar, AA represents the specific response the char was created for and YY represent the peel type of the biochar.

4.4.2 Hydrochar Nomenclature

A similar method of naming samples was used for the hydrochars produced in this study.

Hydrochars produced in the screening stage of the process were labelled as 'HC WW-XX-YY-ZZ', where HC stands for hydrochar, WW represents the HTC temperature (°C), XX the HTC residence time (h), YY the type of peel (O for orange or M for mandarin) and ZZ the post-HTC activation temperature of the sample (°C). For example, a sample produced at 220 °C, with a residence time of 2.5 h, using orange peel and activated at 800 °C would be labelled 'HC 220-2.5-O-800'.

The same nomenclature method was used for the optimisation samples, but without the residence time term as this was fixed; so, samples were named in the form 'OHC WW-YY-ZZ' where 'OHC' stands for optimised hydrochar and WW, YY and ZZ represent the same factors as above.

For the hydrochars produced from the optimised DoE equations, samples were named 'OPH AA YY', where OPH stands for optimal hydrochar, AA represents the specific response the char was created for and YY represent the peel type of the hydrochar.

4.5 N₂ Adsorption Isotherms for Surface Textural Analysis

N₂ adsorption isotherms were measured at -196 °C, on each of the produced chars, using a Micromeritics ASAP 2420 system, Figure 4.17. Approximately 0.2 – 1 g of sample was used, depending on sample availability. This method of analysis assessed the porosity of materials, and helped provide results to inform the DoE process.



Figure 4.17: Micromeritics ASAP 2420 System

Using BET theory (including Rouquerol correction), t-plot method and the Dubinin–Radushkevich (DR) method, analysis was carried out to allow calculation of total and micropore surface areas, and micropore volumes respectively. These methods are discussed in detail in Chapter 3.

4.5.1 Sample Preparation and Degas Procedure

In order to ensure accurate adsorption data was collected, each sample was degassed before undergoing analysis. This process was undertaken to remove any moisture and contamination, or left-over volatiles, from the sample surfaces and pores, which could otherwise affect the adsorption of N_2 molecules and give erroneous results.

For each sample, a clean BET sample tube was chosen and weighed to record its empty mass. Approximately 0.2 – 1 g of the chosen sample was then weighed into the BET tube, see Figure 4.18. As a rule of thumb, for a sample with an expected surface area between 15 – 30 m^2/g ,

1 g of the sample would be required to provide a reliable isotherm. This is an inversely proportional relationship, therefore, for samples of higher surface area, a lower mass of sample is required.

Once the BET tube with sample in it was weighed and recorded, it was secured onto a degas port on the BET instrument. The degas ports can be seen in Figure 4.19. A heating mantle was then attached to the tube and the degas programme started on the system. Each degas cycle began by increasing the temperature to 50 °C with a ramp rate of 5 °C/min and reducing the pressure to 10 µmHg to evacuate the sample, with the sample held at these conditions for 30 min. After this period, the temperature was increased to 250 °C at a rate of 10 °C/min and pressure maintained at 10 µmHg, and the sample held here for 4 h before the process was complete.



Figure 4.18: Biochar Sample in BET Tube



Figure 4.19: Samples Undergoing Degas on Degas Ports

Note that for hydrochar samples that had not been activated, a lower degas temperature was used, as 250 °C was above the production temperature of the material; for these samples

degas was performed at 120 °C for 8 h, with the same ramping conditions and pressure as used for biochars.

4.5.2 Sample Analysis via N₂ Adsorption

The BET sample tube was then removed from the degas port, and its new 'degassed' weight recorded. A filling rod was then placed in the tube, and an isothermal jacket attached to the outside of the tube. A filling rod was used to reduce the free space inside the sample tube, which increases the accuracy of the adsorption measurement, and the isothermal jacket allowed maintenance of a constant temperature across the external surface of the sample tube. The tube was then attached to an analysis port on the instrument, shown in Figure 4.20. The dewar for the chosen port was filled with liquid N₂, and a splash guard placed around the sample. The sample analysis programme was then started on the instrument. For each sample, 49 points were measured on the adsorption branch between 0 and 760 mmHg, across the full range of relative pressure ($0 < \frac{P}{P_0} < 1$), and 32 points on the desorption branch across the same pressure range, measured at a constant temperature of -196 °C.



Figure 4.20: Samples Undergoing BET Analysis on Analysis Ports

After the adsorption and desorption isotherms were complete, specific surface areas (SSAs), and micropore volumes were then determined using the BET method and the DR method.

The Rouquerol correction and t-plot analysis were also applied, due to the microporous nature of the samples [10].

4.6 Proximate Analysis

4.6.1 Sample Preparation

Thermogravimetric analysis (TGA) was conducted to analyse the fixed carbon content in the chars, using a NETZSCH STA 449 F3 Jupiter instrument, see Figure 4.21.



Figure 4.21: NETZSCH STA 449 F3 Jupiter System Used in This Study

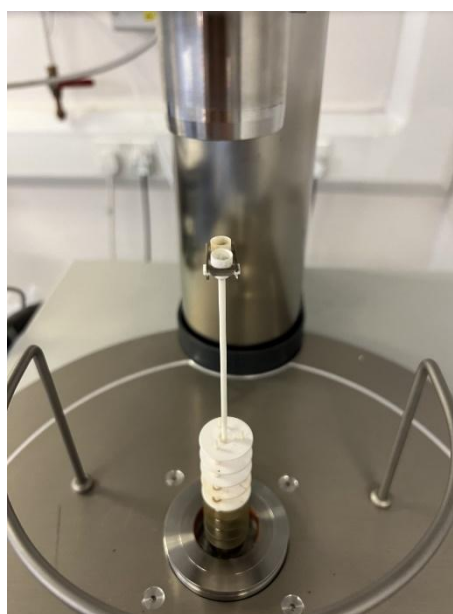


Figure 4.22: STA Furnace Sample Holder of the NETZSCH STA 449 F3 Jupiter System

Initially an aluminium oxide crucible was loaded into the STA furnace sample holder, Figure 4.22, alongside an empty reference crucible made of the same material, exposed to a 50 mL/min flow of N_2 , and the mass tared. The crucible was then removed, filled with char sample and re-loaded. After the mass stabilised, the starting weight was recorded and the temperature program initiated. The range of sample mass used was approximately 10 – 25 mg.

4.6.2 Sample Analysis

The temperature programme followed was based off a standard method found in literature [11]. The programme steps can be seen in Table 4.3. Data from each run was recorded using the Proteus Analysis software, which allowed plots of mass change with respect to time and temperature to be produced and thus, the % mass loss calculated. This allowed the mass losses to be broken down into four definitive sections: moisture, volatiles, fixed carbon and ash.

Table 4.3: Proximate Analysis Temperature Programme Utilised in This Study

Stage type	Target Temp. (°C)	Ramp Rate (°C/min)	Time (min)	Air Flow (mL/min)	N ₂ Flow (mL/min)	N ₂ Protective Flow (mL/min)
Start	25	-	-	0	50	60
Ramp	100	10	7.5	0	50	60
Dwell	100	-	10	0	50	60
Ramp	920	10	82	0	50	60
Dwell	920	-	15	0	50	60
Ramp	820	-10	10	0	50	60
Dwell	820	-	10	0	50	60
Dwell	820	-	30	50	0	60

4.7 Elemental Analysis

Carbon, hydrogen and nitrogen contents of the samples were found by employing elemental analysis, using an FlashSmart Elemental Analyser (CHNS), with residual content (oxygen, sulphur etc) of samples calculated by difference, after calculating the wt% on an ash-free basis, see Equation 4.4.

$$\begin{aligned}
 \text{Residuals (wt\%)} &= 100 - \text{carbon (wt\%)} - \text{hydrogen (wt\%)} \\
 &\quad - \text{nitrogen (wt\%)}
 \end{aligned}
 \tag{Equation 4.4}$$

The analysis was carried out by Mara Knapp in the Department of Civil Engineering, University of Strathclyde. Samples were individually weighed out into tin capsules and loaded into the

CHNS autosampler. The CHNS system is first inerted using helium. When the analysis starts, the helium flow is stopped and oxygen is allowed into the reactor; after a few seconds the tin capsule containing sample is dropped into the reactor. The tin reacts with the oxygen in the environment in an exothermic reaction to raise the temperature of the reactor to 1800 °C, which causes combustion of the sample. At this point the flow of oxygen is stopped and helium is introduced again.

Any nitrogen oxides are reduced to N₂ within the system, and the combustion products are then passed through a filter, of a form of cobalt catalyst, which removes any sulphur and halogenated components from the gas mixture. This leaves a mixture of CO₂, N₂, and H₂O, which are passed into a gas chromatographic column that separates them into the individual gases. Each gas is then passed into a thermal conductivity detector, which determines the wt% of nitrogen, carbon and hydrogen, respectively. Samples were run in duplicate, and calibration of the instrument was carried out prior to operation. The system used can be seen in Figure 4.23 and Figure 4.24.



Figure 4.23: FlashSmart Elemental Analyser CHNS



Figure 4.24: CHNS Autosampler

4.8 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) was carried out by Dr Christopher Kelly in the Department of Chemistry, University of Glasgow. A Kratos AXIS Supra+ instrument was used to obtain both survey and individual element spectra of the char samples and their precursor materials, allowing for quantification of the elemental composition of carbon, nitrogen, oxygen and residual components on the surface of the materials. A dual aluminium and silver monochromatic anode was used as the X-ray source.

Table 4.4: XPS Instrument Analysis Specifications Utilised in This Study

Scans	Pass Energy (eV)	Dwell Time	No. of Sweeps	Step Size (eV)
Survey	160	100 ms	1	1
Carbon	40	239 ms	1	0.1
Oxygen	40	373 ms	1	0.1
Nitrogen	40	397 ms	1	0.1
Calcium, Potassium, Silicon	40	373 ms	4	0.1

The samples were crushed and degassed (at the same conditions used for BET analysis) before undergoing analysis. The instrument specifications used when carrying out the scans is shown in Table 4.4.

The samples were mounted on an XPS sample holder using carbon tape, and placed in the sample chamber, before the chamber was evacuated to create a vacuum. Initially, a survey scan is conducted to identify which elements are present in the sample. To carry out a scan, the X-ray source is directed at the surface of the sample, which excites photoelectrons on the sample surface. The instrument can measure the speed of these electrons, allowing the binding energy to be calculated, and thus, elements to be identified by their peak positions. After identifying the peaks in each sample, high resolution scans are carried out for individual elements to give more accurate spectra.

4.9 Fourier-Transform Infrared Spectroscopy

FTIR spectroscopy was used to identify functional groups on the surface of the chars, and their precursor materials, using an Agilent 4300 Handheld FTIR Spectrometer, see Figure 4.25. A germanium Attenuated Total Reflectance (Ge ATR) attachment was used with this equipment to reduce interference on the collected spectra [12].

In ATR-FTIR spectroscopy, an infrared (IR) beam is passed through a crystal, in this case a germanium crystal, and comes into contact with the sample. At the interface of the sample and the crystal, the majority of the IR light is reflected back to the instrument detector, while a small part of it extends into the sample [13]. This is called the evanescent wave, and at this point specific parts of the IR light are absorbed by the bulk sample. Due to this, the reflected IR light being detected by the instrument is different from the light being projected through the crystal; software can then be used to apply the Fourier transformation to this data, and produce the FTIR spectra used to analyse the sample.

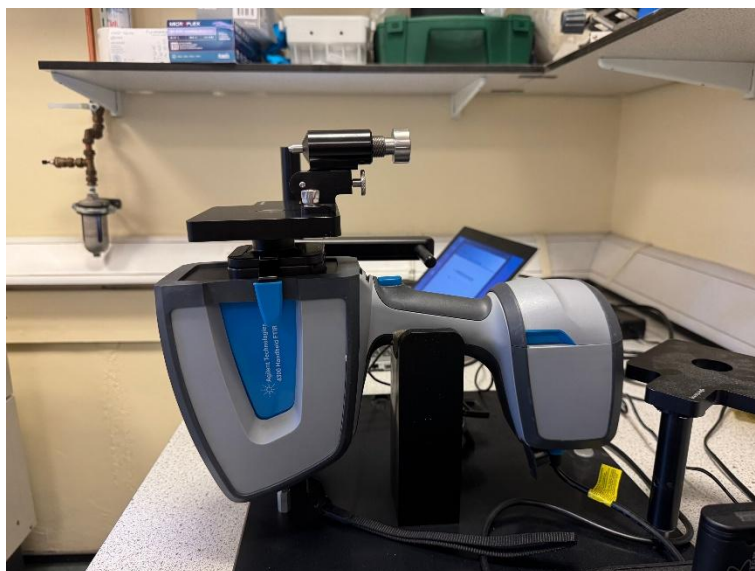


Figure 4.25: Agilent 4300 Handheld FTIR Spectrometer

From the produced spectra, it is possible to relate the peaks (absorbance bands) to specific functional groups, using chemical libraries and literature. This is based on the typical vibrations that occur at different frequencies when the chemical functionalities are stimulated by the IR light [14]; the IR light absorption causes changes to the dipole moments of the functional groups or molecules. These changes can be related to the vibrational energy, and combining this data with the peaks produced at specific frequencies, allows for the identification of the unique group or molecule. As a result, each FTIR spectrum is characteristic to the material for which it has been measured.

A germanium crystal was chosen, in this study, due to its high refractive index, which makes it ideal for use with material that exhibit high light absorbance [12]. Preliminary work with the biochars using a FTIR spectrometer without an additional crystal, an ABB MB3000 Spectrometer, showed high absorbance of the light and poor scan results, which led to the use of the Agilent ATR-FTIR system with germanium crystal.

4.9.1 Sample Preparation

In practice, each sample was crushed with a mortar and pestle until a uniform powder was obtained. Prior to use, the instrument was turned on and allowed to warm up for 30 min. Before analysing samples, a background scan was taken; this provides a clean environment spectrum which is then subtracted from the collected sample spectrum. Ground samples were placed on the FTIR sampling spot, Figure 4.26 and Figure 4.27. 128 scans were recorded per sample with a resolution of 4 cm^{-1} between $650 - 5000\text{ cm}^{-1}$.

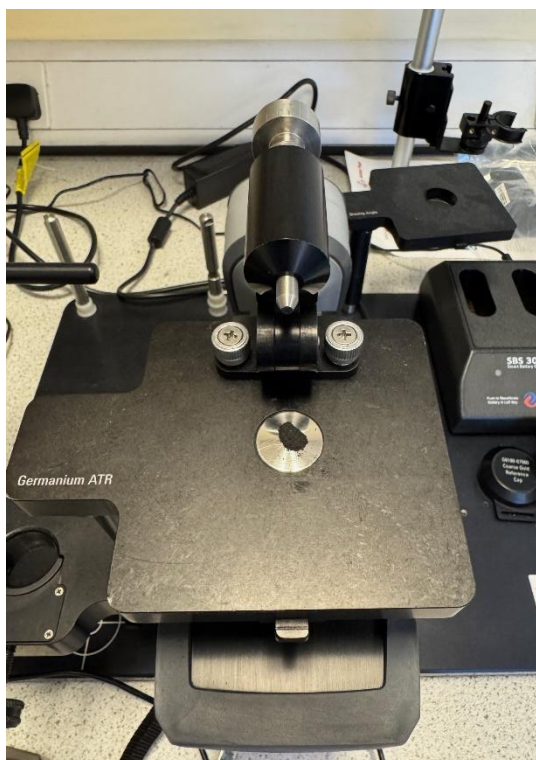


Figure 4.26: Ground Sample On FTIR-Ge Crystal

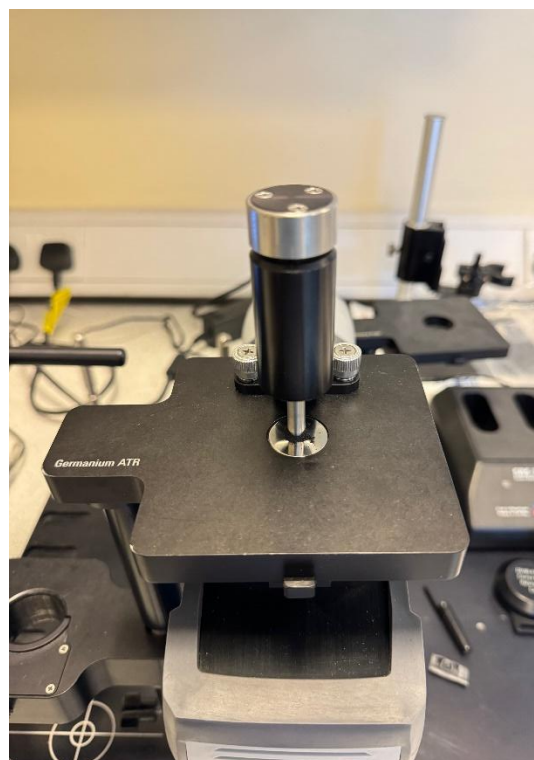


Figure 4.27: Ground Samples During FTIR-Ge Analysis

4.10 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to examine the morphology of biochar and hydrochar samples, along with the precursor material. The instrument uses an electron source to scan the chosen samples and produce a high-resolution image of the surface. The machine was used in backscattered electron mode, which uses a detector to register the electrons which are reflected back from the samples surface after undergoing elastic collisions [15].



Figure 4.28: Example of Biochar Attached to SEM Stubs using Carbon Tape

Samples were prepared using double-sided carbon tape and aluminium SEM stubs. The tape was attached to the stub, before the protective foil was removed from the front of the tape and the sample dispersed onto the stub, see Figure 4.28. The stub was then exposed to a flow of pressurised air to ensure the sample particles were securely attached to the tape and would not be displaced when subjected to a vacuum in the instrument.

A low-vacuum SEM, JEOL JSM-IT100 InTouchScope, with tungsten filament, was used to analyse the chosen samples. The SEM stubs containing sample were placed into the multi-sample holder, see Figure 4.29, before being inserted into the instrument, Figure 4.30. The sample chamber was then sealed, and the chamber evacuated to create a high vacuum environment. The corresponding software, InTouchScope, was loaded and the SEM beam switched on. This set up was then used to analyse the samples. An accelerating voltage of 20 kV was used, and magnification of 150x and 550x were used to collect images at scales of 150 μm and 20 μm respectively.



Figure 4.29: Multi-Sample Holder Used in JEOL SEM

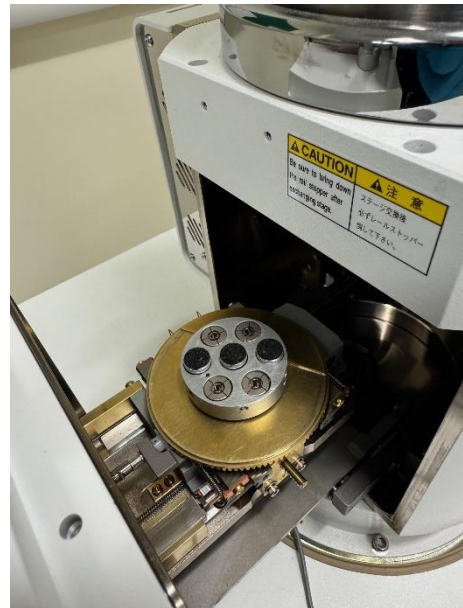


Figure 4.30: Samples Attached to Sample Holder and Placed in Sample Chamber

The area of sample exposed to the electron beam was controlled using the handles seen in Figure 4.31. These were used to move the sample holder within the chamber on the x- and y-axis, allowing different areas of the sample and different samples to be analysed.



Figure 4.31: JEOL JSM-IT100 SEM (Sample Movement Handles Can Be Seen Extending from the Equipment)

4.11 CO₂ Volumetric Adsorption

CO₂ adsorption isotherms were measured at 0 °C, on a selected range of produced biochars and all post-activation hydrochars, using a Micromeritics ASAP 2460 system, Figure 4.32.

Samples were prepared using the same method as described in Section 4.5.1, and degassed with the same procedure and conditions. After degas was complete, the degassed weight of sample and tube was recorded, before a filling rod was placed in the tube and an isothermal jacket attached. The tube was then attached to one of the analysis ports, shown in Figure 4.33, with a splashguard, and the accompanying dewar filled with a mixture of ice and water to create an ice bath. The sample analysis programme was started on the instrument, with a 30-point adsorption isotherm measured for each sample between 0 – 1 bar (approx.), reaching a maximum relative pressure of CO₂ of $\frac{P}{P_0} \approx 0.03$, at a constant temperature of 0 °C.



Figure 4.32: Micromeritics ASAP 2460 System

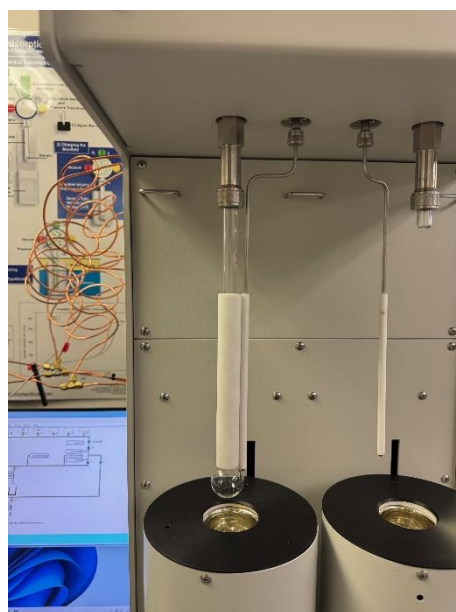


Figure 4.33: Sample Attached to ASAP 2460 for CO₂ Isotherm Analysis

After completion, the micropore volumes and equivalent areas were determined using the DR method, and the CO₂ adsorption capacity at 1 bar also recorded.

4.12 CO₂ Gravimetric Adsorption

Gravimetric adsorption is a technique that allows the mass of a sample to be monitored over time, while varying pressure and/or temperature, under conditions pre-determined by users [16]. For experiments in this study, temperature was maintained as a constant, and pressure was varied to produce isotherms. The system used was capable of carrying out both static and dynamic adsorption experiments; static measurements are used to determine the maximum thermodynamic equilibrium uptake achieved by a sample, whereas dynamic measurements allow the thermodynamic equilibration and mass transfer effects to be examined together.



Figure 4.34: IGA-001 Used in this Study

The instruments used were two Intelligent Gravimetric Analysers (IGAs), supplied by Hiden Isochema Ltd, models IGA-001 and IGA-003 (the 001 model is shown in Figure 4.34). Static

adsorption experiments were carried out using CO₂ at three temperatures (0, 30 and 60 °C) over a pressure range of 0 – 19.5 bar.

4.12.1 Process of Sample Degas

Before loading the sample, the temperature controls were turned off, such that the system was at room temperature and the pressure set to atmospheric (1 bar) in order to ensure that no damage would occur when opening the sample chamber, see Figure 4.35. Once at these conditions, the sample chamber was lowered and removed by unscrewing the six hexagonal bolts holding it in position, to gain access to the sample holder.



Figure 4.35: IGA with Sample Chamber Attached

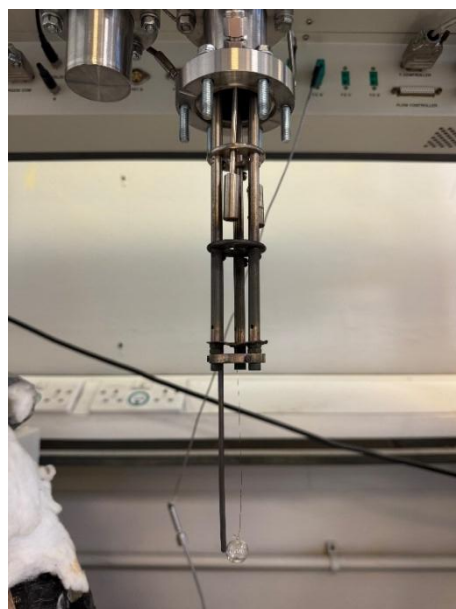


Figure 4.36: IGA with Sample Chamber Removed and Sample Bulb Exposed

When conducting gravimetric analysis, the sample is contained in a small sample bulb. The bulb is hung from the microbalance in the main body of the IGA using a fine tungsten wire. Initially, the bulb was removed from the wire, cleaned with water and then acetone before being dried off and placed back on the tungsten wire, see Figure 4.36. The sample chamber

was loosely re-attached, using the bolts but not fully tightened, and the bulb left to stabilise on the microbalance.

After around 20 – 30 min, the bulb weight would stabilise and the empty bulb weight was recorded. The sample chamber was removed and the sample bulb removed, filled with sample and rehung on the tungsten wire. Note that if the weight of sample exceeded the limit of the standard bulb, a larger bulb could be used but this involved replacing the counterweight inside the microbalance. The bulb filled with sample can be seen in Figure 4.37, and then when it is placed on the IGA in Figure 4.38. The mass range of sample use for this method of analysis within this study was 30 – 75 mg. Once the bulb was in place, the sample chamber was reattached and the chamber fully sealed by placing a fresh copper gasket in the flange formed by the sample chamber and body of the IGA.



Figure 4.37: Sample Bulb Filled with Biochar Sample

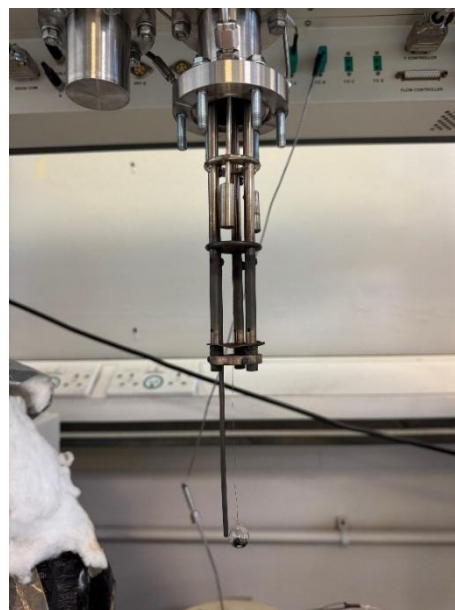


Figure 4.38: Filled Sample Bulb Hanging on Tungsten Wire from IGA

Note that no specific particle size range was selected for the experiments carried out on the IGA. This was due to the heterogenous nature of the char particles, both within samples, and

between different samples, meaning an undefined mixture of particle sizes were used for each experiment. As a result of this, it is acknowledged that the kinetic data may not be truly representative of the samples as a whole; this is due to the fact that the gas will encounter varying levels of resistance during diffusion, based on the difference in particle sizes present within the IGA measuring bulb.

A possible solution would have been to sieve the char materials for a specific particle size, and potentially ball mill or crush larger char particles to achieve a more homogenous material. However, due to the scale of the char synthesis experiments and initial destructive characterisation (elemental analysis, TGA) there was only 0.5 g or less of material available for use in the gravimetric adsorption experiments. In a similar vein, processing them through crushing or ball milling would in turn affect the porosity that had already been created within the materials, and potentially change the intrinsic characteristics of the chars. Note that previous in-house experience within the Fletcher group have found little to no difference in kinetic effects between particles sizes of 10 – 500 μm . Similarly, due to equipment age, description of mass change when the pressure changes from point to point is lost, which also leads to a poorer representation of the kinetic data for each sample.

The sample was subjected to a degas stage to remove any moisture or adsorbed species from the surface prior to undertaking adsorption experiments. A furnace (Model HAS 022163) was attached to the sample setup, see Figure 4.39, and linked to the IGASwin control software. The outgas procedure was initiated using this same software, and the pressure was reduced to 20 mbar using the Vacuubrand diaphragm vacuum pump (Model MD1). At this stage, the Pfeiffer Vacuum turbopump (Model TMU 071 P) engaged and reduced the pressure to around 9×10^{-10} bar. Once the pressure was maintained at this level, the pressure isolation valve (PIV-1) was opened to expose the sample chamber more directly to the vacuum line.

Meanwhile, the temperature on the furnace was set at 120 °C with a dwell time of 14 – 16 h. The combination of heating and vacuum exposure removed any contaminants from the samples, and a new equilibrium weight was reached by the end of the degas stage.



Figure 4.39: Furnace Attached to IGA Sample Chamber



Figure 4.40: Water Bath Attached to IGA Sample Chamber

This setup up was left to run overnight, and in the morning the furnace switched off and PIV-1 closed. The new ‘dry mass’ of the sample was recorded in the IGASwin software to allow for accurate adsorption calculations. At this stage the furnace was then removed, and the Grant Optima TX 150 water bath attached to the setup, see Figure 4.40. This was used to regulate the temperature during measurement of the CO₂ isotherms.

4.12.2 CO₂ Adsorption Isotherms

Single species isotherms were produced using CO₂ as the adsorptive gas. After sample degassing was complete, the IGASwin software was used to set up conditions for the isotherm measurements. A range of pressure points were used to give a full adsorption-desorption isotherm, these are listed in Table 4.5. A minimum equilibration time of 0.5 h was

chosen, and a maximum of 6 h chosen after preliminary experiments, with the long maximum time presenting a compromise between progression towards equilibrium, and an acceptable experiment timescale.

CO₂ adsorption was carried out at three different temperatures: 0, 30 and 60 °C. Temperature of the samples was maintained using a water bath, filled with a mixture of ethylene glycol and water. Once all the above data had been inputted into the software, the isotherm measurements could be started, using the IGASwin software.

Table 4.5: Pressure Points for CO₂ Adsorption and Desorption on IGA

Pressure Points for Adsorption (bar)	Pressure Points for Desorption (bar)
0	19.5
0.05	18
0.1	16
0.2	14
0.4	12
0.6	10
0.8	9
1	8
2	7
3	6
4	5
5	4
6	3
7	2
8	1
9	0.8
10	0.6
12	0.4
14	0.2
16	0.1
18	0.05
19.5	0

4.12.3 Hysteresis Testing

During analysis of single gas adsorption isotherms, a hysteresis loop was witnessed for most biochar samples analysed. To test whether this was a thermodynamic phenomenon or simply

concomitant with slow sorption kinetics exhibited by the sample, an isotherm with a reduced number of points but with increased maximum times was carried out on sample OBC 800-0.5-M. The pressure points measured were 0.4, 1, 2, 5, 10, 19.5 bar for both adsorption and desorption, with a timeout of 48 h used.

4.13 Cyclic Adsorption Isotherms

Cyclic adsorption testing was carried out on selected samples at 60 °C using the IGA system. To begin, the initial sample mass was noted after degas, before the pressure was ramped to 0.05 bar and held for 15 min. After this time elapsed, the pressure was ramped to 1 bar at 0.07 bar/min (≈ 15 min), and then held for 15 min to allow progression towards mass equilibration. Subsequently, the pressure was decreased back to 0.05 bar at the same ramp rate, and held to allow mass equilibration for 15 min. This 0.05-1-0.05 bar regime constituted one cycle, taking approximately 1 h; each sample was tested for a duration of 30 sequential full cycles.

4.14 References

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5 Results I – Biochar Characterisation

5.1 Introduction

This chapter describes the characterisation of the biochars produced in this study. As highlighted in Chapter 2, production of orange peel derived biochars has been previously undertaken, however no studies have combined nitrogen doping using urea and physical activation using CO₂ to produce biochar material from this feedstock. This study will look to fill this research gap, and also include a comparison with mandarin derived biochars produced in the same manner, which has also not been research previously. A Design of Experiment (DoE) statistical method will be used to allow optimisation of the biochar characteristics with the aim of producing effective CO₂ adsorbent materials.

The chapter describes the DoE process and the rationale behind choosing the conditions, and associated ranges, that were tested. The biochars were produced through pyrolysis, before being tested using Fourier Transform Infrared (FTIR) spectroscopy, proximate and elemental analysis, X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM), as well as N₂ sorption, and analysed using Brunauer-Emmett-Teller (BET) and related theory. The DoE process allowed for the optimisation of specific biochars to allow tailored materials to be produced for improved CO₂ capture performance, and these biochars were taken forward to be tested for their CO₂ adsorption capacity.

5.2 Biochar Design of Experiments Plan

To begin, research into biochars produced via pyrolysis or carbonisation and subsequent activation was carried out and a range of process parameters and conditions collated. Upon investigation of each parameter, four main (or significant) types were identified for further examination: pyrolysis temperature, pyrolysis residence time, feedstock type (peel type) and CO₂ gas (activating environment) flowrate.

Other factors identified were heating ramp rate ($^{\circ}\text{C}/\text{min}$), nitrogen doping agent ratio, feedstock particle size, type of activating gas, reactor configuration (vertical or horizontal furnace), and pyrolysis type (fast, slow, or microwave pyrolysis). Feedstock particle size was not considered as it was felt, in order to mimic conditions that would be experienced in larger setups (i.e., industrially), it was appropriate to blend the raw peels to an approximate size range of 1 -2 mm. Any more exact than this was thought to be 'over-processing' of the feedstock, and in opposition to the goal of the project of reducing energy intensive pre-treatment steps. Varying the type of activator gas was not tested, as the goal of the project was to test CO_2 exclusively for its ability to produce microporous materials. Reactor configuration and type of pyrolysis were fixed factors, due to the limitations of the available equipment. Heating rate and nitrogen doping ratio would have been valid factors to consider, but including both factors would have increased the number of required screening experiments alone from 16 to 64. As such, nitrogen doping ratio was fixed, as this was an easier factor to control in terms of preparation of material, where large batches of raw peel could be doped and dried, as and when required. Heating rate was not considered due to a previous DoE study in the research group showing it to be a non-significant factor in the CO_2 gasification of another biomass in the same experimental setup [1]. Nonetheless, it would be beneficial for future studies to investigate these factors, if resources and time constraints allowed.

Firstly, it was decided to carry out a single-stage (one-pot) pyrolysis-activation process. This decision was taken in line with the aims of the project, to reduce energy usage and consumption in order to produce materials for carbon capture in an environmentally friendly manner. Most conventional processes were shown to carry out pyrolysis under an inert atmosphere using N_2 , before a second stage was carried out to physically activate the biochar under a CO_2 or steam atmosphere [2]. The choice to physically activate the biochar instead

of chemically activating was also a conscious decision, and is attributed to 'green chemistry' principles. The most common chemical activator used in previous studies is KOH, which has been shown to give impressive results in terms of development of porosity [3]. This is, however, accompanied by drawbacks, due to the nature of KOH, namely its corrosive characteristics. KOH activation is normally carried out at 700 – 800 °C, and results in the degradation of much of the biochar material; this is very useful in creating a porous structure, but gives a very low yield of material from the original feedstock. The natural characteristics of KOH are also considered to be environmentally harmful and toxic, which makes it an undesired chemical to use from a health and safety standpoint. Other activators such as H_3PO_4 , HCl and NaOH have been used, but can have comparable issues, such as being corrosive or irritants [4]. Alternatively, physical activation can be carried out with either CO_2 or steam [5], both substances that are easier to work with, and do not provide the same level of negative environmental impact.

Both pyrolysis conditions, temperature and residence time, were obvious factors to vary, as much of the literature identifies these both as having significant impacts on the porosity and chemical make-up of the produced chars; this is detailed in depth in Chapter 2. Many different levels of both factors have been tested previously, which allowed for an assessment of upper and lower limits that could be applied to this study. Work previously carried out in the research group was also influential in helping to decide the respective limits. Temperature as a factor is important, in that the lower limit has to be high enough to ensure a sufficient degree of carbonisation is achieved, while too high a level would cause excessive degradation of the samples. From research, a range of 400 – 900 °C has been utilised for biochar production [6], [7], though it should be noted that those in the lower range of 400 °C were further activated after production [8]. Subsequently, a lower temperature limit of 500 °C and an upper limit of 800 °C were chosen for the screening section of this study.

Likewise, the limits used here for residence time reflect the desire to reduce energy consumption; a lower limit of 0.5 h and an upper limit of 3 h were chosen. These fall within the range of values of literature. 0.5 h is generally considered the minimum time required for a pyrolysis process to ensure volatilisation of the biomass can occur. Considering the upper limit, there are instances where high residence times of 6 h have been utilised [9]; while this will admittedly produce 'well' carbonised samples, it is expected that there comes a point where extending the time beyond a certain value will only bring a small increase in carbon content and other characteristics. Thus, 3 h was chosen as the high value for the screening DoE, in order to permit study of a wide range of time values while not excessively using energy.

Peel type was a key factor in the project, with the decision to investigate two related but not identical feedstocks taken early in the planning stage. Orange and mandarin peels originate from the same genus, *Citrus*, which in turn is part of the *Rutaceae* family of plants. As a result, they, unsurprisingly, share many common features, but rudimentary observational analysis shows differences in the thickness and texture of the peels from both fruits. As such, it was considered interesting to study whether these variations would produce significantly different results when tested for biochar production. Note that while the other three factors in the DoE are continuous (i.e., can vary from their initial chosen values and be tested at different levels) this factor is discrete, meaning that there are only two choices with no intermediate levels.

The selection of CO₂ as an activator is ascribed to its proven ability to create micropores in the structures of chars [10], which are the optimal pore size for materials to be utilised in carbon capture systems. Additionally, as the aim of the project is to capture and reduce CO₂ emissions, the use of CO₂ in the production of these materials helps to close the loop in a

circular economy aspect (using waste to create a useful product). In the literature, this is a factor that is considered during experimental planning, but usually at a set value [11]. Thus, to give a definitive answer for this study, it was chosen as a variable to test lower and upper levels of 100 and 400 mL/min CO₂, based on a range of values observed in academic papers.

Once all four factors were chosen and their levels fixed, Minitab 22 software was used to create an experimental plan; 16 runs were planned and were randomised to reduce bias. The runs performed are shown in Table 5.1. Two control experiments were also carried out; these samples were made using orange and mandarin peels respectively, at conditions of 800 °C, 0.5 h and 400 mL/min CO₂, and contained no urea doping, in order to give an example of non-doped biochars.

The responses chosen for the DoE analysis were: yield of biochar (%), micropore surface area determined using the t-plot method (m²/g), and carbon content from elemental analysis (wt%).

5.3 Screening Biochars Results

5.3.1 Yield

The yields of the screening biochars produced within this study are shown in Table 5.1. A clear split can be seen based on pyrolysis temperature used: for the samples produced at 500 °C, the yield varies from 18.6 – 24.1 %, while only one of the samples obtained through pyrolysis at 800 °C exhibited a yield of more than 14 % (BC 800-0.5-O-100 with 19.1 % yield). This is due to the higher pyrolysis temperature removing more volatile components from the peel feedstock, which, in turn, is advantageous in creating the desired porosity and subsequent larger surface areas of the samples [12].

Table 5.1: Conditions Used to Produce Screening Biochars with Subsequent Yield Results

Label	Pyrolysis Temperature (°C)	Residence Time (h)	CO ₂ Flowrate (mL/min)	Peel Type	Yield (%)
BC 500-0.5-O-400	500	0.5	400	Orange	24.0
BC 500-0.5-O-100	500	0.5	100	Orange	24.1
BC 500-0.5-M-400	500	0.5	400	Mandarin	20.2
BC 500-0.5-M-100	500	0.5	100	Mandarin	21.8
BC 500-3-O-400	500	3	400	Orange	22.9
BC 500-3-O-100	500	3	100	Orange	23.9
BC 500-3-M-400	500	3	400	Mandarin	22.9
BC 500-3-M-100	500	3	100	Mandarin	18.6
BC 800-0.5-O-400	800	0.5	400	Orange	12.5
BC 800-0.5-O-100	800	0.5	100	Orange	19.1
BC 800-0.5-M-400	800	0.5	400	Mandarin	13.8
BC 800-0.5-M-100	800	0.5	100	Mandarin	13.0
BC 800-3-O-400	800	3	400	Orange	4.2
BC 800-3-O-100	800	3	100	Orange	3.4
BC 800-3-M-400	800	3	400	Mandarin	5.0
BC 800-3-M-100	800	3	100	Mandarin	4.5
BC Control Orange	800	0.5	400	Orange	9.0
BC Control Mandarin	800	0.5	400	Mandarin	8.0

The 500 °C pyrolysed chars do not show a significant difference in yield between the two residence times, however, this is not the case for chars produced at 800 °C. The higher temperature has already been shown to be more destructive in terms of stripping volatiles from the peel, thus, as the peel is exposed to this higher temperature for a longer period, it is natural that more of the feedstock will be removed during pyrolysis. The higher temperature can be seen to be useful for removing volatiles but prolonged exposure can lead to the carbon, which is the backbone of biochar, becoming excessively degraded and leading to lower yields [13]. It is possible that the low lignin content of orange peel impacts on the pyrolysis process [14]. As this is commonly the last of the three lignocellulosic materials to degrade [15], it has been found to contribute to the structure that remains after pyrolysis; however, if there is a low concentration of it to begin with in the material, this will doubtlessly have an effect on the final char structure.

As the peels are organic materials, their structure comprises of substantial amounts of cellulose, hemicellulose and lignin, which are known to break down during pyrolysis. Hemicellulose and cellulose break down at temperatures in the region of 100 – 400 °C, whereas it can take temperatures of up to and beyond 800 °C to fully decompose lignin within biomass samples [16]. The yield thus decreases as pyrolysis residence time and temperature increase, as there is greater decomposition of the three organic materials described [17]. Urea, and its decomposition products, has been shown to fully degrade by approximately 400 °C, so it would be expected that, in all of the doped chars produced, this has been removed by the pyrolysis process.

In literature studies on orange peel biochars, researchers have reported yields of 31 % after 10 min pyrolysis at 500 °C, 35 % after 1 h of 500 °C, and 31 % after 2 h of 500 °C [18], [19], [20]. These are all slightly higher than the results seen here but this could be due to a variety of reasons, such as experimental setup, gas flow rate and feedstock pre-treatment. A possible explanation for a difference in yields in this study could result from the reverse Boudouard reaction taking places at lower temperatures, during cooling of the chars, or from ingress of oxygen into the experimental setup, once the CO₂ gas flow was shut off due to lab safety policy. This may have resulted in degradation of the sample, and reduced the overall yield of char collected the next day; if N₂ gas had been used during the cooling period, then any reactions with the leftover char would have ceased, and similarly, no reactions with oxygen would have taken place.

From the control samples, we see that they exhibit a reduced yield when compared to the doped samples produced under the same conditions. This suggests that the inclusion of urea helps to retain more of the carbon structure of the biochar, or that it reacts with the material to produce functional groups on the material that are more resistant to the pyrolysis process.

For non-doped orange peel biochar reported in the literature, two similar examples were found; biochar produced at 600 °C for 1 h was obtained at a yield of 10.8 % [21], while another char made at 800 °C for 2 h gave a yield of 10.3 % [17]. The control samples created in this study demonstrate slightly lower yield values, 8 – 9 %, but are still close to the values seen in these previous studies; variation in the values could possibly be attributed to differences in experimental setup, or in peel type used in each study, as the thickness and pith of orange peel can vary between species.

5.3.2 Elemental Analysis and Proximate Analysis

The proximate analysis results obtained for the screening biochars from this study are given in Table 5.2 and the results obtained from elemental analysis are shown in Table 5.3.

Considering the results obtained for the raw orange and mandarin peel samples first, it is evident that the majority of the sample is composed of volatile components (approx. 72 – 74 wt%), with only approx. 21 – 23 wt% fixed carbon from proximate analysis, while the elemental carbon content from elemental analysis is determined as approx. 43 – 44 wt%. This agrees with a previous study on orange peel characterisation, which showed values of 70 wt%, 24.1 wt% and 40.4 wt% for volatiles, fixed carbon and elemental carbon, respectively [21].

The results obtained for proximate analysis of the full suite of biochar samples can be seen in Table 5.2, and it is evident that, as the temperature reaches 500 °C and above, volatile components are still being removed from the biochar. This indicates and confirms that, when pyrolysis is being carried out at 500 °C, this temperature is insufficient to fully carbonise the peels and remove volatile components. This can also help in explaining the lack of porosity in these samples as, at this lower temperature, the CO₂ has not been able to fully penetrate the structure of the peels and create a porous network [22].

Table 5.2: Proximate Analysis Results Obtained for Screening Biochars Produced in this Study

Sample	Moisture (wt%)	Volatiles (wt%)	Fixed Carbon (wt%)	Ash (wt%)
BC 500-0.5-O-400	3.0	29.3	66.2	1.5
BC 500-0.5-O-100	5.0	32.2	58.6	4.2
BC 500-0.5-M-400	5.4	25.8	65.0	3.9
BC 500-0.5-M-100	4.0	23.1	71.4	1.5
BC 500-3-O-400	5.4	36.9	54.5	3.2
BC 500-3-O-100	2.7	27.3	67.4	2.6
BC 500-3-M-400	4.3	23.2	70.7	1.8
BC 500-3-M-100	5.1	28.3	62.3	4.3
BC 800-0.5-O-400	8.5	21.3	61.5	8.7
BC 800-0.5-O-100	7.0	19.1	66.2	7.7
BC 800-0.5-M-400	7.0	19.6	70.6	2.8
BC 800-0.5-M-100	7.3	18.8	69.0	4.9
BC 800-3-O-400	2.1	37.1	35.7	25.1
BC 800-3-O-100	8.5	31.4	42.4	17.7
BC 800-3-M-400	4.1	40.6	46.6	8.7
BC 800-3-M-100	2.5	45.3	37.5	14.7
BC Control Orange	8.7	24.9	48.9	17.5
BC Control Mandarin	10.5	28.9	46.7	13.9
Dried Orange Peel (No Urea)	2.9	73.7	21.2	2.2
Dried Mandarin Peel (No Urea)	3.5	71.9	23.2	1.4
Doped Orange Peel	2.7	86.6	10.7	0
Doped Mandarin Peel	2.7	85.8	11.3	0.2

For the samples obtained for pyrolysis at 500 °C, the fixed carbon content represents more than 50 wt% of the mass of each biochar, in some cases as high as 70 wt%. This suggests that most, but not all, of the volatiles have been removed, along with any moisture, leaving the carbon backbone of the char. Considering the results obtained for the char produced at 800 °C for 0.5 h, it can be seen that these exhibit the lowest range of volatile wt% (approx. 19 – 21 wt%) and fixed carbon contents similar to the samples produced from pyrolysis at 500 °C. The higher level of volatilisation results in an increase in ash content, as minerals, such as potassium and calcium, remain unchanged from the carbonisation process, thus this fraction makes up a larger percentage of the final mass [23]. The results obtained for the chars produced at 800 °C for 3 h are less favourable in terms of the carbon locked away into

the structure, as they are seen to exhibit fixed carbon levels of around 35 – 50 wt%, with several exhibiting significantly higher ash contents, up to 25 wt%. Overall, it appears that the pyrolysis conditions of 800 °C and 0.5 h are the most appropriate for favourable biochar production, considering the ranges of the factors tested in this study.

Fixed carbon contents of 59 – 81 wt% have been previously reported for biochars made from orange peels [17], [24], [25], which is in line with the results reported here. Samples produced at 800 °C for 3 h show a variation from this, likely due to the longer residence time used; where being subjected to a higher temperature for a relatively long period of time leads to greater degradation of the biomass as a result of both the intense heat and the CO₂ gas flow. As a result, as well as volatile components being removed from the peel, the carbon structure is also destroyed and the fixed carbon content reduced. The higher temperatures also lead to higher ash levels, as the remaining minerals and inorganics within the feedstock become a higher relative proportion of the final material [26]. Previous studies have shown that chars produced at lower temperatures, and with shorter residence times, exhibit lower fixed carbon contents compared to those created with higher temperatures and longer residence times [27], indicating that incomplete removal of volatiles from the samples, alongside partial degradation of any lignin content, leads to a lower fixed carbon wt% overall. This would concur with the results reported here.

Elemental analysis was performed on the samples produced within the study, with residual content (oxygen, sulphur etc) determined by difference [19], [26]. The elemental composition, on an ash-free basis, of the screening biochars is seen in Table 5.3. It is clear that the wt% values for nitrogen in the doped samples are much higher than for the non-doped samples, indicating that inclusion of urea in the production stage has increased the nitrogen content of the biochars, as anticipated from the design phase of this work.

Table 5.3: Elemental Compositions Obtained for Screening Biochars Produced in this Study

Sample	C (wt%)	H (wt%)	N (wt%)	Residuals (wt%)
BC 500-0.5-O-400	62.9	2.4	13.3	21.4
BC 500-0.5-O-100	64.0	2.4	12.3	21.3
BC 500-0.5-M-400	61.6	2.4	14.1	21.9
BC 500-0.5-M-100	62.9	2.4	13.5	21.2
BC 500-3-O-400	61.9	2.4	12.3	23.4
BC 500-3-O-100	63.9	2.4	11.7	22.0
BC 500-3-M-400	64.0	2.0	14.3	19.7
BC 500-3-M-100	60.9	2.0	14.6	22.5
BC 800-0.5-O-400	57.2	1.0	9.9	31.9
BC 800-0.5-O-100	59.0	1.1	7.3	32.6
BC 800-0.5-M-400	62.9	1.3	11.2	24.6
BC 800-0.5-M-100	64.2	1.3	11.1	23.4
BC 800-3-O-400	37.1	0.5	7.0	55.4
BC 800-3-O-100	40.9	0.2	7.0	51.9
BC 800-3-M-400	57.6	1.0	9.6	31.8
BC 800-3-M-100	48.5	0.7	7.8	43.1
BC Control Orange	43.7	0.8	2.6	52.9
BC Control Mandarin	49.8	1.3	3.8	45.1
Dried Orange Peel (No Urea)	42.9	6.2	0.7	50.2
Dried Mandarin Peel (No Urea)	44.3	6.2	0.9	48.6
Doped Orange Peel	29.0	6.4	32.2	32.4
Doped Mandarin Peel	32.2	6.3	24.8	36.7

The carbon contents observed for the screening biochar samples show that most chars have between 55 – 65 wt% carbon content, as expected, as the pyrolysis process allows devolatilisation of the peel to occur [28], with the only difference again noted for the biochars obtained at 800 °C for 3 h. Their lower carbon contents can be explained, as above, by the overall degradation of the biochar structure after being subject to the combined harsh conditions of high temperature and long residence time. Elemental carbon content of the control biochars matches with literature data and the doping of urea onto the raw peels can be deemed successful, as the nitrogen content of the DoE biochars are significantly increased compared with the controls [29], [30].

5.3.3 Textural Analysis

Data regarding the porosity of the screening biochars and their precursor materials can be seen in Table 5.4. This has been obtained through N_2 sorption measurements and subsequent analysis and application of the Rouquerol correction, as described in Chapter 3. When considering the raw peels, it is clear that there is no detectable porosity within the material, which vindicates the decision to utilise the process of pyrolysis to treat the waste biomass in order to create a material suitable for use in carbon capture systems. It can also be seen that the preliminary step of doping using urea has little effect on the precursor material and, in both cases, there is no appreciable surface area for either peel type.

Two methods were used for micropore volume determination, as both methods have their own individual limitations in application. The Dubinin-Radushkevich (DR) method assumes an ideal Gaussian pore size distribution of micropores, which is not always the case [31], however, the deviations from linearity in the DR analysis can be used to predict variations in the micropore size distribution. The t-plot method uses a non-porous material, which should be of a similar composition to the sample being analysed, as a reference, to allow for calculation of microporous areas and volumes; however, due to the organic nature of biochars, it can be difficult to apply an exact reference material [32]. This method also works on the assumption that the materials have an 'ideal' flat surface, which does not occur in reality, again due to the organic nature of many samples. As a result of neglecting the curvature of the pores, there is an underestimation of the micropore volume for materials with high levels of microporosity [33]. Thus, due to the limitations of both methods, the results from each are presented to give as wide a view as possible of the porous character.

Table 5.4: Porosity Characteristics of Screening Biochars Produced in this Study

Sample	Specific Surface Area (m ² /g) ¹	Micropore Area (t-plot) (m ² /g) ²	Micropore Volume (t-plot) (cm ³ /g) ³	Micropore Volume (DR) (cm ³ /g) ⁴	t-plot Micropore Area/SSA (%)
BC 500-0.5-O-400	0	0	0	0	0
BC 500-0.5-O-100	0	0	0.001	0	0
BC 500-0.5-M-400	0	0	0	0.001	0
BC 500-0.5-M-100	0	0	0	0	0
BC 500-3-O-400	0	0	0	0	0
BC 500-3-O-100	0	0	0.001	0.001	0
BC 500-3-M-400	0	0	0	0	0
BC 500-3-M-100	0	0	0	0	0
BC 800-0.5-O-400	391	354	0.135	0.154	91
BC 800-0.5-O-100	398	369	0.140	0.155	93
BC 800-0.5-M-400	306	293	0.110	0.120	96
BC 800-0.5-M-100	346	317	0.120	0.135	91
BC 800-3-O-400	382	328	0.127	0.151	86
BC 800-3-O-100	290	263	0.100	0.115	91
BC 800-3-M-400	367	314	0.122	0.145	86
BC 800-3-M-100	420	347	0.135	0.167	83
BC Control Orange	339	273	0.106	0.135	80
BC Control Mandarin	436	357	0.139	0.174	82
Dried Orange Peel (No Urea)	0	0	0	0	0
Dried Mandarin Peel (No Urea)	0	0	0	0	0
Doped Orange Peel	0	0	0	0	0
Doped Mandarin Peel	0	0	0	0	0

A clear divide is seen between the biochar samples produced at 500 °C and those at 800 °C; the lower temperature samples demonstrate negligible surface areas and pore volumes (most results recorded were below the error range of the equipment) while the higher temperature samples show varying degrees of porosity. Results suggest that for the samples produced at 500 °C, in the absence of chemical activators, pyrolysis under CO₂ alone is not sufficient to create any significant form of porosity at this temperature level. The Boudouard

¹ Uncertainties within BET specific surface area (SSA) were calculated to be below 2 m²/g

² Uncertainties within non-zero t-plot micropore surface area values were calculated to be between 2 – 8 m²/g

³ Uncertainties within t-plot micropore volume were calculated to be below 0.003 cm³/g

⁴ Uncertainties within DR micropore volume were calculated to be below 0.001 cm³/g

reaction has been extensively studied in literature, and the thermodynamics of the reaction are well detailed. A previous study calculated the Gibbs free energy of the gasification reaction, where carbon reacts with CO₂ to produce CO; this reaction is only seen to be thermodynamically favourable at temperatures above 700 °C [34]. Below this temperature, the change in Gibbs free energy (ΔG) is positive and therefore the reaction will not proceed spontaneously [35]. Thus, the Boudouard reaction is not significantly active in the 500 °C range used to synthesise the lower temperature biochars. From a kinetic standpoint, an approximate calculation can be carried out to determine the increase of the relative reaction rate between 500 and 800 °C, using an adapted form of the Arrhenius equation, Equation 5.1. Note that the activation energy of the reaction was taken to be 230 kJ/mol; there are a range of values in literature given for the reaction, typically ranging from 200 – 260 kJ/mol [35], [36], [37], [38]. The value of 230 kJ/mol was chosen as this lies in the middle of that range, and the calculation included below is presented to give a simple approximation of the difference in relative reaction rate.

$$\frac{k_{800}}{k_{500}} = \frac{e^{-\frac{Ea}{RT_{800}}}}{e^{-\frac{Ea}{RT_{500}}}} \quad \text{Equation 5.1}$$

Where:

$$\frac{k_{800}}{k_{500}} = \text{relative rate of reaction at 800 °C compared to 500 °C}$$

$$Ea = \text{activation energy of the Boudouard reaction (J/mol)}$$

$$R = \text{universal gas constant (J/mol K)}$$

$$T = \text{temperature the reaction takes place at (K)}$$

Substituting in the relevant temperatures and activation energy gives:

$$\frac{k_{800}}{k_{500}} = \frac{e^{-\frac{23000}{8.3145 \cdot 1073}}}{e^{-\frac{230000}{8.3145 \cdot 773}}} = 22145 \cong 22000$$

Thus, it is seen from the above calculation that the Boudouard reaction is approximately 22,000 times faster at 800 °C than at 500 °C. This further confirms that the temperature of 500 °C is not conducive to the Boudouard reaction taking place, as CO₂ gasification is extremely slow, and thermodynamically unfavourable, below 700 °C.

A study that produced orange peel derived biochar via pyrolysis at 500 °C for 2 h found similar results, reporting the specific surface area (SSA) of the obtained material to be 0.70 m²/g [19]. This is likely due to the pyrolysis temperature being too low to remove a sufficient quantity of volatiles from the material for a microporous structure to be created; subsequent pore blocking could also arise due to the incomplete volatilisation of the feedstock [39]. Pore development may also be inhibited by lignin remaining in the sample, which has not fully degraded. However, an alternative study using orange peel to produce biochar reported a SSA of 230 m²/g, from pyrolysis at 550 °C for 2 h [40]. This raises the possibility that other factors, such as experimental configuration, or feedstock source, could be equally important factors that define the characteristics of these biochars. In any case, it is clear from the results of this study that temperatures higher than 500 °C are required to produce chars with suitable characteristics for CO₂ adsorption.

The samples produced at 800 °C display total SSA results of 290 m²/g or greater, in line with expected values for carbon materials used within adsorption systems. The use of CO₂ as an activating gas is known to be most effective at creating microporosity when used with temperatures of 700 – 900 °C [5]; this explains why there is a vast difference in porosity, considering both the SSAs and pore volumes, between the high and low temperature biochars reported in this study.

No clear trend arises between residence time and SSA but, interestingly, the highest SSA biochar obtained is that for the BC Mandarin control sample, which was not doped with urea. This could indicate that, for the 800 °C chars, there are issues associated with pore blocking due to urea doping, which was also observed in the 500 °C chars. Therefore, although higher SSAs are found for the samples produced at 800 °C, the higher pyrolysis temperature is still inadequate to overcome pore blocking phenomena. Conversely, as reported in Section 5.3.2, the samples obtained for pyrolysis at 800 °C demonstrated higher ash content than their 500 °C equivalents, which can further contribute to pore blocking [23].

By comparison, biochars created using a mix of orange, mandarin, lemon and lime peels, which underwent pyrolysis and CO₂ activation at 900 °C, were reported to exhibit SSAs ranging from 166 – 212 m²/g [41], while another study produced CO₂ activated biochar at 800 °C from orange peels, which had been processed to remove essential oils [42]; the SSA found in this case was 326 m²/g, which falls within the range observed in this study.

Table 5.5: Examples from Literature of Biochars Produced for CO₂ Capture Applications and their Characteristics

Biochar Precursor	Type of Activation	Specific Surface Area (m ² /g)	Micropore Area (m ² /g)	Micropore Volume (cm ³ /g)	CO ₂ Adsorption Capacity (mmol/g)	Ref.
Cucumber	Nitrogen doping and chemical activation	1848	-	0.710	5.96	[29]
Coconut Shells	Nitrogen doping and chemical activation	1596	-	0.820	7	[43]
Soybean Straws	Nitrogen doping and physical activation	491	534	0.210	2.02	[44]
Chicken Manure	Nitrogen doping and chemical activation	301.5	-	0.201	10.15	[45]
Olive Stones	Physical activation	757	-	0.30	5.88	[46]

The results for biochar SSA and micropore volume, Table 5.4, reported in this study are, in general, noticeably smaller than those found in literature, as seen in Table 5.5. Despite this, the microporous surface area results from this study demonstrate an interesting point, when the microporous area is assessed as a percentage of the total SSA. Using this metric, it is found that all ten char samples produced at 800 °C (doped and non-doped) show 80 % or more of the total surface area can be considered to fall within the microporous range. This is encouraging, as CO₂ adsorption is highly dependent on the presence of microporosity, due to the relative size of CO₂ molecules [47], hence these results indicate the 800 °C chars could be suitable for CO₂ adsorption applications.

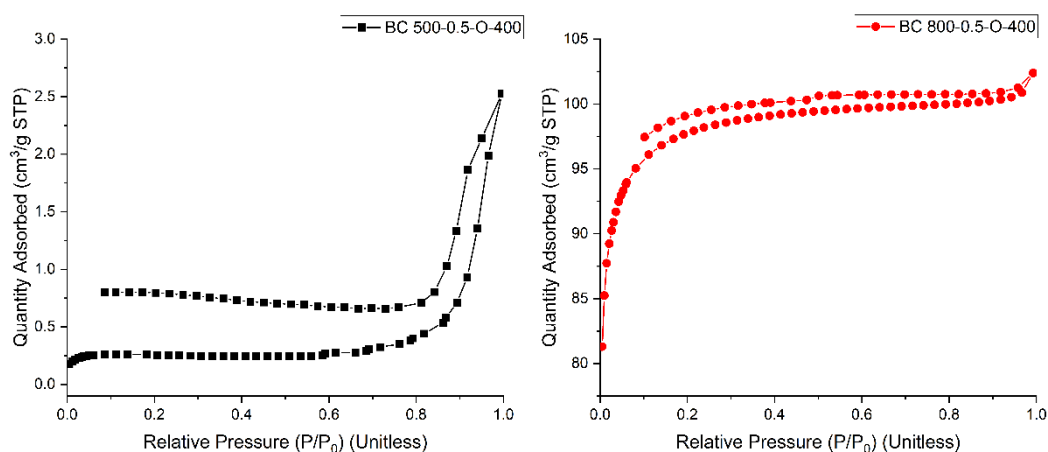


Figure 5.1: Example N₂ Isotherms for Biochar Screening Samples BC 500-0.5-O-400 (left) and BC 800-0.5-O-400 (right)

Figure 5.1 show examples of N₂ adsorption isotherms obtained for the screening biochars produced in this study. The shape of each isotherm represents the general trend found for the high and low temperature chars; the 500 °C pyrolysis sample isotherms resemble the left graph in Figure 5.1 and samples produced at 800 °C exhibit isotherms analogous to the right graph in Figure 5.1. These isotherms can be classified, allowing an indication of the porous character created within the samples. The isotherms obtained for the samples produced at

500 °C are closest to the standard Type II isotherm shape, based on IUPAC classification [48], which shows they are nonporous solids; only minimal adsorption has taken place on their surface, and therefore the pyrolysis temperature was insufficiently high to generate observable porosity. By contrast, the shape of the isotherms observed for the samples obtained through pyrolysis at 800 °C all resemble a Type I(b) isotherm, which indicates that the chars mainly comprise a microporous structure, containing micropores and narrow mesopores. This is confirmed by the relative proportions of micropore surface area to SSA, which is > 80 % for all of these samples. This indicates that the CO₂ activation method has been successful in creating microporous biochars.

5.3.4 Surface Chemical Analysis

FTIR spectroscopy was used to determine the surface chemical groups present in the raw peel and biochar materials produced in this study. The FTIR spectra of the raw precursor materials, orange and mandarin peels, can be seen in Figure 5.2.

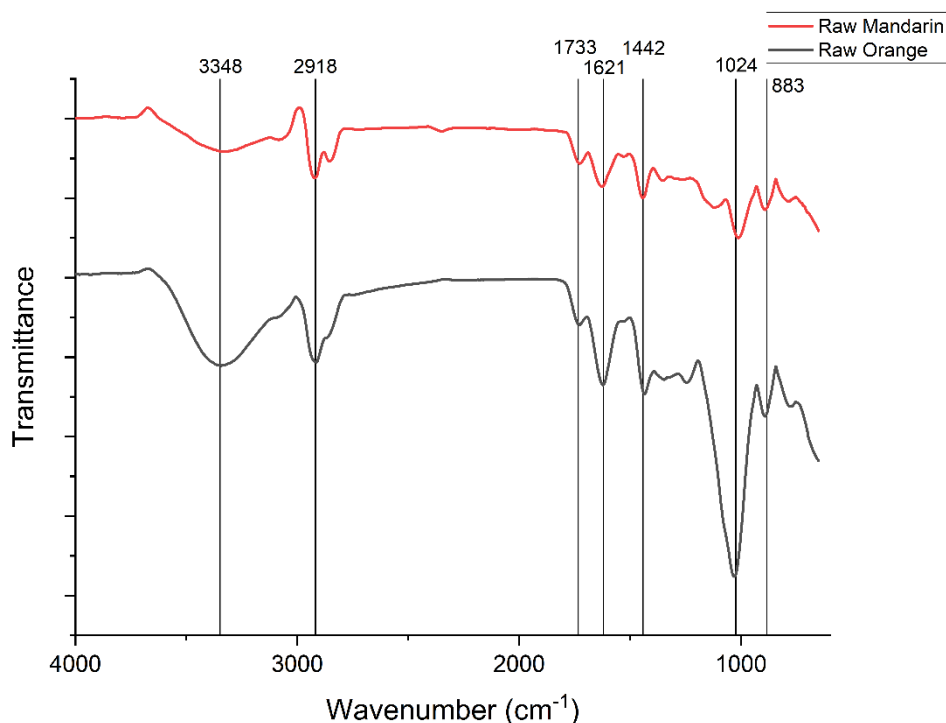


Figure 5.2: FTIR Spectra of Raw Orange and Mandarin Peel Feedstocks

The similarity of both peels is evident, with many of the same peaks shared between the two samples, which is not unexpected due to their association of being from the same taxonomy. A broad peak is found at approx. 3350 cm^{-1} which is characteristic of O-H hydroxyls found in the lignocellulosic structure of the peel, and N-H group stretching from any organic nitrogen in the fruit [49]. C-H stretching is observed at 2918 cm^{-1} likely from methylene groups that are typical of organic materials [50]. Evidence of carbonyl group stretching, C=O, arising from ester groups is seen at 1733 cm^{-1} [51], with aliphatic and aromatic compounds giving rise to the peak around 1620 cm^{-1} [52]. Similarly, aliphatic chains of C-H₃ are seen at 1441 cm^{-1} , which again relates to the fundamental lignocellulosic structure, meanwhile ester and carboxylic C-O bonding is evidenced by the 1023 cm^{-1} peak [53].

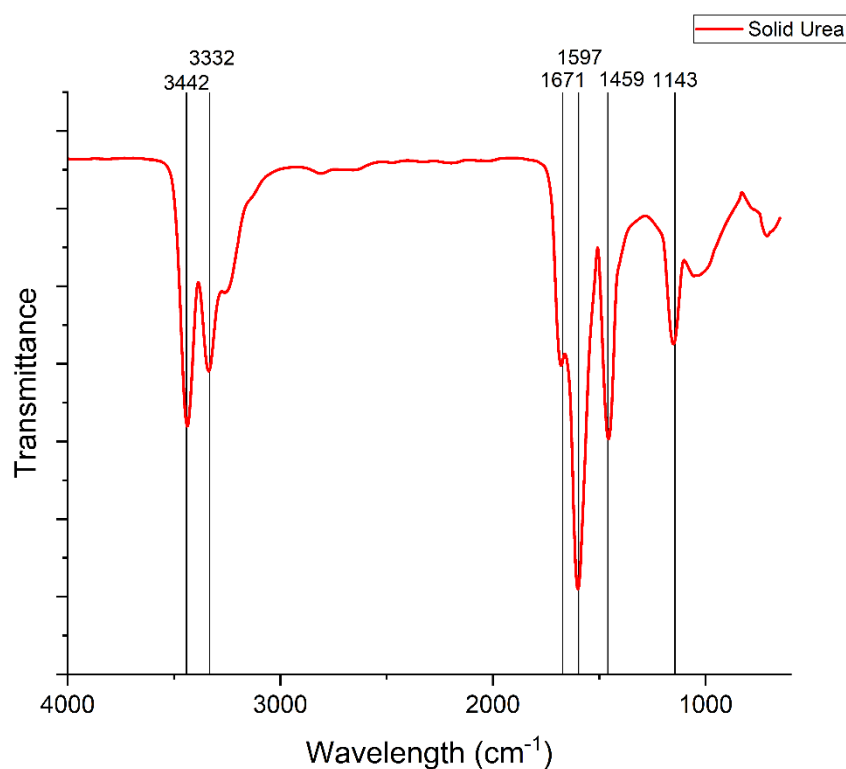


Figure 5.3: FTIR Spectrum of Solid Urea

An FTIR spectrum was collected for the pure urea used to dope the peels, and is shown in Figure 5.3. A large double peak, at around 3400 cm^{-1} , is indicative of N-H bonding, as is the peak at 1597 cm^{-1} [54]. A peak corresponding to C-N is seen at 1459 cm^{-1} , and the stretching of a C=O group at 1672 cm^{-1} . This confirms there is a range of nitrogen groups present in the urea, and therefore the inclusion of it as a doping material would be expected to lead to the transfer of a portion of these groups to the biomass material.

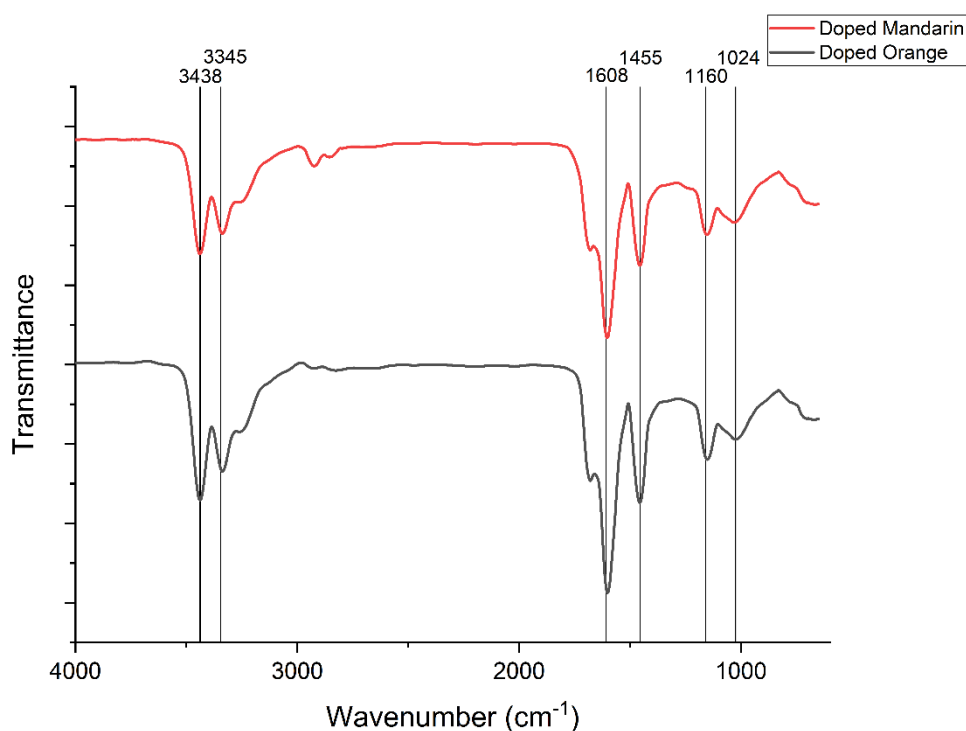


Figure 5.4: FTIR Spectra of Doped Orange and Mandarin Peel Feedstocks

Figure 5.4 shows FTIR spectra obtained for the raw doped orange and mandarin peels, before they were used in the pyrolysis process. The nitrogen peaks of N-H bonding from the urea doping can be seen starkly within the 3400 cm^{-1} range, and the aliphatic and ester peaks also remain within the sample. These spectra are similar to those of the undoped peels; aliphatic, ester and carboxylic bonding peaks all remain visible to a certain degree.

In comparing the raw peels to the produced biochars, seen in Figure 5.5 and Figure 5.6, it is found that many of the peaks disappear after pyrolysis; this could be due to the process of heating the material, causing bonds to be broken between different functional groups and molecules [55]. Alongside this, an issue of poor light penetration in the dark biochars samples was found to occur in practise, which could have contributed to peaks going undetected. As discussed in Chapter 4, a germanium crystal was used during the FTIR spectroscopy practical experiments. This was required due to the dark, carbon black nature of the biochars; due to their colour, they have a high refractive index, which can result in band distortion when using a conventional crystal such as diamond, as there is minimal internal reflection of the light [56]. This displays itself in the spectra as a 'tail off' of the graph in the range of 1500 – 600 cm^{-1} , showing no peaks. The use of the germanium crystal, which has one of the highest refractive indices of those used in FTIR spectroscopy, is known to reduce this effect, and provides more accurate spectra. It should be noted that a downside of this method is that it has a lower penetration depth, so is very much a characterisation technique suited to surface level of the sample only.

Figure 5.5 shows the FTIR spectra obtained for the biochars obtained through heating for 0.5 h and 3 h at 500 °C. It is clear to see all eight samples share very similar surface chemistry, with the same fundamental peaks identified for each one. N-H bending is observed at 1580 cm^{-1} in all samples, indicating some degree of nitrogen doping has been successful [57]. This could, however, also be a sign of C=C alkene stretching, which is common in carbon-based materials [58]. The peak around 1410 cm^{-1} can be attributed to C-H in plane bending, while out of plane bending of C-H is visible around 770 cm^{-1} .

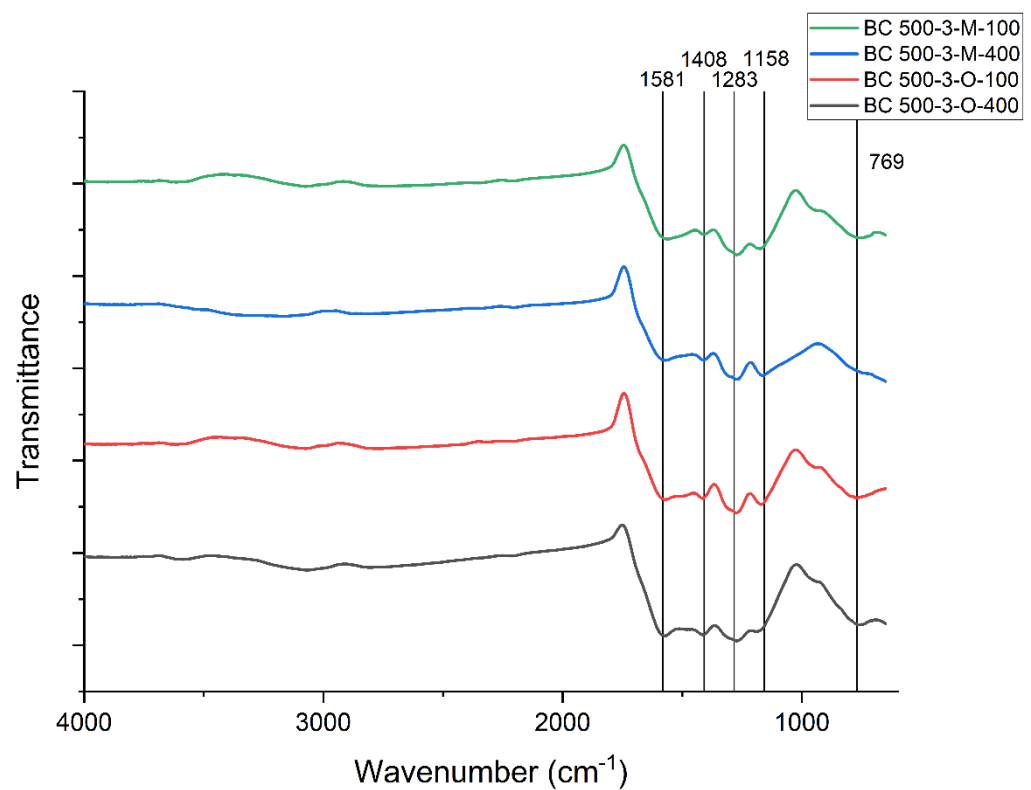
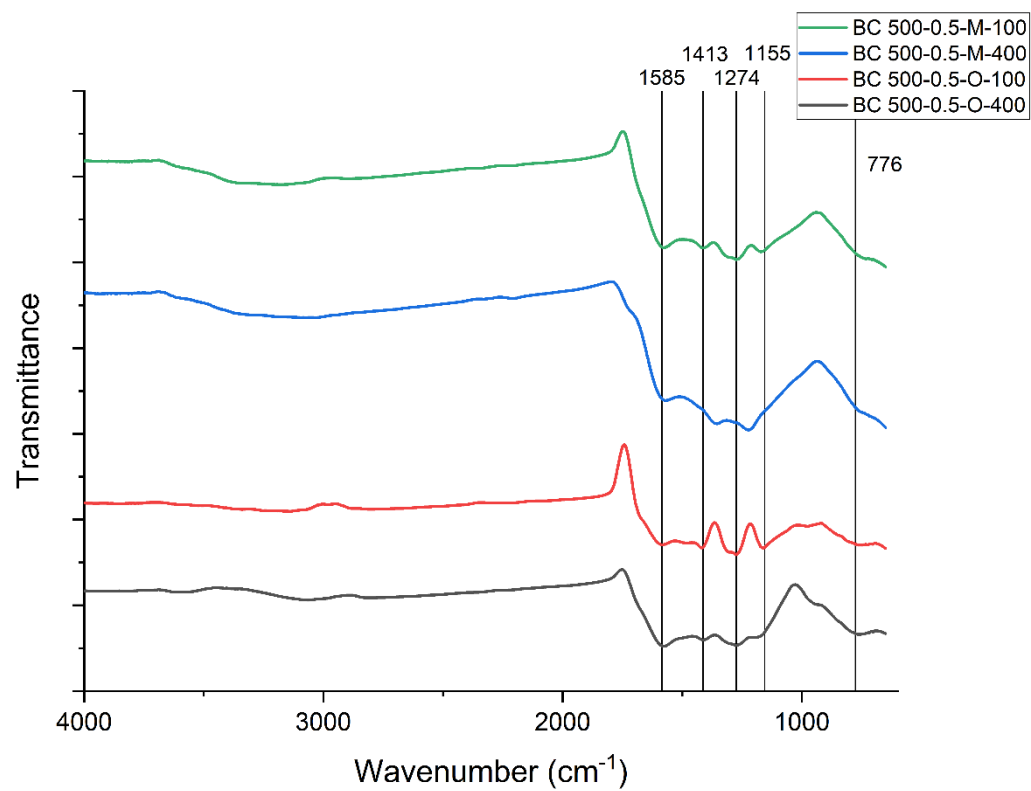


Figure 5.5: FTIR Spectra of Biochar Samples Produced Through Pyrolysis at 500 °C, 0.5 h (top) and 500 °C, 3 h (bottom)

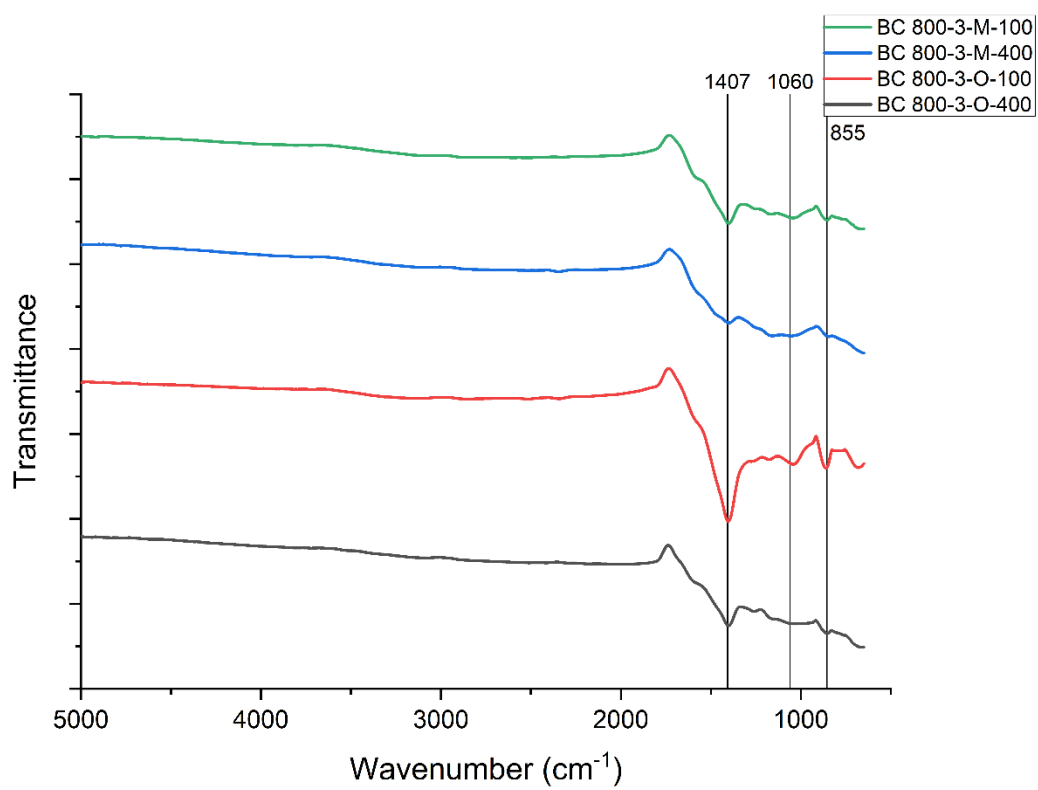
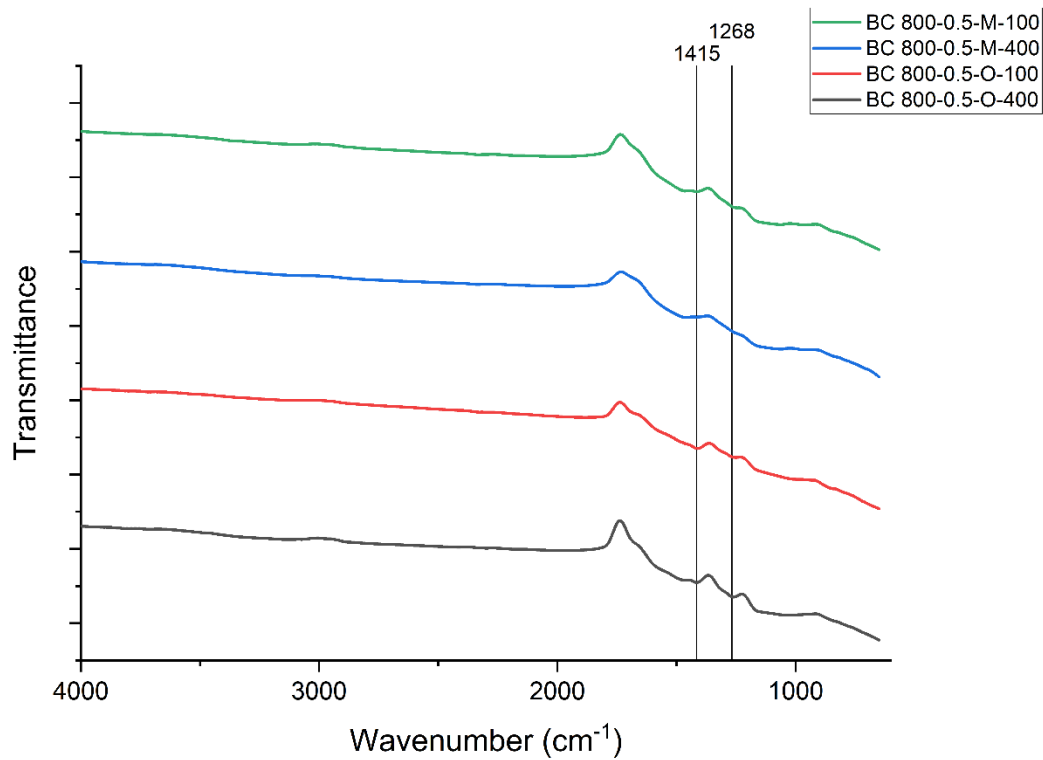


Figure 5.6: FTIR Spectra of Biochar Samples Produced Through Pyrolysis at 800 °C, 0.5 h (top) and 800 °C, 3 h (bottom)

Figure 5.6 show the spectra obtained for the biochars obtained through heating at 800 °C for 0.5 h and 3 h. The issues arising from the dark nature of the biochar are more pronounced for these materials, and the spectra produced are of poor quality with little to no discernible number of peaks available to identify. It is reassuring, despite this, that the two groups of 800 °C biochars both follow the same shape, and exhibit similar peaks to those seen in the lower temperature samples. Nonetheless, the results obtained through FTIR spectroscopy in this study further emphasise the need for a more appropriate analytical technique to characterise the surface of the chosen materials; XPS along with SEM are likely to be more appropriate and accurate.

5.3.5 Screening Design of Experiments Trends and ANOVA

Minitab 22 software was used to carry out regression analysis, and analysis of variance (ANOVA), using three responses: biochar yield, t-plot micropore area and carbon content. Carbon content was informed by elemental analysis. To carry out the analysis, an initial model was created for each response, which contained all four main factors and all two-factor interactions (i.e., AB would represent the interaction between pyrolysis temperature and residence time). Alpha for the model was set equal to 0.05, meaning a confidence level of 95 % was taken. From this, using Pareto Charts and the model summary, specific two-factor interactions were removed from the model when they were deemed to be insignificant, and the model recalculated on this basis. An example of this was the interaction of pyrolysis temperature and CO₂ gas flowrate (termed AD); it was not found to be significant in any of the three models, and thus, was removed from them. The final models were selected on the basis of their inclusion of all significant main factors. The three resulting regression equations can be seen in Equation 5.2 to Equation 5.4, where temperature is in °C, residence time in h and CO₂ flowrate in mL/min.

$$\begin{aligned} \text{Yield} = & 0.3281 - 0.000198 \text{ Temp} + 0.0639 \text{ Time} + 0.0385 \text{ Peel Type} - 0.000012 \text{ CO}_2 \text{ Flow} \\ & - 0.000132 \text{ Temp} * \text{Time} - 0.000035 \text{ Temp} * \text{Peel Type} - 0.00378 \text{ Time} * \text{Peel Type} \end{aligned} \quad \text{Equation 5.2}$$

$$\begin{aligned} \text{Micropore Area} = & -558.6 + 1.1209 \text{ Temp} + 13.8 \text{ Time} + 8.1 \text{ Peel Type} - 0.0038 \text{ CO}_2 \text{ Flow} \\ & - 0.0274 \text{ Temp} * \text{Time} + 0.0170 \text{ Temp} * \text{Peel Type} - 9.26 \text{ Time} * \text{Peel Type} \end{aligned} \quad \text{Equation 5.3}$$

$$\begin{aligned} \text{Carbon Content} = & 61.40 + 0.00674 \text{ Temp} + 6.55 \text{ Time} + 8.11 \text{ Peel Type} - 0.00038 \text{ CO}_2 \text{ Flow} \\ & - 0.01315 \text{ Temp} * \text{Time} - 0.01241 \text{ Temp} * \text{Peel Type} - 0.838 \text{ Time} * \text{Peel Type} \end{aligned} \quad \text{Equation 5.4}$$

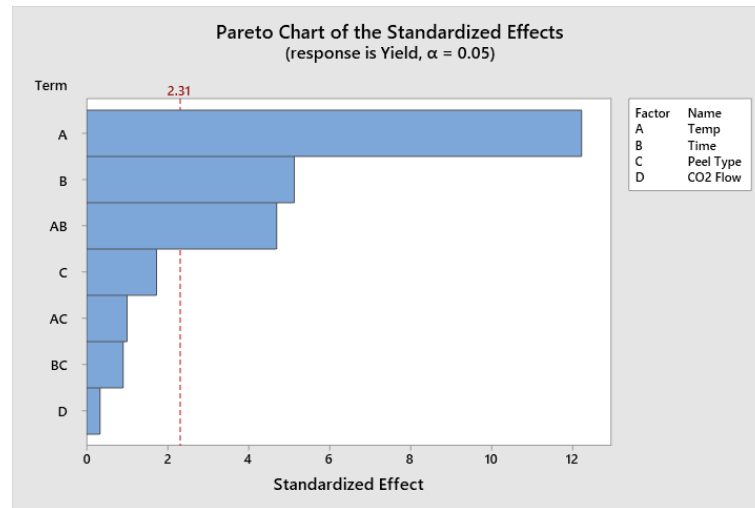


Figure 5.7: Screening Pareto Chart for Biochar Yield as DoE Response

The Pareto charts of standardised effects for all three responses can be seen in Figure 5.7 - Figure 5.9. These show which factors, and two-factor interactions, are significant for each response. It should be noted that for all three responses the CO₂ gas flowrate was found to have little impact on variation in each response.

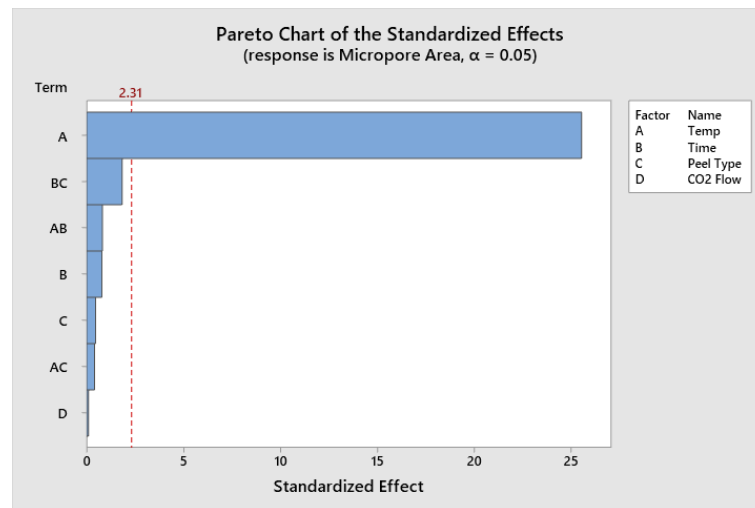


Figure 5.8: Screening Pareto Chart for Biochar Micropore Area as DoE Response

For the micropore area response model, only pyrolysis temperature is seen to be a significant factor, but for the yield and carbon content models there are multiple different factors which show a statistical influence on the response results.

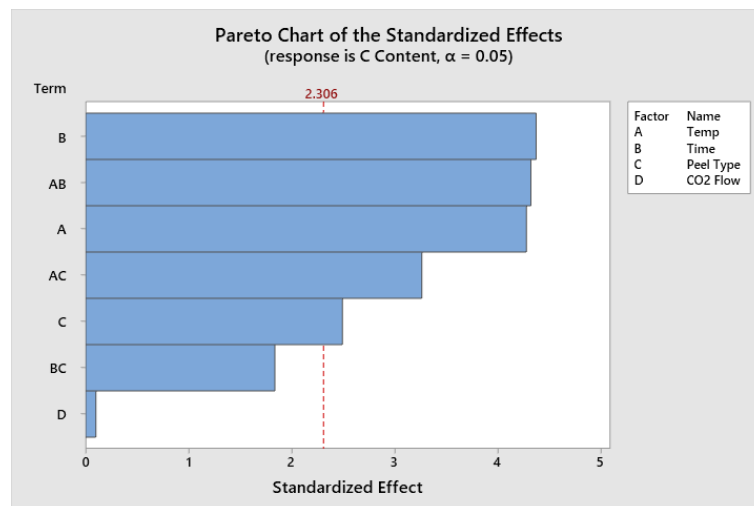


Figure 5.9: Screening Pareto Chart for Biochar Carbon Content as DoE Response

The coefficients of determination (R^2), along with the adjusted (adj) and predicted (pred) values of the same coefficient, are seen in Table 5.6 for each response equation. The R^2 of each equation for the chosen response represents how much of the variation of the response

variable is explained by the chosen model [59]. Looking at the results, the micropore area response is the most well fitted model of the three.

Table 5.6: Screening Coefficients of Determination for Each Response

Response	R ² (%)	R ² -adj (%)	R ² -pred (%)
Yield	96.20	92.87	84.80
Micropore Area	98.80	97.74	95.19
Carbon Content	90.50	82.19	62.00

The full ANOVA results for each response can be seen in Appendix B. As well as Pareto charts, *F* and *p* values from ANOVA analysis can be used to show which factors and interactions are significant in the models for each response. The *p* value is used to determine whether changing the level of a factor has an effect on the response, that is unlikely to have occurred due to chance [60]. At significance level $\alpha = 0.05$, if the *p* value ≤ 0.05 for a given factor, this indicates that the factor significantly affects the measured response. Alternatively, if *p* value > 0.05 for a given factor, then the opposite is true, and the factor is not statistically significant in terms affecting of the measured response.

Through assessment of both Pareto charts and *p* values for each of the three responses, it can be determined that the three factors: pyrolysis temperature, residence time, and peel type are all statistically influential, to some degree, as are several of the two-factor interactions, while CO₂ gas flowrate is not influential. From this, these three influential factors were taken forward for further analysis in the optimisation stage of the DoE.

It should be highlighted that the R²-pred value for the micropore area model must be treated with caution. As only two temperature levels were tested in the screening design, 500 °C and 800 °C, the model is seen to be fitting a binary response; as discussed previously, the Boudouard reaction is not thermodynamically favourable at the lower temperature of 500 °C, while at 800 °C it will proceed and generate a certain degree of porosity. Therefore,

this model is not representative of a continuous relationship, and is instead confirming the thermodynamic behaviour of the CO₂ gasification process. As a result, it should not be used to make predictions for micropore area. This also reiterates the fact that the models presented in the DoE screening process should not be used to optimise or predict any char performance.

Also note from the findings from this screening design that the fact that gas flow rate is not significant in any of the three measured responses may be due to the horizontal configuration of the furnace and the influence this has on the mass transfer of CO₂, as discussed in Chapter 4. As a result, the conclusion that gas flow rate is not a significant process parameter can only be considered valid in the context of this study, which utilises a horizontal tube furnace.

5.4 Optimisation Design of Experiments Plan

After carrying out DoE analysis of the produced screening biochars, three factors of pyrolysis (temperature, residence time and peel type) were deemed significant in at least one of the three responses measured. Thus, these factors were chosen to be investigated further in the optimisation stage. As CO₂ flowrate was deemed not to be significant, it was set at a value of 400 mL/min [61]. This level was chosen to ensure swift removal of gaseous volatiles from the system after their evolution, and to provide a greater rate of cooling to the sample upon completion of pyrolysis. Literature studies have previously show that higher flowrates can increase porosity [12], which directly contradicts the finding of the micropore area response model presented in Section 5.3.5 of this study. An explanation for this could be due to the fact that a horizontal tube furnace setup was utilised in this project, compared to the vertical fixed bed reactor in the aforementioned study [12]. In the horizontal furnace setup, the CO₂ gas will flow over the surface of the biomass, and rely on diffusion into the sample as the

process takes place, whereas in a vertical configuration the CO₂ will flow through and contact more of the biomass sample; as a result, the vertical setup provides more efficient mass transfer and, therefore, possibly has a greater effect on the final properties of the char. It was not possible to test the difference in configurations due to financial and equipment constraints in the project, so in order to best match the available literature, the flowrate was maintained at the higher level of 400 mL/min for the optimisation experiments.

A circumscribed (CCC) design was chosen for use in the optimisation DoE. This allows the testing of levels outwith the previously set limits assigned to each factor, a fundamental feature of this design. For example, in the screening design, 0.5 h and 3 h were used as upper and lower limits for residence time, but in the optimisation stage, values below 0.5 h and above 3 h were assessed to create a full surface response over this range. This also led to a change in the conditions used for the pyrolysis temperature, but did not apply to the factor of peel type due to its discrete nature.

It was clear from the BET results in Section 5.3.3 that samples produced at 500 °C displayed minimal levels of porosity, so testing temperatures below this value would be futile for this response. As literature showed that porosity begins to develop from temperatures of 600 °C or greater, the decision was taken to increase the lower limit for this factor to 650 °C for the optimisation stage, and maintain the upper limit at 800 °C. This allowed for an increase in the likelihood of porosity development in the lower temperature samples produced at 650 °C, and would, in turn, produce more relevant data for the study. Coupled with the fact that CO₂ activation is usually carried out in the range of 700 – 900 °C [4], this gave more samples from this study to compare with literature examples.

Minitab 22 was again used to create the experimental plan, resulting in 18 experiments to be carried out in random order, and the details of these can be seen in Table 5.7. The chosen responses for the analysis were unchanged from the screening stage.

5.5 Optimisation Biochars Results

5.5.1 Yield

The yields of the optimised biochars produced in this study are shown in Table 5.7. Replicate samples from the screening design are shown in Table 5.8 against their corresponding replicate samples from the optimisation design. A general trend is witnessed of yield decreasing with increasing temperature and residence time, similar to observations seen for the screening biochar samples. The samples produced at 650 °C have almost identical yield results (20 – 21 %), however, due to the lower temperature limit of the optimisation DoE stage changing, there are no replicates from the screening stage to allow comparison of results. Nonetheless, it is still pertinent to assess the variation between the chars produced at 500 °C in the screening design and those at 650 °C in the optimisation design, in the cases where the other three factors were constant. For three of the biochars, the yield of the samples produced at 650 °C were lower than those obtained via pyrolysis at 500 °C, and in one case, the 650 °C sample exhibited a slightly higher yield (OBC-650-0.5-M). This implies that increasing pyrolysis temperature will result in increased volatilisation of components within the biomass and, thus, reduce the mass yield of the product; however, variation should still be expected in samples, due to the organic nature of the materials. The 800 °C samples produced during the optimisation stage all exhibit moderately higher yields than those produced from the screening stage; the two samples produced through heating at 800 °C for 3 h increased by 0.2 % each, while the OBC-800-0.5-O sample increased by 3.6 % and the OBC-800-0.5-M sample by 3.2 %. This increase in yield for the samples produced at

0.5 h is possibly due to heterogeneity between the feedstock batches used in each stage of the design. These results suggest there is a high level of repeatability in the sample production process for the higher temperature runs, which is auspicious, as these are the biochars expected to be most applicable to carbon capture technology.

Table 5.7: Conditions Used to Produce Optimisation Biochars and Subsequent Yield Results

Label	Pyrolysis Temperature (°C)	Residence Time (h)	Peel Type	Yield (%)
OBC 650-0.5-O	650	0.5	Orange	21.1
OBC 800-0.5-O	800	0.5	Orange	16.1
OBC 650-3-O	650	3	Orange	20.2
OBC 800-3-O	800	3	Orange	4.4
OBC 619-1.75-O	619	1.75	Orange	20.6
OBC 831-1.75-O	831	1.75	Orange	1.9
OBC 725-0-O	725	0	Orange	20.6
OBC 725-3.52-O	725	3.52	Orange	16.3
OBC 725-1.75-O	725	1.75	Orange	18.8
OBC 650-0.5-M	650	0.5	Mandarin	20.7
OBC 800-0.5-M	800	0.5	Mandarin	17.0
OBC 650-3-M	650	3	Mandarin	20.3
OBC 800-3-M	800	3	Mandarin	5.2
OBC 619-1.75-M	619	1.75	Mandarin	20.5
OBC 831-1.75-M	831	1.75	Mandarin	3.7
OBC 725-0-M	725	0	Mandarin	20.2
OBC 725-3.52-M	725	3.52	Mandarin	18.0
OBC 725-1.75-M	725	1.75	Mandarin	19.7

It is notable that the samples produced at 619 °C and 725 °C demonstrate very similar yields; it could be suggested that, within the 600 – 725 °C range, there is a strong relationship between temperature and residence time. For example, OBC-619-1.75-O has a yield of 20.6 %, which is identical to OBC-725-0-O. Therefore, it may be inferred that using a short residence time and higher temperature as pyrolysis conditions will give a comparable yield to runs with condition of longer residence time and/or lower temperature. This does digress from the overall goal of the work, however, as while material yield is important, the ability to absorb CO₂ is the prime focus; based on results from this study and previous papers,

biochars produced in the temperature range of 650 – 725 °C will likely not be suitable for this application [62].

For the samples produced through heating at 831 °C, very small yields are achieved (< 4 %), which is impractical for real-world applications or even small-scale testing. The samples obtained from pyrolysis at 725 °C show a gradual decrease in yield as residence time increases, a trend that matches with prior knowledge and research, as the biomass undergoes increased volatilisation as time progresses.

Table 5.8: Comparison of Yield Between Replicate Samples of Screening and Optimisation Biochars

Screening Sample	Yield (%)	Corresponding Optimisation Sample	Yield (%)
BC 800-0.5-O-400	12.5	OBC 800-0.5-O	16.1
BC 800-0.5-M-400	13.8	OBC 800-0.5-M	17.0
BC 800-3-O-400	4.2	OBC 800-3-O	4.4
BC 800-3-M-400	5.0	OBC 800-3-M	5.2

5.5.2 Elemental Analysis and Proximate Analysis

The proximate analysis of the screening biochars can be seen in Table 5.9. Replicate samples from the screening design are shown in Table 5.10 against their corresponding samples from the optimisation design. These results show a degree of complexity and must be broken down step by step to be fully analysed. The chars produced at temperatures in the range 619 – 650 °C show similar fixed carbon contents of between 64 – 70 %, which are comparable to those seen for the biochars produced at 500 °C in the screening stage, indicating that this is a suitable temperature range to pyrolyse biomass to produce a carbon rich material.

Table 5.9: Proximate Analysis Results Obtained for Optimisation Biochars Produced in this Study

Sample	Moisture (wt%)	Volatiles (wt%)	Fixed Carbon (wt%)	Ash (wt%)
OBC 650-0.5-O	4.6	27.8	63.9	3.7
OBC 800-0.5-O	5.7	24.8	60.9	8.6
OBC 650-3-O	5.6	20.0	67.7	6.7
OBC 800-3-O	14.8	29.3	45.8	10.1
OBC 619-1.75-O	6.8	19.1	69.8	4.3
OBC 831-1.75-O	12.6	41.8	31.2	14.4
OBC 725-0-O	6.6	18.4	69.8	5.2
OBC 725-3.52-O	7.6	23.3	63.8	5.3
OBC 725-1.75-O	7.0	24.2	63.0	5.8
OBC 650-0.5-M	6.1	18.6	70.5	4.8
OBC 800-0.5-M	8.2	20.7	65.2	5.9
OBC 650-3-M	5.1	22.6	67.3	5.0
OBC 800-3-M	14.4	25.0	53.8	6.8
OBC 619-1.75-M	5.0	22.1	67.3	5.6
OBC 831-1.75-M	6.9	34.8	37.8	20.5
OBC 725-0-M	5.3	21.4	67.6	5.7
OBC 725-3.52-M	4.7	18.8	71.8	4.7
OBC 725-1.75-M	4.5	20.9	68.1	6.5

Increasing the temperature to 725 °C has little perceivable effect; fixed carbon contents for the six samples produced at this level were observed to lie in the range of 62 – 72 %. For the three mandarin biochars the fixed carbon increases as residence time increases, demonstrating that prolonged exposure to higher temperature does increase the removal of volatile matter from the biomass. In contrast, for the orange biochars at this temperature, the highest fixed carbon is found in the sample which experienced a residence time of 0 h.

For the samples produced through heating at 800 °C there is a continuation of the trends observed in the screening experiments; mainly that the 800 °C – 0.5 h samples exhibit fixed carbon contents comparable to the lower temperature samples, while the 800 °C – 3 h samples exhibit less carbon, due to the more destructive heating conditions. This persists for the samples produced at 831 °C, with the lowest fixed carbon levels in the study seen for these materials.

Table 5.10: Comparison of Proximate Analysis Results Between Replicate Samples of Screening and Optimisation Biochars

Screening Sample	Moisture (wt%)	Volatiles (wt%)	Fixed Carbon (wt%)	Ash (wt%)
BC 800-0.5-O-400	8.5	21.3	61.5	8.7
BC 800-0.5-M-400	7.0	19.6	70.6	2.8
BC 800-3-O-400	2.1	37.1	35.7	25.1
BC 800-3-M-400	4.1	40.6	46.6	8.7
Optimisation Sample	Moisture (wt%)	Volatiles (wt%)	Fixed Carbon (wt%)	Ash (wt%)
OBC 800-0.5-O	5.7	24.8	60.9	8.6
OBC 800-0.5-M	8.2	20.7	65.2	5.9
OBC 800-3-O	14.8	29.3	45.8	10.1
OBC 800-3-M	14.4	25.0	53.8	6.8

The 800 °C – 3 h and all 831 °C samples display significantly higher ash contents; again, this is attributable to the mineral components that now contribute a greater relative proportion of the material, as more carbon is released during pyrolysis. The high ash content can become a complication in the application of biochars, as it is an indicator of higher mineral contents within the chars, which, in turn, could adversely affect their performance within remediation technologies [63].

The elemental composition of the biochars produced in the optimisation study, on an ash free basis, are shown in Table 5.11, and comparison between replicate samples from the screening and optimisation design in Table 5.12. Looking at the samples produced using temperatures between 619 – 725 °C, a consistent level of elemental carbon (63 – 65 wt%) is seen, regardless of residence time. This indicates that pyrolysis up to this temperature range is efficient at removing volatiles from biomass and can enhance the carbon content to a predetermined maximum. Therefore, in situations where creation of a carbon rich material is the intention, these conditions can be replicated to provide such an outcome. However, although carbon content is an important factor for biochars, these samples are seen to lack noteworthy porosity, which is fundamentally more important to their performance as carbon

sequestering materials. As such, to achieve the goals of this study, pyrolysis temperatures must exceed 725 °C.

Table 5.11: Elemental Compositions Obtained for Optimisation Biochars Produced in this Study

Sample	C (wt%)	H (wt%)	N (wt%)	Residuals (wt%)
OBC 650-0.5-O	63.3	1.4	12.9	22.4
OBC 800-0.5-O	58.2	1.0	10.9	29.9
OBC 650-3-O	66.0	1.0	13.1	19.9
OBC 800-3-O	30.9	0.6	6.4	62.1
OBC 619-1.75-O	63.6	1.0	10.9	24.5
OBC 831-1.75-O	20.0	0.2	4.3	75.5
OBC 725-0-O	63.5	1.1	11.9	23.5
OBC 725-3.52-O	64.0	0.8	12.3	22.9
OBC 725-1.75-O	63.9	0.7	12.3	23.1
OBC 650-0.5-M	66.2	1.2	13.5	19.1
OBC 800-0.5-M	62.6	1.0	10.7	25.7
OBC 650-3-M	65.6	1.2	12.1	21.1
OBC 800-3-M	49.8	0.9	8.9	40.4
OBC 619-1.75-M	64.9	1.4	12.1	21.6
OBC 831-1.75-M	38.7	0.6	6.7	54.0
OBC 725-0-M	64.5	1.0	11.5	23.0
OBC 725-3.52-M	64.5	0.9	11.7	22.9
OBC 725-1.75-M	65.4	0.6	11.4	22.6

In turn, assessing the results for biochar samples produced at temperatures in the range 800 – 831 °C, there is generally a lower comparative carbon content. The exceptions are the two samples produced at 800 °C for a residence time of 0.5 h, as they show carbon contents of 58 and 63 wt% respectively. This is, in part, due to the shorter residence time; the high temperature ensures that volatiles are driven off from the material, but it is not subject to sustained heating, meaning the carbon backbone remains largely intact. Compare these to the samples produced at 800 °C for 3 h, where the carbon content decreases to 31 wt% for the orange biochar and 50 wt% for the mandarin biochar, and it is clear that exposure to longer residence time at this elevated temperature can be detrimental to the overall biochar structure.

Table 5.12: Comparison of Elemental Analysis Results Between Replicate Samples of Screening and Optimisation Biochars

Screening Sample	C (wt%)	H (wt%)	N (wt%)	Residuals (wt%)
BC 800-0.5-O-400	57.2	1.0	9.9	31.9
BC 800-0.5-M-400	62.9	1.3	11.2	24.6
BC 800-3-O-400	37.1	0.5	7.0	55.4
BC 800-3-M-400	57.6	1.0	9.6	31.8
Optimisation Sample	C (wt%)	H (wt%)	N (wt%)	Residuals (wt%)
OBC 800-0.5-O	58.2	1.0	10.9	29.9
OBC 800-0.5-M	62.6	1.0	10.7	25.7
OBC 800-3-O	30.9	0.6	6.4	62.1
OBC 800-3-M	49.8	0.9	8.9	40.4

The destructive effect of sustained heating is witnessed in the most extreme case for the 831 °C biochar samples; although a shorter residence time of 1.75 h was used, the elemental carbon content for the orange sample was 20 wt%, and 39 wt% for the mandarin sample. This follows the trend of less carbon being locked within the material structure as pyrolysis temperature increases. It is interesting to note for the 831 °C – 1.75 h and 800 °C – 3 h samples that the orange peel biochars have noticeably lower carbon contents than those made from mandarin peel. This could imply there is a meaningful difference in the makeup of each species of peel; note that raw orange peel contained 44 wt% carbon and mandarin peel contained 50 wt%, from the elemental analysis of the raw peels. Naturally this would suggest biochars produced from the orange peel variant would contain less carbon, but a difference of approximately 20 wt% is somewhat unexpected.

Another factor could be that orange peels contain more pith than their mandarin relatives, with the pith itself consisting of a much softer tissue of parenchyma cells; meanwhile the outer layer of the peel (the thicker orange material), is composed of dense collenchyma cells [64]. It is also known that the parenchyma cells contain more cellulose compared to the collenchyma cells [65], and the pith tissue is much less densely arranged on a cellular level than the outer peel [66]. Thus, the orange peels overall are likely to contain more cellulose

than the mandarin peels, with cellulose degrading around 300 °C; therefore, this, in combination, with the different levels of cellular packing, suggests that orange peels may degrade more freely during pyrolysis than the mandarin peels, mirroring what is seen at the high temperatures of > 800 °C. However, the exact effect of pith content was not controlled or explored here.

The elemental nitrogen content remains high relative to the control samples previously produced, replicating the trend from the screening design. Values of 10 – 13 wt% are reported for the majority of samples, and the samples produced at temperatures $\geq$ 800 °C with long residence times, show lower values (4 – 8 wt%); this being a result of the harsh heating conditions, as discussed previously.

High ash contents in samples such as OBC 831-1.75-O and OBC 831-1.75-M result in larger values of residual content, in these cases, greater than 50 wt% of the total material. This is a result of a high proportion of the material degrading to ash, meaning a considerable percentage of the original elemental carbon has been removed and minerals such as potassium and sodium comprise a higher relative wt%. The residual content constitutes approximately 20 wt% for the remaining samples; the majority of this is likely oxygen, but there may be small amounts of elements, such as sulphur, that have not been fully removed from the raw peels and survived the pyrolysis process.

Comparison of the samples produced in the optimisation stage and their replicates from the screening stage, as shown in Table 5.12, demonstrate an encouraging level of consistency between the two sets. The 800 °C – 0.5 h samples have approximately the same carbon content, and their nitrogen content is very similar. The 800 °C – 3 h samples show slightly more variation in carbon content, but may be due to different batches of feedstock being used in each phase of the design.

5.5.3 Textural Analysis

Data pertaining to the porosity characteristics of the optimised biochars can be seen in Table 5.13, and comparison with replicates from the screening design are shown in Table 5.14. It is observed that, despite efforts to produce a wide range of porous samples, the new lower temperature limit of 650 °C was still not high enough to generate meaningful porosity, again, due to the lower temperature lying below the 700 °C point where the Boudouard reaction becomes active for CO₂ gasification to occur. This has been witnessed in literature, where soybean CO₂ activated biochars did not develop any notable porosity until the activation temperature reached 700 °C [44]. The limited degradation of lignin through pyrolysis in this temperature range may also be contributing to the non-porous structure observed.

Table 5.13: Porosity Characteristics of Optimisation Biochars Produced in this Study

Sample	Specific Surface Area (m ² /g) ⁵	Micropore Area (t-plot) (m ² /g) ⁶	Micropore Volume (t-plot) (cm ³ /g) ⁷	Micropore Volume (DR) (cm ³ /g) ⁸	t-plot Micropore Area/SSA (%)
OBC 650-0.5-O	0	0	0	0	0
OBC 800-0.5-O	289	263	0.100	0.114	91
OBC 650-3-O	0	0	0	0	0
OBC 800-3-O	237	193	0.076	0.095	81
OBC 619-1.75-O	0	0	0	0	0
OBC 831-1.75-O	31	22	0.009	0.013	71
OBC 725-0-O	0	0	0	0	0
OBC 725-3.52-O	213	198	0.075	0.086	93
OBC 725-1.75-O	87	85	0.032	0.035	97
OBC 650-0.5-M	0	0	0	0	0
OBC 800-0.5-M	225	203	0.077	0.090	90
OBC 650-3-M	0	0	0	0	0
OBC 800-3-M	355	304	0.118	0.143	86
OBC 619-1.75-M	0	0	0	0	0
OBC 831-1.75-M	319	269	0.105	0.129	85
OBC 725-0-M	0	0	0	0	0
OBC 725-3.52-M	121	116	0.043	0.048	96
OBC 725-1.75-M	0	0	0	0	0

⁵ Uncertainties within BET specific surface area were calculated to be below 1 m²/g

⁶ Uncertainties within non-zero t-plot micropore surface area values were calculated to be between 1 – 5 m²/g

⁷ Uncertainties within t-plot micropore volume were calculated to be below 0.002 cm³/g

⁸ Uncertainties within DR micropore volume were calculated to be below 0.001 cm³/g

Increasing the pyrolysis temperature to 725 °C does show an enhancement of the textural properties of the samples; out of the six biochars produced at this temperature, three are considered porous. OBC 725-3.52-O and OBC 725-3.52-M both demonstrate relative microporosities of greater than 90 %, and OBC 725-1.75-O is almost entirely microporous. The total surface area of each sample is lower than that of the samples produced at 800 °C or above, indicating that it is in this range of temperatures that microporosity development is instigated. For the samples produced at 725 °C with a residence time of 0 h, no porosity is generated, so it should be noted that sustained temperature is required to breakdown the lignocellulosic components of the material. Interestingly for the samples produced at 725 °C with a residence time of 1.75 h, the orange peel biochar exhibits a porous nature but the mandarin biochar does not; so far in this study there have been few noticeable differences between the two species of peel. A possible explanation could be due to the ratio of outer skin peel to pith in the samples; the more pith there is in the sample, the more well developed the porosity. This makes physical sense, as the pith is much softer than the outer peel which could suggest there is less robust components such as lignin present. This in turn relates to the discussion of pith content found in Section 5.5.2. There are other factors, such as pre-processing of the fruit, that may affect the relative biochar properties obtained as, despite the peels being washed before pyrolysis, they will have experienced different processing stages before shipment to the supermarket. Similarly, although the peels share a taxonomy of the same fruit genus, they possess fundamental structural and elemental differences that separate them as different species, which may also affect the outcomes.

The samples produced at temperatures of 800 °C and above prove to be superior chars within this study, in terms of the level of porosity development; all except OBC 831-1.75-O demonstrate total SSAs of greater than 200 m²/g. This confirms observations made from the

screening stage that to attain sufficient pore networks for carbon capture applications, a pyrolysis temperature in the region of 800 °C is required.

Table 5.14: Comparison of Porosity Characteristics Results Between Replicate Samples of Screening and Optimisation Biochars

Screening Sample	Specific Surface Area (m ² /g) ⁹	Micropore Area (t-plot) (m ² /g) ¹⁰	Micropore Volume (t-plot) (cm ³ /g) ¹¹	Micropore Volume (DR) (cm ³ /g) ¹²	t-plot Micropore Area/SSA (%)
BC 800-0.5-O-400	391	354	0.135	0.154	91
BC 800-0.5-M-400	306	293	0.110	0.120	96
BC 800-3-O-400	382	328	0.127	0.151	86
BC 800-3-M-400	367	314	0.122	0.145	86
Optimisation Sample	Specific Surface Area (m ² /g) ¹³	Micropore Area (t-plot) (m ² /g) ¹⁴	Micropore Volume (t-plot) (cm ³ /g) ¹⁵	Micropore Volume (DR) (cm ³ /g) ¹⁶	t-plot Micropore Area/SSA (%)
OBC 800-0.5-O	289	263	0.100	0.114	91
OBC 800-3-O	237	193	0.076	0.095	81
OBC 800-0.5-M	225	203	0.077	0.090	90
OBC 800-3-M	355	304	0.118	0.143	86

Once again, there is a notable difference between the orange and mandarin chars produced at 831 °C, with the mandarin char being highly porous relative to lower temperature samples, and the orange char exhibiting primitive porosity. It is known that OBC-831-1.75-O had degraded heavily under the intense conditions (temperature and residence time), losing a high percentage of its carbon structure in the process, but OBC-831-1.75-M also suffered a notable loss of carbon; thus, it is surprising that there is such a vast difference in porosity terms between the two samples. The values reported for SSA and micropore area, volume

⁹ Uncertainties within Screening BET specific surface area (SSA) were calculated to be below 2 m²/g

¹⁰ Uncertainties within non-zero Screening t-plot micropore surface area values were calculated to be between 2 – 8 m²/g

¹¹ Uncertainties within Screening t-plot micropore volume were calculated to be below 0.003 cm³/g

¹² Uncertainties within Screening DR micropore volume were calculated to be below 0.001 cm³/g

¹³ Uncertainties within Optimisation BET specific surface area were calculated to be below 1 m²/g

¹⁴ Uncertainties within non-zero Optimisation t-plot micropore surface area values were calculated to be between 1 – 5 m²/g

¹⁵ Uncertainties within Optimisation t-plot micropore volume were calculated to be below 0.002 cm³/g

¹⁶ Uncertainties within Optimisation DR micropore volume were calculated to be below 0.001 cm³/g

etc. for the samples in the optimisation runs vary from those obtained for the samples produced in the screening runs at the same conditions, see Table 5.14. This is an unfortunate drawback of using organic biomass material; the very nature of its composition means that there is no guaranteed consistency from batch to batch of oranges or mandarins. Similarly, although the same species of each feedstock were sourced from the same supermarket, they were purchased at different times of the year; the screening biochars were synthesised with peels purchased in the spring, whereas the optimisation biochars were produced from peels purchased in the autumn. It is impossible to accurately discern a full record of factors that would influence the composition or makeup of the fruits, but it is obvious that the changing of seasons and the weather conditions they were subjected to during growth would be key in their impact on the final product. For the samples that do exhibit porosity, there is a high level of microporosity in all, which is promising with a view for testing their ability to adsorb CO₂.

5.5.4 Surface Chemical Analysis

The elemental surface composition (at. %) of each of the optimisation biochars, as calculated from XPS, is shown in Table 5.15. Considering the raw and doped peels; the nitrogen content increases on doping, reaffirming the elemental analysis results, which indicates that urea doping was successful in the initial stage and nitrogen-containing groups did impregnate onto the peels.

Similarly, the samples produced at temperatures between 619 – 725 °C match the trend seen from the bulk elemental analysis (Section 5.3.2), in that their surface is composed mainly of carbon, with all samples demonstrating a carbon at. % of greater than 59 at. %. Although there was no concerted effort to increase oxygen-containing functional groups on the surface

of the materials, it is clear for most that the at. % of oxygen either remained consistent or increased in comparison with the precursor peels.

Table 5.15: XPS Surface Composition Analysis Results of Optimisation Biochars Produced in this Study

Sample	C 1s (at. %)	N 1s (at. %)	O 1s (at. %)	Residuals (at. %)
OBC 650-0.5-O	84.4	7.6	7.2	0.8
OBC 800-0.5-O	83.7	7.3	8.0	1.0
OBC 650-3-O	83.9	7.8	7.5	0.8
OBC 800-3-O	41.3	13.4	32.5	12.8
OBC 619-1.75-O	57.7	19.5	19.3	3.5
OBC 831-1.75-O	22.1	3.8	50.2	23.9
OBC 725-0-O	58.2	17.8	20.6	3.4
OBC 725-3.52-O	57.1	19.2	21.4	2.3
OBC 725-1.75-O	59.1	18.9	20.2	1.8
OBC 650-0.5-M	59.9	20.6	17.7	1.8
OBC 800-0.5-M	58.6	18.2	20.8	2.4
OBC 650-3-M	61.9	21.2	15.6	1.3
OBC 800-3-M	42.1	13.3	33.9	10.7
OBC 619-1.75-M	60.6	19.8	17.9	1.7
OBC 831-1.75-M	34.2	9.1	43.1	13.6
OBC 725-0-M	61.6	19.2	17.5	1.7
OBC 725-3.52-M	60.2	19.7	18.2	1.9
OBC 725-1.75-M	61.8	20.2	16.3	1.7
BC Control Orange	75.5	1.7	18.0	4.8
BC Control Mand	79.9	2.5	14.2	3.4
Raw Orange Peel	76.9	1.6	21.5	0
Raw Mandarin Peel	79.3	1.5	18.5	0.7
Doped Orange Peel	73.8	5.4	20.8	0
Doped Mandarin Peel	76.3	4.7	19.0	0

For the samples produced at 800 °C and above, the carbon content decreases, owing to the harsher pyrolysis conditions, and the residual content is also considerably higher (10 – 20 at. %). This is representative of ash formation, which manifests itself on the surface of chars as minerals such as potassium and calcium. There are considerable quantities of atomic nitrogen on the surface of some of the samples produced at 800 °C, further enhancing their credentials as potential CO₂ capture materials [67].

The different chemical environments of each of the three elements, carbon, nitrogen and oxygen, can be identified based on their peaks that exist within the bonding energy range of each element. For carbon the main peak lies at 284.8 eV; this is commonly known as the adventitious carbon peak of C-C/C-H bonding. It is frequently used as a 'reference peak' to which the spectra are calibrated, due to the abundance of carbon in most organic materials, and as such it is appropriate to use in the analysis of biochars [68]. From this, it is then possible to identify other bonding peaks arising from carbon existing in the sample, and these can include: C-O at 286.5 eV, C=O at 287.8 eV, C=N at 285.9 eV, O-C=O 289 eV and π^* - π^* transitions at 291 eV [69], [70], [71].

Regarding oxygen-containing moieties, there are three main groups which are identified in the biochar samples. Quinone and carbonyl groups (O-1 – C=O) are represented by a peak at approximately 531 eV, phenol or ether groups (O-2 – C-OH, C-O-C) at 532 eV and carboxylic acid groups (O-3 – O=C-OH) at 534 – 535 eV [67].

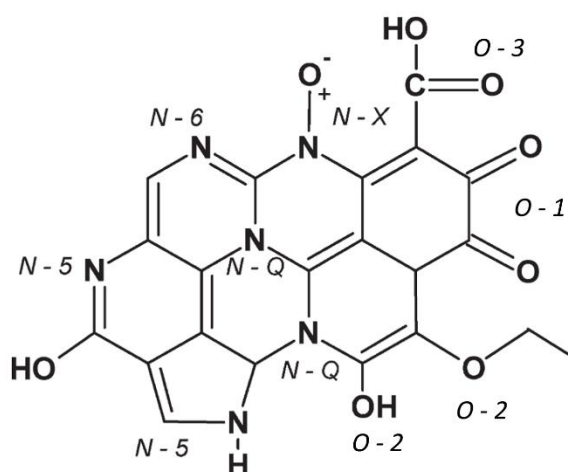


Figure 5.10: Nitrogen and Oxygen-Containing Surface Functional Bonding Groups [72]

In terms of nitrogen-containing groups, there are four notable moieties, although only three are found on the surfaces of the biochars produced in this study. Pyridinic nitrogen (N-6) at 398 eV, pyrrolic and pyridone (N-5) at 400 eV, and quaternary nitrogen (N-Q) at 401 eV are all visible within the spectra of the biochars, while pyridine-N-oxide (N-X) was not present [72]. An example of the different bonding groups that can occur on the surface is shown in Figure 5.10. [73]. During the process of nitrogen doping, the quantity of these chemical groups has increased in the biochar samples through the insertion of nitrogen atoms into cyclic carbon rings [74]. On the edge of the carbon sheets and rings the N-5 groups can be found, appearing as N-H groups [75], while N-6 groups are characteristically found with a single and double bond to two carbon atoms, respectively. The N-Q moieties are similar to N-6, but tend to be firmly embedded inside the aromatic framework of the biochars, existing within the carbon layers. The graphs detailing the peaks for each element for a chosen sample (OBC 619-1.75-M) can be seen in Figure 5.11, Figure 5.12 and Figure 5.13.

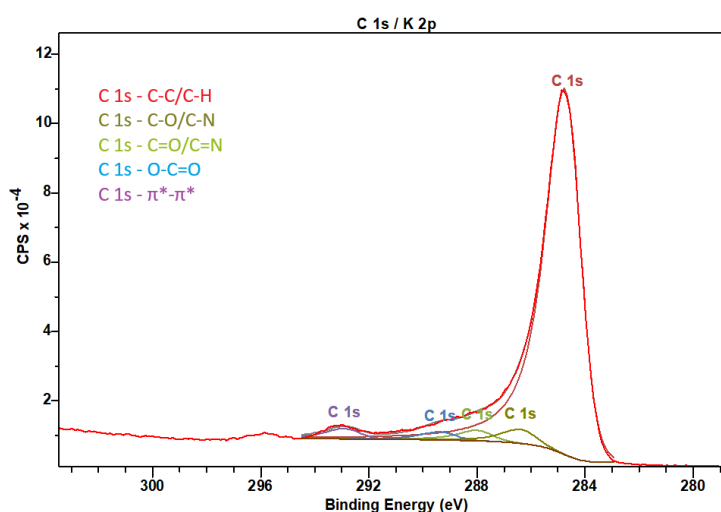


Figure 5.11: XPS Spectrum for Carbon C 1s of OBC 619-1.75-M

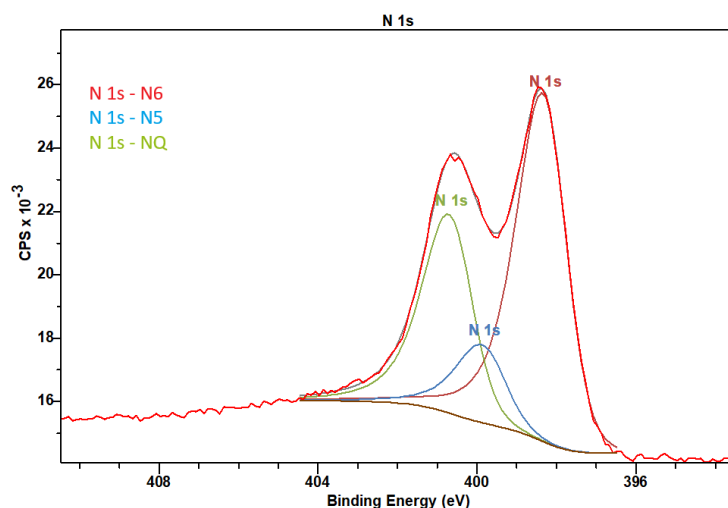


Figure 5.12: XPS Spectrum for Nitrogen 1s of OBC 619-1.75-M

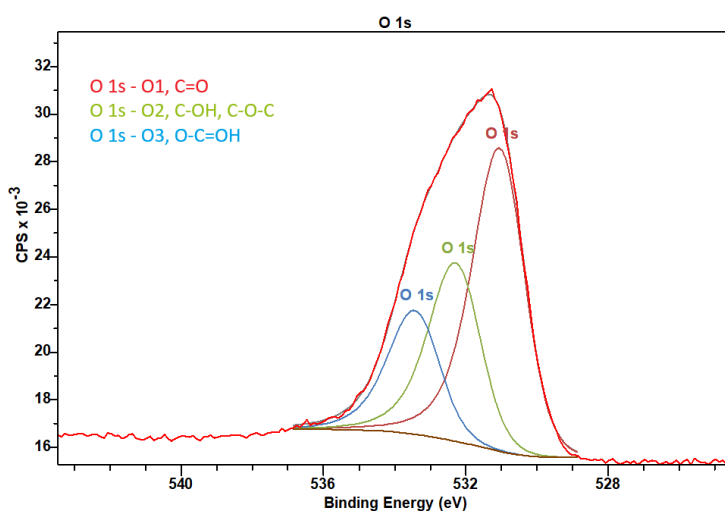


Figure 5.13: XPS Spectrum of Oxygen 1s of OBC 619-1.75-M

The breakdown of nitrogen- and oxygen-containing surface bonding on the biochar samples can be seen in Table 5.16. Pyridinic nitrogen is consistently seen to be the most prominent form of nitrogen on the surface of the chars, with all except one of the samples having a N-6 content of > 50 %. N-Q tends to be the second most prominent surface species of nitrogen, with pyrrolic N-5 being third. At temperatures used for pyrolysis in this study, 619 – 831 °C, the N-5 nitrogen groups are known to convert to N-6 pyridinic forms [76]. This is observed in

this study, as when comparing the raw precursor to the produced biochars, there is a correlation between pyridinic nitrogen increasing and pyrrolic nitrogen decreasing.

When assessing CO₂ adsorption potential, pyridinic and pyrrolic are the most desired species; pyridinic nitrogen interacts with carbon due to its high electronegative nature and by causing Lewis acid-base interactions, while pyrrolic nitrogen has been seen to enhance adsorption through a hydrogen bonding mechanism [77]. Previous studies have also shown a positive relationship between enhanced CO₂ adsorption and pyridinic and pyrrolic moieties, although this was only valid in the pressure range of 0 – 0.5 bar, with tests at atmospheric pressure not providing the same conclusion [78]. For all but one sample, pyridinic nitrogen is the most prevalent form found on the surface of the biochars. The one sample that does not fit this trend is OBC-831-1.75-O, known to be a primarily ashy sample with low carbon and nitrogen content; this would justify why the high-resolution nitrogen scan results differ from other samples.

Interestingly, the pyrrolic nitrogen content is higher in samples produced at higher temperatures (approx. 800 °C) than those at lower temperature (619 – 725 °C). This conflicts with literature knowledge that states pyrrolic nitrogen should change to the pyridinic form with increasing temperature. It is also thought that pyridinic nitrogen should further convert to the quaternary form at temperatures exceeding 800 °C [79], but lower values are seen for N-Q in samples produced at 800 °C than for the samples produced at 725 °C and below.

Table 5.16: XPS Analysis Surface Nitrogen and Oxygen Composition of Optimisation Biochars Produced in this Study

Sample	Bond types and energy ranges (eV)					
	N-6 (pyridinic) (%)	N-5 (pyrrolic) (%)	N-Q (quaternary) (%)	O-1 (C=O) (%)	O-2 (C-O) (%)	O-3 (O-C=O) (%)
OBC 650-0.5-O	56	12	32	54	27	19
OBC 800-0.5-O	55	19	26	59	27	14
OBC 650-3-O	55	10	35	47	34	19
OBC 800-3-O	59	29	12	69	21	10
OBC 619-1.75-O	57	9	34	52	31	17
OBC 831-1.75-O	24	63	13	86	13	1
OBC 725-0-O	56	12	32	41	41	18
OBC 725-3.52-O	54	17	29	55	33	12
OBC 725-1.75-O	53	18	29	51	30	19
OBC 650-0.5-M	55	10	35	51	32	17
OBC 800-0.5-M	54	20	26	59	26	15
OBC 650-3-M	56	9	35	45	34	21
OBC 800-3-M	51	23	26	28	60	12
OBC 619-1.75-M	56	12	32	50	30	20
OBC 831-1.75-M	50	26	24	17	71	12
OBC 725-0-M	55	13	32	52	30	18
OBC 725-3.52-M	55	14	31	48	34	18
OBC 725-1.75-M	53	14	33	48	32	20
BC Control Orange	38	50	12	48	28	24
BC Control Mandarin	69	31	0	27	60	13
Raw Orange Peel	0	97	3	11	74	15
Raw Mandarin Peel	0	88	12	10	65	25
Urea Orange Peel	0	81	19	20	62	18
Urea Mandarin Peel	26	55	19	16	59	25

Oxygen-containing groups deemed important for CO₂ adsorption are generally forms of O-1 and O-3 moieties; O-1 carbonyl bonds provide a quadrupole moment which is favourable for CO₂ molecules, while O-3 carboxylic groups are highly hydrophilic which helps alongside the pyrrolic nitrogen surface groups [29]. O-1 oxygen such as carbonyl and ketone groups are the main groups left on the biochar after the pyrolysis process is completed, as seen from Table 5.16. The predominant type of oxygen on the original precursor peels was O-2, due to

hydroxyl groups being a key functional group in the composition of orange peels [51]. Overall, there is a reasonable spread of the three types of oxygen-containing moieties across each sample, excluding the two biochars produced at 831 °C. The presence of the oxygen-containing surface groups should provide an additional route for CO₂ adsorption onto the samples, by providing ancillary sites for molecules to interact with. For example, although the carbon surface of the chars is hydrophobic, having different hydrophilic oxygen-containing groups available may counter this and encourage adsorption [76].

To compare the levels of nitrogen doping achieved on the external surface of the chars against the nitrogen doping present in the bulk, the elemental analysis results from Section 5.5.2 were converted to atomic percentage, in order to allow a calculation of ratios of XPS determined nitrogen to elemental analysis determined nitrogen. Note that hydrogen was excluded from the atomic percentage calculations, as XPS cannot detect hydrogen. This ratio calculation was also carried out for oxygen, where the value's given for 'residuals' were used to calculate a ratio of XPS determined oxygen to elemental analysis determined oxygen; note again that, the elemental analysis is presented on an ash-free basis. Therefore, it is assumed that the residuals are oxygen, but to confirm this specialised elemental analysis would be required, which was not possible due to financial restrictions.

The results of both ratios can be seen in Table 5.17. For the nitrogen doped biochars, the vast majority of the samples have a ratio > 1, indicating that there is a greater quantity of nitrogen-containing functionalities on the external surface of the materials than on the internal surface areas and the general bulk. This implies that there are more sites on the external surface of the chars for molecules to adsorb to, than there are in the bulk of the material, which is where the porosity exists, and thus, where the majority of adsorption is expected to take place. As a result, the lack of sites within the bulk may limit the adsorption potential of

the chars when being tested for CO₂ uptake. In terms of oxygen containing-functionalities, for most samples the ratio lies in the range of 0.89 – 1.15, which indicates that there is an even spread of these functionalities on both the external and internal surfaces of the chars.

Table 5.17: Ratio of XPS Determined Nitrogen/Elemental Determined Nitrogen and of XPS Determined Oxygen/Elemental Determined Oxygen for the Optimisation Biochars Produced in this Study

Sample	Ratio of XPS Determined Nitrogen/Elemental Analysis Determined Nitrogen	Ratio of XPS Determined Oxygen/Elemental Analysis Determined Oxygen
OBC 650-0.5-O	0.63	0.39
OBC 800-0.5-O	0.70	0.32
OBC 650-3-O	0.64	0.46
OBC 800-3-O	2.03	0.58
OBC 619-1.75-O	1.90	0.96
OBC 831-1.75-O	0.82	0.71
OBC 725-0-O	1.59	1.07
OBC 725-3.52-O	1.66	1.15
OBC 725-1.75-O	1.64	1.07
OBC 650-0.5-M	1.64	1.14
OBC 800-0.5-M	1.82	0.98
OBC 650-3-M	1.88	0.90
OBC 800-3-M	1.54	0.98
OBC 619-1.75-M	1.75	1.01
OBC 831-1.75-M	1.35	0.90
OBC 725-0-M	1.78	0.93
OBC 725-3.52-M	1.80	0.97
OBC 725-1.75-M	1.90	0.89
BC Control Orange	0.65	0.39
BC Control Mandarin	0.67	0.36

The FTIR spectra collected for the samples produced at 619 °C and 650 °C can be seen in Figure 5.14. In the samples produced at 619 °C, small peaks at 2995 cm⁻¹ are indicative of C-H stretching in the material [80], while the peaks at 1738 cm⁻¹ may show evidence of ester (O-C=O) or aldehyde (C=O) groups on the surface. For both samples, the peaks around 1360 cm⁻¹ and 1210 cm⁻¹ again indicate C-H bonding. The quality of spectra for the 650 °C samples is quite poor, with almost no identifiable peaks, indicating that penetration of light into the sample was once again an issue.

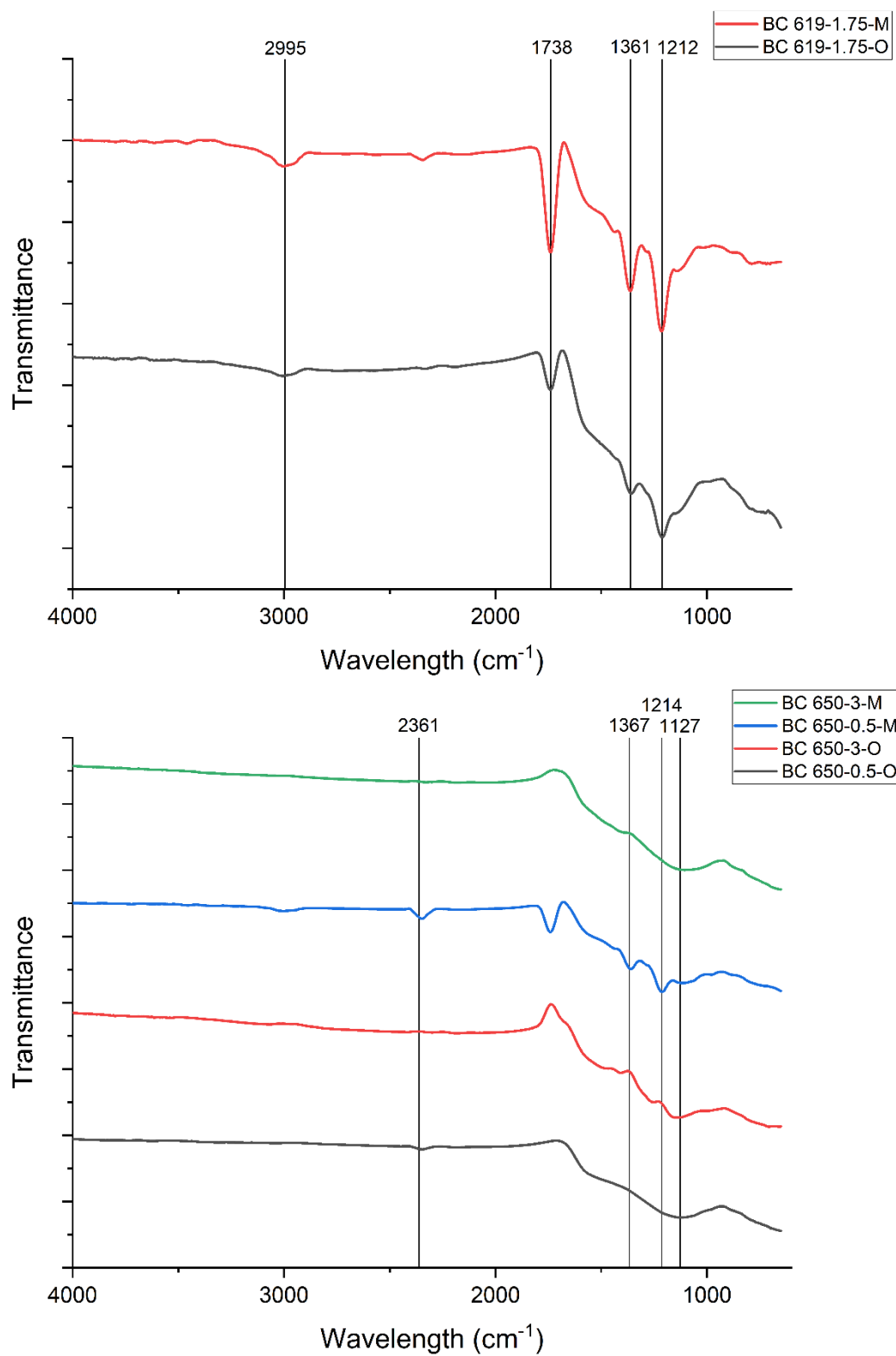


Figure 5.14: FTIR Spectra of Biochar Samples Produced Through Pyrolysis at 619 °C (top) and 650 °C (bottom)

Figure 5.15 shows the spectra of the samples produced at 725 °C. A peak is visible at 2349 cm^{-1} , and seen in approximately the same range for the samples created through pyrolysis at 650 °C; this is attributed to CO_2 in the air near to the instrument that has not been fully compensated for by the background spectra. As with the aforementioned samples, peaks at 1734 cm^{-1} could show evidence of oxygen-containing functional groups on the surface, and C-H bonding is seen once again at 1357 and 1215 cm^{-1} respectively. For the two samples produced using a residence time of 3.52 h there are no visible peaks on either spectrum, emphasising the issues surrounding the use of FTIR spectroscopy characterisation for dark carbon materials; as the carbon content increases, the harder it is for light to penetrate into the sample.

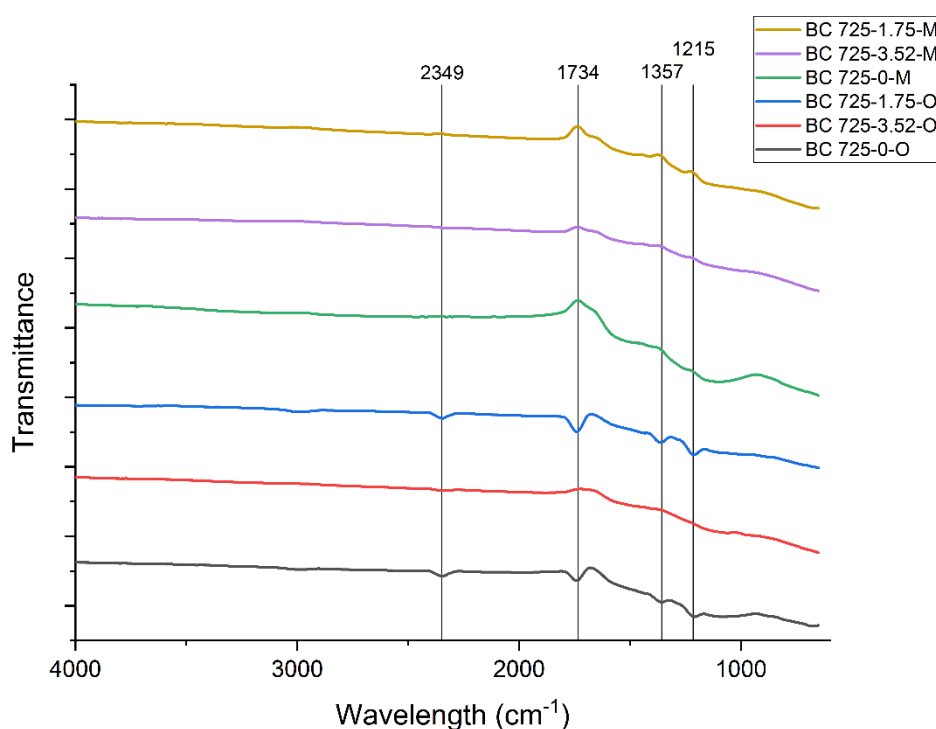


Figure 5.15: FTIR Spectra of Biochar Samples Produced Through Pyrolysis at 725 °C

Spectra obtained for samples produced at 800 °C and 831 °C are shown in Figure 5.16. These are similar to the spectra seen in the screening design, with the two samples produced using

a residence time of 0.5 h showing little to no peaks. The samples obtained using 3 h residence time do show intense peaks, as do the samples produced at 831 °C; but this is suspected to be a product of their high ash content, meaning the minerals that were present in the original material now comprise a higher % of the total sample and thus are more visible in the FTIR spectra.

Overall, the use of FTIR spectra to provide surface analysis of the biochars did not produce quantifiable or meaningful results; although some peaks were identified, the dark characteristics of the materials proved a limitation to providing comprehensive analysis. For future work on biochars, XPS analysis and SEM should be deemed more applicable.

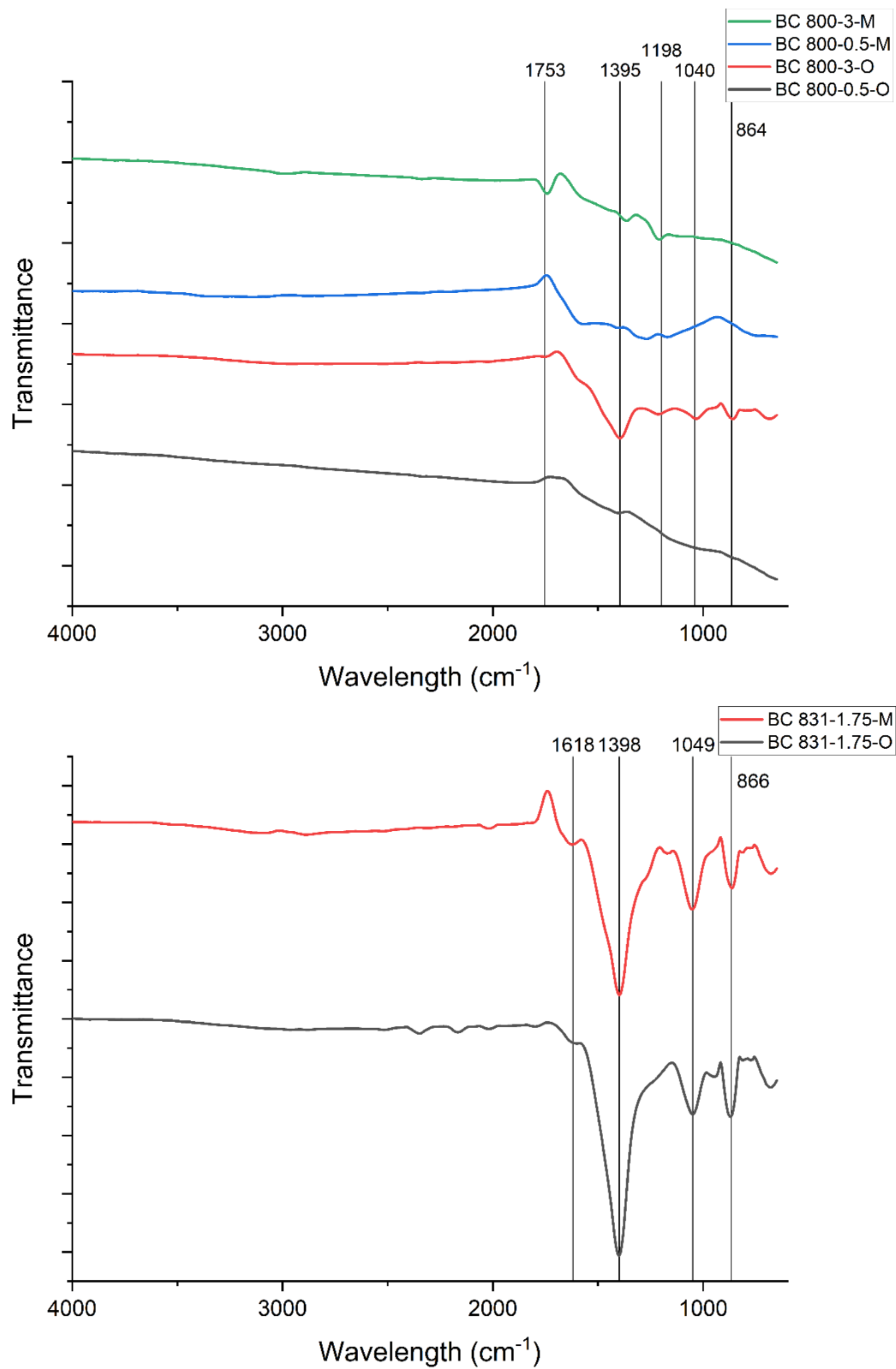


Figure 5.16: FTIR Spectra of Biochar Samples Produced Through Pyrolysis at 800 °C (top) and 831 °C (bottom)

5.5.5 SEM Analysis

SEM was used to examine the optimisation biochars at magnifications of x150 and x550.

Figure 5.17 and Figure 5.18 show the sample OBC 650-0.5-O, while Figure 5.19 and Figure 5.20 show the sample OBC 800-0.5-O.

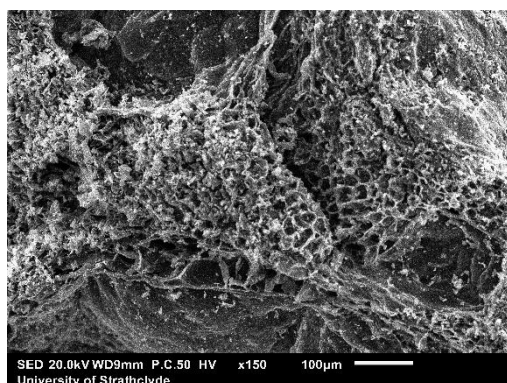


Figure 5.17: SEM Image of OBC 650-0.5-O at Magnification of x150

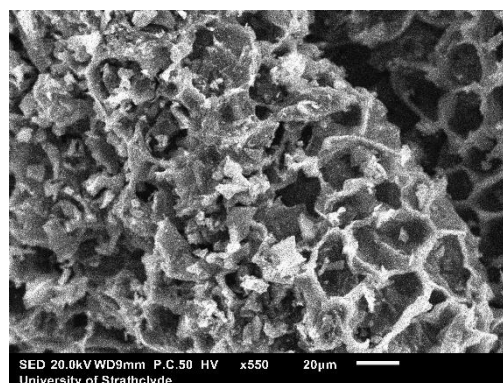


Figure 5.18: SEM Image of OBC 650-0.5-O at Magnification of x550

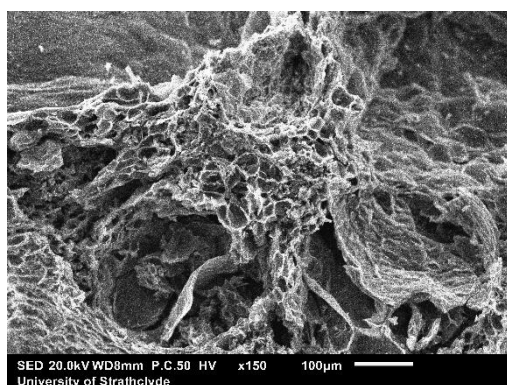


Figure 5.19: SEM Image of OBC 800-0.5-O at Magnification of x150

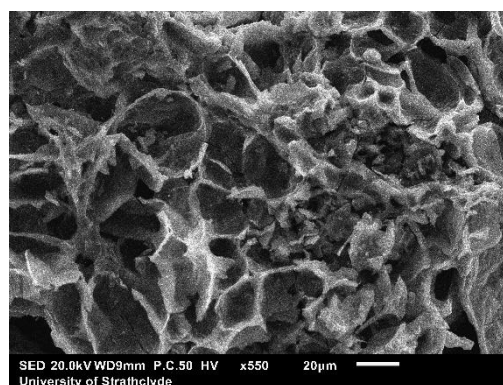


Figure 5.20: SEM Image of OBC 800-0.5-O at Magnification of x550

Firstly, looking at the x150 magnification, similarity between the samples is clear; OBC 650-0.5-O displays a structured network of pores in a honeycomb lattice formation. BC 800-0.5-O has a similar form but is visibly more disordered with larger cavities. When looking at the higher magnification images of x550, pore blocking is visible in the 650 °C sample but not the 800 °C sample; instead, the 800 °C sample contains clear and open pores. The pores identifiable at this magnification are likely to be macropores and large mesopores,

which indicates the higher temperature sample has a better developed pore network, with mesopores likely leading to smaller micropores, which have been identified through textural analysis in Section 5.5.3. This would concur with the pore size data discussed previously and also with literature findings [81].

The sheet-like structure observed in Figure 5.18 and Figure 5.20 is characteristic of biochars produced at these conditions, as other orange peel derived biochars work has shown similar structures through SEM imaging; in the case of biochars produced with and without KOH activation at 800 °C, the sample that did not include KOH shows a close resemblance with those in this project [82]. In that study, the use of KOH was proven to increase the likelihood of honeycomb structures within the material, due to the degradation of K_2CO_3 and its reaction with the carbon framework. Thus, it is possible that for this project, the application of a more common activator could be used to produce a more consistent porous structure if desired.

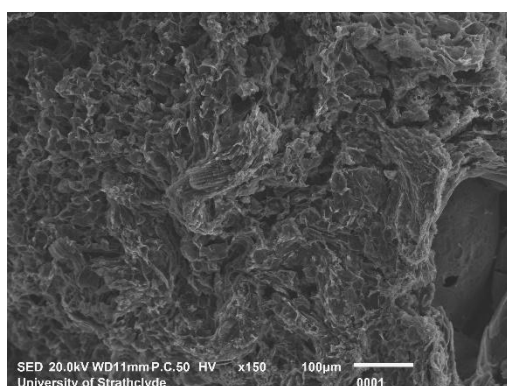


Figure 5.21: SEM Image of OBC 800-3-M at Magnification of x150

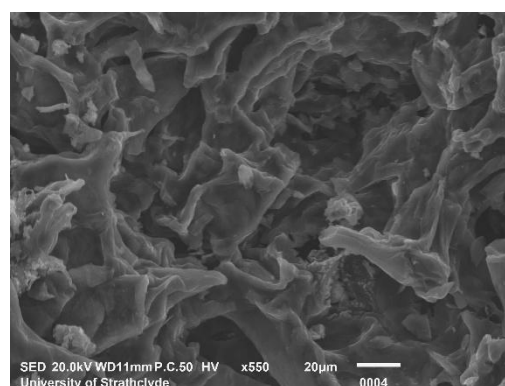


Figure 5.22: SEM Image of OBC 800-3-M at Magnification of x550

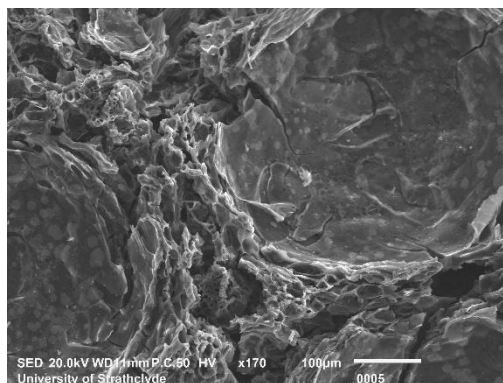


Figure 5.23: SEM Image of OBC 800-3-M at Magnification of x170

OBC 800-M-3 is the most porous biochar produced in the optimisation stage, but its morphology (see Figure 5.21 to Figure 5.23) does not show any large differences to its peers; the same rough outer surface is observed, with intermittent lattice structure throughout. Large cracked craters are seen in Figure 5.23, which could indicate extreme degradation during pyrolysis and activation. The intense synthesis conditions were productive in terms of creating pore development, but also exemplify the trade-off that must be balanced to ensure the structure of the material is not inherently destroyed.

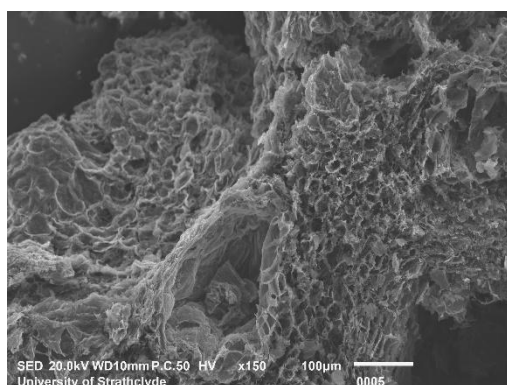


Figure 5.24: SEM Image of BC Control Orange at Magnification of x150

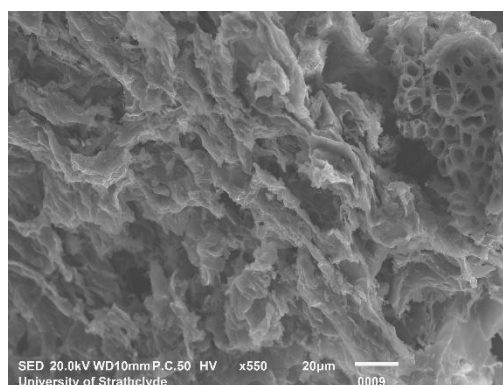


Figure 5.25: SEM Image of BC Control Orange at Magnification of x550

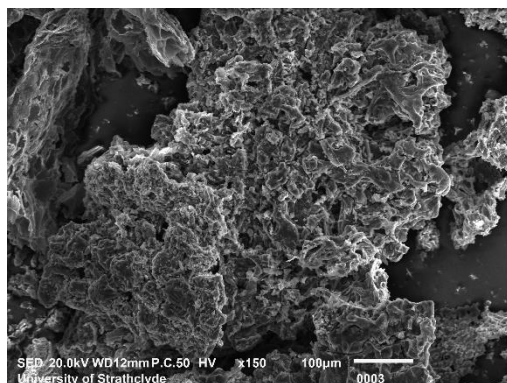


Figure 5.26: SEM Image of BC Control Mandarin at Magnification of x150

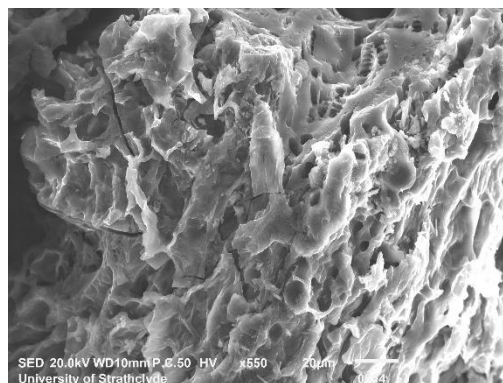


Figure 5.27: SEM Image of BC Control Mandarin at Magnification of x550

The two biochar control samples, Figure 5.24 to Figure 5.27, do not differ significantly in textural terms to the doped biochars. At a magnification of x150 they can be seen to have rough disordered structure with elements of lattice formation, and when increased to x550 the larger mesopores can be seen. Both images at x550 magnification show distinct porous structures, indicating a further porous network exists within these samples, which would concur with the surface area data discussed in Section 5.3.3. In comparison to literature, all the biochar structures presented here show similarities to those reported in other studies [30], [83], [84], [85]; a rough surface coupled with large cavities indicate that pyrolysis has successfully removed volatiles from the material and in turn, has aided the development of a porous network.

5.5.6 Optimisation Design of Experiments Trends and ANOVA

The same process from Section 5.3.5 was followed to produce ANOVA and Pareto charts for the optimisation design. Again, the alpha for the model was set equal to 0.05, resulting in a confidence level of 95 %. Two-factor interactions are described in the same way as before. Pareto charts can be seen in Figure 5.28 – Figure 5.30, and the regression coefficient for each model in Table 5.18.

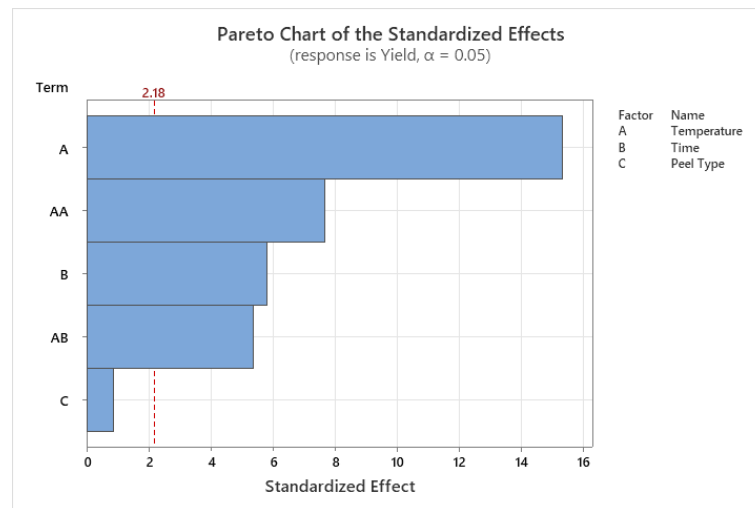


Figure 5.28: Optimisation Pareto Chart for Biochar Yield as DoE Response

On assessment of the Pareto charts it is clear that over the three responses, temperature is the key factor in all. For yield and carbon content, there is also influence from two-factor interactions between temperature and residence time, meanwhile for micropore area temperature is the single defining factor. The R^2 values for the models, in Table 5.18, also give an indication of the accuracy of the optimisation equations (these equations are shown and discussed in Section 5.6); the yield model appears to be the most reliable, while the micropore area model seems poor.

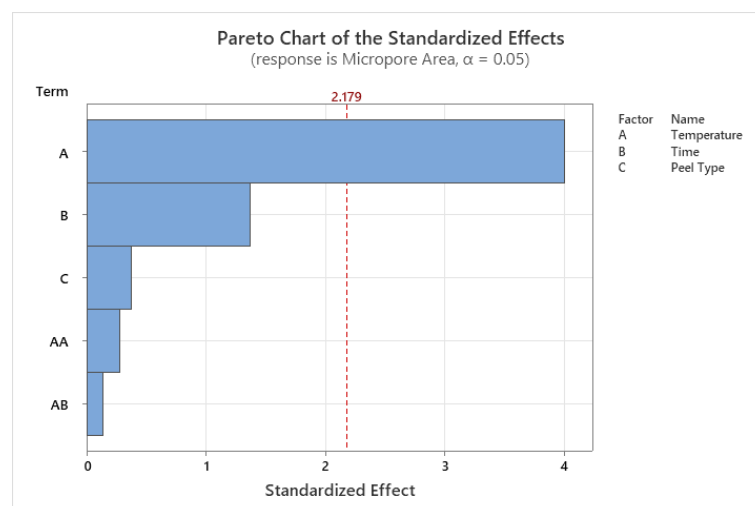


Figure 5.29: Optimisation Pareto Chart for Biochar Micropore Area as DoE Response

Once again, pyrolysis temperature is observed as the single significant factor in the development of micropore area, whereas there are multiple factors and two-factor interactions determined to be influential in the response of yield and carbon content.

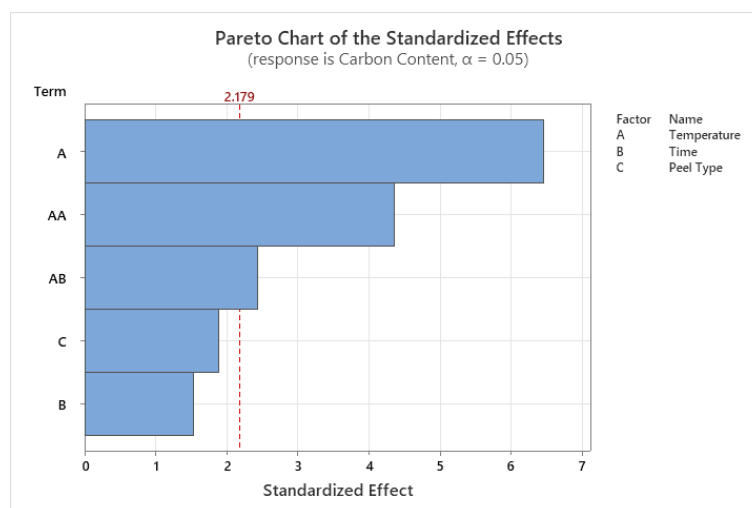


Figure 5.30: Optimisation Pareto Chart for Biochar Carbon Content as DoE Response

Table 5.18: Optimisation Coefficients of Determination for Each Response

Response	R ² (%)	R ² -adj (%)	R ² -pred (%)
Yield	96.74	95.38	92.36
Micropore Area	60.15	43.55	6.93
Carbon Content	85.79	79.87	66.01

The full ANOVA results for each response can be seen in Appendix C. Looking specifically at the micropore area model, the R²-pred for the optimisation model is seen to be vastly different from the screening model (6.93 % optimisation vs 95.19 % screening). The lower range of temperatures within the optimisation design (619 – 650 °C) lie below the 700 °C threshold where the Boudouard reaction becomes thermodynamically favourable and spontaneous; therefore, no CO₂ gasification will occur during the synthesis of these materials, and thus, activation of the samples does not take place. Consequently, CO₂ acts as an inerting gas for these samples rather than an activating gas; nonetheless, due to the atmosphere remaining inert, other pyrolysis reaction mechanisms can still take place. This means limited pore development may be possible, but it will not occur to the same extent as

that observed in the samples produced at 725 – 831 °C, which will be aided by the Boudouard reaction.

Consequently, this results in a non-monotonic response being observed in the micropore area data, for which the polynomial model cannot account, and limits the usefulness of the model for any further predictions. This represents a failing of the experimental design for this response; as seen in the following section (Section 5.6), the micropore area model recognises that a high pyrolysis temperature is required to create notable microporosity, but it cannot predict appropriate synthesis conditions with any degree of reliability (the model also predicts non-zero values at points, which is physically impossible). Due to this, the results drawn from this specific model cannot be framed as successful in terms of optimisation of the process.

5.6 Optimal Biochars Results

Based on the optimised equations produced from analysis of the optimisation DoE in Section 5.5.6, six 'optimal' biochars were produced to ascertain the validity of the optimisation DoE method. This meant two biochars were produced, one from orange peel and one from mandarin peel, for each response variable.

Each optimisation equation is seen in Table 5.19 for each factor. The Microsoft Excel Solver tool was used to find the optimal conditions for each equation based on the limits of the DoE carried out, and on the basis of optimising for maximum yield, micropore surface area and carbon content, respectively. Note that T = temperature (°C), and t = time (h).

Table 5.19: Biochar Optimisation Equations Generated for Each Response Variable

Response Variable and Peel Type	Optimisation Equations
Yield, Orange Peel	$-298 + 0.905 * T + 19.76 * t - 0.00064 * T^2 - 0.0296 * T * t$
Yield, Mandarin Peel	$-297.4 + 0.905 * T + 19.76 * t - 0.00064 * T^2 - 0.296 * T * t$
Micropore Surface Area, Orange Peel	$-23 - 0.88 * T - 8 * t + 0.00133 * T^2 + 0.043 * T * t$
Micropore Surface Area, Mandarin Peel	$-8 - 0.88 * T - 8 * t + 0.00133 * T^2 + 0.043 * T * t$
Carbon Content, Orange Peel	$-707 + 2.165 * T + 38.9 * t - 0.001516 * T^2 - 0.0563 * T * t$
Carbon Content, Mandarin Peel	$-702 + 2.165 * T + 38.9 * t - 0.001516 * T^2 - 0.0563 * T * t$

Using these equations, the following conditions were calculated to be the process parameters to create ‘optimal’ biochars for each response, shown in Table 5.20.

Table 5.20: Conditions for Creating Optimal Biochars Based on Generated Optimisation Equations

Sample	Temperature (°C)	Time (h)	Peel Type
OPB Yield Orange	707	0	Orange
OPB Yield Mandarin	707	0	Mandarin
OPB Micropore Orange	831	0	Orange
OPB Micropore Mandarin	831	3.52	Mandarin
OPB Carbon Orange	650	3.52	Orange
OPB Carbon Mandarin	650	3.52	Mandarin

Each pair of samples was tested only for the response for which they were created. The results of this can be seen in Table 5.21.

Table 5.21: Results of Each Response for Optimal Biochars Created from Generated Optimisation Equations, and the Predicted Result for Each Response

Sample	Yield (%)	Predicted Yield (%)	Micropore Surface Area (m ² /g)	Predicted Micropore Surface Area (m ² /g)	Carbon Content (%)	Predicted Carbon Content (%)
OPB Yield Orange	19.9	21.9	-	-	-	-
OPB Yield Mandarin	18.6	22.5	-	-	-	-
OPB Micropore Orange	16.8	-	61	164	-	-
OPB Micropore Mandarin	0.9	-	0	277	-	-
OPB Carbon Orange	18.5	-	-	-	67.2	67.9
OPB Carbon Mandarin	17.9	-	-	-	65.3	72.9

Overall, it is evident that the biochars created from the optimisation equations do not match all the predicted results accurately. Taking the optimal yield biochars, the actual yield is lower than predicted; this is surprising due to the residence time being used for the production of both was 0 h, thus, it would be expected that the collected yield would be the high. It also contradicts the results for OBC 725-0-O and OBC 725-0-M, as those samples were produced at a marginally higher temperature with the same residence time, yet they display a higher yield than OPB Yield Orange and OPB Yield Mandarin. It is likely that the discrepancies here are due to the inherent reality of using organic materials in this way, such that there will always be a degree of heterogeneity in them. The optimal samples were created around two months after the optimisation run of experiments, but were made from the same batch of feedstock; it is possible that a form of natural degradation has occurred in the dried peels, that then went on to impact the pyrolysis process.

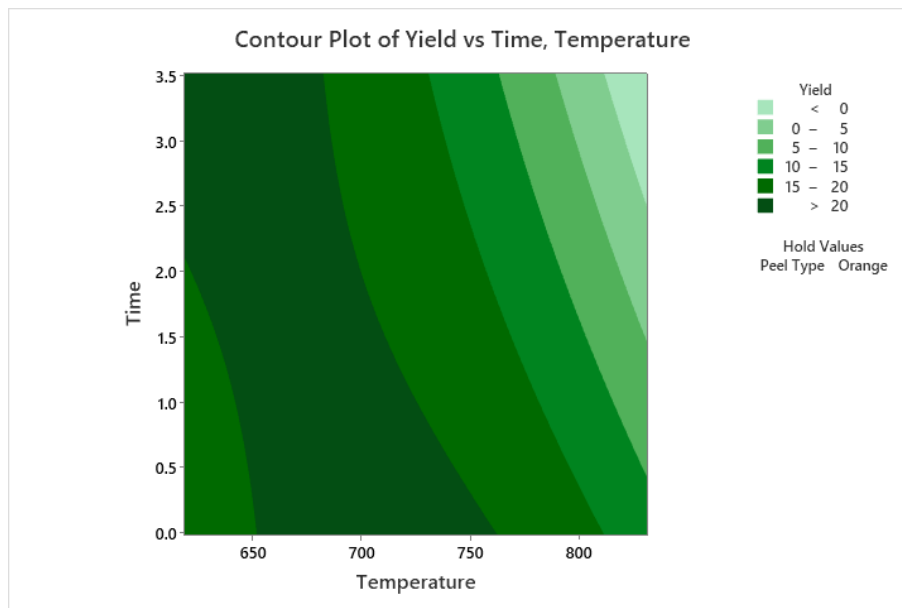


Figure 5.31: Contour Plot for Optimisation of Model for Orange Peel Biochar Yield (%) with Respect to Pyrolysis Temperature (°C) and Residence Time (h)

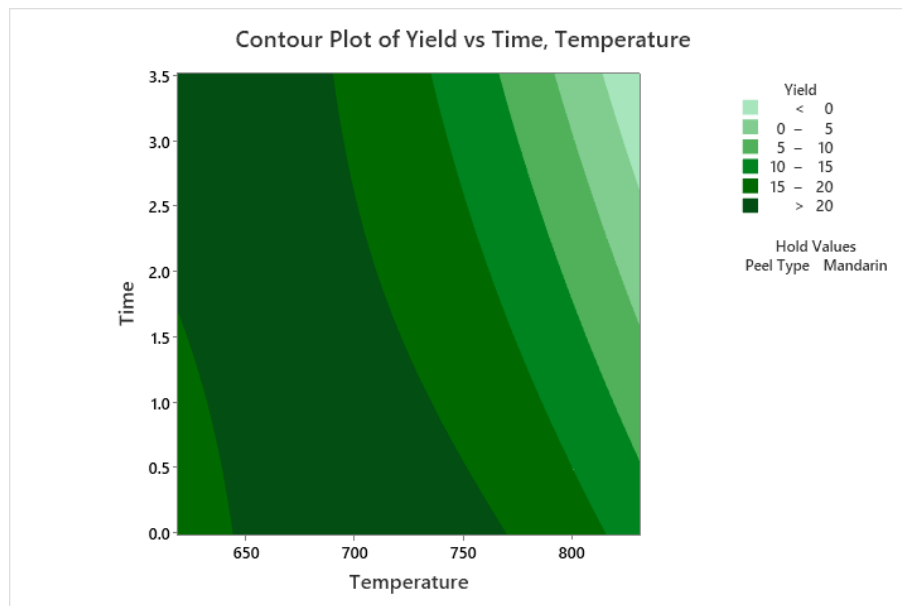


Figure 5.32: Contour Plot for Optimisation of Model for Mandarin Peel Biochar Yield (%) with Respect to Pyrolysis Temperature (°C) and Residence Time (h)

The contour plots for the two yield response models are shown in Figure 5.31 and Figure 5.32. These plots provide a visualisation of the relationship of the continuous process parameter assessed in this study; the colours of the plots indicate the magnitude of the

response for the associated parameter values. For example, the light green areas indicate a low yield result, whereas the dark green areas indicate the highest achievable yield values.

The optimal micropore biochars are the most disappointing of the six created, as they fall well below the prediction of the optimisation model. This should however not come as a surprise, as the R^2 for the model was poor to begin with. The OPB Micropore Orange sample displays a level of porosity, but it is not comparable in a positive sense with other biochars created in the study; likely due to the lack of any residence time, which limits the extent of volatilisation of the material.

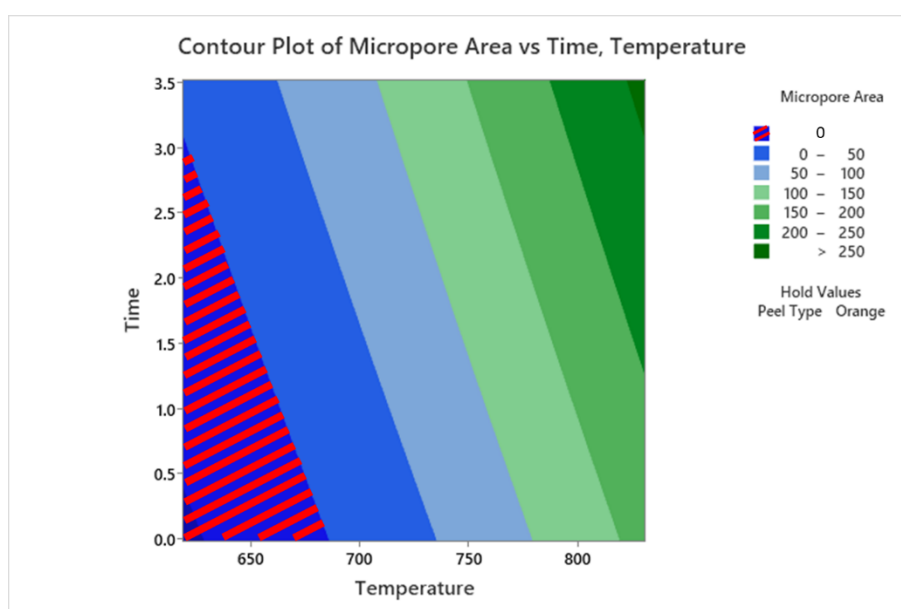


Figure 5.33: Contour Plot for Optimisation of Model for Orange Peel Biochar Micropore Area (m^2/g) with Respect to Pyrolysis Temperature ($^{\circ}C$) and Residence Time (h). Note that this model predicts sub-zero micropore areas, which are physically impossible, hence the associated data has been truncated at $0 m^2/g$.

Meanwhile, the OPB Micropore Mandarin sample was almost completely degraded by the pyrolysis process, leaving mostly ash in the sample and, as a result, exhibited no meaningful porosity. This indicates the recommended levels of temperature and time were too high for the process to successfully produce porous biochars in line with statistical predictions, and indicates a failure of the model in this particular case. The contour plots for both micropore

area models can be seen in Figure 5.33 and Figure 5.34. The contour plots presented in the main body are truncated at 0 m²/g; the models themselves predicts that at low temperature and low residence time the micropore areas will be below 0 m²/g, which is physically impossible, but this discrepancy does exist within the models. The original contour plots, which have not been truncated, can be found in Appendix D.

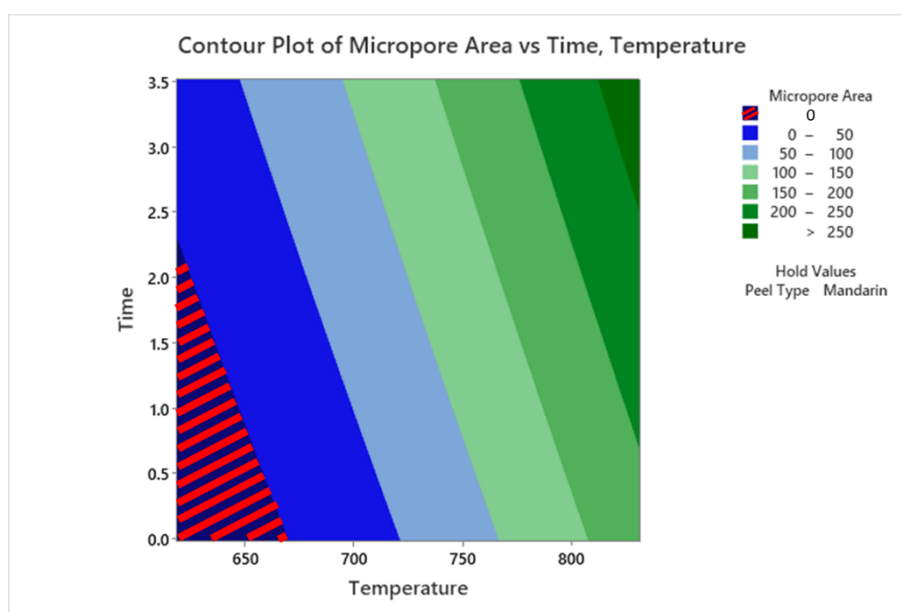


Figure 5.34: Contour Plot for Optimisation of Model for Mandarin Peel Biochar Micropore Area (m²/g) with Respect to Pyrolysis Temperature (°C) and Residence Time (h). Note that this model predicts sub-zero micropore areas, which are physically impossible, hence the associated data has been truncated at 0 m²/g.

The carbon content samples present results closest to those predicted; OPB Carbon Orange essentially matches the expected value, while OPB Carbon Mandarin is close to its expected value. This concurs with literature, as carbon content is often seen to be maximised at low-to-moderate pyrolysis temperatures, and long residence times. It should be noted that although OPB Carbon Mandarin does not meet its predicted value, it is still of similar carbon content to some of the highest mandarin-derived biochars in this study. The contour plots for both carbon content models can be seen in Figure 5.35 and Figure 5.36.

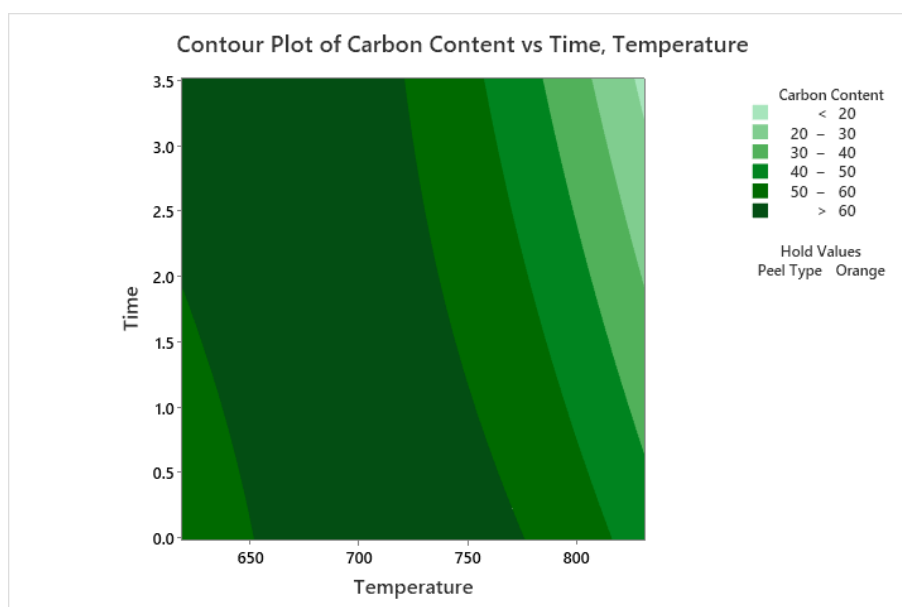


Figure 5.35: Contour Plot for Optimisation of Model for Orange Peel Biochar Elemental Carbon Content (wt%) with Respect to Pyrolysis Temperature (°C) and Residence Time (h)

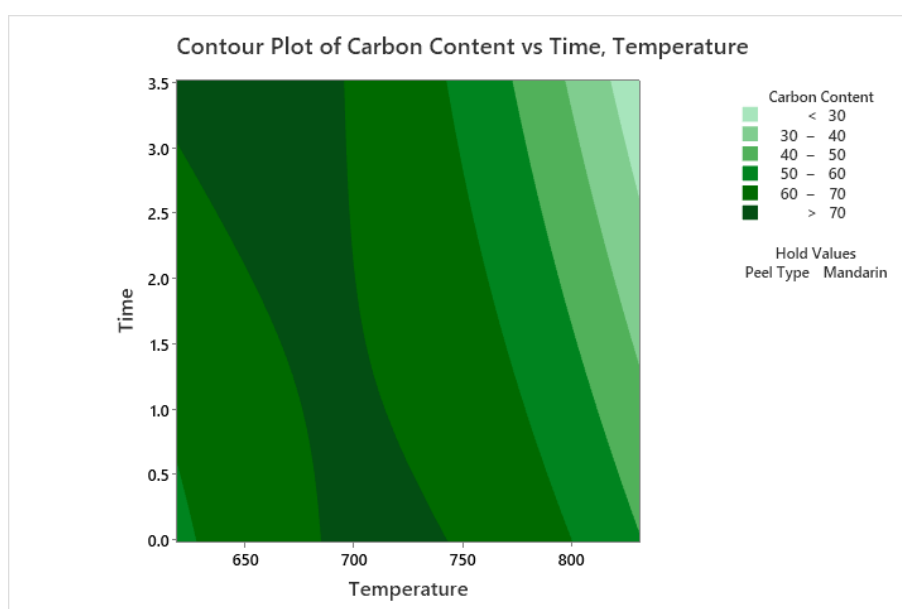


Figure 5.36: Contour Plot for Optimisation of Model for Mandarin Peel Biochar Elemental Carbon Content (wt%) with Respect to Pyrolysis Temperature (°C) and Residence Time (h)

It is difficult to define the optimisation equations above in terms of ‘failure’ or ‘success’, yet on reflection of the results, they provide a mixture picture. The carbon content equations seem to have produced accurate predictions, and the yield equations, while not entirely correct, are within the same magnitude of value. The micropore area equations however are

widely inaccurate, despite agreeing with literature in a sense, in that higher temperature and longer time will increase porosity. In the case of the OPB Micropore Mandarin sample, this likely only holds till a certain level, such as a temperature of 800 °C and time of 3 h (as this was seen during the optimisation stage to produce a porous biochar sample). Beyond these conditions, either the fundamental makeup of the peel feedstock or the increased harsh conditions facilitate a complete degradation of the sample. The OPB Micropore Orange equation contrasts this in that it recommends no residence time, which is insufficient to create meaningful porosity as this means the sample does not undergo pyrolysis for a long enough period.

Overall, it appears that DoE can be utilised to provide reliable prediction models for responses when there are multiple influential factors in a process, such as for yield and carbon content, but when there is one prevailing factor then the model produced is less effective. Assessing the optimal biochars produced from the DoE optimisation in this project, namely OPB Micropore Orange and OPB Micropore Mandarin, both samples display low levels of porosity through N₂ adsorption analysis, and thus are not expected to be suitable for CO₂ adsorption applications. Nevertheless, it is important to explore further characterisation of these samples to confirm this.

5.7 Additional Textural Analysis (Volumetric CO₂ Adsorption)

After the production and characterisation of the biochars in this study was completed, the opportunity to carry out volumetric CO₂ adsorption became available (~9 months after results completion). As a result, the following Chapter 6, which details the hydrochars produced in this study, includes this analysis and incorporates it into the DoE process. Due to time restraints it was not possible to retrospectively analyse all the biochars produced using

this method, but the highest surface area biochar samples were tested to compliment the results presented in Section 5.5.3.

The micropore results calculated from DR analysis of CO₂ isotherms for the selected samples are shown in Table 5.22. It is seen that the trend of porosity derived from N₂ isotherms does not match with that from CO₂ isotherms; out of the nine samples tested, BC Control Mandarin had the highest N₂ adsorption DR micropore area, but only the third highest CO₂ adsorption DR micropore area. These deviations may be a result of the activated diffusion effect (discussed in detail in Chapter 6), where CO₂ molecules at 0 °C possess higher energy than N₂ molecules at -196 °C, meaning the CO₂ molecules are able to penetrate into ultramicropores that are not accessible to the N₂ molecules. Based on this, it follows that a different perspective of the pore structure will be obtained. It is also possible that surface nitrogen-containing functionalities have assisted in increasing the adsorption capacity for samples such as OBC 800-0.5-O.

Table 5.22: Porosity Characteristics Derived from N₂ and CO₂ Isotherms of Selected Optimisation Biochars Produced in this Study

Sample	Equivalent Micropore Surface Area (DR N ₂) (m ² /g) ¹⁷	Equivalent Micropore Surface Area (DR CO ₂) (m ² /g) ¹⁸	Micropore Width (DR CO ₂) (nm)
OBC 800-0.5-O	322	418	0.7
OBC 800-3-O	268	231	0.6
OBC 800-0.5-M	252	391	0.7
OBC 800-3-M	402	327	0.7
OBC 831-1.75-M	362	155	0.7
BC Control Orange	380	298	0.6
BC Control Mandarin	491	380	0.7
OPB Micropore Orange	67	436	0.7
OPB Micropore Mandarin	0	0	-

¹⁷ Uncertainties within DR N₂ equivalent micropore area were calculated to be below 2 m²/g

¹⁸ Uncertainties within DR CO₂ equivalent micropore area were calculated to be 1 – 6 m²/g

The results shown here are evidence that although N₂ adsorption isotherms are considered to be the standard method for porosimetry measurements, it is important to consider alternative methods such as CO₂ adsorption if the selected materials are suspected to contain high levels of microporosity. Further interpretation and experimentation of the CO₂ adsorption of these samples will be discussed further in Chapter 7.

5.8 Biochar Results Summary

This chapter has addressed the production and characterisation of a series of biochars, aided by a DoE methodology. The biochars were synthesised using a one-step method incorporating both pyrolysis and activation; N₂ was used as an inert gas for temperature ramping, and CO₂ as an activating gas. Initially four process parameters were examined in the screening design stage, and textural and elemental characterisation was utilised to quantify the influence of each of these individual factors on chosen responses. These responses were: biochar yield, microporous surface area (determined via t-plot method from N₂ adsorption isotherms) and elemental carbon content. Of the four tested parameters, pyrolysis temperature, pyrolysis residence time and peel type were found to be significant.

This led into the optimisation stage of the process, where these three significant parameters were tested at a wider range of conditions; this allowed models to be developed that could predict the optimal conditions required to maximise each of the three responses. Additional characterisation such as XPS analysis confirmed the increased presence of nitrogen-containing functionalities on the surface of the biochars, and SEM showed honeycomb-like porous structures within the materials. The prediction models were then tested experimentally, resulting in the production of six optimal biochars; the yield and carbon content response models were deemed to be accurate, while the micropore area response model performed more poorly.

It is important to note that due to the use of natural biomass, there exists inherent variability both throughout a single feedstock batch, and between different batches. There is also the potential for degradation in samples upon storage for prolonged periods. While these factors cannot necessarily be controlled, further work could be undertaken to understand the potential implications that they have upon char characteristics.

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6 Results II – Hydrochar Characterisation

6.1 Introduction

This chapter aims to provide detailed characterisation of nitrogen-doped orange and mandarin derived hydrochars which were physically activated using CO₂, a synthesis method not previously tested in literature for these feedstocks. This is accompanied by a Design of Experiment (DoE) methodology, which utilises both screening and optimisation designs, to create model designs for each chosen response. Once produced, these models can be used to synthesise an optimal hydrochar for each response.

This chapter consists of the characterisation of the hydrochars produced in this project. It takes an almost identical form to Chapter 5, in that it will follow through the DoE process and rationale for process decisions. The hydrochars were produced through hydrothermal carbonisation (HTC) before being activated via pyrolysis with CO₂. Limited textural characterisation was carried out on the pre-activated hydrochars, with full characterisation carried out on the activated hydrochar materials. This was due to the pre-activation hydrochars being of little interest in the context of this project. Proximate and elemental analysis alongside textural analysis (Brunauer-Emmett-Teller (BET) and Fourier Transform Infrared (FTIR) spectroscopy) were carried out on the hydrochars produced in the screening phase, with full characterisation undertaken for the hydrochars produced in the optimisation stage; this included X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM) and gravimetric CO₂ adsorption.

6.2 Hydrochar Design of Experiments Plan

As for the biochars in Chapter 5, an extensive review of the literature was undertaken for hydrochars and the process conditions used to create them. Four main parameters identified to influence the characteristics of hydrochar were selected from this review to be tested:

HTC temperature, HTC residence time, feedstock type (peel type), and activation temperature (in a CO₂ environment). These parameters are also comparable to those used to produce the aforementioned biochars, enabling a more detailed comparison of the production methods as well as the final characterisation results.

In literature methodologies it was commonly observed that materials created by HTC alone possessed negligible porosity, and as such would be of little interest to this study. Therefore, a two-step production method was employed, with the further activation stage chosen to induce a level of porosity that is desired for CO₂ adsorption. Physical activation with CO₂ as the activating gas was used to mirror the biochar activation method. This was due to the ability of CO₂ to create microporosity, but also allowed for further comparison opportunities to the biochars made in this study.

HTC temperature and HTC residence time were identified from other studies as having a marked effect on the process, but conflicting data was presented on their overall influence [1], [2], [3], [4]. Upper and lower temperature limits were chosen, again based on previous literature. There is an inherent limit on the upper range, as going above 250 °C would bring about the risk of overpressure and loss of containment of the HTC vessel, so it was decided to work at a safe range below this. Low temperatures (< 150 °C) were seen to give poor levels of carbonisation [5], so a range of 180 – 220 °C was used for hydrochar production in the screening design (parameters are compiled in Table 6.1).

In the literature, HTC residence time has been tested at a wide range, ranging from 0 h up to multiple days (48 h) [6]. Due to the inclusion of urea in the HTC process, this introduced safety concerns about the reaction pathways that could occur, meaning it was preferred to carry out the synthesis process overnight when there were no occupants in the laboratory. As such, each sample was prepared and loaded into the HTC autoclave vessel at the end of each day,

before being placed in a specialised oven that could be pre-programmed. The process was then allowed to run overnight, and the sample removed the following morning for drying and further analyses. This then meant that the upper limit for residence time had to be short enough that the process could be started at 5 pm and finished by 9 am the following day. It was decided to use 12 h as the upper limit, to ensure the process would be complete and the heating and cooling times accounted for. The lower limit was set at 2.5 h.

For the activation stage, the chosen temperatures were based on the findings of Chapter 5, and how the pyrolysis temperature had been seen to affect porosity. 800 °C was seen to be effective, and contrastingly 500 – 650 °C was not; thus, a narrower range of 750 – 800 °C was chosen in an attempt to create a set of samples that all presented characteristics concomitant with the potential for CO₂ adsorption.

Minitab 22 was again used to create an experimental plan, and the experiments are detailed in Table 6.1. Two control experiments were carried out without urea, using orange and mandarin peels respectively at conditions of 220 °C (HTC), 2.5 h and 800 °C (activation), with no urea doping to examine the effect of the doping process.

The chosen responses for this DoE analysis were: overall yield of hydrochar (%), micropore surface area determined using the DR CO₂ method (m²/g), and carbon content from elemental analysis (wt%). These responses are similar to those used for the biochar DoE process, however, they differ slightly. Firstly, overall yield was used as a parameter for this investigation as the final hydrochar product is produced through a two-step procedure rather than the one-step method employed for the biochars. Secondly, the possibility to measure adsorption via volumetric CO₂ isotherms was available for the second half of the project and this was determined to be more appropriate for the overall scope of the project than just measuring porosity from N₂ isotherms. As result, the CO₂ isotherms could be used along with

the DR method to give data relating to the surface area of the samples that was more suitable to the study. Carbon content was measured using elemental analysis.

6.3 Screening Hydrochar Results

6.3.1 Yield

The conditions used to produce the screening hydrochars in this study are reported in Table 6.1, along with the HTC yield and the overall hydrochar product yield.

Table 6.1: Conditions Used to Produce Screening Hydrochars with Subsequent Yield Results

Sample	HTC Temp. (°C)	HTC Time (h)	Peel Type	Activation Temp. (°C)	HTC Yield (%)	Overall Yield (%)
HC 180-2.5-O-750	180	2.5	Orange	750	31.7	10.5
HC 220-2.5-O-750	220	2.5	Orange	750	34.4	10.8
HC 180-12-O-750	180	12	Orange	750	29.1	9.6
HC 220-12-O-750	220	12	Orange	750	32.6	12.5
HC 180-2.5-M-750	180	2.5	Mandarin	750	30.4	9.0
HC 220-2.5-M-750	220	2.5	Mandarin	750	31.2	10.4
HC 180-12-M-750	180	12	Mandarin	750	29.0	9.8
HC 220-12-M-750	220	12	Mandarin	750	29.3	9.7
HC 180-2.5-O-800	180	2.5	Orange	800	28.3	7.9
HC 220-2.5-O-800	220	2.5	Orange	800	27.9	8.8
HC 180-12-O-800	180	12	Orange	800	29.9	9.8
HC 220-12-O-800	220	12	Orange	800	33.2	9.7
HC 180-2.5-M-800	180	2.5	Mandarin	800	27.7	7.5
HC 220-2.5-M-800	220	2.5	Mandarin	800	30.4	9.1
HC 180-12-M-800	180	12	Mandarin	800	28.4	8.6
HC 220-12-M-800	220	12	Mandarin	800	30.6	10.0
HC Control Orange	220	2.5	Orange	800	40.1	15.1
HC Control Mandarin	220	2.5	Mandarin	800	40.2	14.1

From the data obtained for HTC Yield, Table 6.1, it is clear that the results for all 16 screening samples fall within approximately the same range of around 30 %, with the lowest at 27.7 % and the highest at 34.4 %. Most samples fall within the 29 – 31 % range, indicating a degree of homogeneity between them, no matter the HTC conditions used in the synthesis step; the average HTC yield is 30.2 %, with a standard deviation of 2 %. The hydrochar control samples,

produced with no urea doping, both exhibit higher HTC yields of 40 %, which indicates that the urea doping has resulted in lower yields. When urea decomposes in hydrothermal conditions, it leads to the production of CO_2 and NH_3 [7]; it could be possible that these gases are produced during the HTC process, and go on to aid in the decomposition of the biomass, reducing the solid mass fraction obtained from HTC and leading to lower yields for samples that had been doped with urea. However, note that a fraction of these gases will be dissolved in the liquid phase which is present; CO_2 would typically enhance the acidity of the mixture, and NH_3 would cause an increase in basicity. Thus, it is difficult to quantify the individual effect these gases have on reactions occurring in the mixture.

Assessing the difference between samples produced at 180 °C versus those at 220 °C, the higher temperature samples have a higher HTC yield. This conflicts with previous literature studies into hydrochar production using microalgae, coconut shells and loblolly pine biomass respectively [8], [9], [10], which indicate that higher HTC temperature should cause the hydrochar yield to decrease. There are reports that during the HTC process around 180 °C, hemicellulose and glucose derivatives in the biomass precursor can break down to form 5-hydroxymethylfurfural (HMF). The HMF present in the mixture can then adsorb onto the solids in the mixture, and as a result can give the impression of an apparent increase in hydrochar yield [11]. It was then reported that increasing the temperature beyond 200 °C in that study was seen to bring about the expected decrease in yield; but in the range of 180 – 200 °C there is the possibility that this event can occur, which may explain the higher yields at higher temperature observed here. This has also been described in another study using microalgae for hydrochar production [12].

Residence time is commonly found to have an inversely proportional relationship to HTC yield, such that as it increases, yield will decrease [13], [14]. While detected for some of the

hydrochars here, it is not seen universally in the sample set, indicating further research is required on it. It has been reported that while it does influence the yield from hydrothermal process, it is not as significant a factor as HTC temperature [15].

When considering the overall yield of hydrochar materials, the 750 °C activated samples have, on average, a slightly higher mass of final product than the 800 °C samples. This is not unexpected, as the use of a higher activation temperature is likely to drive off more volatile material [16], and give a lower yield, as seen previously for the biochar samples produced in this study (Chapter 5). Nonetheless, there is an overlap of overall yields between the two activation temperatures, with the 750 °C activated samples falling within 9 – 12.5 %, compared to 7.5 – 10 % for the 800 °C samples. In the overall context this is a small variation. Thus, if those developed at a higher activation temperature are later seen to have improved porous properties, the trade-off in lower yield could be found to be acceptable. As described in Section 6.3.3, the resulting porosities of these materials mean that the variation in yield is tolerable.

Again, the hydrochar control samples activated at 800 °C have the highest overall yield of those produced, suggesting that the inclusion of urea must have some added effect on the degradation of the material structure during both the HTC and the activation step. The values of 14 – 15 % yield for the control peels are similar to literature, where non-doped orange peel hydrochar was produced at HTC conditions of 200 °C and 20 h, then activated under CO₂ at 750 °C and displayed a yield of 17.3 % [17].

This is an interesting result as it contrasts with what is found for the biochar materials. When assessing the biochars post-pyrolysis, the samples produced with nitrogen doping via urea soaking were found to have higher yields than those made from raw peels alone; whereas the opposite is true for the hydrochars. An explanation for this could be that urea causes

more degradation to occur during the hydrothermal stage by offering additional reaction pathways for the biomass. It was not possible to find precedent for this in literature, but it has been seen to be true for instances when urea was used as a doping agent in the activation stage of hydrochars and helped to produce more porous structures [18].

6.3.2 Elemental Analysis and Proximate Analysis

The proximate analysis results for the screening hydrochars can be seen in Table 6.2. Note that both these and the elemental analysis data are based on the post-activation hydrochars. On the whole, the data shows all 16 screening samples to contain high levels of fixed carbon, ranging from 65 – 76 wt%. The range of results is narrow, with no clear trend emerging: they all lie within the typical range for fixed carbon, as observed in literature [19], [20], [21]. In fact, for each of the four measured parameters (moisture, volatiles, fixed carbon and ash), the samples are all reasonably consistent, with no one sample or samples standing out as exceptionally higher in any one aspect. HTC is known to drive off volatiles from the biomass feedstock, in this case the raw peels, and increase the fixed carbon content [22] and the activation stage continues this process, leading to a further increase in the fixed carbon percentage [23]. When comparing with the proximate data for the raw peels, included in Chapter 5, it is evident this has taken place as expected in this study.

The HC Control Mandarin sample exhibits what could be described as the ‘best’ results of all 18 tested here; it contains very little moisture, and similarly has an ash content which is on the lower end of those seen in this study. Most importantly, it displays a fixed carbon level of 79.6 wt%, the highest found for hydrochars in this study. A study using general citrus fruit waste to produce activated hydrochars at 800 °C reported the fixed carbon in their sample as 76.4 wt% [24], which matches well with results shown below.

Table 6.2: Proximate Analysis Results Obtained for Screening Hydrochars Produced in this Study

Sample	Moisture (wt%)	Volatiles (wt%)	Fixed Carbon (wt%)	Ash (wt%)
HC 180-2.5-O-750	5.3	20.9	70.4	3.4
HC 220-2.5-O-750	3.1	24.8	65.6	6.5
HC 180-12-O-750	1.8	19.9	70.0	8.3
HC 220-12-O-750	1.6	16.8	74.6	7.0
HC 180-2.5-M-750	2.8	15.2	74.3	7.7
HC 220-2.5-M-750	3.1	17.0	72.6	7.3
HC 180-12-M-750	2.3	17.9	73.6	6.2
HC 220-12-M-750	1.3	18.9	70.3	9.5
HC 180-2.5-O-800	5.0	19.3	68.4	7.3
HC 220-2.5-O-800	1.5	23.4	66.0	9.1
HC 180-12-O-800	4.9	18.6	67.1	9.4
HC 220-12-O-800	3.5	13.3	74.4	8.8
HC 180-2.5-M-800	3.0	14.0	75.2	7.8
HC 220-2.5-M-800	2.5	20.0	69.6	7.9
HC 180-12-M-800	3.2	14.5	77.0	5.3
HC 220-12-M-800	4.8	14.4	73.2	7.6
HC Control Orange	0.2	16.5	76.3	7.0
HC Control Mandarin	0.5	13.3	79.6	6.6

Elemental analysis of the post-activation hydrochars is shown in Table 6.3. In terms of the screening hydrochars, the carbon content lies within a range of 58 – 69 wt%, which is a typical range for hydrochar materials [21], although for activated hydrochars the figures are usually higher; values up to 94 – 97 wt% have previously been found [25], [26]. It is likely that the doping of urea has therefore resulted in the comparably lower values here. Previous study has proven this, with nitrogen-doped and non-doped activated hydrochars from the same biomass precursor given elemental carbon content of 63 wt% and 79.4 wt% respectively [9]; the increase of nitrogen between non-doped and doped in this case was from 0.8 wt% to 12.5 wt%.

Table 6.3: Elemental Compositions Obtained for Screening Hydrochars Produced in this Study

Sample	C (wt%)	H (wt%)	N (wt%)	Residuals (wt%)
HC 180-2.5-O-750	67.2	0.8	6.8	25.2
HC 220-2.5-O-750	65.2	0.8	7.4	26.6
HC 180-12-O-750	60.5	0.8	5.7	33.0
HC 220-12-O-750	63.6	0.8	7.8	27.8
HC 180-2.5-M-750	64.8	0.8	6.2	28.2
HC 220-2.5-M-750	64.9	0.9	6.8	27.4
HC 180-12-M-750	66.0	0.8	6.3	26.9
HC 220-12-M-750	64.0	0.9	7.3	27.8
HC 180-2.5-O-800	62.5	0.7	5.0	31.8
HC 220-2.5-O-800	58.9	0.7	5.9	34.5
HC 180-12-O-800	61.3	0.6	6.0	32.1
HC 220-12-O-800	59.2	0.9	6.3	33.6
HC 180-2.5-M-800	64.1	0.7	5.6	29.6
HC 220-2.5-M-800	64.9	0.7	6.6	27.8
HC 180-12-M-800	69.7	0.7	6.9	22.7
HC 220-12-M-800	65.7	0.7	7.6	26.0
HC Control Orange	75.9	0.6	1.7	21.8
HC Control Mandarin	79.9	0.6	2.3	17.3

Activation temperature does not seem to have a clear influence on fixed carbon content: the highest value of 69.7 wt% and also the lowest of 59.2 wt% were both achieved in samples activated at 800 °C. In the case of some samples, increasing HTC temperature while other factors remain constant is seen to result in a small decrease in elemental carbon, but this is not universal within the sample set; some display no change and for HC 180-12-O-750 and HC 220-12-O-750 the increase in temperature leads to an increase in carbon. Due to this, it can be said that varying both HTC and activation temperature within these tested ranges does not appear to have a noticeable influence on the elemental carbon content of the hydrochars. Typically, increase in HTC temperature has been shown to increase elemental carbon content [27], [28], as the hydrothermal process increases the degree of aromatisation in the samples [29]. However, in this project it is likely that the activation stage obscures the relationship between HTC temperature and carbon content. If the carbon content was to be measured after HTC but before the CO₂ activation process, it would be expected that higher

HTC temperatures would result in noticeably higher carbon content in the samples. In the case of this study, the proximate and elemental analysis was carried out after the activation process, by which point any relationship between carbon content and HTC temperature will have been obscured by the further carbonisation that has taken place during activation; thus, most of the hydrochar samples are reported to have similar carbon levels.

The variation in peel type between samples does however show some change in elemental carbon. For the samples activated at 750 °C, there are mixed results which show no correlation, but for 800 °C activated samples it is clear to observe that the mandarin derived samples all show higher carbon content than the corresponding orange derived samples. This is likely to be due to the physical make up of both peel types; orange peels contain more pith (cellulose fibre component) than mandarin peels [30], which will result in a greater state of decomposition during HTC and pyrolysis (activation). As a consequence, more of the carbon structure of the materials is destroyed during the production process of the orange peel hydrochars than for the mandarin peel hydrochars.

In terms of nitrogen doping using urea, the results confirm this has been successful: there is an approximate 5 wt% increase in elemental nitrogen in the doped samples compared to the two control samples. Theoretically this should enhance CO₂ adsorption through increased numbers of nitrogen-containing functionalities, and the same can be said for oxygen-containing functional groups which appear to exist in the sample too, based on the high residual content for each sample. The two control samples tested both exhibit higher carbon content than the screening hydrochars, and lower nitrogen content; the lack of urea will result in less nitrogen being present, which in turn will increase the carbon content as it will make up more of the samples by convention. There is also the potential that the carbonisation process in both HTC and activation occurs in a different manner as a result of

no urea inclusion, and in the case of the control samples a higher degree of carbonisation is achieved. An orange peel derived hydrochar (HTC at 200 °C, 20 h) which was activated under CO₂ at 750 °C from literature reported elemental carbon content of 83.9 wt% [17], indicating that non-doped hydrochars indeed display high levels of carbon. Similarly, *Tectona grandis* seeds were used to produce hydrochars and subsequently activated with CO₂ at 750 – 850 °C, and showed elemental carbon levels of 79 – 83 wt% [31].

6.3.3 Textural Analysis

Porosity data for the screening hydrochar prior to their activation is shown in Table 6.4.

Table 6.4: Porosity Characteristics Determined from N₂ Isotherms of Screening Hydrochars (Pre-Activation) Produced in this Study

Sample	Specific Surface Area (m ² /g)	Micropore Area (t-plot) (m ² /g)	Micropore Volume (t-plot) (cm ³ /g)	Micropore Volume (DR) (cm ³ /g) ¹⁹
HC 180-2.5-O	0	0	0	0.001
HC 220-2.5-O	0	0	0	0.002
HC 180-12-O	0	0	0	0.001
HC 220-12-O	0	0	0	0.002
HC 180-2.5-M	0	0	0	0.001
HC 220-2.5-M	0	0	0	0.001
HC 180-12-M	0	0	0	0.001
HC 220-12-M	0	0	0	0.001
HC 180-2.5-O	0	0	0	0.001
HC 220-2.5-O	0	0	0	0.002
HC 180-12-O	0	0	0	0.001
HC 220-12-O	0	0	0	0.001
HC 180-2.5-M	0	0	0	0.002
HC 220-2.5-M	0	0	0	0.001
HC 180-12-M	0	0	0	0.002
HC 220-12-M	0	0	0	0.001

¹⁹ Uncertainties within t-plot micropore volume were calculated to be below 0.001 cm³/g.

Table 6.5: Porous Characteristics Determined from N₂ Isotherms (-196 °C) and CO₂ Isotherms (0 °C) of Screening Hydrochars (Post-Activation) Produced in this Study

Sample	N ₂ Adsorption Isotherm Data ²⁰					CO ₂ Adsorption Isotherm Data ²¹		
	Specific Surface Area (m ² /g)	Micropore Area (t-plot) (m ² /g)	Micropore Volume (t-plot) (cm ³ /g)	Micropore Volume (DR) (cm ³ /g)	t-plot Micropore Area/SSA (%)	Micropore Volume (DR) (cm ³ /g)	Equivalent Micropore Surface Area (m ² /g)	Micropore Width (nm)
HC 180-2.5-O-750	0	0	0.002	0.002	0	0.135	336	0.7
HC 220-2.5-O-750	0	0	0.003	0.001	0	0.129	322	0.7
HC 180-12-O-750	N/A	N/A	N/A	N/A	N/A	0.136	340	0.7
HC 220-12-O-750	0	0	0.001	0.001	0	0.133	331	0.7
HC 180-2.5-M-750	N/A	N/A	N/A	N/A	N/A	0.136	340	0.7
HC 220-2.5-M-750	N/A	N/A	N/A	N/A	N/A	0.149	372	0.7
HC 180-12-M-750	N/A	N/A	N/A	N/A	N/A	0.148	368	0.7
HC 220-12-M-750	0	0	0	0.003	0	0.144	359	0.7
HC 180-2.5-O-800	88	92	0.034	0.034	0	0.142	354	0.7
HC 220-2.5-O-800	82	74	0.027	0.033	90	0.154	385	0.7
HC 180-12-O-800	46	43	0.016	0.019	93	0.134	334	0.7
HC 220-12-O-800	N/A	N/A	N/A	N/A	N/A	0.119	297	0.7
HC 180-2.5-M-800	64	64	0.024	0.024	100	0.143	358	0.7
HC 220-2.5-M-800	11	12	0.004	0.005	100	0.146	365	0.7
HC 180-12-M-800	10	12	0.004	0.003	100	0.164	409	0.7
HC 220-12-M-800	0	0	0	0.001	0	0.140	348	0.7
HC Control Orange	394	363	0.136	0.152	92	0.195	486	0.7
HC Control Mandarin	390	356	0.134	0.152	91	0.182	453	0.7

²⁰ Uncertainties within the BET specific surface area (SSA) were calculated to be below 2 m²/g, below 2 m²/g for the t-plot micropore surface area and below 0.001 cm³/g for the t-plot micropore volume. Uncertainties within DR N₂ micropore volume were calculated to be below 0.001 cm³/g.

²¹ Uncertainties within DR CO₂ micropore volume were calculated to be below 0.002 cm³/g, and below 4 m²/g for the DR CO₂ micropore surface area.

It is clear to see from Table 6.4 that the pre-activation hydrochars demonstrate no notable porosity; thus, the HTC process alone is not suitable for the production of porous chars in this study, and a secondary method must be subsequently employed.

Data pertaining to the porosity of the screening activated hydrochars is shown in Table 6.5, and example of both N_2 and CO_2 isotherms are seen in Figure 6.1. Note that not all samples were tested via N_2 adsorption, as at this stage in the project the equipment capable of recording volumetric CO_2 isotherms became available for use. Therefore, it was decided to focus on carrying out these tests as they were more relatable to the overall goal of the project. N_2 isotherms were still deemed necessary, however, to give a complete characterisation of the hydrochars. In the interest of time remaining in the project, it was decided to prioritise the optimisation hydrochars for this full N_2 adsorption characterisation.

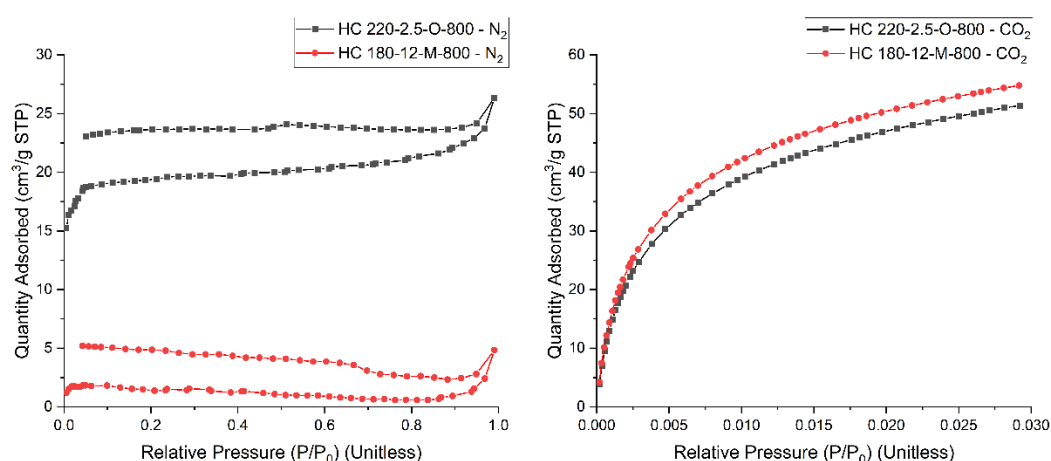


Figure 6.1: Example N_2 (left) and CO_2 (right) Isotherms for Hydrochar Screening Samples HC 220-2.5-O-800 and HC 180-12-M-8000

From the N_2 adsorption data, the tested samples clearly show that activation temperature is the influential factor, with the majority of those produced at 800 °C showing a degree of porosity ($10 < SSA, m^2/g < 90$), compared to the 750 °C activated hydrochars which display a distinct lack of a porous network ($SSA < 10 m^2/g$). This matches trends from Chapter 5, which

showed that the pyrolysis temperature was often required to be 800 °C or greater to produce char materials with observable porosity. HTC residence time also seems to show some influence, as the samples produced with a time of 12 h appear to display lower porosity than those with 2.5 h, in this small sample size. This could be due to carbonisation occurring after initial hydrolysis in the HTC process, meaning any porosity that was created is then destroyed over the increased timescale [4]. The control samples exhibit enhanced porosity compared to the screening hydrochars, suggesting a difference in pore development between the doped and non-doped samples.

The porosity data calculated from CO₂ isotherm data displays a stark contrast to the N₂ porosity data. All of the 16 doped samples tested display values of DR equivalent microporous surface area in the approximate range of 300 – 400 m²/g, even those samples which displayed negligible surface area when measured via N₂ adsorption. This situation highlights the importance of using the appropriate analysis techniques when assessing microporous materials. While CO₂ is known to possess a smaller kinetic diameter than N₂ (0.33 nm vs 0.36 nm) [32], this parameter does not take into account the molecular orientation of either molecule, and thus, cannot be used to determine whether the molecules will enter smaller ultramicropores. Instead, the critical dimensions are more applicable, and in this case, N₂ is observed to have a smaller minimum cross-sectional dimension than CO₂ [33]. In reality, the reason that CO₂ can access smaller micropores in the ultramicroporous regime (<0.7 nm) is due to the activated diffusion effect; activated diffusion is a method of diffusion where molecules must overcome an energy barrier to move or hop across sites [34]. In the case of narrow pores, such as ultramicropores, issues can arise when the molecules are a similar size to the pore, and thus, they encounter a large energy barrier at the entry to the pore. As adsorption of N₂ is tested at -196 °C, the N₂ molecules encounter this barrier but do not possess the appropriate kinetic energy to enter the pore; if left for an

infinite period of time adsorption would occur, but within the allotted experiment measurement time this does not occur. Conversely, CO₂ adsorption measurements are carried out at 0 °C, and therefore, the CO₂ molecules have higher energy, which, in turn, enhances the likelihood that they can overcome the energy barrier and diffuse into the ultramicropores; this is therefore why the data derived from the CO₂ isotherms differs to that derived from N₂ isotherms.

From these CO₂ results, the sample with the largest DR equivalent surface area is still seen to be HC Control Orange, with HC 180-12-M-800 presenting the highest DR equivalent surface area of the nitrogen-doped samples. Based on this data, it could be suggested that using urea aids in the development of ultramicroporous materials, but limits the creation of larger pores in the meso- and macroporous domain. This may relate to the way in which CO₂ in the activation stage interacts with nitrogen-containing functionalities which are present in the samples. In terms of the influence of process factors on this CO₂ derived microporosity, there are no stark relationships that can be found from comparison within the data set. Varying HTC residence time and temperature between sample sets is seen to give differing results throughout the range of samples, so it is not possible to identify any trends. Similar can be stated for activation temperature, where no clear correlations are seen. Only the factor of peel type shows some relationship: mandarin derived hydrochars have, on average, higher micropore surface areas compared to orange derived hydrochars, indicating that mandarin peels provide the opportunity for greater micropore development.

Literature around orange peel derived hydrochar produced at 210 °C for 2 h, doped with urea and KOH and then physically activated under argon, has shown that inclusion of urea in the HTC step is more effective at porosity creation in activated hydrochars than introducing it after HTC but before activation [35]. This conflicts with the data in this project; it is possible

that the use of KOH as activator had an additional impact that could not be replicated by the use of CO₂, thus, further investigation would be required.

Looking at surface areas calculated from N₂ isotherms presented in other studies, hydrochar prepared from orange peels at 200 °C and 20 h (HTC) before being activated under CO₂ at 750 °C was seen to have a surface area of 117 m²/g pre-activation and 301 m²/g post activation (and a DR N₂ micropore volume of 0.154 cm³/g post-activation) [17]. Regrettably, the porosity characteristics of the pre-activated control hydrochars were not measured in this project so cannot be compared. In future it would be interesting to see if they presented similar results. Considering the post-activation data, for the eleven screening hydrochars examined, all present much lower N₂ derived surface areas (0 – 88 m²/g), but the control samples have greater surface areas than this example; this could be due to a greater activation temperature of 800 °C, or the higher HTC temperature used. It should not be forgotten however, that the doped samples have been shown to possess high levels of microporosity that cannot be accessed via N₂ adsorption.

The general difference from the data in this study and the reports from literature is that the urea doping carried out has not led to well-developed pore structures forming in the hydrochar materials. While the overall process has produced microporous hydrochars after nitrogen doping and CO₂ activation, this microporosity was not detectable under N₂ adsorption, indicating that the overall pore development has been restricted beyond these small ultramicropores. In contrast, the two control samples are seen to be microporous via both CO₂ and N₂ adsorption analysis. It has been repeatedly reported in other studies that urea doping results in increases in surface area [18], [36], [37]. The difference between these studies and this project is that they have incorporated urea after HTC, whereas here it was introduced during the HTC stage, which could imply that the reactions between the feedstock

and urea under hydrothermal conditions must influence the porosity development. Alternatively, it could simply be the case that CO₂ is very effective at micropore creation but unable to enhance mesopore development.

An additional study looking at hydrochar derived from orange peels and activated by KOH at 700 °C tested three different HTC temperature: 180, 200 and 220 °C. The sample produced at 220 °C displayed the highest surface area after activation, 457 m²/g, while the 180 °C sample was found to be 51 m²/g [28]. Considering these were activated using KOH, the highest surface area is lower than expected, but nonetheless, it is still greater than those presented in this report and show a trend of higher HTC temperature resulting in higher surface area.

6.3.4 Surface Chemical Analysis

To examine the surface chemistry of the hydrochar samples pre- and post-activation, FTIR spectroscopy was used. This allows different surface functionalities to be identified, and can provide evidence of successful doping through the presence of nitrogen-containing functionalities. A selection of the pre-activation FTIR spectra are shown below: hydrochars produced at 180 °C and 220 °C are shown in Figure 6.2, with the rest of the data presented in Appendix E.

All of the samples present similar spectra, indicating a high degree of chemical similarity between all produced hydrochars. The majority of differences observed are related to the intensity of peaks between individual samples. A relatively wide peak at 3340 – 3280 cm⁻¹ is observed due to the presence of hydroxyl groups in the hydrochar structures [38], also indicated by C-O hydroxyl bending at around 1270 cm⁻¹. A small peak at 2930 – 2915 cm⁻¹ can be attributed to stretching of aliphatic C-H bonds [39]; leftover C-H₂ and C-H₃ aliphatic chains are also seen at 1430 – 1420 cm⁻¹ in some samples [40]. Around 1740 – 1720 cm⁻¹ a distinct

carbonyl peak related to C=O vibrations is observed from ketone or aldehyde groups [41]. Peaks at approximately 1600 cm^{-1} can be ascribed to C=C bonding that arises from aromatic rings in the structure [42]. Phenol C-O stretches can be seen around $1225 - 1220\text{ cm}^{-1}$, and possible C-N stretches at 1360 cm^{-1} ; alternatively, instead of C-N, these may prove to be simply more evidence of methyl C-H stretching [43]. Finally, ester bonds of C-O-C are clear at 1035 cm^{-1} likely from the carbohydrate content of the feedstock [44], and C-H bending is visible at around 750 cm^{-1} [45]. Little variation is seen between the orange and mandarin samples, indicating there are many common functionalities shared between the two types of citrus species, as evidenced in the FTIR section of Chapter 5. Generally, more intense peaks are seen for the samples produced at 2.5 h compared to 12 h. This could suggest that longer residence time results in higher carbonisation and removal of more functional groups [46].

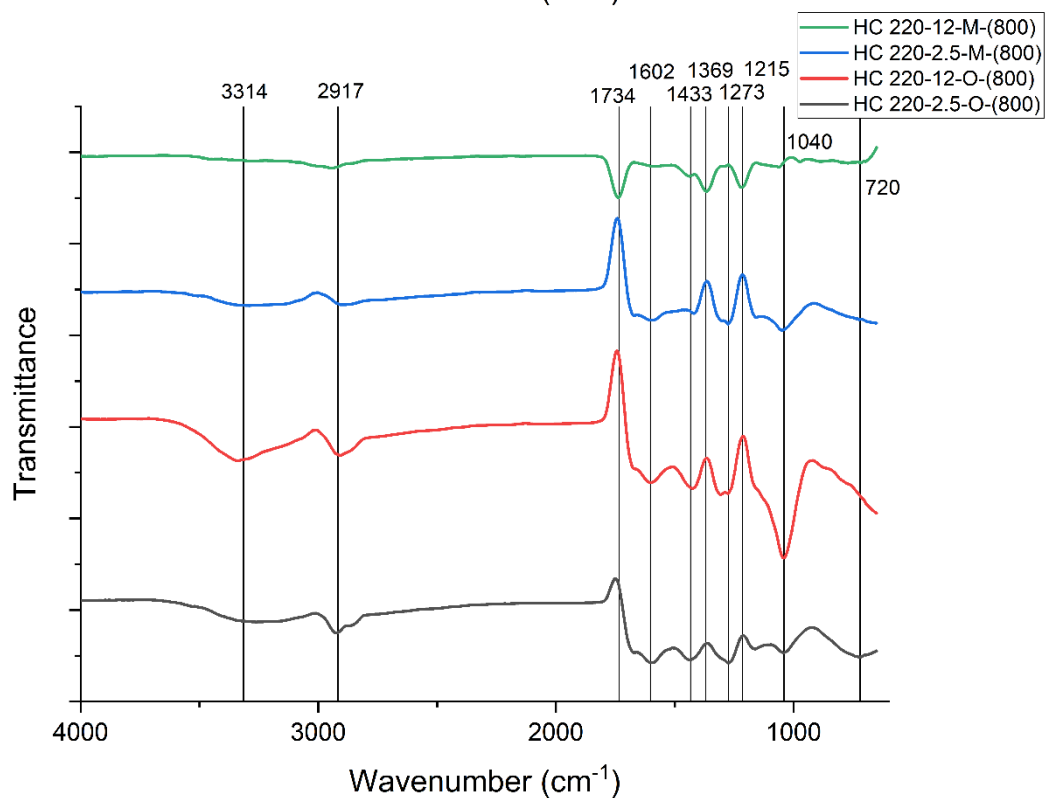
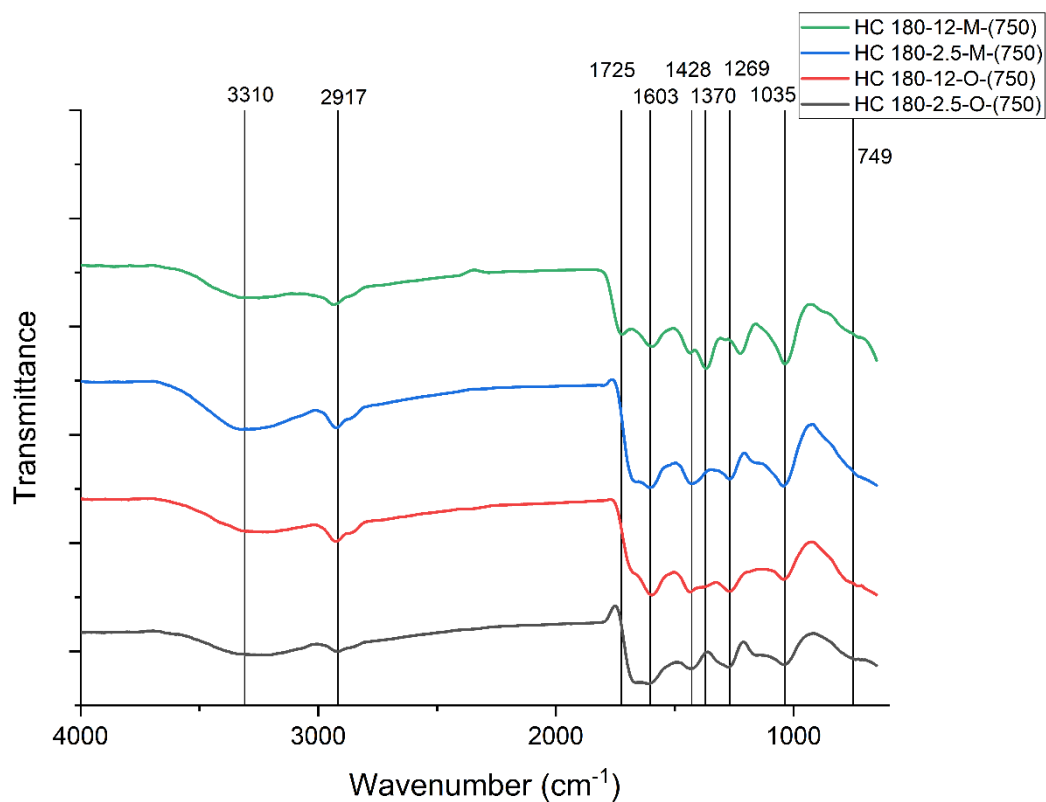


Figure 6.2: FTIR Spectra of Hydrochar Samples Produced Through HTC at 180 °C (top) for Activation at 750 °C and 220 °C (bottom) for Activation at 800 °C

The FTIR spectra produced from the two control hydrochar samples prior to activation are seen in Figure 6.3. They exhibit, in the main, the same peaks as the hydrochars produced using urea doping, indicating that the inclusion of urea does not change the HTC process in any fundamental way.

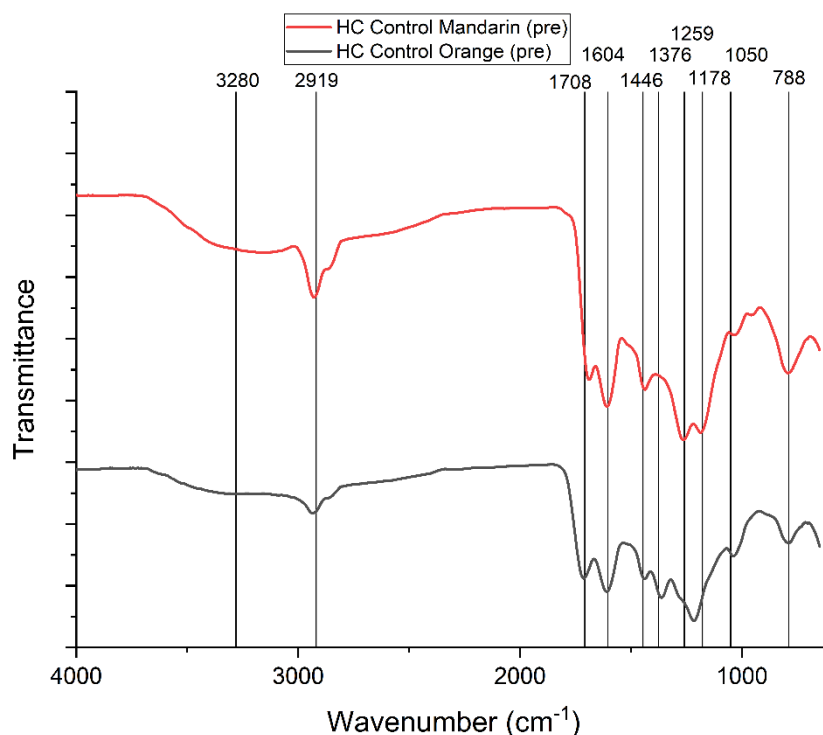


Figure 6.3: FTIR Spectra of Hydrochar Control Samples Produced Through HTC at 220 °C for Activation at 800 °C

The post-activation FTIR spectra are shown below in Figure 6.4, showing hydrochars produced at 180 °C and activated at 750 °C, and hydrochars produced at 220 °C and activated at 800 °C. These spectra are notably different from the pre-activation ones described above, in the main, due to their lack of absorbance bands, indicating loss of functional groups. This matches with behaviour noted in Chapter 5, in that high pyrolysis temperature of approximately 800 °C results in high levels of carbonisation and devolatilisation of the char material. Some groups remain: C=O carbonyl stretching is seen from 1740 – 1735 cm^{-1} , and C-N bonding remains at approximately 1370 – 1360 cm^{-1} . Likewise, C-O groups are still observed at 1200 cm^{-1} , and C-H stretching at 870 cm^{-1} [39].

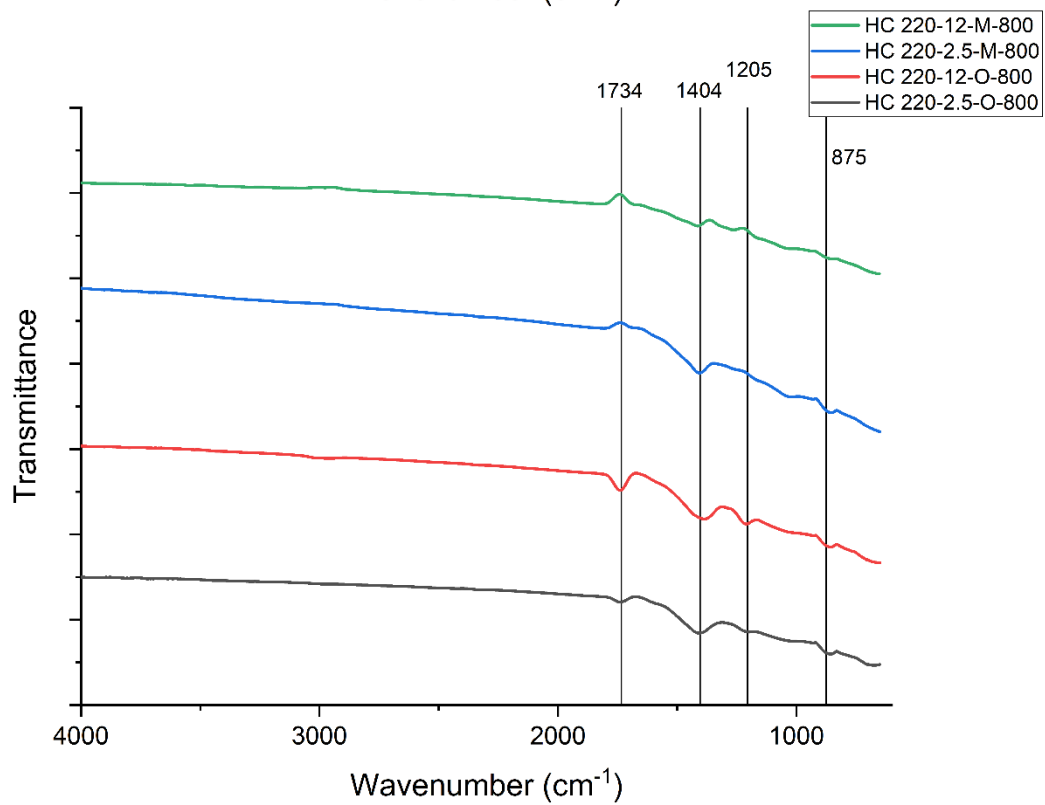
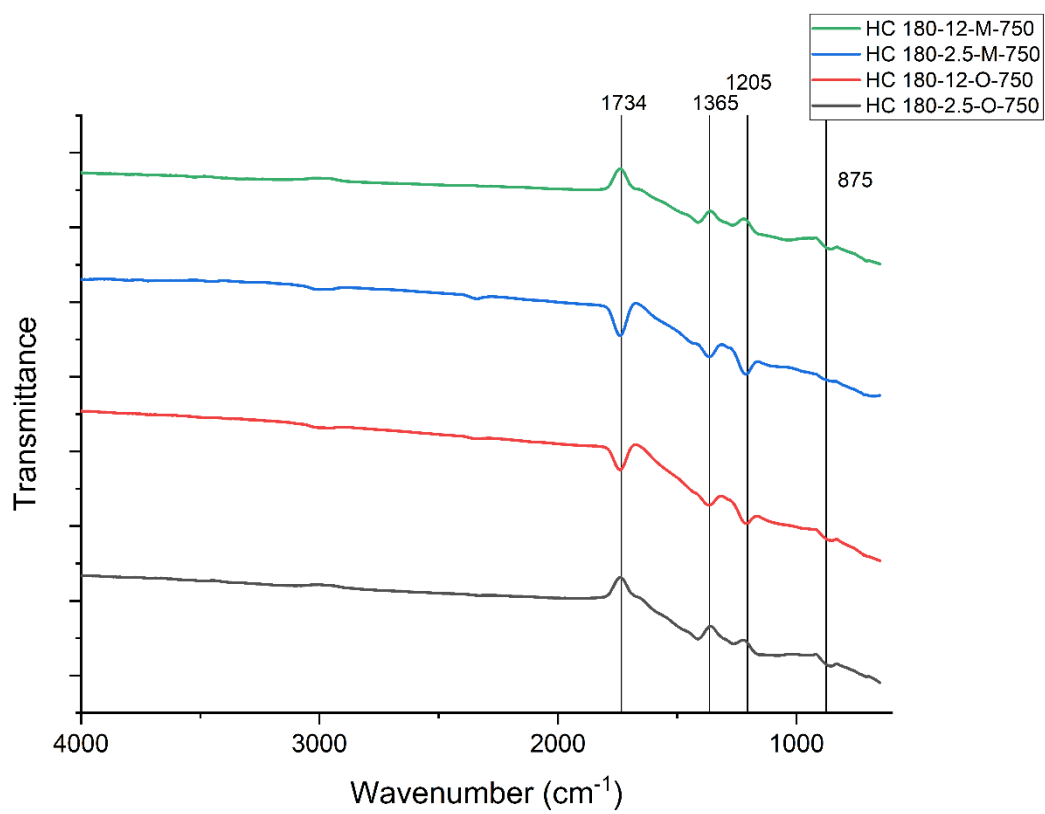


Figure 6.4: FTIR Spectra of Hydrochar Samples Produced Through HTC at 180 °C and Activated at 750 °C (top), and at 220 °C and Activated at 800 °C (bottom)

The pyrolysis process of activating the hydrochars is useful for porosity creation, but it is clear it removes many of the functional groups that were previously present; this is due to the breaking of structural bonds associated with different functionalities and decomposition of many of the intrinsic structures from the initial feedstock [17], [39].

Finally, the FTIR spectra produced from the two control hydrochar samples post-activation are seen in Figure 6.5. No absorbance bands are witnessed in the either spectra, reminiscent of some of the spectra seen for biochars in this study, see Chapter 5, where a combination of pyrolysis removing the vast majority of functional groups and the dark nature of the char material prevented collection of high-quality spectra.

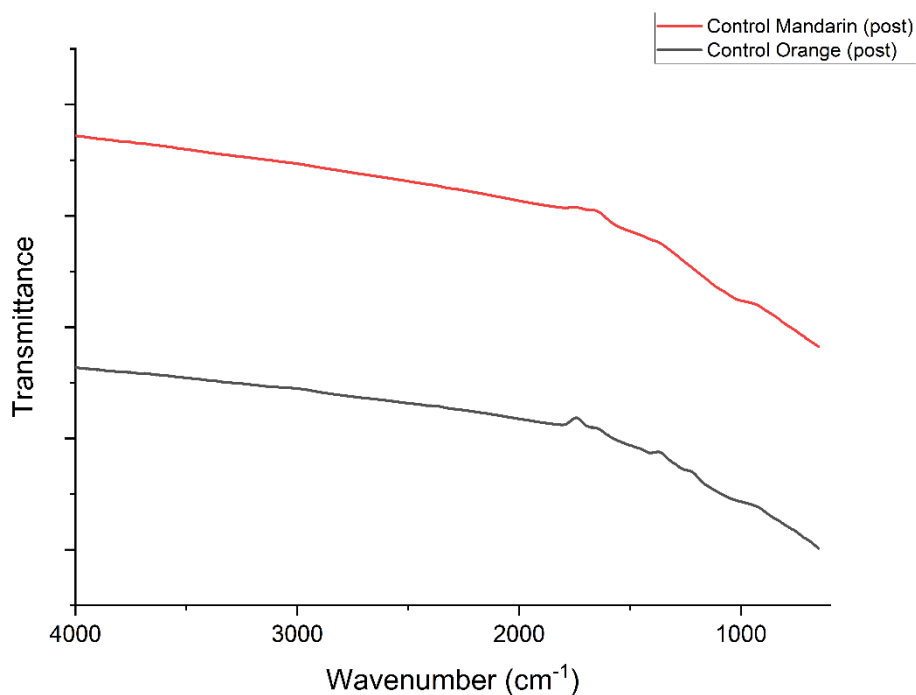


Figure 6.5: FTIR Spectra of Hydrochar Control Samples Produced Through HTC at 220 °C and Activated at 800 °C

6.3.5 Screening Design of Experiment Trends and ANOVA

The same process, method and materials were used to carry out Analysis of Variance (ANOVA) and regression analysis of the hydrochar screening results as had been used for the biochar screening results in Chapter 5. The only major difference that should be noted is that for the hydrochar samples, the response of micropore area was now based on the data obtained from the volumetric CO₂ adsorption isotherms, rather than N₂ adsorption isotherms. This was due to the overall goal of the project being directed towards CO₂ adsorption, thus, when the ability to carry out testing in this manner arose during the course of the study, it was deemed appropriate to utilise it. While this meant that the hydrochar DoE differed from the biochar DoE, it was suspected that the same trend would be followed through both types of analysis method in that the more porous chars would give higher levels of adsorption. The use of CO₂ would simply help better facilitate analysis of microporosity due to its ability to travel into smaller pores than N₂ [47].

The regression equations for each of the three responses are seen in Equation 6.1 – Equation 6.3, with temperature in °C, residence time in h and CO₂ flowrate in mL/min.

$$\text{Yield} = 25.33 + 0.02613 \text{ HTC Temp} - 7.09 \text{ Peel Type} - 0.02705 \text{ Activation Temp} + 0.00870 \text{ Peel Type} * \text{Activation Temp} \quad \text{Equation 6.1}$$

$$\text{Micropore Area} = 231 - 0.189 \text{ HTC Temp} + 12 \text{ Peel Type} + 0.204 \text{ Activation Temp} + 0.002 \text{ Peel Type} * \text{Activation Temp} \quad \text{Equation 6.2}$$

$$\text{Carbon Content} = 88.7 - 0.0302 \text{ HTC Temp} - 35.7 \text{ Peel Type} - 0.0242 \text{ Activation Temp} + 0.0482 \text{ Peel Type} * \text{Activation Temp} \quad \text{Equation 6.3}$$

The Pareto charts for each response are seen in Figure 6.6 – Figure 6.8, and the regression coefficients for each model in Table 6.6.

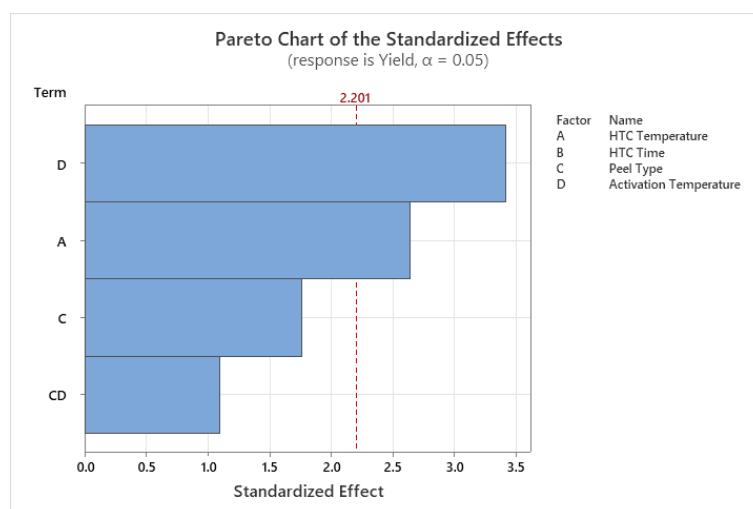


Figure 6.6: Screening Pareto Chart for Hydrochar Yield as DoE Response

All three models have poor regression coefficients, indicating that they could be improved, likely by removing more factors as the ones remaining are complicating each model. For instance, the yield model could be improved by removing the factor of peel type and the interaction between peel type and activation temperature, however, as this factor was found to be influential in one of the other two responses, it was kept in all three models. It should be reiterated that the screening models in this study are used to identify the factors to take forward for further investigation, and should not under any circumstances be used to make any detailed predictions of the responses tested.

In terms of the micropore area model, it displays a R^2 of 34.41 % and R^2 -pred of 0 %, and suffers similar failings that were present in the biochar screening model, as discussed in Chapter 5; however, in this case it is due to the choice of the activation temperature range, i.e. 750 – 800 °C. While this lies within the window in which the Boudouard reaction occurs, it is too narrow to generate meaningful changes in microporosity between the 750 °C and 800 °C samples. While a small effect from this factor may be present, it is likely hidden by experimental noise and a poor signal-to-noise ratio. Therefore, the effect of activation

temperature is not fully captured in this DoE model. Due to CO₂ being present during the ramp and dwell stages of activation, the hydrochar material that enters the dwell phase in each experiment is not consistent, as different dwell temperatures of 750 °C and 800 °C are utilised. This introduces a level of variability that the model cannot interpret.

The above explanation can also, in part, be applied to the carbon content response. As the hydrochar is subjected to an activation process, it is likely that the activation temperature is an important factor in the degree of carbonisation that will be achieved. Yet, as described above, the chosen range of 750 – 800 °C is too narrow to display the true effect that this factor has on the response. In both cases, to improve the models, a wider range of activation temperature could be tested in future, as long as the chosen range lay within the active window for the Boudouard reaction.

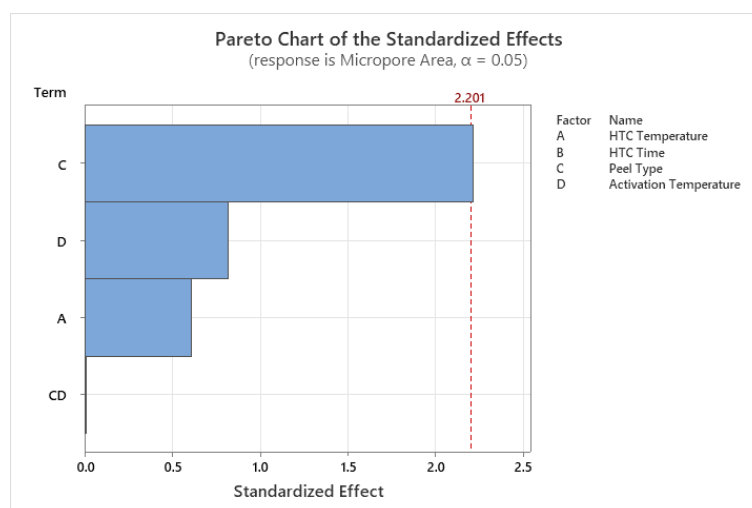


Figure 6.7: Screening Pareto Chart for Hydrochar Micropore Area as DoE Response

Despite this, it can be observed that HTC temperature, peel type and activation temperature are all determined to be influential in at least one of the three responses measured. Therefore, these process parameters were taken forward for further analysis in the optimisation stage. HTC residence time was set at a fixed value for future experiments.

The ANOVA and associated *p* values for each response can be seen in Appendix F.

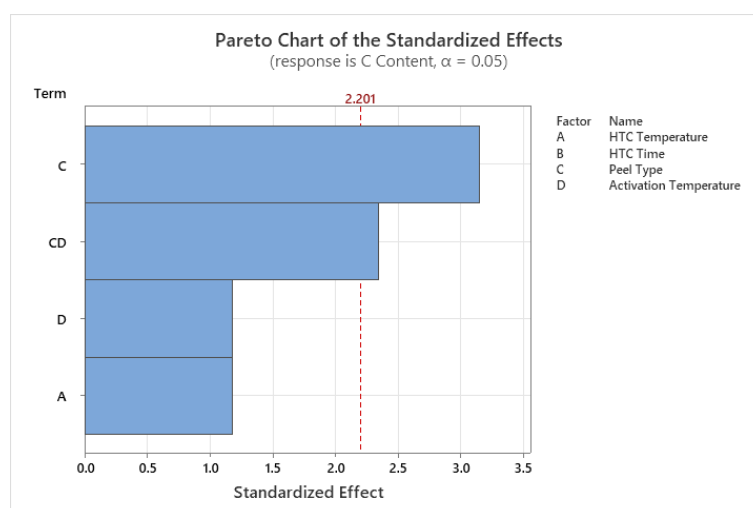


Figure 6.8: Screening Pareto Chart for Hydrochar Carbon Content as DoE Response

Table 6.6: Screening Coefficients of Determination for Each Hydrochar Response

Response	R ² (%)	R ² -adj (%)	R ² -pred (%)
Yield	67.59	55.80	31.43
Micropore Area	34.41	10.55	0.00
Carbon Content	62.24	48.52	20.12

6.4 Optimisation Design of Experiments Plan

From the DoE results, three of the four factors were determined to be influential: HTC temperature, peel type and activation temperature. This therefore meant HTC residence time would not be included in the optimisation stage of the process, and must be set at a constant value. It was decided to use the lower level of time from the screening experiments of 2.5 h; this was in part due to literature suggesting a longer residence time had no significant impact on the final product's porosity, and partly due to the safety concerns that had surrounded the experimental setup. By choosing the lower time period for HTC, the setup was running for less time which was preferential. Additionally, using a shorter

residence time would reduce energy consumption, in line with the green chemistry focus of the project.

A circumscribed (CCC) design was used for the optimisation experiments, identical to that used in Chapter 5. HTC temperature and activation temperature were tested at five levels instead of two, and the peel type remained set as orange and mandarin, respectively. Minitab 22 was used to create the new experimental plan, see Table 6.7, leading to 18 experiments being undertaken, and the chosen responses were the same as those used for the screening design: overall hydrochar yield, DR microporous surface area, and elemental carbon content.

6.5 Optimisation Hydrochars Results

6.5.1 Yield

The process conditions and calculated yield of the optimisation hydrochars are shown in Table 6.7, and comparisons with their replicates from the screening design in Table 6.8.

Table 6.7: Conditions Used to Produce Optimisation Hydrochars and Subsequent Yield Results

Sample	HTC Temperature (°C)	Peel Type	Activation Temperature (°C)	HTC Yield (%)	Overall Yield (%)
OHC 200-O-740	200	Orange	740	30.4	10.4
OHC 180-O-750	180	Orange	750	27.4	8.7
OHC 220-O-750	220	Orange	750	30.8	9.9
OHC 172-O-775	172	Orange	775	26.2	7.9
OHC 200-O-775	200	Orange	775	32.2	10.6
OHC 228-O-775	228	Orange	775	31.3	10.7
OHC 180-O-800	180	Orange	800	28.4	8.4
OHC 220-O-800	220	Orange	800	31.6	9.9
OHC 200-O-810	200	Orange	810	30.9	10.0
OHC 200-M-740	200	Mandarin	740	27.3	9.0
OHC 180-M-750	180	Mandarin	750	24.4	7.6
OHC 220-M-750	220	Mandarin	750	27.0	8.2
OHC 172-M-775	172	Mandarin	775	21.4	6.1
OHC 200-M-775	200	Mandarin	775	29.0	9.3
OHC 228-M-775	228	Mandarin	775	27.0	8.9
OHC 180-M-800	180	Mandarin	800	23.0	6.1
OHC 220-M-800	220	Mandarin	800	27.9	9.7
OHC 200-M-810	200	Mandarin	810	26.2	8.0

There is a wider range of initial HTC yield in these samples, with some showing yields of 21 – 23 %, however, the higher range of values remains consistent at around 31 – 32 %. On the whole, most lie around the 26 – 30 % range, which is congruent with the results from the screening samples. It is noticeable that the majority of the lower yield values originate from the mandarin hydrochar samples, possibly due to harsher degradation of the feedstock structure during HTC. This was a new trend that had not been seen in the screening phase.

The same relationship is present in the overall yield data, with mandarin derived hydrochars displaying lower values. This is likely a follow-on effect from the HTC process, and the lower yield are purely due to less material being available to activate after the HTC stage. In terms of activation temperature, it does not present any strong relationship with the overall yield results. Nonetheless, the HTC temperature does, as it is clear to see that samples produced at lower HTC temperatures such as 172 °C and 180 °C show the lowest yields; the description of HMF production and adsorption onto the solid hydrochar during HTC which was provided in Section 6.3.1 remains the only explanation found so far to describe this increased yield for samples produced at a higher HTC temperature. The yields obtained for the optimisation samples appear to be lower than those for the screening samples; this may again be due to different batches of feedstock being used in each phase of the design. If more time and resources were available, further replicates could be produced to allow for calculation of errors and variation within each sample set.

Table 6.8: Comparison of Yield Between Replicate Samples of Screening and Optimisation Biochars

Screening Sample	HTC Yield (%)	Overall Yield (%)	Corresponding Optimisation Sample	HTC Yield (%)	Overall Yield (%)
HC 180-2.5-O-750	31.7	10.5	OHC 180-O-750	27.4	8.7
HC 220-2.5-O-750	34.4	10.8	OHC 220-O-750	30.8	9.9
HC 180-2.5-M-750	30.4	9.0	OHC 180-M-750	24.4	7.6
HC 220-2.5-M-750	31.2	10.4	OHC 220-M-750	27.0	8.2
HC 180-2.5-O-800	28.3	7.9	OHC 180-O-800	28.4	8.4
HC 220-2.5-O-800	27.9	8.8	OHC 220-O-800	31.6	9.9
HC 180-2.5-M-800	27.7	7.5	OHC 180-M-800	23.0	6.1
HC 220-2.5-M-800	30.4	9.1	OHC 220-M-800	27.9	9.7

6.5.2 Elemental and Proximate Analysis

The proximate analysis results for the post-activation optimisation hydrochars can be seen in Table 6.9, and a comparison with their replicate samples from the screening design in Table 6.10. The 18 samples all lie within a range of 65 – 75 wt% for their fixed carbon content, matching expectations from the screening design and from literature [48], [49]. No observable trend is seen for activation temperature in the data. It may have been expected that higher temperature would give lower fixed carbon due to more burn-off, but this was not observed. The lowest fixed carbon content for both peel types is seen in the two samples produced at a HTC temperature of 228 °C, OHC 228-O-775 and OHC 228-M-775, which could imply the higher temperature has resulted in enhanced degradation during the HTC process and, thus, produced a poorer carbon structure at the end of the process. The ashiest samples in this section (those > 10 wt%) are activated at temperatures of 775 °C or higher, which can be a sign of increased volatilisation or of further degradation of the carbon structure. In either case, the ash is produced from minerals that inherently exists within the feedstock [50].

Table 6.9: Proximate Analysis Results Obtained for Optimisation Hydrochars Produced in this Study

Sample	Moisture (wt%)	Volatiles (wt%)	Fixed Carbon (wt%)	Ash (wt%)
OHC 200-O-740	4.3	15.6	73.0	7.1
OHC 180-O-750	2.5	15.4	74.4	7.7
OHC 220-O-750	3.2	16.0	73.8	7.0
OHC 172-O-775	2.1	16.6	71.2	10.1
OHC 200-O-775	2.3	14.0	74.8	8.9
OHC 228-O-775	2.1	20.2	65.2	12.5
OHC 180-O-800	2.1	18.5	69.3	10.1
OHC 220-O-800	2.1	15.3	73.1	9.5
OHC 200-O-810	1.9	14.2	74.1	9.8
OHC 200-M-740	3.6	20.3	68.1	8.0
OHC 180-M-750	1.1	13.7	75.5	9.7
OHC 220-M-750	1.7	17.3	75.0	6.0
OHC 172-M-775	1.8	14.6	73.8	9.8
OHC 200-M-775	2.2	13.4	75.9	8.5
OHC 228-M-775	3.5	22.1	67.4	7.0
OHC 180-M-800	1.34	13.6	74.7	10.3
OHC 220-M-800	5.4	14.0	72.9	7.7
OHC 200-M-810	3.1	15.6	72.7	8.6

Some of the samples from this section can also be directly compared to those from the screening design which were created at the same conditions, see Table 6.10, and it is notable that most of them displayed slightly higher fixed carbon than the corresponding screening samples. This serves to highlight the lack of consistency that can be achieved when working with natural organic samples, but equally, the variation is small enough to leave no concerns with the synthesis process. From a general point of view, the samples produced in both the screening and optimisation designs have a consistent level of fixed carbon, which is crucial for a high quality of hydrochar.

Table 6.10: Comparison of Proximate Analysis Results Between Replicate Samples of Screening and Optimisation Hydrochars

Screening Sample	Moisture (wt%)	Volatiles (wt%)	Fixed Carbon (wt%)	Ash (wt%)
HC 180-2.5-O-750	5.3	20.9	70.4	3.4
HC 220-2.5-O-750	3.1	24.8	65.6	6.5
HC 180-2.5-M-750	2.8	15.2	74.3	7.7
HC 220-2.5-M-750	3.1	17.0	72.6	7.3
HC 180-2.5-O-800	5.0	19.3	68.4	7.3
HC 220-2.5-O-800	1.5	23.4	66.0	9.1
HC 180-2.5-M-800	3.0	14.0	75.2	7.8
HC 220-2.5-M-800	2.5	20.0	69.6	7.9
Optimisation Sample	Moisture (wt%)	Volatiles (wt%)	Fixed Carbon (wt%)	Ash (wt%)
OHC 180-O-750	2.5	15.4	74.4	7.7
OHC 220-O-750	3.2	16.0	73.8	7.0
OHC 180-M-750	1.1	13.7	75.5	9.7
OHC 220-M-750	1.7	17.3	75.0	6.0
OHC 180-O-800	2.1	18.5	69.3	10.1
OHC 220-O-800	2.1	15.3	73.1	9.5
OHC 180-M-800	1.34	13.6	74.7	10.3
OHC 220-M-800	5.4	14.0	72.9	7.7

The elemental analysis results for the post-activation optimisation hydrochars can be seen in Table 6.11, and their comparison with replicate samples from the screening phase in Table 6.12. The hydrochars have a very consistent elemental carbon content of 60 – 65 wt%, and as before with the screening hydrochars, Section 6.3.2, there is little correlation between the carbon content and the respective HTC and activation temperatures. The same trend of higher levels of elemental carbon in the mandarin derived hydrochars compared to the orange hydrochars is observed, giving further indication that the difference in structure between mandarin and orange peels has an influence over the final hydrochar product.

Table 6.11: Elemental Compositions Obtained for Optimisation Hydrochars Produced in this Study

Sample	C (wt%)	H (wt%)	N (wt%)	Residuals (wt%)
OHC 200-O-740	61.6	0.8	7.5	30.1
OHC 180-O-750	62.6	1.0	7.1	29.3
OHC 220-O-750	63.8	0.8	8.2	27.2
OHC 172-O-775	61.9	0.6	6.3	31.2
OHC 200-O-775	64.0	0.7	7.8	27.5
OHC 228-O-775	60.9	0.7	8.2	30.2
OHC 180-O-800	62.7	0.7	7.1	29.5
OHC 220-O-800	60.2	0.6	7.7	31.5
OHC 200-O-810	63.0	0.6	7.3	29.1
OHC 200-M-740	64.1	0.9	7.6	27.5
OHC 180-M-750	65.0	0.9	6.8	27.3
OHC 220-M-750	65.9	0.9	8.5	24.7
OHC 172-M-775	61.6	0.8	6.4	31.2
OHC 228-M-775	64.4	0.6	8.4	26.6
OHC 200-M-775	65.0	0.8	7.4	26.8
OHC 180-M-800	62.5	0.7	6.6	30.2
OHC 220-M-800	65.2	0.7	8.0	26.1
OHC 200-M-810	65.3	0.6	7.6	26.5

Urea doping is seen to continue to be successful by providing an enhanced level of elemental nitrogen content, compared to non-doped control samples analysed previously. It should be noted that the nitrogen content in this set of hydrochars is slightly higher than that reported for the screening hydrochars, see Table 6.12. This is possibly due to a different batch of peels being used, and the associated variation this brings. Conversely, the carbon content of the samples is broadly similar in comparison. This serves to highlight the degree of variation and unpredictability that is present when working with organic materials. It should also be noted that elemental analysis has been reported to be an unreliable technique in terms of reproducibility [51]. This may be a contributor to the variation in nitrogen content.

Table 6.12: Comparison of Elemental Analysis Results Between Replicate Samples of Screening and Optimisation Hydrochars

Screening Sample	C (wt%)	H (wt%)	N (wt%)	Residuals (wt%)
HC 180-2.5-O-750	67.2	0.8	6.8	25.2
HC 220-2.5-O-750	65.2	0.8	7.4	26.6
HC 180-2.5-M-750	64.8	0.8	6.2	28.2
HC 220-2.5-M-750	64.9	0.9	6.8	27.4
HC 180-2.5-O-800	62.5	0.7	5.0	31.8
HC 220-2.5-O-800	58.9	0.7	5.9	34.5
HC 180-2.5-M-800	64.1	0.7	5.6	29.6
HC 220-2.5-M-800	64.9	0.7	6.6	27.8
Optimisation Sample	C (wt%)	H (wt%)	N (wt%)	Residuals (wt%)
OHC 180-O-750	62.6	1.0	7.1	29.3
OHC 220-O-750	63.8	0.8	8.2	27.2
OHC 180-M-750	65.0	0.9	6.8	27.3
OHC 220-M-750	65.9	0.9	8.5	24.7
OHC 180-O-800	62.7	0.7	7.1	29.5
OHC 220-O-800	60.2	0.6	7.7	31.5
OHC 180-M-800	62.5	0.7	6.6	30.2
OHC 220-M-800	65.2	0.7	8.0	26.1

Overall, the nitrogen content of the optimisation post-activation hydrochars is typically lower than that of the optimisation biochars presented in Chapter 5; the biochars showed an average nitrogen content of 10.8 wt% compared to an average of 7.5 wt% for these hydrochars. This could be due to the different doping techniques that the precursor peels were subject to. Peels for use in biochar synthesis were soaked in a urea solution for 5 h, before being drained and dried in an oven for 24 h prior to pyrolysis, to introduce urea into the materials. Conversely, the peels for hydrochar synthesis were washed in deionised water and dried; their first interaction with urea was when they were mixed with a urea solution in the autoclave prior to undergoing HTC. It is also possible that different reaction pathways are encountered in the two processes (pyrolysis and HTC), therefore as a result, the nitrogen content will undoubtedly vary between the two types of materials.

6.5.3 Textural Analysis

Data regarding the porosity of pre-activation optimisation hydrochars from N₂ isotherms is displayed in Table 6.13. These show an overall lack of porosity and further emphasise the fact that HTC alone is not suitable for creating porous materials, and matches with data obtained from the screening design.

Table 6.13: Porosity Characteristics Determined from N₂ Isotherms of Selected Optimisation Hydrochars (Pre-Activation) Produced in this Study

Sample	Specific Surface Area (m ² /g)	Micropore Area (t-plot) (m ² /g)	Micropore Volume (DR) (cm ³ /g)	Micropore Volume (t-plot) (cm ³ /g)
OHC 180-O-750	0	0	0	0.001
OHC 220-O-750	0	0	0	0.002
OHC 180-O-800	0	0	0	0.001
OHC 220-O-800	0	0	0	0.002
OHC 200-O-775	0	0	0	0.001
OHC 180-M-750	0	0	0	0.001
OHC 220-M-750	0	0	0	0.003
OHC 180-M-800	0	0	0	0.002
OHC 228-M-775	0	0	0	0.002
OHC 200-M-810	0	0	0	0.002

Table 6.14 below shows further porosity characteristics of the pre-activation hydrochars, in this case derived from CO₂ isotherms. The data from this form of analysis is more positive than that of the N₂ isotherms, yet the micropore areas reported are not remarkably large, with most results lying within the 20 – 30 m²/g range. Once again, this adds credence to the judgement that non-activated hydrochars do not possess the characteristics to be utilised in carbon capture technologies. As the data obtained from both the N₂ and CO₂ isotherms for this subsection of hydrochars are consistent, it follows that the other pre-activated hydrochars that have not been tested would very likely show the same level of porosity as those displayed here.

Table 6.14: Porous Characteristics Determined from CO₂ Isotherms of Selected Optimisation Hydrochars (Pre-Activation) Produced in this Study

Sample	Micropore Volume (DR) (cm ³ /g) ²²	Equivalent Micropore Surface Area (m ² /g) ²³
OHC 180-O-750	0.008	19
OHC 220-O-750	0.012	29
OHC 180-O-800	0.009	23
OHC 220-O-800	0.011	27
OHC 200-O-775	0.010	25
OHC 180-M-750	0.011	28
OHC 220-M-750	0.011	29
OHC 180-M-800	0.011	29
OHC 228-M-775	0.011	26
OHC 200-M-810	0.011	27

Porosity characteristics determined after activation had taken place are presented below in Table 6.15, showing data obtained via N₂ and CO₂ isotherms, and the comparison of CO₂ porosity data with replicates from the screening design in Table 6.16. The N₂ specific surface area (SSA) results show a slight contrast to the pre-activation samples: ten of the optimised samples present discernible porosity using this method, although only three of them are greater than 100 m²/g. These three specific samples were activated at either 800 °C or 810 °C, and also produced using a HTC temperature of 200 °C or above. This would suggest that higher temperature is required in both parts of the process to enable sufficient pore network development. Most of these samples are of a similar standard in terms of SSA to the post-activation screening hydrochars, discussed in Section 6.3.3, but some of the samples within the optimisation subset that are produced at the same conditions show differing results. For example, HC 180-2.5-O-800 presents a SSA of 88 m²/g, whereas OHC 180-O-800 shows non-porous characteristics under N₂ analysis. Contrastingly, the SSA of HC 220-2.5-O-800 was 82 m²/g, compared to 207 m²/g for OHC 220-O-800. This again shows the consequences of

²² Uncertainties within DR CO₂ micropore volume were calculated to be below 0.001 cm³/g.

²³ Uncertainties within DR CO₂ micropore surface area were calculated to be below 1 m²/g.

using natural organic materials as a feedstock, as the optimisation samples were produced from a different batch of peels to the screening samples, so natural variation in the raw material could have influenced results.

The results from CO₂ isotherm analysis show all the post-activation optimisation samples possess high levels of microporosity, higher than that seen from N₂ analysis. This is similar to the results seen in Section 6.3.3, where the post-activation screening samples were seen to be microporous under CO₂ analysis compared to the low or non-porous results obtained via N₂ analysis, and is likely a result of CO₂ activation generating an abundance of micropores [52]. This further emphasises the importance of choosing the most appropriate porosity analysis technique for solid adsorbent materials. As seen before in the screening hydrochar samples, there is not an immediate identifiable relationship between the tested factors and the equivalent micropore surface area measured via CO₂ adsorption. On average the mandarin-derived hydrochars present marginally higher microporous surface areas. The highest result is seen by OHC 180-M-800, giving 407 m²/g, which is an impressive level of porosity. In comparison to the screening hydrochars, Section 6.3.3, this matches the porosity level of sample HC 180-12-M-800 which reported a microporous surface area of 409 m²/g. Looking at other comparisons between the two sample sets, for those made at the same conditions, the results show mild variation but still lie in the same approximate range.

The set of samples analysed here all present microporous surface areas within a tight 100 m²/g range, and it is difficult to distinguish any trends. The key takeaway appears to be the requirement for an activation stage, in this case with CO₂ as activating agent, to create this level of microporosity within the samples themselves, which subsequently gives them the characteristics to be potential CO₂ adsorbents.

Table 6.15: Porosity Characteristics Determined from N₂ and CO₂ Isotherms of Optimisation Hydrochars (Post-Activation) Produced in this Study

Sample	N ₂ Adsorption Isotherm Data ²⁴					CO ₂ Adsorption Isotherm Data ²⁵		
	Specific Surface Area (m ² /g)	Micropore Area (t-plot) (m ² /g)	Micropore Volume (t-plot) (cm ³ /g)	Micropore Volume (DR) (cm ³ /g)	t-plot Micropore Area/SSA (%)	Micropore Volume (DR) (cm ³ /g)	Equivalent Micropore Surface Area (m ² /g)	Micropore Width (nm)
OHC 200-O-740	0	0	0.000	0.002	0	0.126	315	0.7
OHC 180-O-750	0	0	0.001	0.003	0	0.139	347	0.6
OHC 220-O-750	0	0	0.001	0.002	0	0.139	346	0.7
OHC 172-O-775	0	0	0.003	0.003	0	0.125	311	0.7
OHC 200-O-775	25	27	0.010	0.010	100	0.129	322	0.7
OHC 228-O-775	62	63	0.028	0.022	100	0.133	332	0.6
OHC 180-O-800	0	0	0.001	0.001	0	0.147	366	0.7
OHC 220-O-800	207	195	0.080	0.073	94	0.150	367	0.7
OHC 200-O-810	135	127	0.052	0.048	94	0.137	343	0.6
OHC 200-M-740	0	0	0.000	0.001	0	0.146	364	0.7
OHC 180-M-750	0	0	0.000	0.001	0	0.137	343	0.7
OHC 220-M-750	10	11	0.003	0.004	1	0.139	346	0.7
OHC 172-M-775	83	79	0.032	0.030	95	0.122	304	0.6
OHC 200-M-775	24	28	0.009	0.009	100	0.154	383	0.7
OHC 228-M-775	10	13	0.004	0.005	100	0.141	353	0.6
OHC 180-M-800	11	10	0.004	0.004	91	0.163	407	0.7
OHC 220-M-800	0	0	0.000	0.001	0	0.134	333	0.7
OHC 200-M-810	119	112	0.047	0.042	94	0.148	369	0.7

²⁴ Uncertainties within the BET specific surface area were calculated to be below 2 m²/g, below 2 m²/g for the t-plot micropore surface area and below 0.001 cm³/g for the t-plot micropore volume. Uncertainties within the DR N₂ volume were calculated to be below 0.003 cm³/g.

²⁵ Uncertainties within DR CO₂ micropore volume were calculated to be below 0.002 cm³/g, and below 4 m²/g for the DR CO₂ micropore surface area.

Table 6.16: Comparison of Porosity Characteristics Results Between Replicate Samples of Screening and Optimisation Hydrochar

Screening Sample	Micropore Volume (DR) (cm ³ /g)	Equivalent Micropore Surface Area (m ² /g)
HC 180-2.5-O-750	0.135	336
HC 220-2.5-O-750	0.129	322
HC 180-2.5-M-750	0.136	340
HC 220-2.5-M-750	0.149	372
HC 180-2.5-O-800	0.142	354
HC 220-2.5-O-800	0.154	385
HC 180-2.5-M-800	0.143	358
HC 220-2.5-M-800	0.146	365
Optimisation Sample	Micropore Volume (DR) (cm ³ /g)	Equivalent Micropore Surface Area (m ² /g)
OHC 180-O-750	0.139	347
OHC 220-O-750	0.139	346
OHC 180-M-750	0.137	343
OHC 220-M-750	0.139	346
OHC 180-O-800	0.147	366
OHC 220-O-800	0.150	367
OHC 180-M-800	0.163	407
OHC 220-M-800	0.134	333

6.5.4 Surface Chemical Analysis

The elemental surface composition (at. %) of each of the post-activation optimisation hydrochars, as calculated from XPS, is shown in Table 6.17. A large percentage of the surface is seen to be carbon based (> 80 at. %) for all samples, indicating that the HTC and activation processes have succeeded in creating a carbon rich-material. It is also observed that there is a consistent level of atomic nitrogen incorporated into each of the samples, around 4 – 6.3 at. %. In contrast, the two control samples which were not doped have atomic nitrogen contents of 1.8 – 1.9 at. %. While not a huge difference, it is notable and corroborates that the urea doping process has been successful. Atomic oxygen content for most samples is within the range of 7 – 10 at. %, indicating the presence of oxygen-containing functionalities, which in turn, is promising in terms of the materials potential for CO₂ adsorption.

Table 6.17: XPS Surface Composition Analysis Results of Post-Activation Optimisation Hydrochars Produced in this Study

Sample	C (1s) (at. %)	N (1s) (at. %)	O (1s) (at. %)	Ca (2p) (at. %)	Si (2p) (at. %)	Residuals (at. %)
OHC 200-O-740	85.9	5.7	7.1	0.8	0.6	0
OHC 180-O-750	84.7	5.2	8.5	0.8	0.8	0
OHC 220-O-750	84.1	6.3	8.1	0.6	0.9	0
OHC 172-O-775	86.3	4.7	7.7	0.6	0.7	0
OHC 200-O-775	84.7	5.6	8.2	0.9	0.6	0
OHC 228-O-775	86.2	6.6	6.1	0.8	0.3	0
OHC 180-O-800	83.3	4.2	10.1	1.8	0.6	0
OHC 220-O-800	83.6	5.7	8.5	1.3	0.9	0
OHC 200-O-810	85.5	4.8	8.2	0.7	0.8	0
OHC 200-M-740	86.3	5.8	6.7	0.7	0.5	0
OHC 180-M-750	87.2	4.5	7.0	0.6	0.7	0
OHC 220-M-750	86.1	6.3	6.6	0.5	0.5	0
OHC 172-M-775	86.1	4.0	8.3	1.1	0.4	0.2
OHC 200-M-775	86.8	5.2	6.8	0.9	0.1	0.1
OHC 228-M-775	85.0	5.3	8.3	1.0	0.5	0
OHC 180-M-800	83.1	4.6	10.0	1.5	0.4	0.3
OHC 220-M-800	85.6	4.8	8.0	1.1	0.5	0
OHC 200-M-810	83.8	5.2	9.0	1.2	0.4	0.4
HC Control Orange	92.1	1.9	5.2	0.5	0.3	0
HC Control Mandarin	92.5	1.8	5.2	0.2	0.2	0

Considering the two controls, they have significantly high atomic carbon on their surface in comparison to their precursor material, see the XPS data presented in Chapter 5. The two-step process of HTC and activation clearly results in a well-carbonated sample, as the oxygen content is seen to greatly reduce, matching what is seen in literature where oxygen/carbon ratios decrease after both processes [37], [46], [53], [54].

Calcium is observed as this is a common component of ash, and the higher at. % of it are seen for the samples activated at the higher range of activation temperatures, which matches with ash formation being more prominent at these temperatures. Interestingly, calcium is common in hydrochar ash as during the HTC process it is not reduced as efficiently by the carbonisation process as other common ash elements such as potassium and sodium [24].

Assessing the atomic carbon between individual samples, there is a general slight decrease as activation temperature increases: most of the hydrochars produced at 800 °C and 810 °C contain approximately 83 at. %, while those activated at 775 °C or below show 85 – 87 at. %. As a whole, the activated hydrochars appear to exhibit a large degree of homogeneity across their outer surface, indicating that both the carbonisation and doping processes have been successful across the range of samples. In comparison to the elemental analysis carried out in this project, the overall XPS data matches well. High carbon content is found on the surface of the hydrochars, as well as throughout the bulk, a sign of successful carbonisation, and nitrogen-containing functionalities are present too. The presence of oxygen-containing functionalities on the hydrochar surface is reasonably consistent between samples, although lower than the residual content reported in Section 6.5.2. Nonetheless, it must be remembered that the residual content from elemental analysis will include other components such as the calcium and silica identified in the XPS analysis.

The explanation of different nitrogen- and oxygen-containing moieties has been covered in the XPS analysis presented in Chapter 5 and can be consulted for reference. The types of nitrogen and oxygen environments present on the surface of the activated hydrochars are seen in Table 6.18.

Table 6.18: XPS Analysis of Surface Nitrogen and Oxygen Composition of Post-Activation Optimisation Hydrochars Produced in this Study

Sample	Bond types and energy ranges (eV)					
	N-6 (pyridinic) (%)	N-5 (pyrrolic) (%)	N-Q (quaternary) (%)	O-1 (C=O) (%)	O-2 (C-O) (%)	O-3 (O-C=O) (%)
OHC 200-O-740	44	25	31	42	39	19
OHC 180-O-750	45	16	39	15	64	21
OHC 220-O-750	47	12	41	16	64	20
OHC 172-O-775	41	16	43	20	60	20
OHC 200-O-775	44	29	27	42	46	12
OHC 228-O-775	42	14	44	53	39	8
OHC 180-O-800	44	12	44	14	63	23
OHC 220-O-800	48	17	35	17	65	18
OHC 200-O-810	41	29	30	17	68	15
OHC 200-M-740	42	28	30	17	61	22
OHC 180-M-750	40	25	35	20	60	20
OHC 220-M-750	42	23	35	19	60	21
OHC 172-M-775	49	22	29	26	61	13
OHC 200-M-775	42	25	33	17	72	11
OHC 228-M-775	38	28	34	13	65	22
OHC 180-M-800	51	31	18	11	68	21
OHC 220-M-800	41	23	36	21	59	20
OHC 200-M-810	42	29	29	52	30	18
HC Control Orange	33	19	48	40	33	27
HC Control Mandarin	34	21	45	10	76	14

The urea method of doping is known to incorporate nitrogen components into the aromatic structures that are created in the material [37], and appears to have been successful. Across the range of doped hydrochars, pyridinic nitrogen is the most common bonding type found, comprising approximately 40 % of the overall detected nitrogen. This is promising, as pyridinic nitrogen is one of the most useful forms for enhancing CO₂ adsorption [55], although other reports suggest pyrrolic is equally if not more important [56]. Spent coffee grounds hydrochars doped with urea and physically activated showed a similar tendency, where after activation pyrrolic nitrogen has decreased and led to the subsequent increase in pyridinic nitrogen [57].

Compared to the biochars in this study (Chapter 5), the hydrochars have higher levels of pyrrolic nitrogen, and lower levels of pyridinic nitrogen. The doped hydrochars display an average pyrrolic level of 22.4 % compared to 15.7 % in the biochars, and the average pyridinic level in the hydrochars is 43.5 % versus 53 % in the biochars. This suggests that the nitrogen is more stable in the hydrochars, as it would be expected that the pyrrolic form would change to pyridinic at these activation temperatures, and then in turn, change to quaternary nitrogen above 800 °C [58], [59]. No clear trend is seen between the process factors and the different levels of each form of nitrogen. The range of tested factors is potentially too narrow to highlight any differences.

The hydroxyl form of oxygen, O-2, is the most prominent type of bonding on the surface of the activated hydrochars, with varying levels of carbonyl bonding, O-1, and carboxylic bonding, O-3, also found throughout. The O-3 forms of oxygen are the more desired form in this project, as they can increase CO₂ adsorption through increasing electrostatic interactions between the hydrochar surface and the CO₂ molecules [25]. However, O-2 forms are still considered useful as they increase the overall basicity of the surface which in turn also contributes to higher affinity for CO₂ molecules [60]. From analysing the hydrochar data, there is a sufficient level of oxygen functionality on the surface of the samples, and in turn a promising level of O-2 and O-3 groups within that which should contribute to the goal of CO₂ adsorption. In a similar manner to the nitrogen data, there is little in the way of trends or relationships that can be drawn from the data. No direct correlation between HTC or activation temperature can be found in any of the three forms of oxygen. Examples of each elemental XPS spectrum collected for a given sample, OHC 220-O-750, can be seen in Figure 6.9 to Figure 6.11.

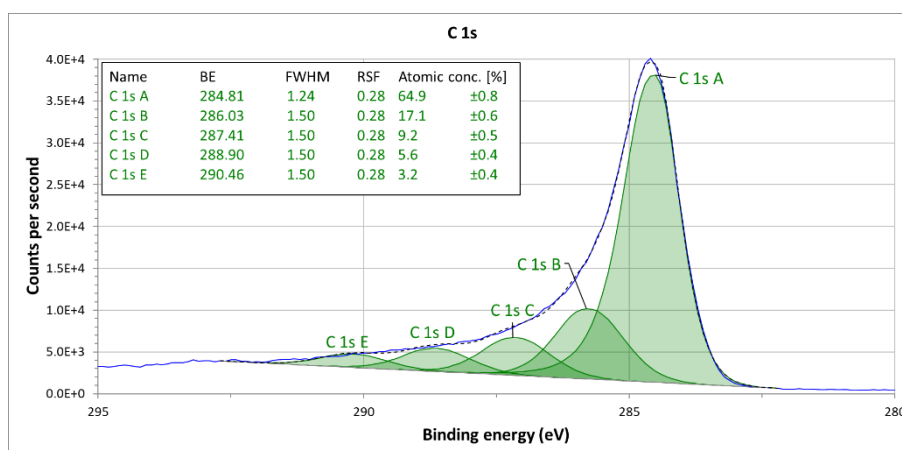


Figure 6.9: XPS Spectrum for Carbon C 1s of OHC 220-O-750

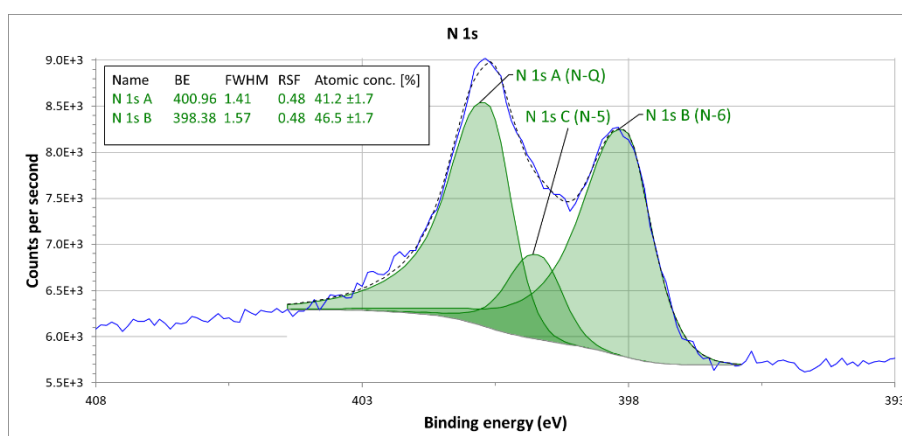


Figure 6.10: XPS Spectrum for Nitrogen N 1s of OHC 220-O-750

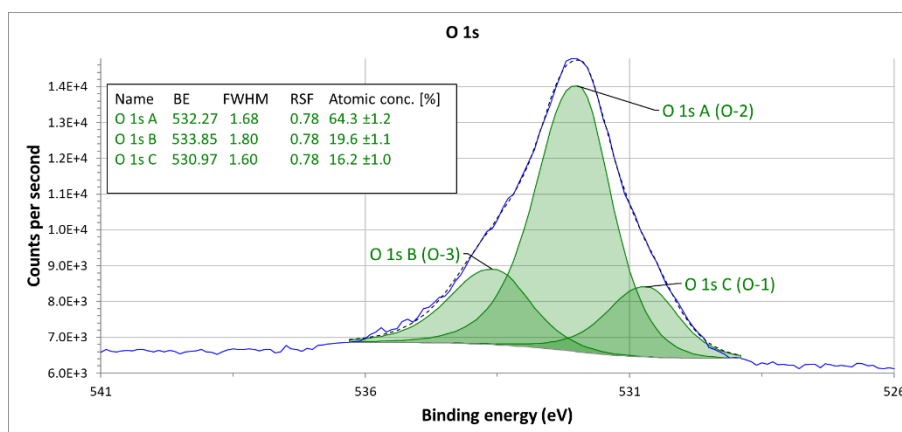


Figure 6.11: XPS Spectrum for Oxygen O 1s of OHC 220-O-750

Calculations of the ratios of XPS determined nitrogen to elemental analysis determined nitrogen, and XPS determined oxygen to elemental analysis determined oxygen, were carried

out for the hydrochars, in the same manner as had been followed for the biochars obtained in this study, as described in Chapter 5. The results can be seen in Table 6.19.

Table 6.19: Ratio of XPS Determined Nitrogen/Elemental Analysis Determined Nitrogen and of XPS Determined Oxygen/Elemental Analysis Determined Oxygen for the Optimisation Hydrochars Produced in this Study

Sample	Ratio of XPS Determined Nitrogen/Elemental Analysis Determined Nitrogen	Ratio of XPS Determined Oxygen/Elemental Analysis Determined Oxygen
OHC 200-O-740	0.80	0.28
OHC 180-O-750	0.78	0.35
OHC 220-O-750	0.82	0.36
OHC 172-O-775	0.79	0.30
OHC 200-O-775	0.76	0.36
OHC 228-O-775	0.85	0.24
OHC 180-O-800	0.63	0.41
OHC 220-O-800	0.78	0.33
OHC 200-O-810	0.70	0.34
OHC 200-M-740	0.81	0.30
OHC 180-M-750	0.71	0.31
OHC 220-M-750	0.79	0.33
OHC 172-M-775	0.66	0.32
OHC 200-M-775	0.75	0.31
OHC 228-M-775	0.68	0.38
OHC 180-M-800	0.73	0.40
OHC 220-M-800	0.64	0.37
OHC 200-M-810	0.73	0.41
HC Control Orange	1.23	0.30
HC Control Mandarin	0.86	0.38

For all of the doped samples, the nitrogen ratio is < 1 (within an approximate range of 0.65 – 0.8), which indicates that there are more nitrogen-containing functionalities within the bulk of the material (i.e., the internal surface area) than on the external surface area. The same can be said for the oxygen-containing functionalities, although the ratios are much lower, with the majority of values lying in the range 0.3 – 0.4; this implies that there are significantly more oxygen-containing functionalities within the bulk of the material, and present on the internal surface area, than on the external surface. This would be expected to be favourable in terms of CO₂ uptake, as the combination of internal microporosity which contains nitrogen

adsorption sites should be attractive to the adsorbate molecules. The results for these hydrochars are distinctly different to those found for the biochars discussed in Chapter 5, as those biochar samples were seen to have greater levels of functionalisation on the external surface of the materials compared to the bulk. Assessing both sets of results, it is clear to see that the hydrothermal synthesis step has helped increase the level of functionalisation observed in the bulk/internal surface area. This may be due to the urea solution being present in the reaction mixture during HTC and potentially facilitating different reaction pathways within the materials.

The FTIR spectra for the optimisation hydrochars pre-activation are presented based on their intended activation temperatures: samples to be activated at 740 °C and 775 °C are seen in Figure 6.12. Again, as the collected spectra are all similar and easily comparable, only a selection are included here; the rest can be found in Appendix G.

The same trends and peaks are observed which were seen in the range of screening samples (see Section 6.3.4), with some slight variations in intensity seen. The main groups identified remain hydroxyl bonds (-OH), carbonyl stretching (C=O), phenols (C-O), aromatic structures (C=C) and methyl stretches and bending (C-H and CH₂/CH₃). It is encouraging that the same principle bonds and groups are seen to exist between samples in the screening and optimisation design, implying that there is a degree of chemical consistency between both sample sets. To avoid repetition, in-depth discussion of the identified peaks which are seen here can be found in Section 6.3.4. It is notable in some samples that there is a peak around 2300 cm⁻¹ (not highlighted). This belongs to CO₂ that is present in the room due to breathing when the FTIR spectra were measured [44]. Attempts were made to ensure this had minimal effect on the results, but in some cases, it was impossible to avoid.

The accompanying post-activation hydrochar spectra can be seen in Figure 6.13. Once again, the pyrolysis process is seen to strip the chars of functional groups, leaving little behind in the activated forms. Similarly, it is the same groups seen to remain as it was for the screening hydrochars after activation, Section 6.3.4; carbonyl C=O around $1740\text{--}20\text{ cm}^{-1}$, aliphatic CH_2 and CH_3 at 1400 cm^{-1} , phenol C-O at 1200 cm^{-1} and C-H bending at 870 cm^{-1} [40], [41], [43], [45]. Overall, while little quantitative data can be garnered from these spectra, they present evidence of the high degree of carbonisation of the samples that matches with elemental and XPS analysis results. Similarly, through the phenol and carbonyl associations, oxygen-containing functional groups are demonstrated to still exist within the hydrochar structure.

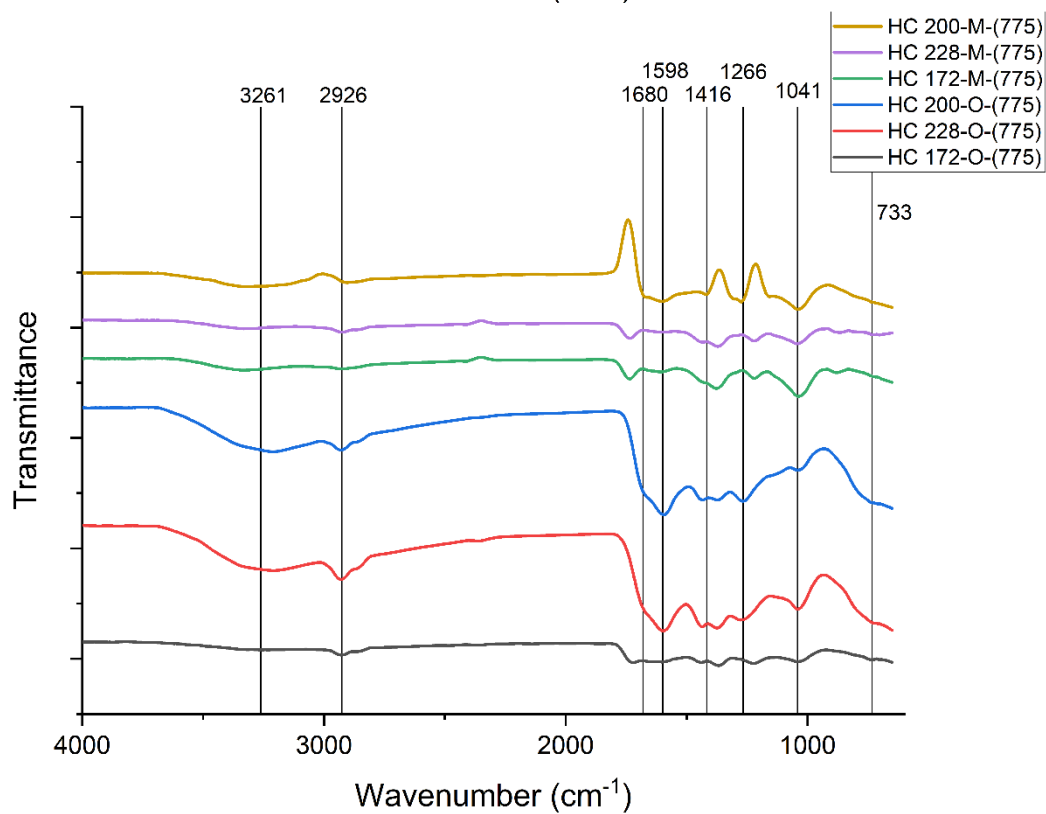
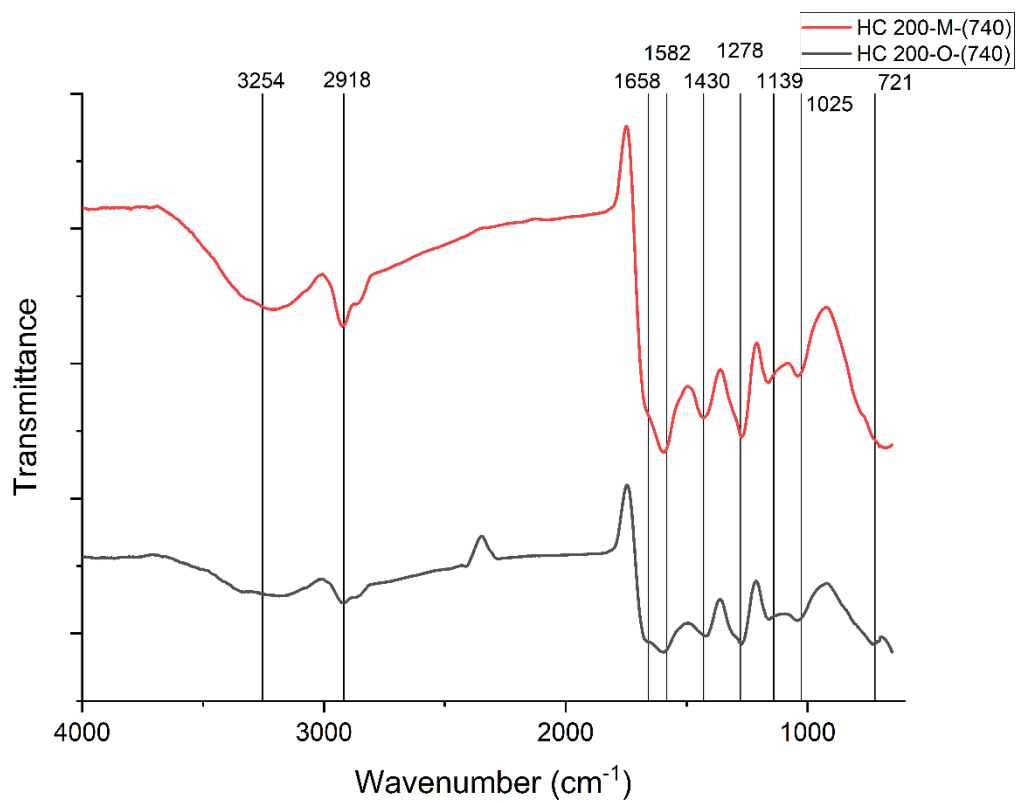


Figure 6.12: FTIR Spectra of Hydrochar Samples Produced Through HTC for Activation at 740 $^{\circ}\text{C}$ (top) and 775 $^{\circ}\text{C}$ (bottom)

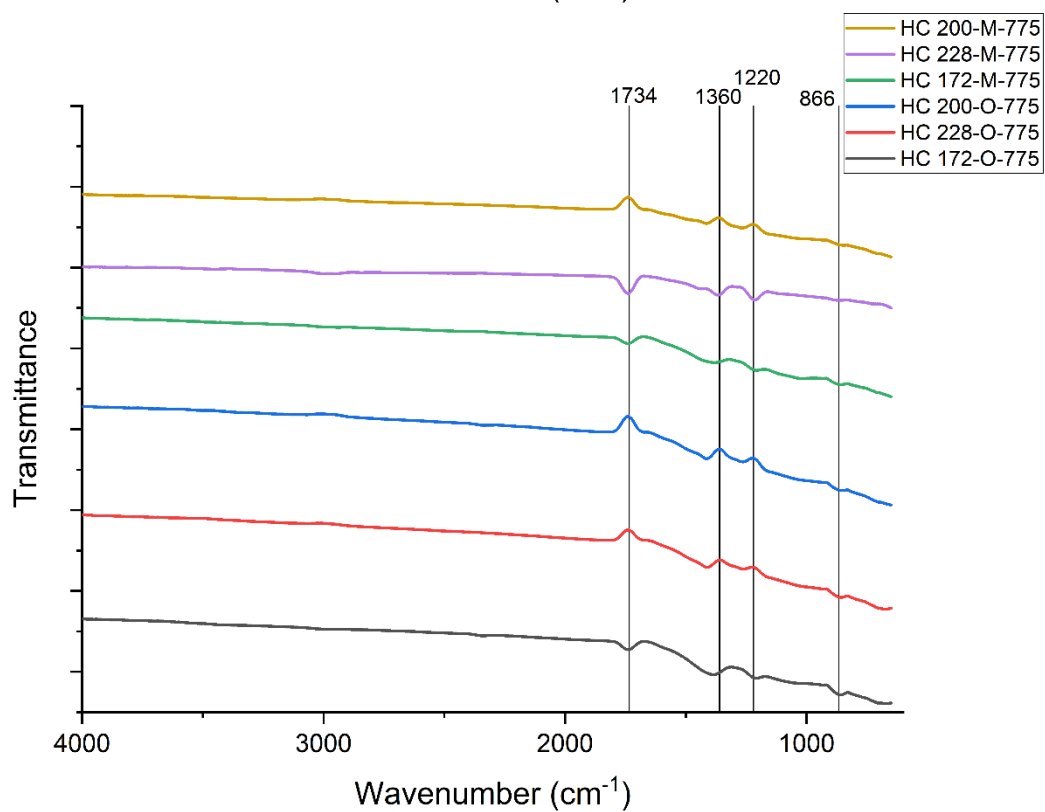
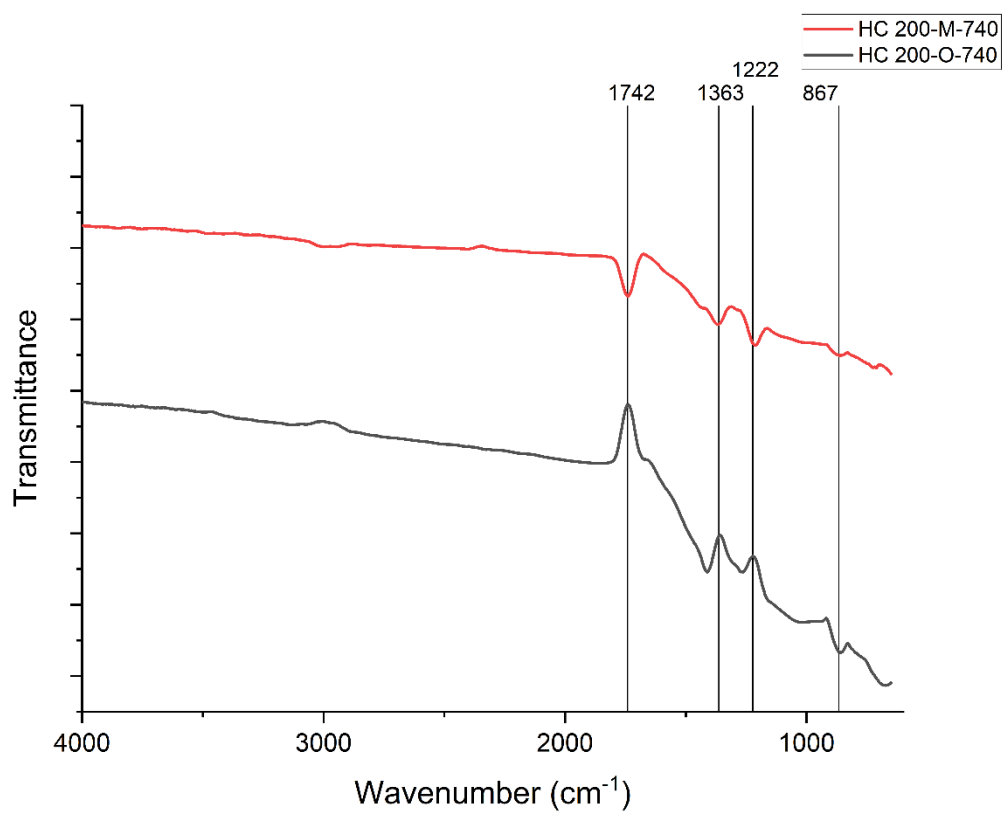


Figure 6.13: FTIR Spectra of Hydrochar Samples Produced Through HTC and Activated at 740 °C (top) and 775 °C (bottom)

6.5.5 SEM Analysis

A selection of activated hydrochar samples were selected to be tested by SEM to analyse the surface morphology and examine, if any, porous structures that were developed in the samples. Selection was based on demonstrating the difference between synthesis conditions. Nine samples were chosen: four urea-doped orange peel derived samples and another four urea-doped mandarin peel derived samples, with the final one being the HC Control Orange sample. Microspheres can be seen on the surfaces of most of the hydrochars; these are created through the interactions between HMF and the hydrochar during the HTC process [11]. This occurs by hemicellulose and cellulose being removed from the lignocellulosic structure of the biomass, undergoing a conversion process in the hydrothermal mixture before adsorbing back onto the solid char structure in the form of these microspheres [61]. The spherical nature is due to the hydrophobicity exhibited by the particles – by adopting a sphere shape this provides minimal contact with the aqueous media that they are present in during HTC [17].

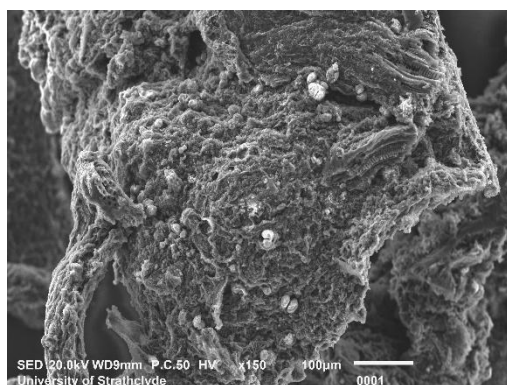


Figure 6.14: SEM image of OHC 180-O-750 at Magnification of x150

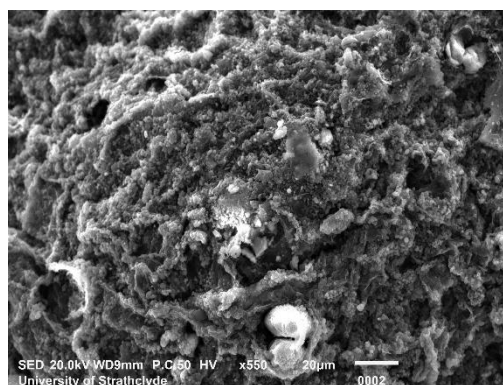


Figure 6.15: SEM Image of OHC 180-O-750 at Magnification of x550

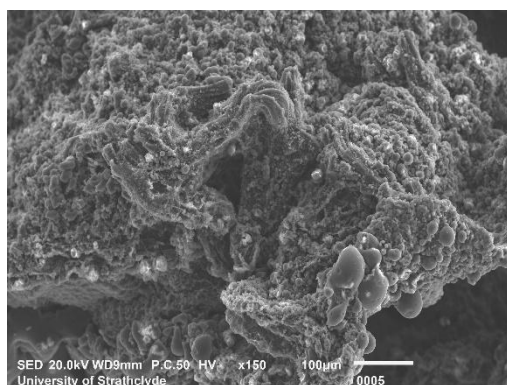


Figure 6.16: SEM image of OHC 220-O-800 at Magnification of x150

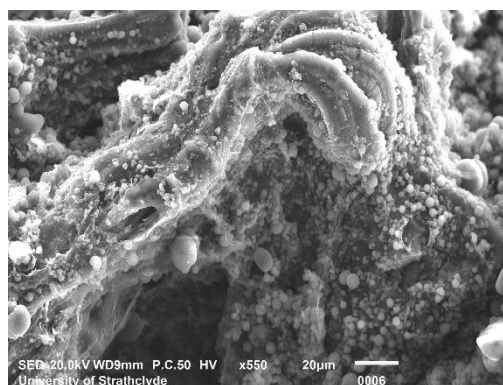


Figure 6.17: SEM image of OHC 220-O-800 at Magnification of x550

All hydrochars visualized present some form of microsphere on their surface from the SEM results, with OHC 220-O-800 showing a variety of them in different sizes in Figure 6.17. The size and frequency of them across each sample varies, likely a result of the different process conditions tested during synthesis, and also due to natural variation in the chosen feedstock. It is thought that this occurs for temperatures of 190 °C and above in the HTC [17]. In general, this matches with the micrographs presented in this project, but for some of the 180 °C HTC temperature samples, Figure 6.15 and Figure 6.19, there are visible spherical particles with rough surfaces that could be the initial formations of these spheres. The sample produced at 172 °C HTC temperature also displays these particles, Figure 6.20, indicating that the formation of them is possible at lower temperature than previously reported.

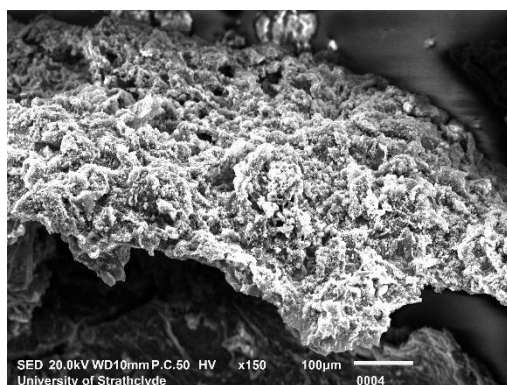


Figure 6.18: SEM image of OHC 180-M-800 at Magnification of x150

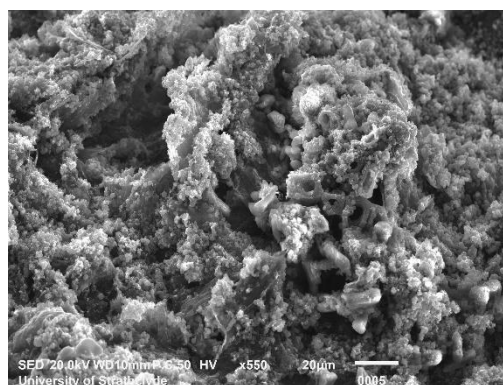


Figure 6.19: SEM image of OHC 180-M-800 at Magnification of x550

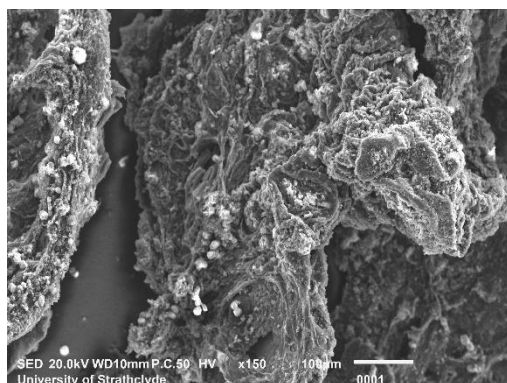


Figure 6.20: SEM image of OHC 172-M-775 at Magnification of x150

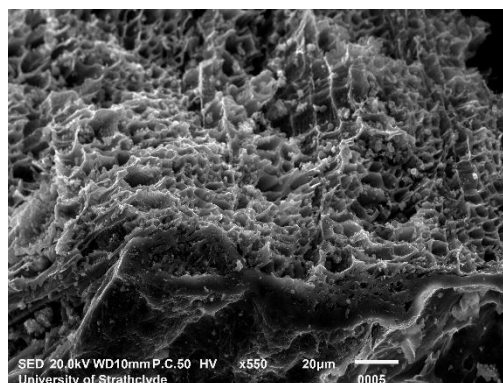


Figure 6.21: SEM image of OHC 172-M-775 at Magnification of x550

The 172 °C sample also showed an example of the honeycomb structures seen in the hydrochar samples tested, Figure 6.21. This is reminiscent of the structures seen in the biochar samples, Chapter 5; this follows, as the hydrochars are subject to the same process during their activation stage, so similarities in morphology are not surprising.

The overall surface of the samples appears to be quite rough and heterogenous, with deposits of microspheres visible but also spaces where CO₂ activating gas has penetrated the structure and led creation of a porous network. Although the magnification used cannot provide observation of micropores, it is clear the activation process has led to the formation of a transport pore network that will be useful for gas sorption applications.

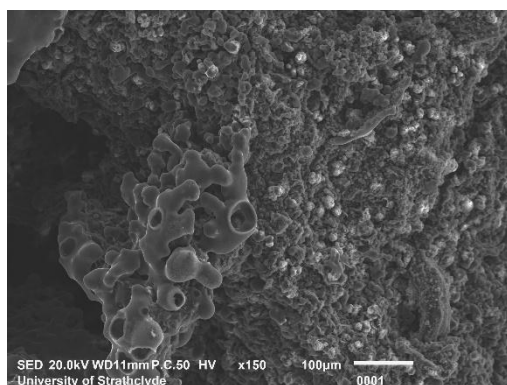


Figure 6.22: SEM image of OHC 228-O-775 at Magnification of x150

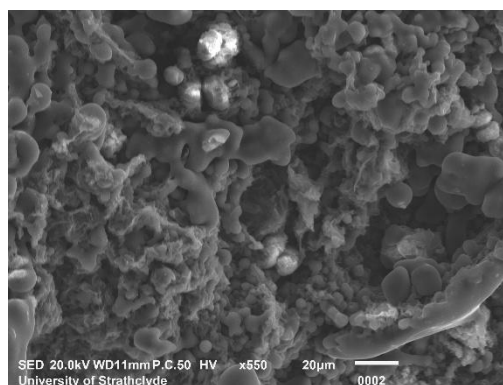


Figure 6.23: SEM image of OHC 228-O-775 at Magnification of x550

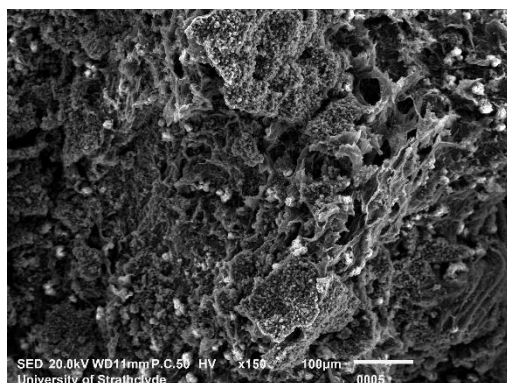


Figure 6.24: SEM image of OHC 200-O-810 at Magnification of x150

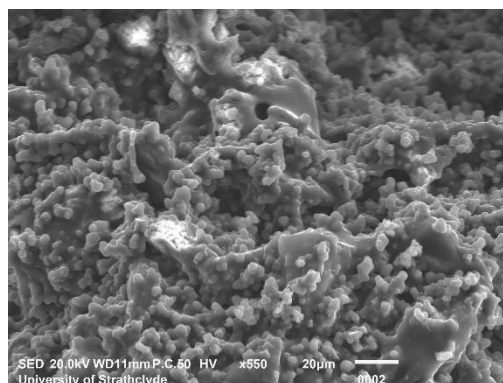


Figure 6.25: SEM image of OHC 200-O-810 at Magnification of x550

For the samples synthesised at HTC temperatures of 200 °C and above, examples shown in Figure 6.22 to Figure 6.25, many of the microsphere structures are present. In some cases, there are larger structures with smooth surfaces, which could be examples of agglomeration that has occurred where there were concentrated deposits of the microspheres. It is assumed that these structures have not been affected by the CO₂ activation, but to confirm this future work would need to be carried out i.e., carrying out SEM imaging on hydrochars pre- and post-activation.

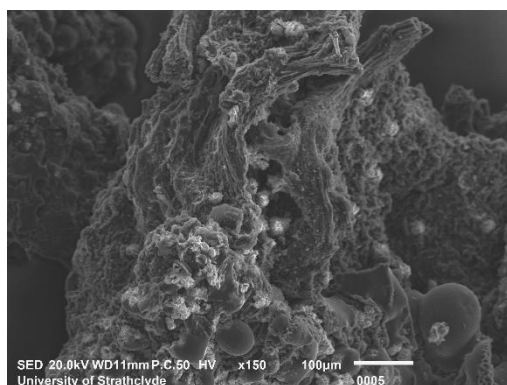


Figure 6.26: SEM image of OHC 200-M-810 at Magnification of x150

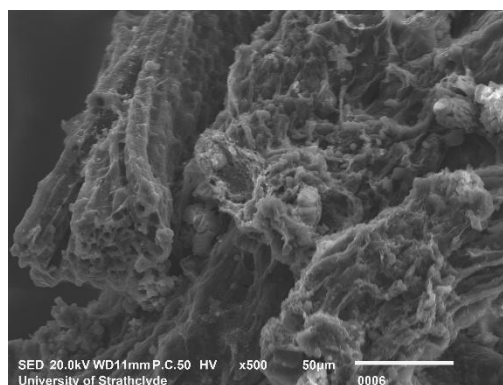


Figure 6.27: SEM image of OHC 200-M-810 at Magnification of x500

Typical cylindrical pore like structures can be seen in Figure 6.19 and Figure 6.27; these are likely transport pores which will lead into the wider pore network within the material. The shape of the pores are heterogenous, suggesting that they have been created by a combination of the removal of volatiles being driven out of the biomass material and the CO₂ activating gas penetrating the samples.

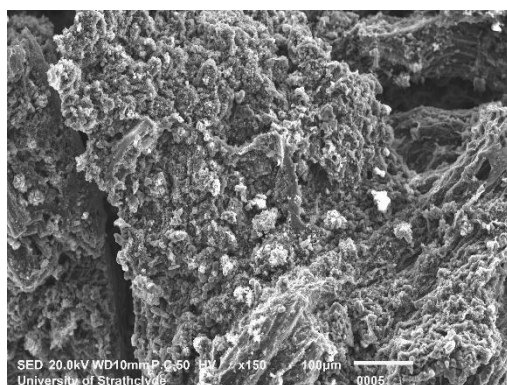


Figure 6.28: SEM image of OHC 200-M-775 at Magnification of x150

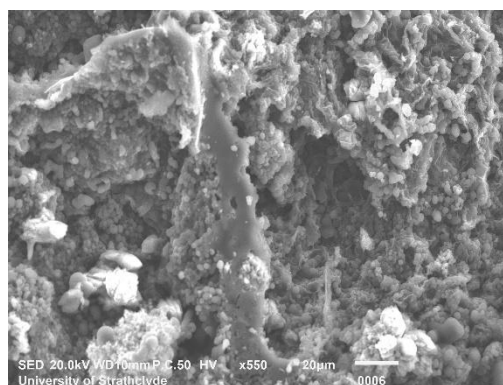


Figure 6.29: SEM image of OHC 200-M-775 at Magnification of x550

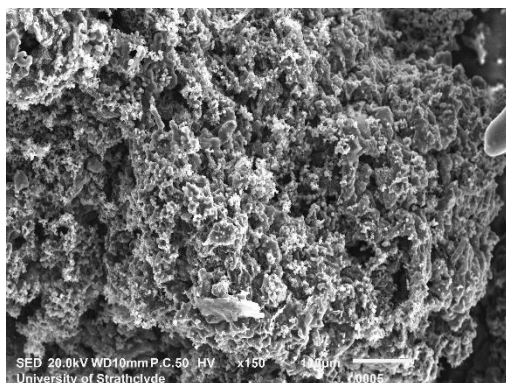


Figure 6.30: SEM image of HC Control Orange at Magnification of x150

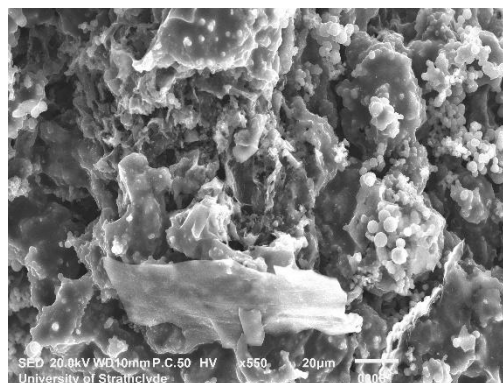


Figure 6.31: SEM image of HC Control Orange at Magnification of x550

Overall, the SEM images of the activated hydrochars present pictures typical of materials produced through HTC and activated through pyrolysis. Other orange peel derived hydrochars produced through HTC have been reported in literature; for example, a study of non-doped sample activated with CO₂ showed a comparable smooth, microsphere, coral-like structure that bares resemblance to Figure 6.25 [17]. This study also suggests that higher activation temperature may have an influence on the fusion of microspheres. Comparing the two samples activated at 810 °C, Figure 6.24 to Figure 6.27, this would concur with the images of OHC 200-O-810 but not so much for OHC 200-M-810. OHC 220-O-800, activated at 800 °C, presents a high quantity of microspheres but the agglomeration process is not as pronounced. Another study using orange peels reported similar microsphere fusion after activation with CO₂ [24].

Assessing the HC Control Orange sample, Figure 6.30 and Figure 6.31, from the x150 magnification it displays a similar general structure to the doped hydrochar samples. Upon increasing the magnification to x550 there is a noticeable flakier nature to the structure, resembling that of the biochars from Chapter 5, but microsphere particles are also still clearly visible indicating the same fundamental degradation process has occurred during HTC regardless of the inclusion of urea doping.

Literature has shown examples of hydrochars produced using orange peels as having comparable characteristics, with both microspheres and sheet-like structures present in the materials framework [28], while the rough texture seen in many of the samples is commonly observed, and credited to the release of volatiles during both HTC and activation [62], [63], and the CO₂ activating gas.

6.5.6 Optimisation Design of Experiments Trends and ANOVA

Pareto charts for the optimisation design are shown in Figure 6.32 – Figure 6.34 and the regression coefficients in Table 6.20. From the three factors examined, and their two-factor interactions, it is notable that activation temperature was not deemed influential for any of the three responses. This could be due to the fact that a narrow range of 750 – 800 °C was initially chosen for the study (based on literature values and previous experience with biochar production). As such, due to using a proven range of activation temperatures, the effect of varying it within this range was minimal.

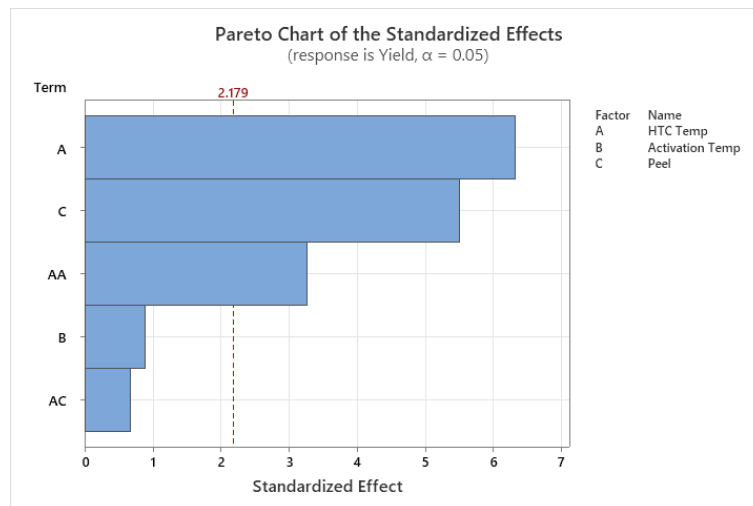


Figure 6.32: Optimisation Pareto Chart for Yield as DoE Response

In terms of the yield response, both HTC temperature and peel type are identified as influential to the results, highlighting the improved yields observed for orange peel compared

to mandarin. The phenomenon of higher HTC temperature producing higher yields is also evidenced by this analysis.

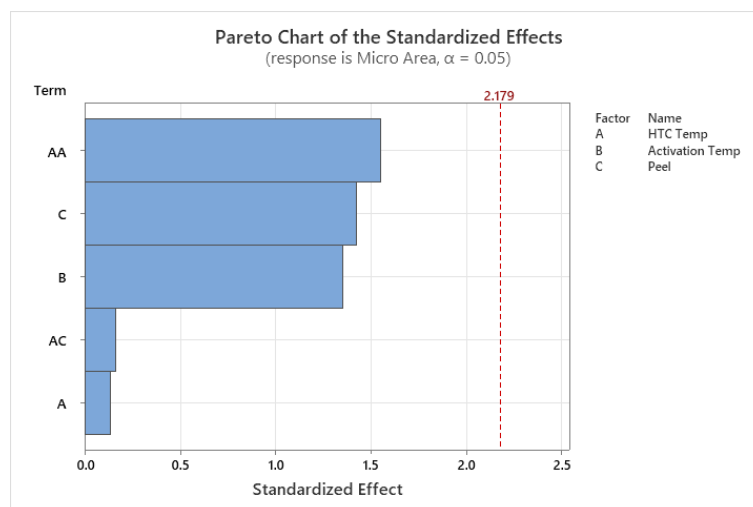


Figure 6.33: Optimisation Pareto Chart for Micropore Area as DoE Response

The micropore area response model shows that none of the three tested main factors are statistically significant at the applied 95 % confidence level. This could relate to the narrow range of activation temperature as discussed above, where regardless of the positive values of microporosity that were found, the variation between them was not large enough to show any significance. The R^2 -pred is also 0 % for this model; the explanation discussed in Section 6.3.5 remains valid and applies here. Consequently, the result from Figure 6.33 that suggests no factor is influential on the response of micropore area must be treated with caution; in reality, the factor of activation temperature will certainly have an influence on the porous characteristics of the hydrochar material, however, this effect is not noticeable in this study due to the narrow range of activation temperatures considered by this model. Similarly, the model presented here has no predictive power and should not be used to investigate the response of micropore area.

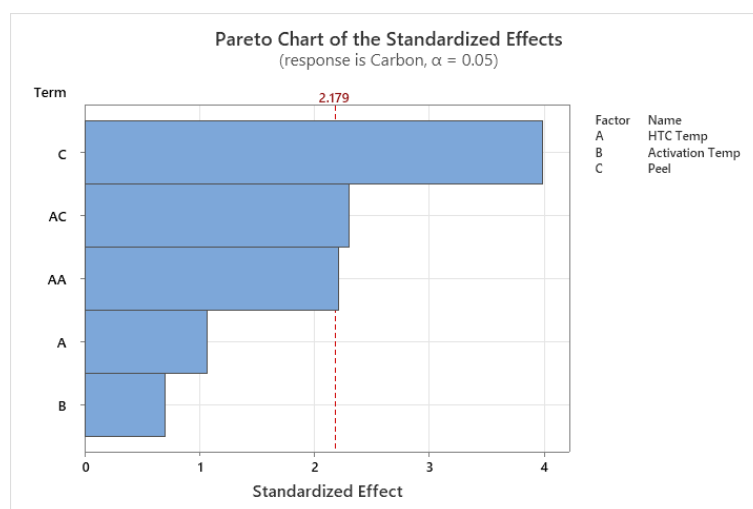


Figure 6.34: Optimisation Pareto Chart for Carbon Content as DoE Response

For carbon content of samples, peel type is the defining factor, with some two-factor interactions also playing a part. From analysis of the initial optimisation elemental analysis results it was already clear that mandarin derived hydrochars had a higher carbon content, with DoE analysis simply confirming this fact.

Table 6.20: Optimisation Coefficients of Determination for Each Hydrochar Response

Response	R ² (%)	R ² -adj (%)	R ² -pred (%)
Yield	87.24	81.92	72.93
Micropore Area	34.44	7.12	0.00
Carbon Content	69.77	57.18	36.68

Assessing each of the regression models, Table 6.20, it is notable that the yield and carbon content models have improved; this should not be a surprise, as the inclusion of more experimental points should by definition lead to an enhanced accuracy in a model. As a result, it would be expected that predictions made using these two should be close to the value found during experimental trials. Conversely, the micropore area model remains poor and thus, likely unreliable for basing estimations. The ANOVA and associated *p values* for each response can be seen in Appendix H, while the optimisation equations are addressed in Section 6.6.

6.6 Optimal Hydrochars Results

Six optimal hydrochars were produced using the optimisation equations produced from the analysis of the optimisation design, Section 6.5.6. The equations can be seen in Table 6.21 for each response, where HT represents HTC temperature (°C) and AT represents activation temperature (°C).

Table 6.21: Hydrochar Optimisation Equations Generated for Each Response Variable

Response Variable and Peel Type	Optimisation Equations
Yield, Orange Peel	$-55.3 + 0.654 * HT - 0.00524 * AT - 0.000153 * HT^2$
Yield, Mandarin Peel	$-58.8 + 0.664 * HT - 0.00524 * AT - 0.000153 * HT^2$
Micropore Surface Area, Orange Peel	$-1192 + 12.67 * HT + 0.342 * AT - 0.0314 * HT^2$
Micropore Surface Area, Mandarin Peel	$-1154 + 12.57 * HT + 0.342 * AT - 0.0314 * HT^2$
Carbon Content, Orange Peel	$-4.4 + 0.749 * HT - 0.0076 * AT - 0.001914 * HT^2$
Carbon Content, Mandarin Peel	$-14.8 + 0.811 * HT - 0.0076 * AT - 0.001914 * HT^2$

Using the limits for each factor that were defined in the optimisation stage, optimisation was performed using the Microsoft Excel Solver tool. The optimal conditions for both continuous factors to maximise each response for each peel type are shown in Table 6.22.

Table 6.22: Conditions for Creating Optimal Hydrochars Based on Generated Equations

Sample	HTC Temperature (°C)	Activation Temperature (°C)	Peel Type
OPH Yield Orange	211	740	Orange
OPH Yield Mandarin	217	740	Mand
OPH Micropore Orange	202	810	Orange
OPH Micropore Mandarin	200	810	Mand
OPH Carbon Orange	196	740	Orange
OPH Carbon Mandarin	212	740	Mand

The results of the production of activated hydrochars using each of the sets of optimal conditions is shown in Table 6.23, alongside their predicted values.

Table 6.23: Results of Each Response for Optimal Hydrochars Created from Generated Optimisation Equations, and the Predicted Result for Each Response

Sample	Yield (%)	Predicted Yield (%)	Micropore Surface Area (DR CO ₂) (m ² /g)	Predicted Micropore Surface Area (DR CO ₂) (m ² /g)	Carbon Content (%)	Predicted Carbon Content (%)
OPH Yield Orange	11.94	9.68	-	-	-	-
OPH Yield Mandarin	11.34	9.36	-	-	-	-
OPH Micropore Orange	11.46	-	351	363	-	-
OPH Micropore Mandarin	8.64	-	372	381	-	-
OPH Carbon Orange	12.32	-	-	-	65.9	63.3
OPH Carbon Mandarin	9.30	-	-	-	68.3	65.5

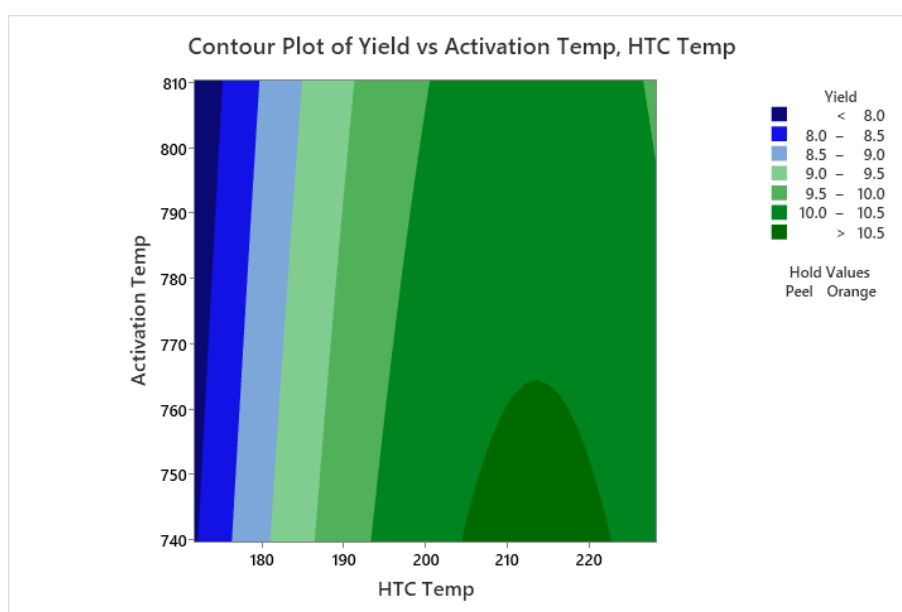


Figure 6.35: Contour Plot for Optimisation of Model for Orange Peel Hydrochar Yield (%) with Respect to Activation Temperature (°C) and HTC Temperature (°C)

The results for these optimisation equations are proven to be quite accurate for all three responses. Assessing the yield response, the experimental yield values found for both the orange and mandarin hydrochars are higher than the predicted values from the models. It is possible that the feedstocks batches that these two hydrochars were derived from were more robust than previous batches, meaning less of the materials structure was degraded.

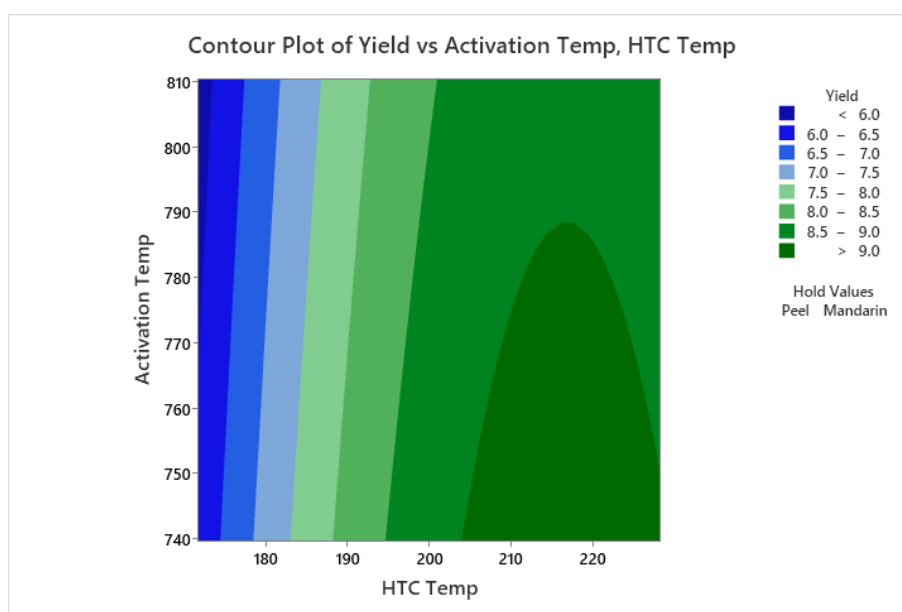


Figure 6.36: Contour Plot for Optimisation of Model for Mandarin Peel Hydrochar Yield (%) with Respect to Activation Temperature (°C) and HTC Temperature (°C)

The contour plots for each of the yield response models are shown in Figure 6.35 and Figure 6.36. The areas of the plot coloured dark blue represent the conditions that are predicted to result in a low yield, and the areas in dark green describe those conditions predicted to give a high yield result. The change in colour gradient through the plots indicates the change in predicted results. The subsequent contour plots presented display model predictions in the same manner.

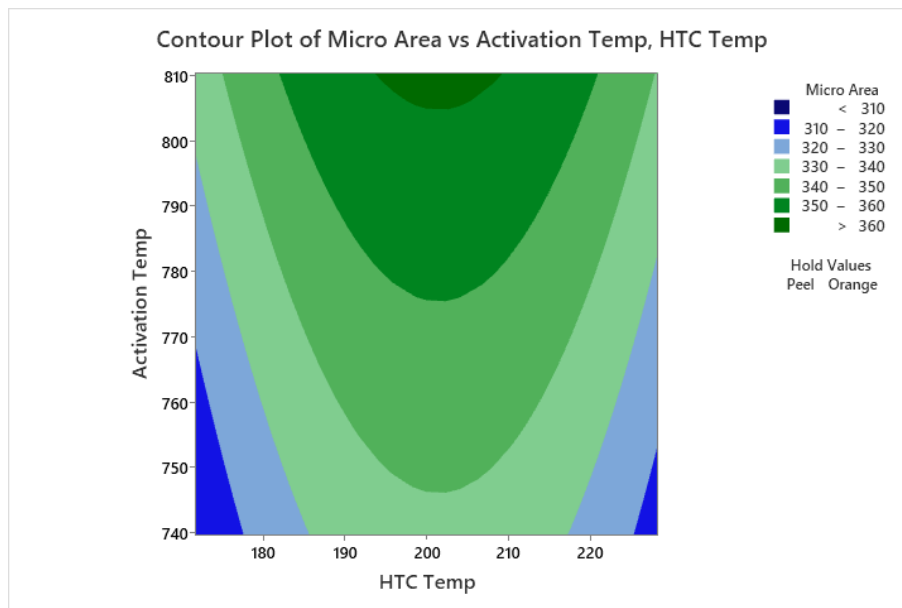


Figure 6.37: Contour Plot for Optimisation of Model for Orange Peel Hydrochar Micropore Area (m^2/g) with Respect to Activation Temperature ($^{\circ}\text{C}$) and HTC Temperature ($^{\circ}\text{C}$)

For the micropore area samples, there is approximately a 5 % reduction in the experimentally measured values compared to the predicted values. This is presumed to be due to chance, as the models used have an R^2 -pred of 0 %, thus, cannot be validated in reality. The chosen temperature range for this optimisation study ranged from 740 – 810 $^{\circ}\text{C}$, which lies entirely within the active window for the Boudouard reaction. Therefore, it is most likely that, as described in Section 6.3.5 and 6.5.6, this window is too narrow to accurately identify a relationship between the factors and response (due to the small differences in microporosity in the samples), and subsequently the two models are not reliable. The contour plots for both orange and mandarin micropore area models are shown in Figure 6.37 and Figure 6.38.

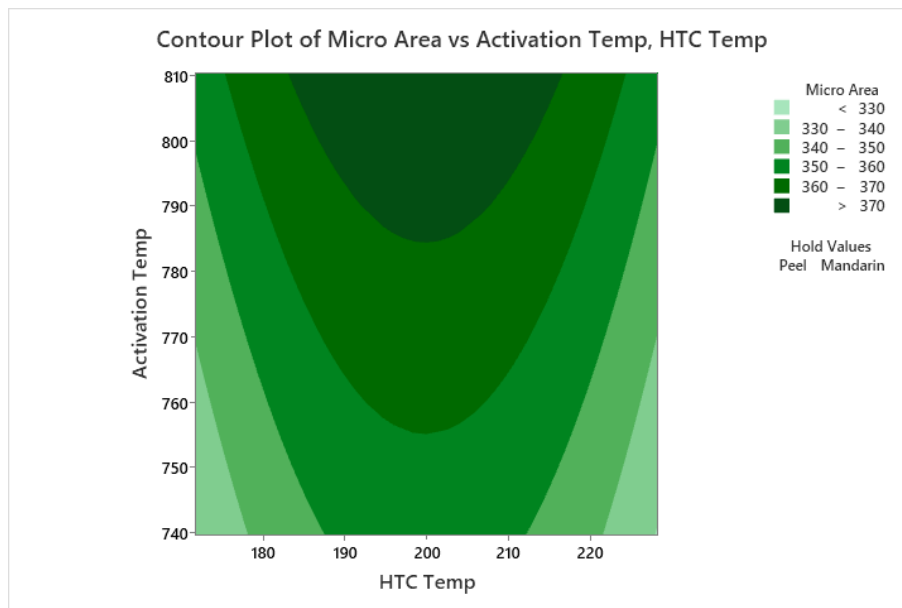


Figure 6.38: Contour Plot for Optimisation of Model for Mandarin Peel Hydrochar Micropore Area (m^2/g) with Respect to Activation Temperature ($^{\circ}\text{C}$) and HTC Temperature ($^{\circ}\text{C}$)

Finally, for the carbon content response, as with the yield response, the experimental testing provided superior results to the predictions given by the model: both were found to give 5 % more elemental carbon than expected, validating the model in reality. The choice of 740 $^{\circ}\text{C}$ for activation temperature no doubt ensured that a high level of carbonisation was achieved, but did not result in excess degradation of the hydrochar structure. The contour plots for both orange and mandarin carbon content models are shown in Figure 6.39 and Figure 6.40.

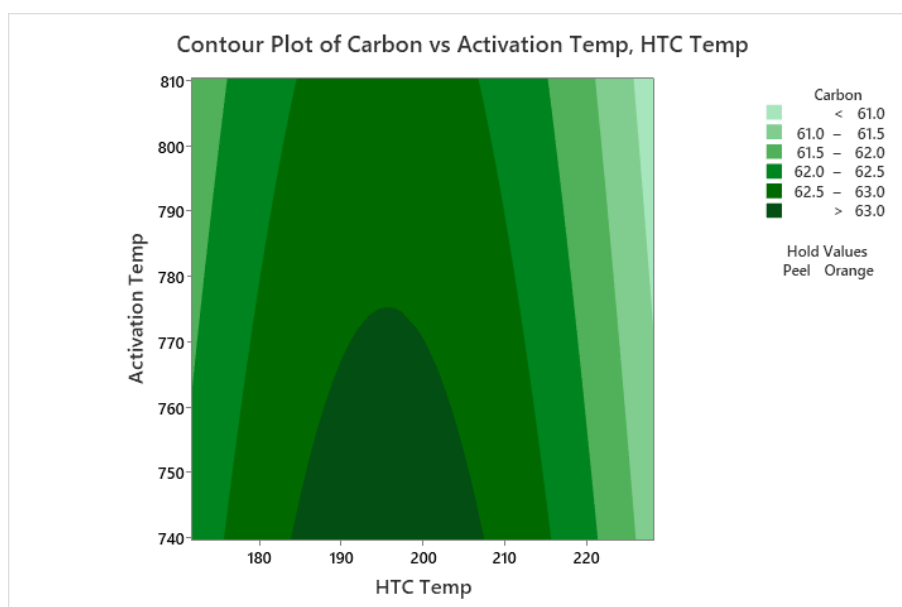


Figure 6.39: Contour Plot for Optimisation of Model for Orange Peel Hydrochar Elemental Carbon Content (wt%) with Respect to Activation Temperature (°C) and HTC Temperature (°C)

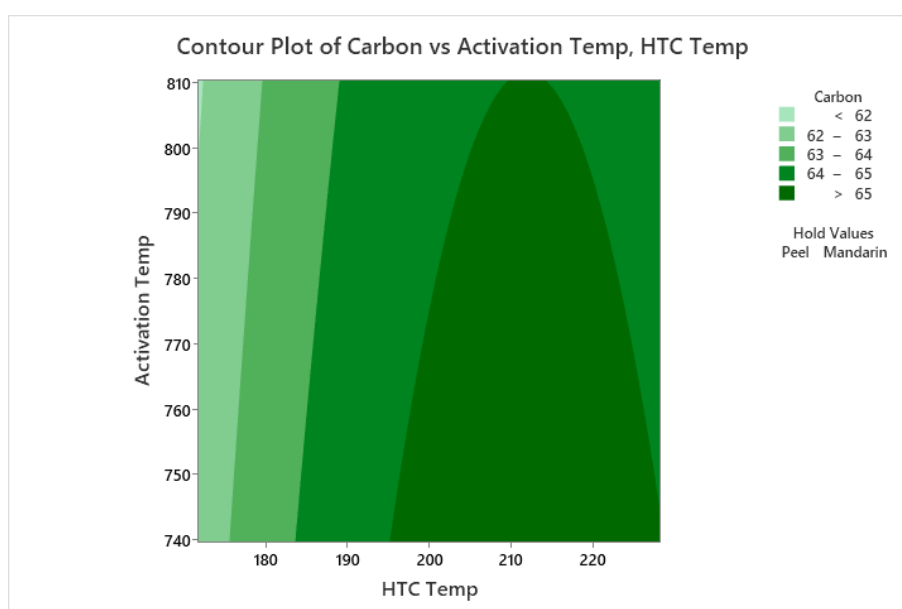


Figure 6.40: Contour Plot for Optimisation of Model for Mandarin Peel Hydrochar Elemental Carbon Content (wt%) with Respect to Activation Temperature (°C) and HTC Temperature (°C)

Overall, all three models have had reasonable success towards the goal of producing optimal hydrochars for each response. The two yield-optimised hydrochars have the second and third highest yields in the study; ironically the OPH Carbon Orange sample had the highest (12.32 %). The optimal micropore area hydrochars do not possess the highest DR CO₂

micropore surface area from all the hydrochars produced, but they are within the top range of samples for their respective peel types when compared to the optimisation design set of samples. Similar can be said for the carbon content response results: the large carbon content in both samples proves high quality hydrochars have been produced, and while they are not the highest recorded in this study, there are in the overall top range.

6.7 Hydrochar Results Summary

This chapter has discussed the production and characterisation of hydrochars using a Design of Experiment methodology. The hydrochars were produced through a two-step process of HTC followed by activation with CO₂ gas. In the initial screening stage, textural and elemental characterisation was used to determine the influence of the tested process parameters on responses from the produced activated hydrochars. The three chosen responses were overall hydrochar yield, microporous surface area (determined via DR method from CO₂ adsorption isotherms) and elemental carbon content. Of the four parameters tested, HTC temperature, activation temperature and peel type were found to be significant.

The optimisation stage of process was used to test these three aforementioned parameters at wider conditions, allowing the creation of prediction models to determine the optimal conditions for each response. Further in-depth characterisation was carried out on the optimisation hydrochar samples; volumetric CO₂ adsorption experiments showed the activated hydrochars contained high levels of microporosity that were not accessible through volumetric N₂ adsorption experiments. SEM showed the presence of microspheres on the surface of the activated hydrochars, while XPS and elemental analysis confirmed an increase in nitrogen content of the samples due to urea doping during the activation process. The optimisation models were tested experimentally, and the majority of the collected results

concurred with the predicted results, validating the process for the yield and the carbon content models, but not for the micropore area model.

6.8 References

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7 Results III – CO₂ Adsorption

This chapter will describe the CO₂ adsorption experiments (volumetric, gravimetric and cyclic) and subsequent results that have been collected during the project, and compare performance to similar competitors in literature.

The novelty aspect of this chapter arises from the testing of physically activated, nitrogen-doped biochars and hydrochars for their CO₂ adsorption potential. As highlighted in Chapter 5 and 6, these are innovative materials that have been produced through a Design of Experiments (DoE) methodology in order to optimise and tailor their characteristics towards those typically required for CO₂ adsorbents. The use of orange and mandarin peels feedstocks to produce different types of char allows for a variety of comparisons between the two feedstocks, and two production methods, by measuring the CO₂ adsorption capacity of these chars, which has not been documented in previous studies. Finally, CO₂ adsorption of these materials will be tested under temperatures analogous to flue gas conditions, which is often found missing from related literature surrounding solid adsorbents designed for post-combustion carbon capture.

7.1 Volumetric CO₂ Adsorption

The ability to carry out volumetric CO₂ adsorption tests was only available in the final year of the project, and due to time and budget constraints, it was not possible for all of the biochar samples to be tested using this method. As a result, selected biochars from the optimisation design (Chapter 5) were tested to assess the smaller pores in their network. The biochars with the highest surface area measured using N₂ isotherms were chosen, along with three random samples that had been deemed to have low or no porosity. All the hydrochars in the study (Chapter 6) were tested using this method.

The uptake of CO₂ by the screening hydrochars is shown in Table 7.1, by the optimisation and optimal hydrochars in Table 7.2 and by the select range of the biochars in Table 7.3.

Table 7.1: CO₂ Adsorption Uptake (0 °C, 1 bar) of Screening Activated Hydrochars and Control Activated Hydrochars Measured Using Volumetric Adsorption Method

Hydrochar Sample	CO ₂ Uptake at 0 °C, 1 bar (mmol/g)
HC 180-2.5-O-750	2.01
HC 220-2.5-O-750	1.98
HC 180-12-O-750	2.02
HC 220-12-O-750	1.97
HC 180-2.5-M-750	2.08
HC 220-2.5-M-750	2.29
HC 180-12-M-750	2.26
HC 220-12-M-750	2.23
HC 180-2.5-O-800	2.15
HC 220-2.5-O-800	2.31
HC 180-12-O-800	2.01
HC 220-12-O-800	1.79
HC 180-2.5-M-800	2.17
HC 220-2.5-M-800	2.19
HC 180-12-M-800	2.46
HC 220-12-M-800	2.05
HC Control Orange	2.91
HC Control Mandarin	2.80

The range of results seen from the screening samples are positive in the sense they confirm that the hydrochars are microporous, with the highest doped activated screening hydrochar providing an uptake of 2.46 mmol/g at 0 °C, 1 bar, while the two hydrochar control samples were slightly higher than this, at 2.91 mmol/g for the orange sample and 2.80 mmol/g for the mandarin sample. This indicates that the inclusion of urea in the hydrochar production process has had a limiting effect on the adsorption of CO₂. It is clear the doping process has increased the nitrogen content of the samples, implying there are more available nitrogen-containing functional sites available to aid in adsorption. However, despite literature suggesting these sites assist in adsorption of CO₂ [1], [2], the CO₂ capacity of the doped hydrochars in this work is lower, which could be indicative of a form of pore blocking, or

general inhibition of pore development during the activation process. It is possible that activation using CO₂ has been successful in developing an abundance of micropores [3], as discussed in Chapter 6, yet has resulted in an underdeveloped overall pore network. This may be limiting the ability of CO₂ molecules to diffuse and contact with the available adsorption sites, in microporous regions or otherwise.

Table 7.2: CO₂ Adsorption Uptake (0 °C, 1 bar) of Optimisation Activated Hydrochars Measured Using Volumetric Adsorption Method

Hydrochar Sample	CO ₂ Uptake at 0 °C, 1 bar (mmol/g)
OHC 180-O-750	2.21
OHC 220-O-750	2.20
OHC 180-O-800	2.31
OHC 220-O-800	2.31
OHC 172-O-775	1.93
OHC 228-O-775	2.07
OHC 200-O-740	2.00
OHC 200-O-810	2.16
OHC 200-O-775	2.11
OHC 180-M-750	2.13
OHC 220-M-750	2.18
OHC 180-M-800	2.55
OHC 220-M-800	2.14
OHC 172-M-775	1.94
OHC 228-M-775	2.25
OHC 200-M-740	2.29
OHC 200-M-810	2.28
OHC 200-M-775	2.33
OPH Micropore Orange	2.14
OPH Micropore Mandarin	2.21

The results obtained from the activated optimisation hydrochars are not markedly different from the screening samples. They lie within the same approximate range, however, the highest performing doped hydrochar produced in the project is found in this subset, with OHC 180-M-800 adsorbing 2.55 mmol/g of CO₂ at 0 °C, 1 bar. Those samples which were produced with a HTC residence time of 2.5 h in the screening design can be compared with their ‘repeat’ samples in the optimisation design; as the optimisation design set HTC

residence time at a constant value of 2.5 h, there are eight repeats with identical conditions between the two studies. All but one of the repeats present results within ± 0.22 mmol/g of the corresponding original screening sample, indicating a high degree of repeatability between the samples. The only sample exhibiting significantly higher uptake was the aforementioned OHC 180-M-800. Considering the variation in the natural composition of the peel precursors, these results are positive and indicate an acceptable level of repeatability in the hydrochar production process.

HTC temperature appears to have limited effect on the CO₂ adsorption capacity, as although the samples synthesised at 172 °C do show the poorest level of CO₂ uptake of the 18 optimisation hydrochars, for the HTC temperatures above this there is no identifiable trend. Equally, within the range of activation temperatures tested, there is no strong correlation with CO₂ capacity; comparing some sample pairs shows an increase in uptake, but other pairs display a decrease or no change in uptake. Finally, in terms of peel type, there is a slight increase in CO₂ uptake on the mandarin peel-based samples compared to the orange peel derived samples, which matches with porosity data gathered previously. This could signal, unsurprisingly, that the physical makeup of the two types of peel plays an important role in the porosity development and functionalities present on the final char material. However, a basic DoE model was created for the response of CO₂ uptake using the results in Table 7.2; the results of this suggested that no parameter was significant. Further experiments and repeatability studies would be required to investigate this, along with detailed characterisation of the peels used in this study.

The two optimal hydrochar samples, OPH Micropore Orange and OPH Micropore Mandarin, have lower CO₂ capacity than the best performing hydrochar samples produced in the project; this is thought to be due to the inability of the micropore optimisation model from

Chapter 6 to successfully optimise the Dubinin-Radushkevich (DR) micropore surface area response, thus, impacting on the subsequent CO₂ uptake capacity. Despite this, the results are acceptable in the scope of the study and show that CO₂ does have adsorption affinity for the microporous activated hydrochars. Note that the OPH Micropore Mandarin has a higher CO₂ uptake than OPH Micropore Orange, matching the difference between peel types that was observed in the optimisation design.

Table 7.3: CO₂ Adsorption Uptake (0 °C, 1 bar) of Optimisation Biochars and Control Biochars Measured Using Volumetric Adsorption Method

Biochar Sample	CO ₂ Uptake at 0 °C, 1 bar (mmol/g)
OBC 800-0.5-O	2.74
OBC 650-3-O	2.00
OBC 800-3-O	1.59
OBC 725-1.75-O	2.51
OBC 800-0.5-M	2.58
OBC 800-3-M	2.20
OBC 831-1.75-M	1.13
OBC 725-1.75-M	2.56
BC Control Orange	2.07
BC Control Mandarin	2.76
OPB Micropore Orange	2.41

The results obtained from the CO₂ isotherms collected from the biochar samples, Table 7.3, highlight an unexpected finding: the three samples OBC 650-3-O, OBC 725-1.75-O and OBC 725-1.75-M, previously thought to contain low porosity or be entirely non-porous, in fact display high levels of CO₂ uptake, even relative to the other biochars produced in the project. This is evidence of the successful nature of using CO₂ as an activating gas, as it has resulted in highly microporous samples; it also raises the point that in order to provide detailed characterisation of porosity, CO₂ isotherms are an important tool to be used alongside N₂ isotherms. An example of this situation was seen in a study using *Populus nigra* wood to produce biochars which resulted in the production of material that appeared non-porous based on surface area informed by N₂ isotherm analysis, but then displayed

microporosity through the presence of ultramicropores which were discovered after surface area analysis with CO₂ isotherm data [4]. This was also observed for nitrogen-doped biochars produced at 600 °C from pomelo peels [5]. From the samples tested, the highest CO₂ adsorption result is seen from BC Control Mandarin of 2.76 mmol/g, slightly higher than OBC 800-0.5-O which displayed uptake of 2.74 mmol/g. Overall, most of the biochar samples displayed CO₂ uptake in the range 2 – 2.76 mmol/g. The higher-performing samples are those produced at predominantly higher pyrolysis temperatures and lower residence times. These conditions were demonstrated in Chapter 5 to result in well-developed microporosity, thus it would be expected that these samples display the highest performance. The OPB Micropore Orange sample produced from the optimisation model for micropore area does not give the highest CO₂ adsorption capacity, but nonetheless sits in the higher end of the results range.

Comparing the CO₂ uptake between the biochar and hydrochar samples highlights a degree of similarity, with the majority of both materials providing a CO₂ adsorption capacity in the range of 2 – 3 mmol/g. Likewise, the spread of results within each suite of samples is analogous, and with no clear stand outs. Both hydrochar control samples and BC Control Mandarin have the highest CO₂ uptake of samples produced in the overall project, which suggests that while urea doping has been successful and has increased the nitrogen content of the samples, it is not key to enhancing CO₂ adsorption with these materials. Instead, the more pressing focus should be on maximising the microporosity of the samples to give high CO₂ uptake at low pressures of 0 – 1 bar.

To evidence this, it has been reported in literature that for pressures of 0 – 1 bar, it is the quantity of narrow micropores (ultramicropores, <0.7 nm) that is the most important factor for CO₂ adsorption [6]. This can validate a number of observations from this study. Firstly,

the high uptake at 0 °C and 1 bar, relative to the low BET calculated surface area of many of the chars. Thus, this impressive CO₂ adsorption performance can be attributed to the high levels of microporosity the samples in question contain. Secondly, the fact that biochars and hydrochars that were thought to be non-porous are capable of adsorbing CO₂; this is due to them possessing narrow micropores in their structure that cannot be detected using N₂ adsorption techniques, and, therefore, they are only found when tested directly with CO₂ adsorption techniques.

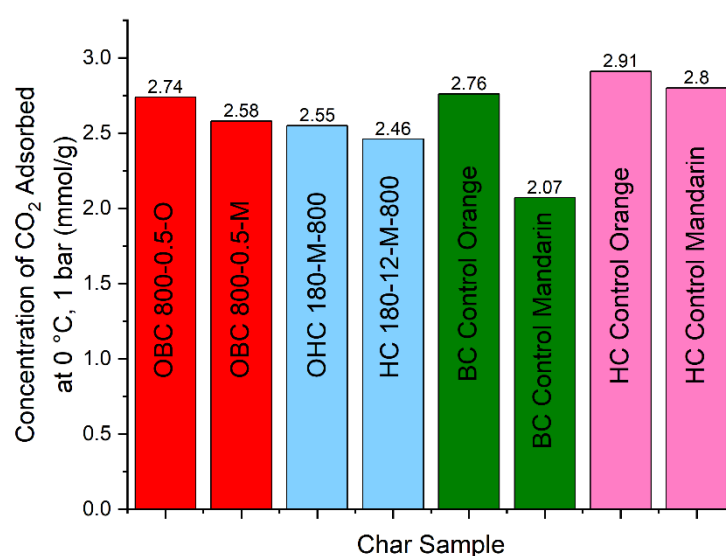


Figure 7.1: A Selection of the Best CO₂ Volumetric Adsorption Uptake Results at 0 °C, 1 bar in This Project

A selection of the best and notable adsorption results are shown in Figure 7.1. Figures showing all of the volumetric results can be found in Appendix I. To assess the performance of these materials with literature, these values are compared with those reported in other studies in Table 7.5, found in Section 7.2.3. Across the range of literature presented, the orange and mandarin derived chars from this study lie in the middle to lower range of CO₂ adsorption values. One specific orange peel study presented a biochar with uptake of

1.02 mmol/g at 0 °C [7], while another reported orange peel derived hydrochars delivering CO₂ adsorption of 2.23 – 6.67 mmol/g at 0 °C. In a similar vein, a group of pomelo peel derived biochars were shown to have a CO₂ capacity in the range 0.86 – 5.74 mmol/g at 0 °C [5]. Both the orange peel hydrochar and pomelo peel biochar studies reference the importance of microporosity in delivering their respective best CO₂ adsorbing chars. Despite nitrogen content appearing to have little effect on CO₂ adsorption in this project, another study using urea-doped bamboo shoots to produce biochars reported that when assessing materials for carbon capture, attention should be given to the optimisation processes of both producing narrow micropores, and increasing nitrogen content, as the two factors are interlinked in their influence on CO₂ adsorption capacity [8].

7.2 Gravimetric CO₂ Adsorption

7.2.1 Biochar Samples Selected for CO₂ Adsorption

To assess the CO₂ adsorption capacity of the biochars produced in this project, the four biochars from the optimisation sample set with the highest specific surface area (SSA) were chosen to be tested using gravimetric adsorption analysis at three temperatures (0, 30 and 60 °C) from 0 – 19.5 bar. These samples were selected over the high performing alternatives from the screening set on the basis that the optimisation samples had undergone a more complete characterisation process. The two control biochars were also tested using this method due to their high SSAs. Finally, the optimal biochar, OPB Micropore Orange, was tested at 60 °C. The single temperature was used for this sample as there was not enough time to test its performance at all three.

Gravimetric adsorption was utilised after the volumetric adsorption experiments, as the gravimetric method offers the opportunity to collect more detailed data on the adsorption performance of the chars, such as adsorption kinetics. It was also possible to measure

adsorption at a wider variety of temperatures using this method, as the laboratory setup for volumetric CO₂ adsorption only allowed for measurements at 0 °C. Therefore, volumetric adsorption experiments served as a screening process for the hydrochar materials, but not for the biochars, as the ability to carry out this technique only became available towards the end of the project. The gravimetric adsorption experiments carried out in this study were performed using an IGA in static mode. This allowed the maximum thermodynamic equilibrium uptake of the selected chars to be measured, which, in turn, allowed the best performing samples to be identified, with a view to taking them forward for further testing, if the possibility to do so arose. Additionally, the volumetric CO₂ adsorption measurements presented in Section 7.1 were collected in static mode on the ASAP 2460 system, so the choice of static mode for IGA experiments allowed a comparison between the volumetric and gravimetric adsorption results.

7.2.2 Hydrochar Samples Selected for CO₂ Adsorption

For the hydrochar samples produced in this study, the doped sample from the optimisation set which displayed the highest DR micropore surface area (OHC 180-M-800) was selected to be tested in the same manner, along with the HC Control Orange sample. These were again preferred to the screening samples due to their enhanced characterisation profile. Finally, the optimal hydrochar, OPH Micropore Mandarin, was tested at 60 °C; again, this was only carried out at one temperature due to time restrictions within the project.

7.2.3 Gravimetric CO₂ Adsorption Results

The 0, 30 and 60 °C isotherms for the four urea-doped biochar samples can be seen in Figure 7.2, while Figure 7.3 shows the isotherms of the two control biochars, the highest performing urea-doped activated hydrochar and the best control hydrochar, and Figure 7.4 shows the isotherms of the two tested 'optimal' char samples.

The four doped biochar samples, as shown in Figure 7.2, present comparable isotherm shapes and CO₂ uptake capacities. Each isotherm takes the form of Type I (a) as per IUPAC classification, indicating that the materials are primarily microporous, with many pores in the range of < 1 nm [9], which agrees with previous results obtained via DR analysis. The highest uptake for each sample can be seen at the lowest isotherm temperature, 0 °C, and a decrease in uptake is observed as temperature increases. This indicates that the predominant adsorption mechanism is physisorption [10], as the increase in temperature provides the CO₂ molecules with more kinetic energy, which in turn makes it more thermodynamically difficult for the molecules to adsorb onto the surface of the chars [11].

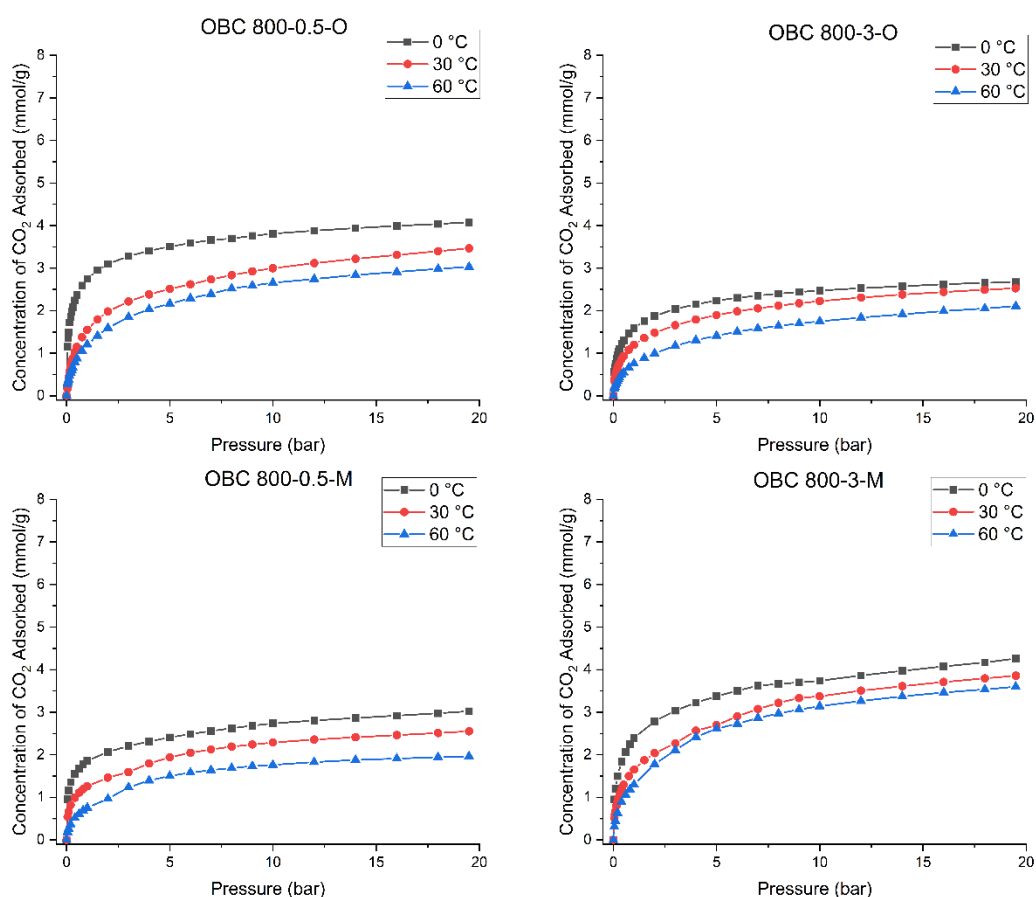


Figure 7.2: 0 °C, 30 °C and 60 °C Isotherms Measured Using Gravimetric Analysis for Samples OBC 800-0.5-O, OBC 800-3-O, OBC 800-0.5-M and OBC 800-3-M, Respectively

The high level of uptake at low pressure (0 – 1 bar) can be attributed in the main to the highly microporous nature of the char samples. Adsorption of CO₂ in this range has been proven to have a large dependence on the presence of ultramicropores, which these samples are known to contain; these narrow micropores have a diameter of 0.7 nm or smaller, and CO₂ molecules have a kinetic diameter of 0.33 nm. Thus, the combination of overlapping electric potential fields from the pore walls [12], and the wall-to-wall Van der Waals interactions with CO₂ molecules leads to enhanced adsorption, causing rapid micropore filling [2]. Due to this, it is widely agreed that for adsorption at lower pressures, the microporous surface area and volume is a much more important factor than the overall total surface area of a material [13], [14], [15].

Likewise, the presence of different functionalities such as nitrogen- and oxygen-containing groups, which can occur throughout the material, has been seen in literature to aid adsorption through Lewis acid-base interactions or hydrogen bonding [1], [16]. Oxygen-containing groups can also increase hydrophilicity of the char samples, heightening the local polarity of the sample surfaces and further assisting CO₂ adsorption. Note that these functionalities should be expected to promote adsorption at any pressure, not just the low range. The results presented here do not concur with expectations from literature, and instead show that the nitrogen-doped samples have no enhanced level of CO₂ adsorption, and instead the best performing sample is seen to be a non-doped control sample, BC Control Mandarin. The reasoning behind the poor performance of the doped samples could be attributed to a number of reasons; the doping process may have led to pore blocking, meaning the accessible micropore volume within the chars is limited. Alternatively, the inclusion of urea in the process may have inhibited pore development in both the micro- and mesoporous range, in turn reducing the adsorption capacity. The XPS analysis of both types of chars in Chapter 5 and 6 respectively, showed that N-6 nitrogen was prominent in most of

the samples, but N-Q was also seen to be present in modest quantities in most chars; this species of nitrogen is not as influential in the adsorption mechanisms of CO₂ in chars as N-5 and N-6. Therefore, while the nitrogen content of the materials has been increased by doping, not all of the nitrogen species present are necessarily deemed useful towards the overall goal of increasing the CO₂ capacity of the chars.

Similarly, there is little to no correlation seen with regards to the CO₂ uptake and the ratio of XPS determined nitrogen to elemental analysis determined nitrogen presented in Chapters 5 and 6 for each type of char. The doped biochars generally showed higher levels of nitrogen and oxygen functionalisation on the external surfaces of the materials, while the hydrochars showed enhanced functionalisation within the internal bulk structure of the materials. Despite this, these doped samples all exhibited gravimetrically measured CO₂ capacities within the range of 0.76 – 1.30 mmol/g (at 60 °C, 1 bar). Note that in order to facilitate a full analysis, and comparison of the effect of surface-to-bulk enrichment, each of the optimisation chars from both the hydrochar and biochar stage would have to be tested for their gravimetric CO₂ adsorption capacity, but this was not possible due to time and financial restraints. However, from this small sample size it not possible to draw major conclusions on the effect that functionalisation of different areas of the material has on their CO₂ adsorption ability. Ultimately however, it is clear that nitrogen doping has not been successful in improving the CO₂ capacity of the chars, when compared to the non-doped chars produced in this study.

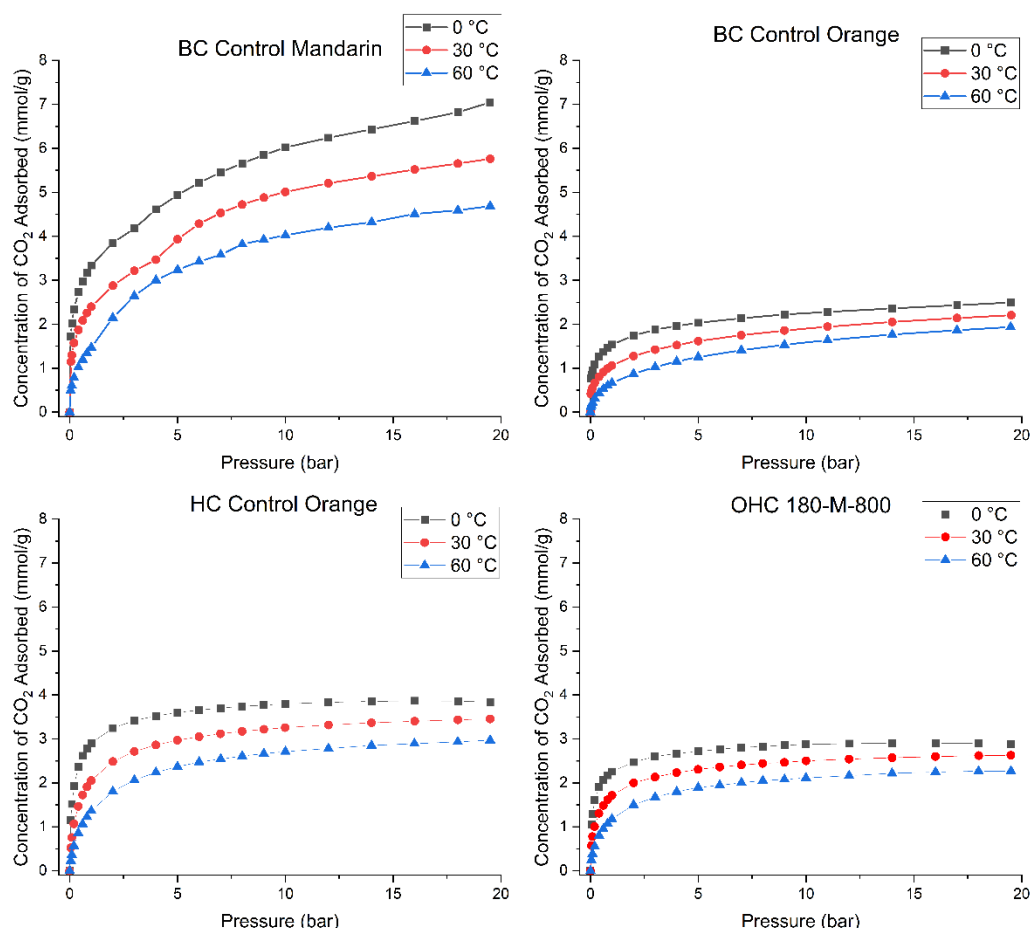


Figure 7.3: 0 °C, 30 °C and 60 °C Isotherms Measured Using Gravimetric Analysis for Samples BC Control Orange, BC Control Mandarin, HC Control Orange and OHC 180-M-800 Respectively

Of the four samples shown in Figure 7.3, OHC 180-M-800, HC Control Orange and BC Control Orange all match with the doped biochars in that they present Type I (a) isotherm behaviour. BC Control Mandarin is the outlier, as it closer resembles a Type I (b) isotherm, which is indicative of a wider pore size distribution than Type I (a) and may include small mesopores [9]. Interestingly, this sample also displays the highest CO₂ capacity at both 1 bar and 19.5 bar for all three temperatures tested, and was not part of the nitrogen doping experiment aspect of the project. In fact, at 19.5 bar, 0 °C the uptake of 7.04 mmol/g is 65 % higher than the second-best char (OBC 800-3-M, 4.26 mmol/g). Therefore, to have such significantly higher CO₂ uptake capacity, the BC Control Mandarin sample must contain a more developed and

balanced pore structure than the other nine chars tested. This type of structure would allow for ease of diffusion for CO₂ molecules through the pore network and to the important micropores; compare this to the other chars, which are predominantly microporous, which may raise challenges in the overall diffusion process. This aforementioned pore network is likely to have been responsible for the superior adsorption at low pressure; in contrast, at high pressures the existence of larger pores, such as mesopores, will then have provided the opportunity for pore filling to occur after all the micropores have been filled. Whether it is due to this, or simply easier access to favourable adsorption sites such as those with oxygen-containing functionalities, the BC Control Mandarin sample displays the highest adsorption results of the whole project.

Two of the samples produced from the optimisation models in Chapter 5 and 6, OPB Micropore Orange and OPH Micropore Mandarin, are shown in Figure 7.4. The isotherm for each sample presents Type I(a) isotherm behaviour, agreeing with the DR analysis data which showed both materials were highly microporous. The performance of both optimal chars in the range of 0 – 1 bar is similar to the rest of samples discussed in this section, with no clear improvement in CO₂ capacity. They also present similar results in the range 1 – 19.5 bar, where the lack of large mesopores and a fully developed pore network appears to limit their adsorption capacity.

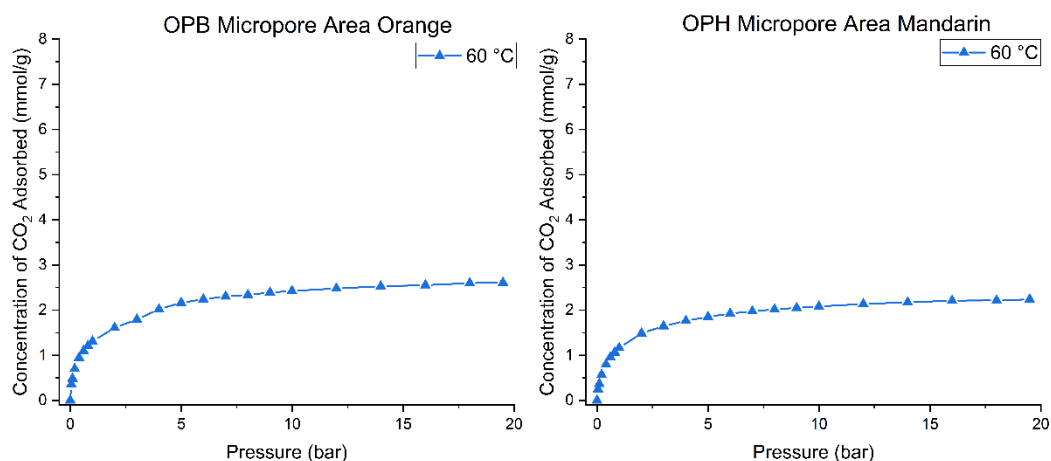


Figure 7.4: 60 °C Isotherms Measured Using Gravimetric Analysis for Samples OPB Micropore Orange and OPH Micropore Mandarin

When assessing adsorption in the higher-pressure range, in the case of this study up to 19.5 bar, it is notable that above 5 bar most of the isotherms plateau, although it can be said for BC Control Mandarin that there is a still a steady increase in the amount adsorbed. At these elevated pressures, adsorption in ultramicropores is no longer dominant as they have likely been filled, and larger micropores and mesopores become important as previously mentioned. This marks the point where total Brunauer-Emmett-Teller (BET) surface area and overall pore volume is considered more relevant, as materials which report high values for these two properties are commonly found to have well developed pore networks that combine both micro- and mesopores [6]. As a result of these networks, filling of the larger pores occurs freely, and individual interactions CO₂ molecules have between ultramicropores and functional group sites have less of an influence on adsorption [17].

Tabulated results for the gravimetric adsorption isotherms can be seen in Table 7.4. As discussed, apart from the BC Control Mandarin sample, the other nine chars present very similar results. For these samples, the 0 °C, 1 bar results all lie between 1.53 – 2.91 mmol/g, and for the same temperature and 19.5 bar, the results lie between 2.50 – 4.26 mmol/g. It

can be concluded from this that despite adequate adsorption at low pressure, there is no significant increase in capacity at higher pressure, which is likely due to saturation of micropores and an inadequate pore network for pore filling to deliver increased uptake. Sample BC Control Mandarin does demonstrate improved adsorption in comparison, but the uptake at 0 °C, 19.5 bar is only around double the uptake at 0 °C, 1 bar; in comparison other studies have reported the increase in uptake at 20 bar to be three or four time larger than the uptake at 1 bar [6], [18].

Table 7.4: Gravimetric CO₂ Uptake Capacity at 1 and 19.5 bar for Selected Chars Produced in This Study at 0, 30 and 60 °C

Sample	Pressure	Temperature		
		0 °C	30 °C	60 °C
OBC 800-0.5-O	1 bar	2.75	1.55	1.21
	19.5 bar	4.08	3.46	3.03
OBC 800-3-O	1 bar	1.59	1.19	0.76
	19.5 bar	2.67	2.53	2.11
OBC 800-0.5-M	1 bar	1.86	1.26	0.76
	19.5 bar	3.02	2.55	1.96
OBC 800-3-M	1 bar	2.39	1.65	1.30
	19.5 bar	4.26	3.86	3.60
OHC 180-M-800	1 bar	2.26	1.72	1.18
	19.5 bar	2.88	2.63	2.27
BC Control Orange	1 bar	1.53	1.06	0.66
	19.5 bar	2.50	2.20	1.94
BC Control Mandarin	1 bar	3.34	2.40	1.47
	19.5 bar	7.04	5.76	4.69
HC Control Orange	1 bar	2.91	2.05	1.36
	19.5 bar	3.84	3.45	2.97
OPB Micropore Orange	1 bar	-	-	1.31
	19.5 bar	-	-	2.61
OPH Micropore Mandarin	1 bar	-	-	1.16
	19.5 bar	-	-	2.24

The adsorption results obtained gravimetrically can be compared to other carbon-based materials found in literature, which are shown in Table 7.5 (note the samples from this study included in the table present only the gravimetric CO₂ adsorption capacity and not the volumetric results). The adsorption results obtained at 1 bar from this study lie within the

range observed from literature; this does imply a sufficient level of microporosity exists in the samples, and can concur with the findings that pores in this size range are vital for low pressure adsorption. For other studies which utilise orange peel in the synthesis of chars [2], [7], [12], [19], the results of this study lie in the lower range of those observed. At higher pressures, the results are poor, even compared to other studies which have only tested to 10 bar.

BET surface area data has been included in Table 7.5, despite the argument made above that this is not the most important property for chars being used in CO₂ adsorption. However, BET calculated surface area is the only characteristic that is consistently reported across all the studies, due to its ease of experimental measurement. Thus, instead of reporting various different types of microporous data, it was deemed more fitting to provide one common value for each sample that allows for easy comparison. Information on the microporous data of each individual study can be found via their reference.

Table 7.5: Table of CO₂ Uptake Capacities Reported in Literature for Different Biochar and Hydrochar Materials, at a Range of Temperatures and in a Pressure Range of 1 - 20 bar

Material	Biochar or Hydrochar	BET Surface Area (m ² /g)	Temperature (°C)	CO ₂ Capacity (mmol/g)		Ref.
				1 bar	20 bar	
Orange Peels ²⁶	Biochar	0 – 391	0	1.59 – 2.74	2.50 – 4.08	This Study
			30	1.06 – 1.55	2.20 – 3.46	
			60	0.66 – 1.31	1.94 – 3.03	
Mandarin Peels ²⁶	Biochar	0 – 436	0	1.13 – 2.76	3.02 – 7.04	This Study
			30	1.26 – 2.40	2.55 – 5.76	
			60	0.76 – 1.47	1.96 – 4.69	
Orange Peels ²⁶	Hydrochar	0 – 394	0	1.79 – 2.91	3.84	This Study
			30	2.05	3.45	
			60	1.36	2.97	
Mandarin Peels ²⁶	Hydrochar	0 – 390	0	1.94 – 2.80	2.88	This Study
			30	1.72	2.63	
			60	1.16 – 1.18	2.24 – 2.27	
Orange Peel	Biochar	40	0	1.02		[7]
Orange Peel	Hydrochar	457	25	2.46 – 3.05		[19]
Orange Peel	Biochar	309 – 1768	25	2.60 – 4.31		[12]
			50	1.64 – 2.59		
Orange Peel	Hydrochar	87 – 2130	0	2.23 – 6.67		[2]
			10	2.12 – 5.41		
			25	1.72 – 3.97		
Banana and Orange Peel	Hydrochar	154 – 222	25	2.46 – 3.81		[20]
Garlic Peel	Hydrochar	306 – 1262	0	2.49 – 6.25		[14]
			25	1.65 – 4.22		
Pine Sawdust	Hydrochar	522 – 2171	25	1.78 – 3.30		[13]
			50	1.01 – 1.96		

²⁶ The CO₂ Capacity data presented in the '20 bar' column is the data which was measured at 19.5 bar and presented in this thesis.

Material	Biochar or Hydrochar	BET Surface Area (m ² /g)	Temperature (°C)	CO ₂ Capacity (mmol/g)		Ref.
				1 bar	20 bar	
<i>Delonix regia</i> Seeds	Hydrochar	300 – 1299	35	2.60		[21]
Corncob	Hydrochar	42 – 1222	15	2.95 – 4.50		[22]
			30	2.25 – 3.39		
Lemon Peels	Hydrochar	1113 – 2143	0	3.2 – 4		[10]
			25	2 – 2.8		
			40	1.4 – 2		
Pomelo Peel	Biochar	252 – 1088	0	0.86 – 5.74		[5]
			25	1.96 – 3.41		
Jujun Grass and <i>Camellia japonica</i>	Hydrochar	1048 – 3537	25	2.8 – 5	8.7 – 21.1	[6]
Bamboo Shoots	Biochar	387 – 1985	0	2.39 – 7.52		[8]
			25	1.76 – 3.60		
Cotton Stalk	Biochar	95 – 627	20	2.26		[23]
Coconut Shells	Biochar	563 – 1495	0	5.16 – 7.85		[24]
Banana Peels	Hydrochar	72 – 243	25	3.18 – 3.80		[25]
Vine Shoots	Biochar	405 – 536	25	2.35 – 2.67		[26]
			50	1.65 – 1.90		
Wheat Straw	Biochar	459 – 514	25	2.44 – 2.63		[26]
			50	1.78 – 1.91		
Camphor leaves	Biochar	721 – 1736	0	4.50 – 5.86		[27]
			25	2.42 – 3.74		
			50	1.45 – 2.28		
Bacterial Cellulose	Biochar	329 – 916	0	4.89		[28]
<i>P. nigra</i> Wood and Cellulose Fibres	Biochar	6 – 593	25	1.12 – 2.33		[4]
Lignin – Eucalyptus and Spruce	Hydrochar	1380 – 2875	0	2.1 – 6		[15]

Material	Biochar or Hydrochar	BET Surface Area (m ² /g)	Temperature (°C)	CO ₂ Capacity (mmol/g)		Ref.
				1 bar	20 bar	
Glucose with Acrylic Acid	Hydrochar	659 – 1192	0	2.73 – 5.86		[29]
			25	1.05 – 3.82		
Cashew Nutshell	Biochar	1693	25	4	10 bar: 11	[30]
Coffee Grounds	Biochar	1624 – 2785	0	5.09 – 7.55	10 bar: 13.34 – 23.27	[31]
			25	2.81 – 4.42	10 bar: 11.59 – 16.81	
			50	1.52 – 2.86		
Lignin Waste	Hydrochar	1157 – 1924	25	4.6	17.3	[18]
<i>Arundo donax</i>	Biochar	1122	0	6.3	30 bar: 15.4	[32]
Grape Marc Biomass	Biochar	1640 – 2473	0	4.9 – 6.7	30 bar: 17.2 – 26.8	[33]
			25	2.7 – 3.9	30 bar: 10.4 – 19.9	
Lotus Seed	Biochar	1614 – 2230	0	4.6 – 6.9	30 bar: 20.1 – 26.4	[34]

Four isotherm models were tested against the collective gravimetric isotherm adsorption data: Langmuir, Freundlich, Temkin and Dual Site Langmuir. The Dual Site Langmuir model was found to consistently be the best model fit for the data, which matches with the type of adsorption mechanisms expected to be seen from the samples. This model assumes that there are two types of adsorption sites available to the CO₂ molecules, with one type of site having a higher energy than the other. This can apply to sites in terms of their functionalities, i.e., sites with nitrogen- and oxygen-containing moieties would be more favourable for CO₂ adsorption than non-functionalised sites, due to stronger intermolecular interactions. Conversely, it can also apply to pores of different sizes, for example narrow micropores potentially present more favourable sites for CO₂ molecules to adsorb than larger mesopores. As this model assumes there are two types of adsorption sites, this suggests that the surface of the materials are heterogenous, and this in turn concurs with the double exponential kinetic model, which is discussed further in Section 7.4.

The Dual Site Langmuir model has been successfully used to describe adsorption of CO₂ onto nitrogen-doped microporous activated carbons produced from pitch [35]. In this study, the types of sites were split into type one and two, with type one representing adsorption sites in narrow micropores, and type two attributed to other adsorption sites available throughout the material. The equilibrium constants for the type one sites were consistently higher than for type two; this indicates that there is a higher affinity for CO₂ at the type one sites. Adsorption on the type one sites also dominated the process from pressure of 0 to 0.3 bar, and from 0.3 to 1 bar the type two sites took over. This is further evidence of ultramicropores providing the driving force for adsorption at low pressure ranges, with pore filling becoming more relevant once those sites have been occupied. It is possible that the type of mechanism proposed by this study can be applied to the adsorption data of the orange and mandarin derived chars of this project.

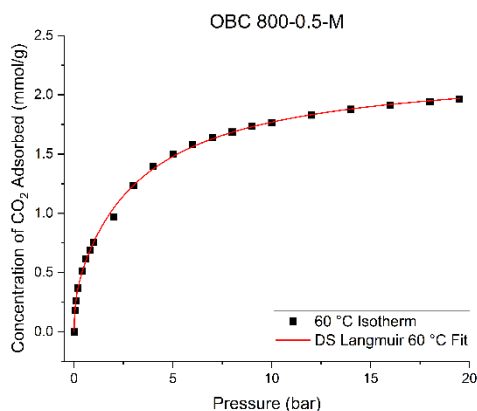


Figure 7.5: Dual Site Langmuir Fit for 60 °C Isotherm of OBC 800-0.5-M

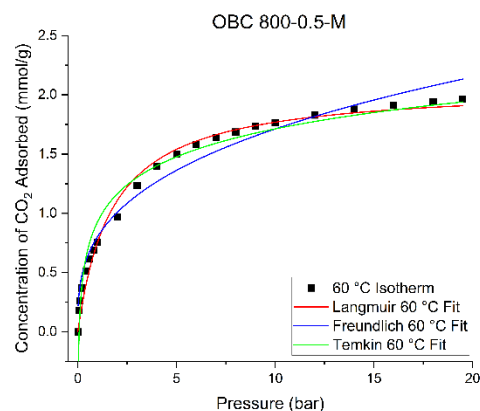


Figure 7.6: Langmuir, Freundlich and Temkin Fits for 60 °C Isotherm of OBC 800-0.5-M

The Dual Site Langmuir fit for the 60 °C isotherm of OBC 800-0.5-M is shown in Figure 7.5 (Dual Site is shortened to DS in the legend), and for comparison the other three tested fits for the same isotherm are shown in Figure 7.6.

Table 7.6: Model R^2 Values for Fits Applied to 60 °C Isotherm of OBC 800-0.5-M

Isotherm Model Fits	Dual Site Langmuir	Langmuir	Freundlich	Temkin
Model R^2 (unitless)	0.99911	0.98616	0.97345	0.96835

The R^2 for each of the four fits are shown in Table 7.6. All four models were tested for each gravimetric isotherm collected, and the Dual Site Langmuir model was found to be the best fit for 25 of the 26 isotherms. All Dual Site Langmuir fittings can be found in Appendix J, along with the associated fittings parameters for each fit, and the R^2 for each of the fits is displayed in Table 7.7. In every case, $R^2 > 0.996$, indicating a good fit to the model.

Table 7.7: Model R^2 Values for Dual Site Langmuir Fits for Each Gravimetric Isotherm in This Study

Sample	Dual Site Langmuir Model R^2 (Unitless)		
	0 °C Isotherm	30 °C Isotherm	60 °C Isotherm
OBC 800-0.5-O	0.99870	0.99986	0.99965
OBC 800-3-O	0.99932	0.99936	0.99951
OBC 800-0.5-M	0.99890	0.99893	0.99911
OBC 800-3-M	0.99810	0.99932	0.99956
OHC 180-M-800	0.99929	0.99951	0.99978
BC Control Orange	0.99684	0.99759	0.99955
BC Control Mandarin	0.99911	0.99826	0.99966
HC Control Orange	0.99963	0.99972	0.99989
OPB Micropore Orange	-	-	0.99918
OPH Micropore Mandarin	-	-	0.99978

In industrial settings, flue gas streams are commonly found to contain CO_2 on a volumetric basis of between 5 – 15 %, although it can be as high as 33 % in some cases [36], [37], and they are released at temperatures of 50 – 150 °C [38]. For amine post combustion systems, it is desirable for the flue gas stream temperature to be in the range of 50 – 60 °C [39], [40].

As the aim of this study is to produce adsorbent materials for use in carbon capture technology, it is important to test them under relevant conditions and benchmark them against other materials reported in literature and used in industry. To give a broad view of char materials' performance, the CO_2 uptake at 60 °C at two pressures is shown in Table 7.8. The 0.1 bar pressure was chosen to represent a lean CO_2 flue mixture, and the 0.2 bar pressure to represent a rich CO_2 flue mixture. As is expected, CO_2 uptake is higher at 0.2 bar than 0.1 bar, with the level of uptake increasing by 28 – 54 % in the range of samples tested. BC Control Mandarin again is the best performing sample in this pressure range, indicating good levels of ultramicroporosity, and OPB Micropore Orange is the best of the doped char samples tested.

Table 7.8: CO₂ Adsorption Capacity of Selected Chars at 60 °C and Pressures of 0.1 and 0.2 bar, Respectively

Sample	CO ₂ Uptake at 60 °C	
	0.1 bar (lean flue gas composition comparison)	0.2 bar (rich flue gas composition comparison)
OBC 800-0.5-O	0.38	0.55
OBC 800-3-O	0.25	0.35
OBC 800-0.5-M	0.26	0.37
OBC 800-3-M	0.45	0.64
OBC 180-M-800	0.38	0.55
BC Control Orange	0.22	0.31
BC Control Mandarin	0.61	0.78
HC Control Orange	0.37	0.57
OPB Micropore Orange	0.48	0.70
OPH Micropore Mandarin	0.37	0.57

Table 7.9 shows a range of post-combustion CO₂ style adsorption tests found in literature. While these offer opportunity for comparison with this study, flue gas is commonly found to exit process streams at temperatures of 50 °C or higher, thus, the experiments carried out in this project are closer to real life conditions than other literature studies.

Few examples could be found in literature that reported CO₂ uptake at both low pressure (0.1 – 0.3 bar) and high temperature (> 50 °) which is characteristic of flue gas conditions. Despite this, a general comparison can still be made between this study and other work. For the vine shoots and wheat straw biochars [26], the values of 0.6 – 0.74 mmol/g of CO₂ adsorbed at 0.14 bar, 50 °C is very similar to the uptake of BC Control Mandarin in this study, and a comparable range of 0.58 – 0.68 mmol/g is reported at 0.15 bar, 50 °C for almond shell and olive stone biochars [41]. It is commonly known that high ultramicroporosity is key to high uptake of CO₂ at low pressures such as this [26], [42], [43], which again concurs with the results obtained for samples in this work. Overall, it can be suggested that while not achieving the highest CO₂ uptake at atmospheric conditions in literature, BC Control Mandarin and OPB Micropore Orange provide impressive performance at conditions representing a flue gas stream. It should also be noted that many of the samples in Table 7.5 report relatively large

capacities at 0 or 25 °C; if they were to be tested at 60 °C as has been done in this project, it is likely they would report smaller CO₂ capacities, and importantly, more similar capacities to the orange and mandarin derived chars produced here.

Table 7.9: CO₂ Adsorption Capacity of Chars from Literature at Pressure Range Commonly Found in Flue Gas Streams

Material	Biochar or Hydrochar	Pressure (bar)	Temp. (°C)	CO ₂ Capacity (mmol/g) ²⁷	Ref.
Jujun Grass and <i>Camellia japonica</i>	Hydrochar	0.15	25	0.6 – 1.5	[6]
Bamboo Shoots	Biochar	0.15	0	1.06 – 2.23	[8]
			25	0.55 – 1.02	
<i>P. nigra</i> Wood and Cellulose Fibres	Biochar	0.15 and 0.3	25	0.5 – 0.9 (0.15 bar) 0.75 – 1.4 (0.3 bar)	[4]
Lignin – Eucalyptus and Spruce	Hydrochar	0.15	0	0.5 – 1.8	[15]
Glucose with Acrylic Acid	Hydrochar	0.15	25	0.72 – 1.33	[29]
Two Phase Olive Mill Waste	Hydrochar	0.15	0	0.76 – 1.55	[44]
Rice Husks	Hydrochar	0.15	25	1.90	[45]
Sawdust and Lignin	Hydrochar	0.15	0	1.3 – 2.3	[46]
			25	0.5 – 2.0	
Sawdust	Hydrochar	0.15	25	0.7 – 1.4	[47]
Olive Stones	Biochar	0.15	25	1.02	[41]
			50	0.58	
Almond Shells	Biochar	0.15	25	1.08	[41]
			50	0.68	
Banana Peels	Hydrochar	0.15	25	1.40	[25]
Vine Shoots	Biochar	0.14	25	1.02 – 1.16	[26]
			50	0.60 – 0.70	
Wheat Straw	Biochar	0.14	25	1 – 1.3	[26]
			50	0.63 – 0.74	

7.3 Isosteric Heat of Adsorption and Heat of Entropy

The isosteric heat of adsorption was calculated using the 0, 30 and 60 °C isotherms for all eight char samples that were tested in this range using gravimetric adsorption. To perform

²⁷ Accuracy is reported to the level in the original literature.

this calculation, the heat of adsorption is assumed constant across the utilised temperature range. Note, 0 – 60 °C is a relatively large range for this assumption, and therefore precise values should be treated with caution, however trends between samples are expected to be representative. Figure 7.7 presents the calculated isosteric heat of adsorption against CO₂ uptake for the eight samples, with a version including error bars found in Appendix K. Note that the real values for the isosteric heat of adsorption in this study are negative, thus, the processes described here are exothermic; but for ease of understanding and by general convention, they are presented as positive values in the relevant figure.

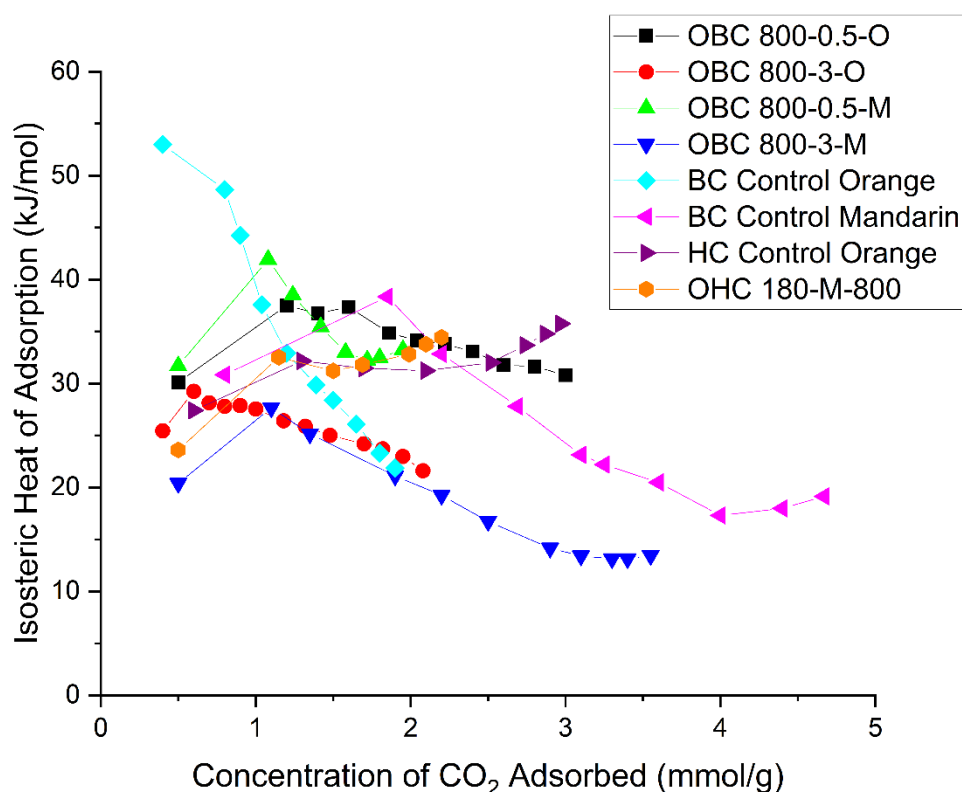


Figure 7.7: Isosteric Heat of Adsorption of Selected Biochar and Hydrochar Samples (Across Temperature Range of 0 – 60 °C)

High initial values of heat of adsorption for most of the samples, approximately 25 – 52 kJ/mol, is a sign of strong affinity from the CO₂ molecules for the surface of the chars, and

it would be expected that the narrow ultramicropores they possess have aided in the initial adsorption of CO₂ [2], [12]. As previously discussed, narrow micropores will enhance adsorption through Van der Waal's forces and electrostatic forces due to the proximity of the pore walls, and potential for bridging interactions across pores [29]. When the capacity increases, these more favourable sites reach saturation, which leads to the less favourable sites then being used for adsorption, and the heat of adsorption subsequently decreases, and reaches a plateau [5]. This decrease in enthalpy is indicative of heterogeneity on the surface of the chars, thus, confirming that the ultramicropores and elemental functionalities are present and active during the adsorption process [8], [45].

The adsorption processes here are exothermic, thus, follow Le Chatelier's principles in that an increase in temperature will cause adsorption capacity to decrease, which agrees with the experimental data presented in Section 7.2.3. As the range of values found are < 60 kJ/mol, this confirms that physisorption is dominant in the adsorption of CO₂ onto the samples [14]. This can be linked to the lifecycle of the chars: the relatively low heat of adsorption values indicate that they may possess good regenerative abilities, as desorption should be readily achievable with mild temperatures, compared to if chemisorption bonds were required to be broken. Finally, most values lie within the range of 30 – 55 kJ/mol, which is the recommended range for post-combustion carbon capture applications [4].

Considering other values reported in literature, the samples here are consistent with expectations. Other chars with narrow micropores and nitrogen-containing functionalities have reported initial high heats of adsorption values which follow the trend of decreasing as CO₂ uptake increases [8], [28], [48], [49]. In terms of physical values, orange peel hydrochars showed initial heats of adsorption of 27.8–38.9 kJ/mol before decreasing to ~15 – 20 kJ/mol, and garlic peel hydrochars reported initial values of approximately 40 kJ/mol before

decreasing to 20 kJ/mol as coverage increased [2], [14]. A study using nitrogen-doped cucumber peel biochars reported higher values of 43.9 – 57.3 kJ/mol for the initial heats of adsorption, but these decreased to 30 kJ/mol range as adsorption sites became saturated [49].

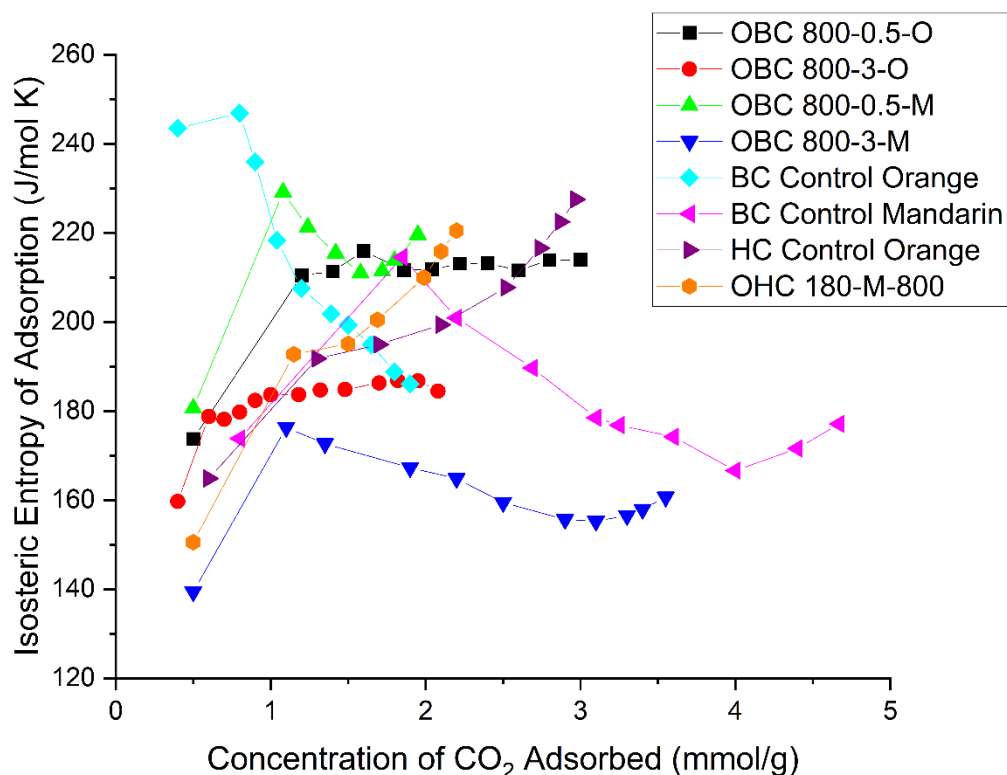


Figure 7.8: Isosteric Entropy of Adsorption of Selected Biochar and Hydrochar Samples (Across Temperature Range of 0 – 60 °C)

The isosteric entropy of adsorption for the same eight samples discussed above can be seen in Figure 7.8, and a version including error bars in Appendix K. There is no clear trend for the dataset as a whole, as the change in entropy is seen to vary between samples. The entropy values of the biochar control samples are seen to decrease as CO₂ uptake increases, while the opposite is observed for the two hydrochar samples. Meanwhile for the urea-doped

biochar chars, entropy appears to be generally constant within a narrow window for each sample.

In principle, a decrease in entropy with increasing uptake can suggest an ordering effect of the CO₂ molecules as they adsorb onto the available active sites on the material. Conversely, an increase in entropy with increasing uptake can indicate more disorder occurring on a molecular level, potentially signalling that disordered multilayer adsorption is taking place.

7.4 CO₂ Adsorption Kinetics

As described in Chapter 3, the stretched exponential and double exponential models were applied to the CO₂ adsorption kinetic data, collected via gravimetric adsorption experiments, to describe the adsorption processes occurring on the char samples. Through the course of fitting the models to the adsorption data, the double exponential model was consistently found to give better model fits over the range of individual samples tested. This implies there are two distinct mechanisms that are governing the adsorption kinetics.

The k_1 values for the 60 °C isotherms are displayed in Figure 7.9, and the k_2 values for the same isotherms in Figure 7.10 (note that y-axis scales are not consistent between graphs in these figures, due to differences in magnitudes of k_n values). The k_1 and k_2 plots vs pressure for the 0 °C and 30 °C isotherms can be found in Appendix L.

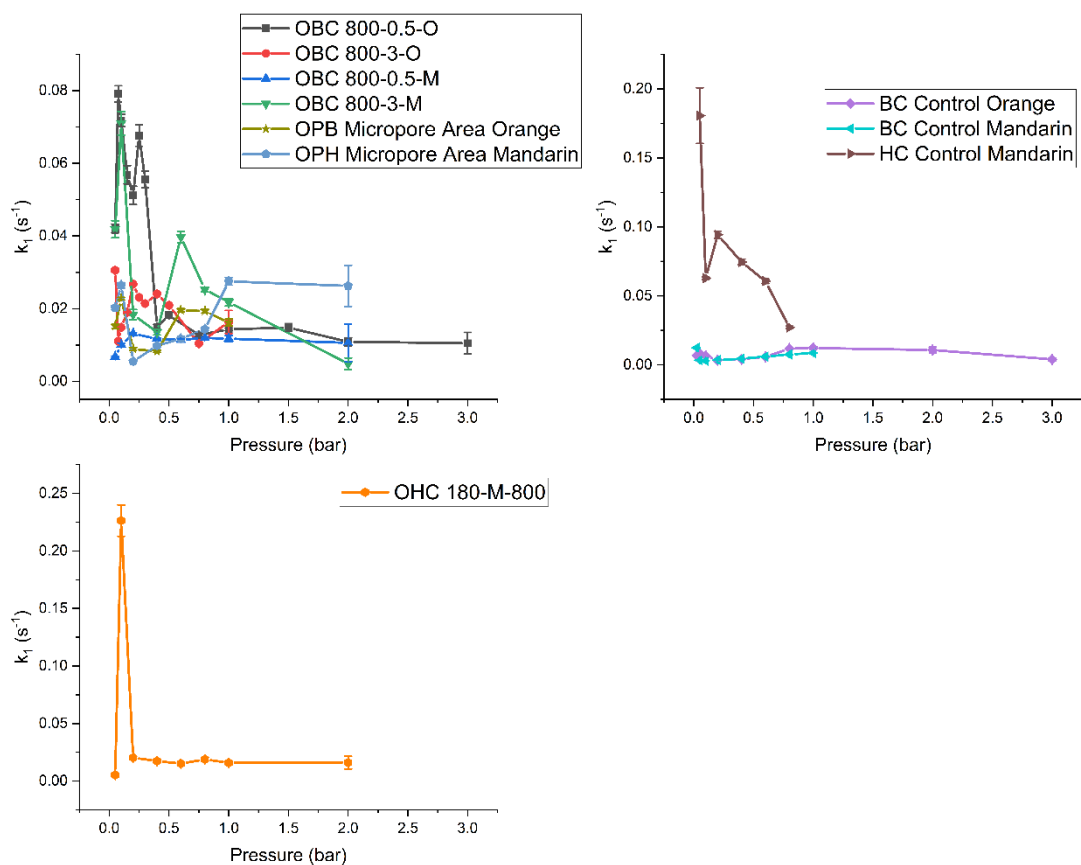


Figure 7.9: k_1 Values for 60 °C CO₂ Adsorption Isotherms of Selected Chars Produced in this Study

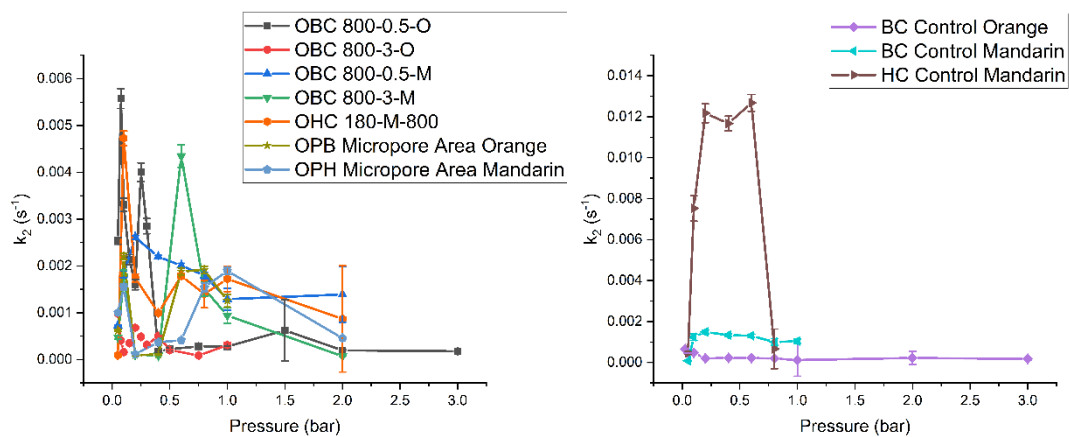


Figure 7.10: k_2 Values for 60 °C CO₂ Adsorption Isotherms of Selected Chars Produced in this Study

The double exponential model is used to describe scenarios where there are two processes occurring simultaneously, with each process have their own unique rate constant. In terms of adsorption, this has been interpreted in various ways for different adsorbate-adsorbents.

The main theory around this model describes the steps as follows: (1) the fast step can represent diffusion of molecules through internal and external means, and (2) the slow step represents intraparticle diffusion, which has been observed in adsorption of metals in solution previously [50]. Regarding the adsorption kinetics within this study with gas adsorption, the fast and slow barriers may be due to diffusion at pore entrances. It has been reported that the rate-limiting step can be the process of molecules adsorbing into the pores, with the faster step being linked to diffusion through the pores [51]. Alternatively, the fast and slow steps can be used to describe scenarios when an adsorbent presents two distinct types of adsorption sites, where one type of site is more favourable than the other [52], [53]. It is also possible that the two different mechanisms discussed above can occur concurrently. The profiles presented and the values of k_1 and k_2 suggest the adsorption of CO₂ by the chars in this project is controlled by two distinct kinetic processes, with one consistently faster than the other up to pressures of 3 bar. No data is presented beyond this pressure point, as the mass change at each subsequently measured pressure point is too small to fit a kinetic curve too. It should also be noted that for the first few low-pressure points where the kinetics are faster, it is hard to capture the event entirely as the initial adsorption could not be measured while the pressure was still ramping.

Focusing on the 60 °C experimental data, the fast process in the case of the biochars show k_1 values of 0.0067 – 0.0791 s⁻¹, while the slow process ranges from 0.00008 – 0.0056 s⁻¹. A general trend of the highest rate of adsorption occurring at low pressure, 0.1 – 0.3 bar, before decreasing and plateauing around 1 bar is witnessed for both the fast and slow process descriptors. The hydrochar samples also exhibit a similar trend, however with higher k_1 values, with peak values of 0.226 s⁻¹ at 0.1 bar for OHC 180-M-800 and 0.094 s⁻¹ at 0.2 bar for HC Control Orange. The control biochars do not exhibit values as high as this. The high rate observed around 0.1 – 0.3 bar is likely associated with enhanced uptake of CO₂ in this range,

attributed to the high proportion of ultramicropores in all the samples tested. The nitrogen doping is also thought to contribute to this increased uptake in this pressure range, by providing favourable adsorption sites for the CO₂ molecules [2]. The same general trend is observed for the k_1 and k_2 values calculated from the 30 °C and 0 °C isotherms, indicating consistency of behaviour across the temperature range tested.

Very generally, the value of k_1 was found to be a factor of 10 larger than k_2 , indicating that the mechanism associated with k_2 was the rate limiting step. As the chars in this study have been demonstrated to contain high quantities of ultramicropores, possessing a diameter around double the size of CO₂ molecules, it is likely that the slow step here relates to the diffusion of CO₂ into the pores. A certain molecular orientation may be required for molecules to gain access to the pores. High concentration of molecules at the pore entrance could cause clustering which would similarly limit the diffusion of CO₂ into the pores. However, once they successfully enter, they are likely to adsorb onto sites quickly due to the high electrostatic potential originating from the pore walls and associated Van der Waals interactions, both discussed in Section 7.2.3. A similar mechanism has been reported where the double exponential model has related the slow process to diffusion through pores with high activation energy requirements, while the fast process is linked to diffusion along pore cavities which present low activation energies [54].

Equally, the double exponential model is capable of describing adsorption in a two-site mechanism, where there is heterogeneity on a material's surface [52], [53]. The materials in this study are expected to have a heterogenous surface, as shown by the high levels of nitrogen and oxygen in them which suggests the presence of chemical functionalities, and the relatively high heats of adsorption presented in Section 7.3 substantiates this. Therefore, this could also be used to interpret the rate constants calculated, where carboxyl oxygen

groups or pyrrolic nitrogen groups provide more favourable sites for CO₂ molecules compared to non-functionalised sites on the carbon structure of the char. Oxygen-containing groups have been demonstrated to increase the surface basicity which attracts acidic CO₂ molecules [16], with nitrogen-containing functional groups also acting in the same way, as well as promoting intermolecular hydrogen bonding [49]. CO₂ may be more likely to interact with these sites, and adsorb on them ahead of non-functionalised sites.

In reality, it is highly likely that CO₂ molecular diffusion and adsorption onto heterogeneous sites (whether that be due to different functionalities present or pores of differing activation energies) is happen simultaneously and collectively impacting the adsorption kinetics of the system. More detailed experiments would be required to isolate and identify each of the mechanisms in the process. Little was found in literature around separating the effects of these phenomena, thus, it could provide an interesting study in future work. Two-step CO₂ adsorption has been identified in clays, where the fast step was associated with adsorption on outer layer sites, and the slow step with adsorption on sites in the interlayer which were harder to access [55]. Adsorption of CO₂ on copper materials reports similar, fitting the double exponential mode to describe fast diffusion seen in larger pores, and subsequent slower diffusion in the smaller pores [56]. It has also been reported in simpler terms from a copper-carbon catalyst study, with fast CO₂ adsorption reported on the external surface sites which are more freely accessible, and the slow rate of adsorption taking place due to diffusion of CO₂ through pores and the pore network [57]. The kinetics of CO₂ adsorption on fly-ash derived adsorbent, a material similar to biochar, was seen to follow the double exponential model, highlighting a difference between chemisorption and diffusion of CO₂ in this case. Apart from this example, the only other evidence of fitting the double exponential model to CO₂ adsorption data was from the thesis of a previous research group member. In that project, data from the testing of CO₂ adsorption on torrefied carbons produced from

wood was seen to fit the aforementioned model and reported values of $0.005 - 0.05 \text{ s}^{-1}$ for k_1 , and $0 - 0.007 \text{ s}^{-1}$ for k_2 (approximately) [58], which are of a similar magnitude to those reported in Figure 7.9 and Figure 7.10.

The pre-exponential factors A_1 and A_2 represent the proportion of adsorption uptake associated with each adsorption event, for a given pressure point. The pre-exponential factors from this kinetic model were calculated but no clear trend was seen between samples or temperatures; as such the data has not been included here, but is available on request. It should be noted that the pre-exponential factor for the fast event, k_1 , was likely to be an underrepresentation of its 'true' value, due to the fact the early stages of adsorption for each pressure point could not be measured due to it occurring during the pressure ramping stage between points.

During the collection of the gravimetric isotherms, the biochar samples were observed to contain a large hysteresis upon desorption. In order to ascertain if this hysteresis was a thermodynamic effect or simply a result of slow kinetics, an isotherm was repeated with longer equilibration timeout periods. The 60°C isotherm for OBC 800-0.5-M was re-measured using timeout periods of 48 h for each point. Note that less points were used than in the original isotherm, as it would not be time-effective to re-run a 42-point isotherm using these conditions. The resulting isotherm is shown alongside the original isotherm, which was collected using a 6 h equilibration timeout for each point, in Figure 7.11. It can be seen that increasing the timeout period led to an increase in adsorption, bringing the adsorption branch of the isotherm closer to the desorption branch. This implies that the adsorption kinetics are extremely slow; the mass increase on the sample was still slowly increasing at each pressure point when 48 h equilibration was used. This suggests that a fully equilibrated isotherm would display adsorption and desorption branches that are even closer together. It

is possible that there is some degree of chemisorption of CO₂ on to the samples, but the isosteric heats of adsorption calculated in Section 7.3 suggest that physisorption is the dominant mechanism. If there is indeed chemisorbed CO₂ on the biochar materials, then increasing the equilibration time for any given pressure point would not be sufficient to completely remove it from the samples and an increase in temperature (such as a degas process) would be required.

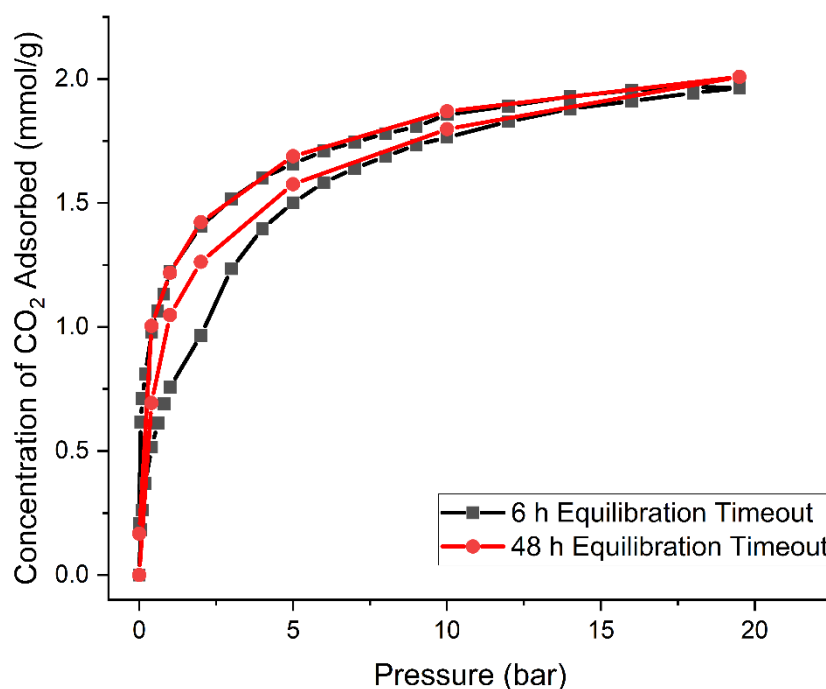


Figure 7.11: 60 °C CO₂ Adsorption Isotherms Showing the Difference in Adsorption for Different Equilibration Periods for OBC 800-0.5-M

7.5 Cyclic CO₂ Adsorption

7.5.1 Sample Selection

Due to time restraints, it was not possible to test all samples for their cyclic adsorption capabilities. A selection of the produced samples which presented the highest CO₂ capacities in this work at 1 bar and 60 °C were chosen to be analysed. BC Control Mandarin was chosen due to its excellent performance compared to the other chars in the study. OBC 800-0.5-O

and OBC 800-3-M were chosen as the best doped biochars to be tested, and HC Control Orange and OHC 180-M-800 chosen to allow for comparison between biochars and hydrochars. The two optimal char samples, OPB Micropore Orange and OPH Micropore Mandarin, were also tested to assess the validity of the optimisation models.

7.5.2 Cyclic CO₂ Adsorption Results

Cyclic CO₂ sorption, and thus regeneration, of the selected char samples was carried out at 60 °C and between pressures of 0.05 bar and 1 bar, with 15 min equilibration times used for each adsorption and desorption point, and 30 full adsorption-desorption cycles carried out. The cyclic adsorption tests can be seen in Figure 7.12 to Figure 7.18. The calculated working CO₂ adsorption capacity for each sample is presented in Table 7.10. The working capacity was calculated for two scenarios: (1) the capacities were taken at the end of the equilibration time for each pressure point, and (2) capacities taken immediately after the pressure had reached the set-point, i.e. with no equilibration time. This second scenario models what is known as vacuum swing adsorption (VSA). The VSA test figures can be found in Appendix M.

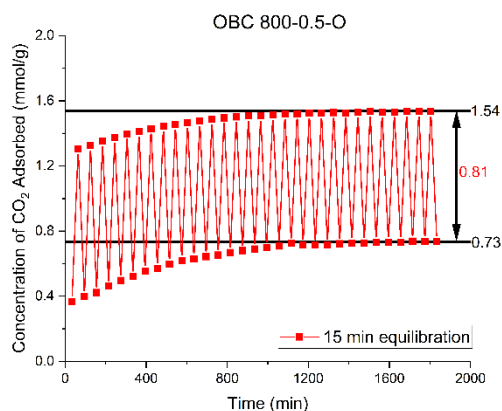


Figure 7.12: Cyclic Adsorption Results for OBC 800-0.5-O (0.05 - 1 bar cycling, 60 °C, 15 min Equilibration)

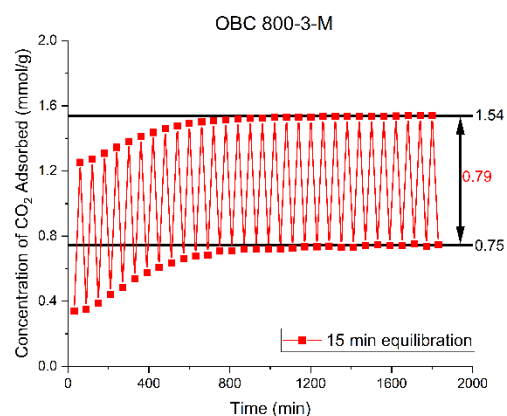


Figure 7.13: Cyclic Adsorption Results for OBC 800-3-M (0.05 - 1 bar cycling, 60 °C, 15 min Equilibration)

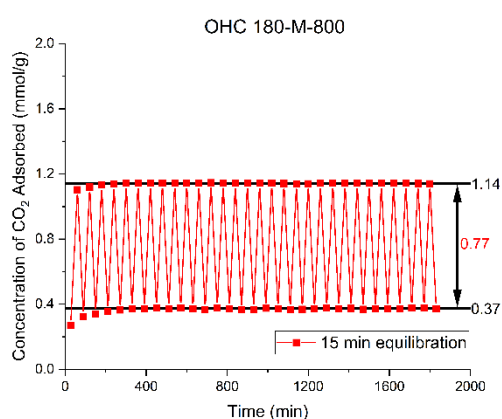


Figure 7.14: Cyclic Adsorption Results for OHC 180-M-800 (0.05 - 1 bar cycling, 60 °C, 15 min Equilibration)

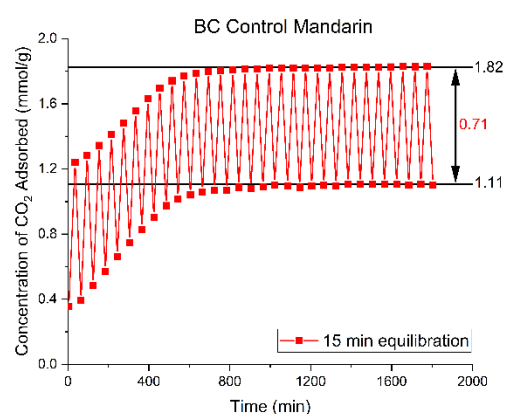


Figure 7.15: Cyclic Adsorption Results for BC Control Mandarin (0.05 - 1 bar cycling, 60 °C, 15 min Equilibration)

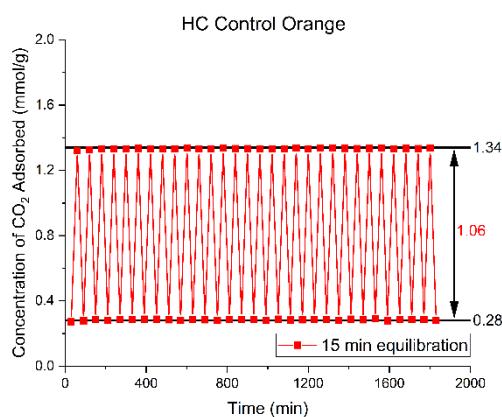


Figure 7.16: Cyclic Adsorption Results for HC Control Orange (0.05 - 1 bar cycling, 60 °C, 15 min Equilibration)

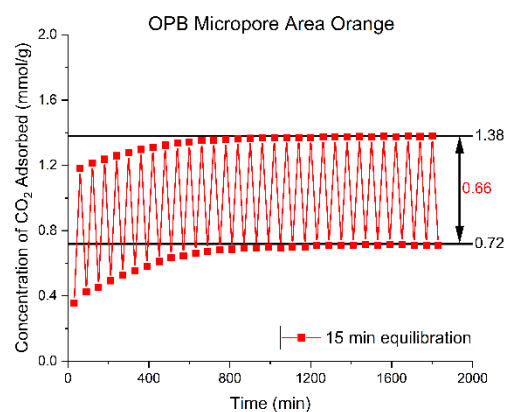


Figure 7.17: Cyclic Adsorption Results for OPB Micropore Area Orange (0.05 - 1 bar cycling, 60 °C, 15 min Equilibration)

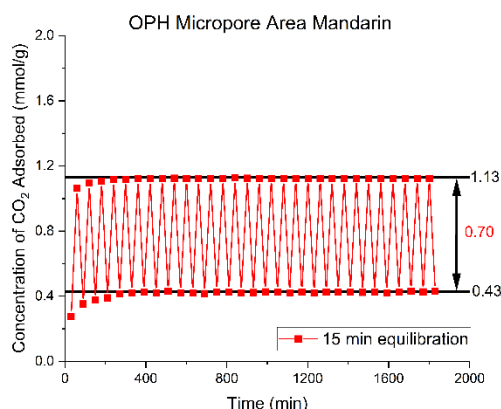


Figure 7.18: Cyclic Adsorption Results for OPH Micropore Mandarin (0.05 - 1 bar cycling, 60 °C, 15 min Equilibration)

From the figures above, it can be seen that it takes approximately 15 cycles for the capacity of the biochar samples to stabilise at a high and low level, but after this the working capacity is sustained for the remainder of the cycles. In contrast, the hydrochar samples do not appear to require this initial stabilisation period, instead reaching a steady working capacity almost instantly. Nonetheless, once each of the chars have stabilised they show excellent regenerative ability, with negligible loss of capacity over the period of 30 cycles. The best performing sample was HC Control Orange, achieving a working capacity of 1.06 mmol/g. Notably, this sample also showed stable capacities from the first adsorption cycle. Despite BC Control Mandarin's high CO₂ uptake at 1 bar, 60 °C, discussed in Section 7.2.3, it in fact has the lowest working capacity of the tested chars. This demonstrates the fine balance of uptake capacity, kinetics, and ease of desorption that must be found for optimal sorbent materials. The two optimal samples, OPB Micropore Orange and OPH Micropore Mandarin, show the lowest capacities of the seven chars tested. Interestingly however, both these samples see the largest increase in capacity when changing from VSA to 15 min equilibration times; there is no obvious explanation behind this, and further characterisation of these optimal chars would be required to give definitive conclusions.

In the biochar samples, there is a visible lag in reaching the maximum uptake observed in this cyclic testing, which is likely due to the slow kinetics of the biochar samples, as discussed in Section 7.4. The same principle explains why the capacity at low pressure cycles for these samples is around 0.7 – 1.11 mmol/g instead of desorbing down to ~0 mmol/g. If subject to 0.05 bar for a sustained period after adsorbing CO₂ at 1 bar, it would be expected that a larger quantity of CO₂ would desorb from these samples than that already removed in the 15 min, however this would likely take many hours or even days, which would not be viable for the desired application of the chars.

Table 7.10: Cyclic CO₂ Adsorption Working Capacities for Chars Produced in this Study

Sample	VSA Working Capacity (mmol/g)	15 min Equilibration Working Capacity (mmol/g)	Increase from VSA Capacity to 15 min Equilibration Capacity
OBC 800-0.5-M	0.68	0.81	19 %
OBC 800-3-M	0.73	0.79	8 %
OHC 180-M-800	0.65	0.77	18 %
BC Control Mandarin	0.63	0.72	13 %
HC Control Orange	1.03	1.06	3 %
OPB Micropore Orange	0.49	0.66	35 %
OPH Micropore Mandarin	0.56	0.70	25 %

Due to the relatively slow adsorption kinetics, there was a concern that the cyclic experiments would require a longer equilibration period to produce acceptable results. The first sample tested, BC Control Mandarin, was therefore tested through 30 cycles with two separate equilibration times: 15 min and 45 min, with the results of this shown in Figure 7.19. These values were chosen to test the rapid adsorption capacity of the materials and allow for a high number of cycles to be tested. In the same vein, it was expected that in industrial scenarios that short equilibration timescales would be implemented. From Figure 7.19, it is clear to see that equilibrium is reached within 15 min, therefore, there is no need for a longer

equilibration time to be used; the working capacity for the 45 min equilibration time experiment is the same as the working capacity for the 15 min equilibration time experiment. Therefore, all further experiments utilised a 15 min equilibration time.

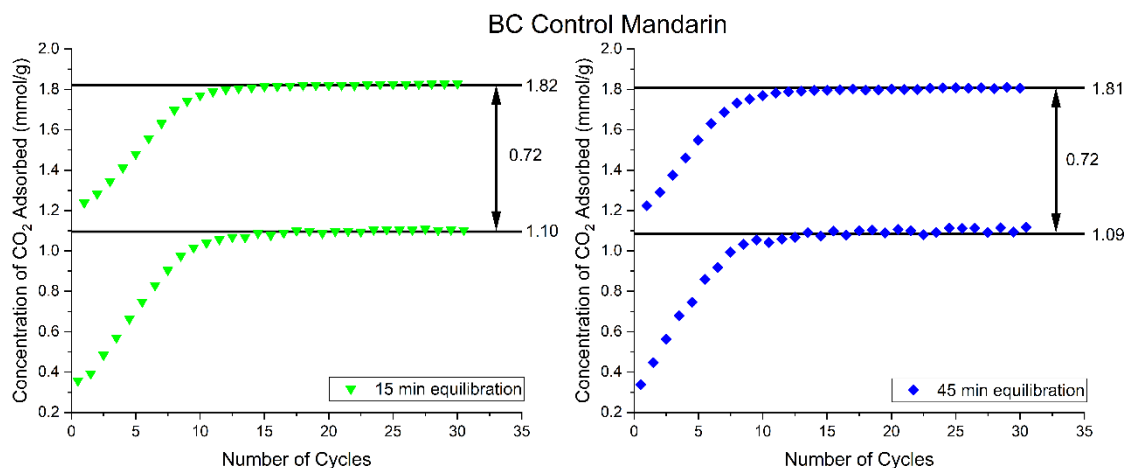


Figure 7.19: Comparison of 15- and 45-min Equilibration Times During Cyclic CO₂ Adsorption Testing for BC Control Mandarin Sample

Examples of cyclic CO₂ adsorption testing from literature is displayed in Table 7.11. Again, it is difficult to compare data from this study to these examples as many are reported at 25 °C, thus the temperature effect of adsorption must be considered. In addition to this, the experimental conditions between each cyclic experiment from literature vary, thus adding more uncertainty in the comparisons. It can be seen that the working capacities of other char materials are higher than those found in the orange and mandarin chars, but many of these are measured at 25 °C. If this was factored into the results, it could be suggested that the results from this project would be closer to the capacities found in literature. For example, in this work when the temperature was reduced from 60 °C to 30 °C, the CO₂ uptake for sample HC Control Orange increased from 1.36 mmol/g to 2.05 mmol/g, which is a not-insignificant change. It is positive to see that the ~100 % retention of capacity observed in the chars here matches with other studies, but also that this is maintained over a period of 30 cycles,

whereas some examples such pomelo peel and coffee ground chars begin to degrade after 10 cycles [5], [59].

Table 7.11: Comparison of Cyclic CO₂ Adsorption Capacity of Chars from Literature

Sample	Temp. (°C)	Cycling Conditions	Working CO ₂ Capacity (mmol/g) ²⁸	Cycles	Retained Capacity	Ref.
Bamboo Shoot BC	25	0 – 1 bar	3.5 *	5	90 %	[8]
Bamboo Sawdust BC	25	Temp. swing (25 – 70 °C)	1.7 *	10	100 %	[60]
Orange Peel BC	25	0 – 1 bar	4.3 *	5	97.3 %	[12]
Pine Sawdust HC	25	0 – 1 bar	3.0 *	5	100 %	[13]
<i>Delonix regia</i> seeds HC	25	Temp. swing (25 – 200 °C)	2.60	10	95 %	[21]
Pomelo Peel BC	10	0 – 1 bar	3.74	10	90.7 %	[5]
Bacterial Cellulose BC	25	Temp. swing (25 – 120 °C)	-	10	95 %	[28]
Andiroba Shells HC	25	0 – 1 bar	3.25 *	15	100 %	[61]
<i>Citrus aurantium</i> HC	25	0 – 1 bar	4 – 6.51	7	95 and 93 %	[1]
Pinewood and Sewage Sludge BC	25	0 – 1 bar	3.9 *	6	98 %	[62]
Coffee Grounds BC	35	Temp. swing (35 – 75 °C)	2.7 *	10	94 %	[59]

7.6 Chapter Summary

The volumetric CO₂ adsorption capacity was measured for all of the activated hydrochars produced in this study, and a selection of the produced biochars. The vast majority of these samples showed adsorption in the range of 2 – 3 mmol/g at 0°C, 1 bar, which is comparable to other carbon materials presented in literature, albeit lying in the lower range.

²⁸ * represent values that were approximated from figures as no definitive value was stated in research papers.

Gravimetric CO₂ adsorption across the range of 0 – 19.5 bar was carried out for the biochar and hydrochar samples presenting the highest micropore areas. Of the samples tested, BC Control Mandarin was the best performing, showing a CO₂ capacity at 0 °C of 3.4 mmol/g (1 bar) and 7.04 mmol/g (19.5 bar) respectively. The gravimetric adsorption results agree with literature findings that microporosity is the most important characteristics that influences CO₂ adsorption at low pressures (0 – 1 bar); similarly, the subsequent poorer level of adsorption at higher pressure for most samples concurs with suggestions that overall surface area, pore volume, and developed pore networks are key to aiding pore filling after the micropores become saturated.

The gravimetric isotherms were found to best fit the Dual Site Langmuir model, suggesting that there is a heterogenous array of adsorption sites on the surface of the chars; this is likely attributable to adsorption sites in ultramicropores and then adsorption sites in other areas of the material. The decrease in isosteric heat of adsorption of the samples with increasing CO₂ uptake concurred with this, and indicated surface heterogeneity. The calculated values of the isosteric heat of adsorption were < 60 kJ/mol, indicating that the main adsorption mechanism was physisorption. The double exponential model was used to fit the kinetic data of each sample as two simultaneous events were seen to occur, one fast and one slow for each relaxation time period. The use of this model provides further evidence to support the claims of surface heterogeneity, however, it can also be used to describe the process of molecular diffusion into and through the material's pores.

Finally, for a selection of chars with the highest CO₂ uptake, cyclic CO₂ adsorption was carried out between 0.05 – 1 bar at 60 °C to simulate industrial conditions. HC Control Orange was found to be the best performing char in this part of the study, displaying a working capacity

of 1.06 mmol/g. All the samples tested in this section showed negligible capacity loss over the period of 30 cycles, which shows their viability as reusable CO₂ adsorbents.

7.7 References

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8 Conclusions and Future Work

This chapter provides a summary of the research work carried out in this thesis, aiming to contextualise it within the current research landscape. It highlights the main achievements of the study, from the production of nitrogen-doped biochar and hydrochar using waste streams, addresses their capabilities in the field of CO₂ adsorption, and emphasises the circular economy credentials of these materials. Areas that could be investigated in more depth through future studies are proposed, and experiments that could have further complemented the body of work are highlighted.

8.1 Conclusions

The persistent, high volumes of industrial CO₂ emissions are the primary driver of climate change worldwide and, as such, it is key that research is carried out into technologies that can be utilised to curtail, and ultimately reduce, these emissions. A potential solution to this problem is the use of solid adsorbents in post-combustion carbon capture systems; it is, however, vital that these adsorbent materials perform effectively under typical flue gas conditions, and that they can be scaled to industrial levels. Additionally, the synthesis process for these materials should aim to be as sustainable and low cost as possible, and meet with circular economy principles.

This work focussed on a comparison of biochar and hydrochar sorbent materials produced from orange and mandarin peels, with and without the incorporation of nitrogen doping, using urea. These materials were synthesised and activated using CO₂, before undergoing chemical and textural characterisation, and subsequent testing for their CO₂ adsorption capabilities under conditions analogous to industrial flue gas streams. A Design of Experiments (DoE) process, including surface response methodology, was utilised to optimise the development of these materials and tailor them towards capture of CO₂ molecules.

Specific attention was given to porosity development and nitrogen doping, as these factors have been highlighted in the literature as vital to enhancing CO₂ adsorption.

Focusing on the biochar synthesis route, which was a one-step processing route, combining pyrolysis and activation; a screening design was carried out to assess the impact of four process parameters on three chosen responses: yield, microporous surface area (informed via N₂ sorption isotherms), and carbon content. Pyrolysis temperature, pyrolysis residence time, and peel type were all found to be influential in at least one of the responses, while CO₂ activating gas flow rate was not a significant factor. A subsequent optimisation design tested these three influential factors at a wider range and at multiple levels, allowing the development of optimisation models, which were used to produce six optimal biochars (three for each peel type) in order to maximise each response. The models for yield and carbon content were experimentally validated with acceptable predictions. However, the model for micropore area was not successfully validated, and consequently produced materials with lower microporosity than predicted. This was possibly due to the range of tested pyrolysis temperature and pyrolysis residence time values being too wide to accurately define an optimal point.

Nitrogen doping of the biochars was confirmed to be successful through elemental and surface chemical analysis (Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy). Textural porosity analysis evidenced the development of structured pore networks in samples produced at high temperatures, and confirmed the creation of micropores through CO₂ activation. Scanning electron microscopy was also helpful in identifying the development of larger mesopores. The doped sample with highest surface area produced during the optimisation phase, i.e. OBC 800-3-M, was found to have a N₂ calculated surface area of 355 m²/g, of which 86 % was attributable to micropores.

Nonetheless, the sample with the largest surface area was BC Control Mandarin, which had been produced as a control sample that was not subject to nitrogen doping; this sample displayed a N_2 calculated surface area of $436 \text{ m}^2/\text{g}$, with 82 % of this attributable to micropores. The samples produced to obtain optimal micropore areas displayed low N_2 surface areas of only $61 \text{ m}^2/\text{g}$ (OPB Micropore Orange) and $0 \text{ m}^2/\text{g}$ (OPB Micropore Mandarin). In terms of peel types, neither orange or mandarin peels were seen to be consistently superior in the production of porous biochars. However, it is key to acknowledge the limitations of N_2 as a probe gas for the determination of microporosity. Fortunately, within the timeframe of the study, equipment became latterly accessible that allowed for volumetric CO_2 sorption experiments to be carried out. Initial testing of the high surface area biochar samples via this method indicated increased microporosity compared to the results from N_2 adsorption, therefore, CO_2 sorption was used for future characterisation of hydrochars.

The production of hydrochars was carried out using a two-step process of hydrothermal carbonisation (HTC) followed by CO_2 activation. A similar screening design was utilised to investigate four hydrochar synthesis parameters, and their effect on the same three responses of yield, microporous surface area (now informed via CO_2 sorption isotherms), and carbon content. HTC temperature, activation temperature, and peel type were all ascertained to be influential with respect to at least one of the responses, while HTC residence time was not deemed to be statistically significant. Once again, an optimisation design tested the three influential parameters at a wider range and optimisation models were created in the same manner as previously undertaken for the biochar samples. These models were then tested experimentally, resulting in the synthesis of six optimal hydrochars. The results for optimal micropore area samples were very close to the predicted values: $351 \text{ m}^2/\text{g}$ actual vs $363 \text{ m}^2/\text{g}$ as predicted for OPH Micropore Orange, and $372 \text{ m}^2/\text{g}$ actual vs

381 m²/g as predicted for OPH Micropore Mandarin. However, this was likely due to the narrow range of activation temperatures tested, as the models had an R²-pred of 0 %, which meant they had no prediction power; thus, the micropore area models could not be experimentally validated. The carbon content models resulted in both OPH Carbon Orange and OPH Carbon Mandarin displaying elemental carbon content's that were approximately 5 % higher than model predictions. The yield models were less accurate, as the two samples produced experimentally, OPH Yield Orange and OPH Yield Mandarin, also outperformed the model, reporting yields approximately 22 % higher than the predicted values.

Hydrochar characterisation verified successful nitrogen doping, based on elemental and surface chemical analysis, although the elemental nitrogen content was lower for the hydrochars than it had been for the biochars. This was possibly due to different pre-treatment methods between the biochar and hydrochar synthesis routes, or different reaction pathways occurring in the pyrolysis and HTC steps in each process. In a similar contrast to the biochars, the majority of hydrochars were found to be non-porous, when analysed using N₂ adsorption techniques; the subsequent use of CO₂ adsorption techniques revealed an abundance of ultramicropores, which were not accessible to N₂ molecules at -196 °C. Sample OHC 180-M-800 was seen to have the highest CO₂ calculated micropore surface area of 407 m²/g. Meanwhile, the hydrochar control samples produced with no nitrogen doping displayed high porosity accessible via both N₂ and CO₂ adsorption techniques; the HC Control Orange sample was reported to have a N₂ calculated surface area of 394 m²/g, and CO₂ calculated micropore area of 486 m²/g. This raised the possibility that urea inclusion caused a change in reaction pathways during the hydrothermal carbonisation process, which inhibited the formation of well-developed pore networks, primarily resulting in the creation of micropores. Mandarin derived hydrochars were also seen to have slightly higher micropore areas on average than their orange derived counterparts; this could be a

result of compositional differences between the feedstock materials but further investigation is required.

A selection of the highest surface area biochar and hydrochar samples were tested for their CO₂ adsorption performance using a gravimetric adsorption system at temperatures of 0, 30 and 60 °C, in the pressure range 0 – 19.5 bar. Sample BC Control Mandarin was seen to be the best performing adsorbent, showing CO₂ capacities of 3.34 mmol/g (1 bar) and 7.04 mmol/g (19.5 bar), at 0 °C. The presence of ultramicropores was seen to be the most important characteristic for CO₂ adsorption at low pressure (below 1 bar), while total pore volume was more imperative for successful adsorption at higher pressures (5 – 19.5 bar). The presence of nitrogen-containing functionalities upon the doped samples was not found to give any notable increase in CO₂ adsorption capacity for either biochars or hydrochars; this is notable, as much of the literature in this area of study states that the inclusion of these nitrogen-containing functionalities leads to an increase in CO₂ adsorption through enhanced interactions with nitrogen-containing moieties. It is important to highlight this finding, as it is significant to recognise that nitrogen doping should not be seen as a definitive method for improving the adsorption capacity of porous chars; instead, its impact can be varied depending on the chosen precursor material, and applied synthesis process. The isotherms collected for each of the ten samples best fit a Dual Site Langmuir adsorption isotherm model, which is indicative of surface heterogeneity within the materials. The samples displayed a range of heats of adsorption, in the range 25 – 52 kJ/mol, which suggests physisorption is the dominant adsorption mechanism, and a general trend of decreasing heat of adsorption as CO₂ uptake increases offers further evidence of surface heterogeneity. A double exponential kinetic model was used to describe the kinetic data for each sample, indicating that there were two rate-determining steps in the adsorption process. These could describe kinetics limited by pore diffusion effects (slow rate due to diffusion into pores and fast rate once

inside them) or by the heterogenous nature of the surface of the chars (slow rate due to adsorption onto less favourable sites and fast rate of adsorption onto more favourable sites). Finally, the samples with the highest CO₂ capacity were tested for their cyclic adsorption properties. The HC Control Orange sample presented the highest CO₂ working capacity of 1.06 mmol/g in the range of 0.05 – 1 bar, at 60 °C. It was notable that the biochars tested in this manner required around 10 cycles to reach stability, while the hydrochar materials reached steady working capacity almost immediately. Over the course of 30 cycles, all samples tested showed negligible capacity loss, which is favourable in terms of their suitability for CO₂ capture applications.

In reference to the aims of the thesis, presented in Chapter 2, it can be said that the majority of those set out have now been achieved. The production of nitrogen-doped biochars and hydrochars was successfully carried out using urea as doping agent and CO₂ as an activating agent. Material characterisation was then carried out for each of the produced chars, and these results were analysed to provide an assessment of the process conditions and parameters. These results were also used to inform the DoE methodology which was in turn utilised to tailor the synthesis of each char type. Optimisation models were produced from each DoE in an attempt to maximise the CO₂ adsorption performance of the chars; this gave mixed results in terms of response optimisation, but did not ultimately produce the most superior materials in the study. Testing CO₂ adsorption for a selection of the produced materials resulted in a non-doped control sample, BC Control Mandarin, displaying the highest CO₂ capacity in the study under conditions analogous to industrial flue gas streams, and at higher pressures up to 19.5 bar. The optimisation process of peel-derived chars doped with urea was carried out, but ultimately the inclusion of nitrogen-containing functionalities within the char did not lead to an improvement in CO₂ adsorption; this conflicts with previous studies in the literature. As a consequence, the results presented in this study should serve

to highlight that the use of nitrogen doping does not guarantee an increase in the adsorption capacity of the final sorbent material.

When comparing between the two feedstock materials, and the two synthesis routes, no one factor is overall superior. The difference in CO₂ adsorption capacity between orange derived and mandarin derived chars was not significantly different. Similarly, the CO₂ capacities of the tested biochars and hydrochars fall within the same approximate range for each set of tested conditions. The cumulative characterisation and CO₂ adsorption testing of the synthesised biochar and hydrochar materials presented here demonstrates the suitability of these materials for use in the field of carbon capture, and sets out foundations for the future use of these sorbents in industrial applications. This work has successfully valorised a waste biomass stream, specifically within carbonaceous char materials for CO₂ capture, in line with circular economy principles. Collectively, the process has contributed new materials and insights to the field of sustainable engineering.

8.2 Future Work

This project has presented a detailed study into two carbonaceous char production process routes, including characterisation of the materials and proof of their applicability to CO₂ adsorption applications. However, in order to drive innovation and development of sustainable materials for use in carbon capture to achieve set environmental goals, research into the field of solid adsorbents must continue. Some areas for consideration in related future studies are, therefore, proposed below.

Although the impact of four process parameters were investigated for each synthesis route in this study, there remain other factors that could be varied to measure their impact on char characteristics. Examples of these include pyrolysis/HTC ramp rate, initial feedstock particle size, feedstock variation (different species of orange and mandarin peel), pressurised

carbonisation, and ratio of doping agent (urea) to feedstock. For hydrochar synthesis, the ratio of feedstock to solution, and autoclave filling ratio are factors that require further research. This study does not claim to be exhaustive in regards to its conclusions around all synthesis process factors, however, findings presented here are clearly foundational for future work with the same feedstock.

When using biomass as a feedstock for these types of processes, it is common for issues to arise surrounding the storage and subsequent aging of both the feedstock and the produced materials. In future, it would be interesting to examine the effect of precursor material aging on the final char product, and similarly, the effect that aging has on the char over a defined time period. A possible experiment could be using the same batch of feedstock to produce char samples at identical conditions but a defined period of time apart, and testing the produced chars at several time points to monitor the change in characteristics and capacity. This is a topic that is important to address for all biological based feedstocks.

In general, there are many aspects of the experimental design that could be altered to examine other aspects of char production or application. The optimisation process followed in this study can be applied to different feedstocks, if more suitable precursor materials are identified. Alternatively, different nitrogen doping agents could be introduced to the process, providing they match with the environmentally-conscious design goals of the project, as literature heavily suggests nitrogen doping results in performance enhancement through provision of favourable binding sites. The use of nitrogen rich precursors could be implemented to avoid the need for a doping agent entirely. In terms of application of the chars already mapped in this work, preliminary testing could also be carried out in other areas, such as water remediation, to identify other potential uses. Similarly, any changes to the synthesis process could lead to modifications in porosity or surface functionalities, which

would, in turn, present opportunities to target other pollutant molecules, in either gaseous or liquid phase sorption.

To ensure accuracy in the models produced through DoE statistical analysis, it is important to carry out replicate experiments in order to increase precision within the analysis. Due to the large numbers of both biochars and hydrochars synthesised in this study, it was not possible to produce many replicate samples and fully characterise them. In future it would be beneficial to repeat syntheses and characterise the samples, which would reduce the standard error in measurements and enable more accurate modelling of the significant factors in the process(es). This, in turn, would lead to an increase in the prediction accuracy of the optimisation models. Similarly, replication of centre points in the optimisation designs would allow for confirmation of process stability and provide an inherent test for curvature in the processes being examined. The utilisation of Multi-Response Surface Optimisation would allow for the three chosen responses to be optimised in an individual model, producing one optimal sample; thus, if successful, this could result in the production of a highly microporous char with both high elemental carbon content, and a suitable yield that would be more amenable for process scale up studies. The need for high elemental carbon contents is especially important, as this maximises the carbon that is stored within the carbonaceous char materials, thus, reducing associated emissions from waste degradation.

As the ability to carry out volumetric CO₂ adsorption was not available during the biochar DoE study, it would be interesting to assess the significance of process factors in relation to the microporous characteristics derived from CO₂ data rather than the microporous surface area measured via N₂ adsorption as has been done. This may result in a more precise and appropriate optimisation model for the biochar synthesis process being produced.

This study has measured CO₂ adsorption capacity at temperatures equivalent to those of flue gas emissions streams; however, to achieve more industrially applicable results, it would be more appropriate to also test adsorption at this temperature and with a mixed gas stream of comparable CO₂ concentration. As CO₂ is commonly found at approximately 15 vol% in flue gas streams, a mixed stream containing CO₂ and the balance of N₂ would give more realistic adsorption predictions and allow for determination of the materials selectivity for CO₂ over N₂. Additionally, the inclusion of water vapour and trace contaminants would bring more accurate representation of practical scenarios; note that these are complex experiments to undertake and required specialised equipment. Cyclic adsorption could be examined further by performing lengthier cycling, allowing determination of long-term stability under relevant process conditions, and the subsequent reusability of the samples. Furthermore, packed bed/column setups could be utilised for adsorption experiments to simulate the technology used in post-combustion carbon capture systems.

If these tests were successful, the next stage would be to consider scale up of the synthesis process. The choice of reactor for production at scale should be examined, and testing of different configurations may be required, such as a move towards a vertical reactor, which could provide more equal exposure to CO₂ activating gas, and thus, enhanced mass transfer. This, in turn, may require additional characterisation to ensure consistency in the char properties. Choices, such as plant location, would require detailed planning to ensure close proximity to a reliable source of raw peel feedstock; this would be essential in order to minimise transport emissions. Additionally, the pre-processing of the peels at an industrial scale would require important consideration, including issues such as the size of equipment required, how to maintain feedstock consistency being fed to the process, and how to avoid biological degradation of the raw peels. Testing the chars in breakthrough systems for multicomponent gases, including contaminants, would also be an important next step to

carry out in assessing their capability in industrial systems. Similarly, methods for sorbent regeneration would require rigorous experimentation and study to ensure that the most environmental and energy efficient method was utilised. This would be a vital factor to consider, as the level of regeneration that can be achieved will ultimately define the maximum capacity that the char materials can provide in the final CO₂ capture system. To determine the true environmental impact of the production process of these adsorbent materials, a Life Cycle Assessment and accompanying Techno-Economic Assessment could be carried out. This would examine the energy and economic cost of production of the char materials in-depth, the net-environmental impact, and the feasibility of scaling the process up to an industrial level. This would also allow for more rigorous comparison with current industrial post-combustion carbon capture techniques, and more precise definition of the circular economy, and sustainable engineering credentials, of this work.

Appendices

Appendix A: Literature Findings of Biochar and Hydrochar Production

Parameters

Appendix Table A.1 and Appendix Table A.2 present an overview of literature studies that have produced biochar and hydrochar materials respectively.

Note: if data was not provided by study, then it is marked by ‘-’ in the table.

Appendix Table A.1: Previous Literature Studies That Have Produced Biochar Materials

Feedstock	Pyrolysis Temperature (°C)	Pyrolysis Time (h)	Pyrolysis Ramp Rate (°C/min)	Nitrogen Doping (With Focus On Urea)	N ₂ Flowrate (mL/min)	Further Activation	Ref.
Camphor Leaves	500	2	-	No	-	Chemically activated with KOH	[167]
Celtuce Leaves	600	-	-	No	-	Chemically activated with KOH	[168]
Garlic Skin	600	2	5	No	-	Chemically activated with KOH	[237]
<i>P. nigra</i> Wood and Cellulose Fibres	480, 600 and 700		5	No	-	No	[165]
Potassium Citrate	700, 750, 800 and 900 (after freeze drying)	2	3	8 g of urea dissolved in 60 mL water along with feed	-	No	[238]
<i>Medulla tetrapanacis</i>	70	2	-	1:1 and 2:1 mass ratios of urea to feed	-	No, but NaHCO ₃ included in mixture	[239]
Litchi Branch	400, 600 and 800	1.5	10	1:1 mass ratio of urea to feed	400	No, but NaHCO ₃ included in mixture	[240]
Bamboo	700	2	10	0, 1 and 4:1 ratios of urea to feed	400	No but KHCO ₃ included in the mixture	[241]
Corn Stalk	500, 600 and 700	2	10	2:1 mass ratio of urea to feed	400	No but NaHCO ₃ included in the mixture	[242]

Cocoa Shell	400 and 700	2	10	3:1:1 mass ratio of feed:urea:NaHCO ₃ was used	400	No but NaHCO ₃ included in mixture	[243]
Coconut Shells	145, 600 and 700	6	5	Urea, but quantity not specified	-	Partial carbonization, followed by activation with ionic KOH and finally pyrolysis	[244]
Rice Straw	700	2	5	6 g of urea with 5 g of feed, and FeCl ₃ .6H ₂ O also included	-	No	[245]
Stillage (waste from winery)	600 and 900	1	10	Urea phosphate, ammonia phosphate and ammonia polyphosphate, each tested at 1:1 mass ratio	-	No	[246]
Sugarcane Bagasse	600	0.5	10	Urea solution, at 5, 10, 15, 20 and 25 wt% urea	-	Chemical activation with KOH	[132]
Sawdust	600 – 900	2	-	Urea phosphate, at 0.5, 1 and 2:1 mass ratios of UP:feed	150	No	[175]
Microalgae Powders	800	0.333	-	1:1 mass ratio of urea to char after initial step	250	Chemical activation with KOH	[247]

Orange Peel Wastes after Oil Extraction	550	1	10	No	20	Physical with CO ₂ – 800 °C, assumed 20 mL/min, with mix of CO ₂ :N ₂ of 1:2.	[184]
Whitewood	500	1 second	-	No	-	Activation with CO ₂ , steam and KOH all carried out. CO ₂ – heated to 890 °C at 3 °C/min, CO ₂ flow of 130 mL/min, for 1.2 h	[248]
Olive Pomace	500	0.25	10	No	100	Chemical activation with K ₂ CO ₃ , physical activation with steam, and a combination of both.	[249]
Cherry Stones	750, 790, 850, 909 and 950	Not stated – duration was based on targeted yield	10, 12, 15, 18 and 20	No	Single stage under CO ₂ – 100 mL/min	No	[229]
Corn cob, Grape Seeds and Birch	700	1	283	No	Argon – 10 mL/min	Physical activation with steam	[250]
Elm, Fir and Bamboo Forest Waste	500	0.5	10	No	300	CaO included in pyrolysis stage	[251]
Eucalyptus Woodchip	400	1	25	No	100	Physical activation with CO ₂ – 100 mL/min flowrate, 600-900 °C, and between 1-5 h	[228]

Pine Sawdust	550	2	7	No	-	Some physically activated BC were produced using steam	[252]
Pine Bark	250, 300, 350, 500, 600, 700, 750 and 850	1	0.1, 0.5, 10 and 5	No	100	Physical activation with steam and CO ₂ – for CO ₂ flowrate of 100 mL/min used, 0.5 h, 500, 700 and 850 °C with rate of 20 °C/min. Chemical activation also carried out with KOH	[253]
Orange Peels	700	2	-	No	-	Chemically activated with KOH	[185]
Orange Peels	450-550	-	10	No	400	Chemically activated with ZnCl and H ₃ PO ₄	[186]
Orange and Lemon Peels	600	3	-	No	-	Chemically activated with H ₃ PO ₄	[187]
Orange Peels	700	-	-	No	150	Char mixed with K ₂ CO ₃ pellets and activated in a microwave method	[188]
Passion Fruit Peel	450	0.5	-	No	-	Chemically activated with potassium oxalate monohydrate and EDA at 700 °C	[254]
Alpha-d-glucose, Defatted Soya Flour and Microalgae	750-800	1	3	No	-	One-pot – mixed with potassium oxalate monohydrate and calcium carbonate nanoparticles	[255]

Camphor Seed Husks	600-800	1	5	No	-	Mixed with hydroxylamine hydrochloride prior to pyrolysis	[256]
Alkali Lignin	750	3	-	No	-	Washed with acid.	[257]
Hairy Crab Shell	500	1	10	No	200	Chemically activated with KOH at 600-900 °C	[258]
Pine Wood Sawdust	500-700	0.333	-	No	60	No	[259]
Coconut Shells	800	-	-	No	-	Chemically activated with KOH and NaOH	[260]
Cucumber Peels	700	2	-	No	200	Chemically activated with KOH and melamine	[68]
Solid Digestate	600	1	10	No	-	Chemically activated with H ₃ PO ₄	[261]
Pine Nut Shells	500	1.5	5	No	200	Chemically activated with KOH	[169]
Palm Oil Residue	650	1	10	No	-	Physically activated with CO ₂ (900 °C, 6.5 – 18.8 h, 12 mL/min) Chemically activated with NaOH (700 °C, 1 h)	[262]
Soybean Straw	500	-	-	No	400	Physically activated with CO ₂ , NH ₃ and a mixture of both (500 – 900 °C, 0.5 h, 500 mL/min)	[174]

<i>Sargassum</i> and Enteromorpha Seaweed	400, 600 and 800	2	-	No	-	Chemically activated with KOH	[263]
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Appendix Table A.2: Previous Literature Studies That Have Produced Hydrochar Materials

Feedstock	HTC Temp (°C)	HTC Time (h)	HTC Ramp Rate (°C/min)	Ratio of Feed:Water	Dry or Wet Feed	Nitrogen Doping (With Focus On Urea)	Further Activation	Ref.
Jujun Grass and Camellia japonica	250	2	-	-	Dry	No	Chemically with KOH	[164]
Olives Stones	220	16	-	30-50 wt% of dry olives, balance made up by water	Dry	Doped with ammonium sulphate	Chemically activated with 3 activating agents	[27]
Sugar Cane Biomass	220	12, 24, 36 and 48	10	0.5 g of feed and 20 mL of water	Dry	No	Chemical with KOH	[103]
Acrylic Acid	190	14	-	1, 5 and 10 wt% acid added to 60 mL of 0.1 g/mL glucose solution	-	No	Chemically activated with KOH	[264]
Silver Fir Sawdust	200	0 and 2	-	7:1 ratio of water to biomass	Dry	No	Chemically activated with KOH	[100]
Sargassum horneri	180	2	-	10 g feed to 40 mL water	Dry	Doped with ammonium iron (II) sulfate hexahydrate	Chemically activated with KOH	[57]
Orange Peels	240	2	-	6 g feed and 60 mL water	Dry	Doped with melamine	Chemically activated with K ₂ C ₂ O ₄	[130]
Cocoa Shell Powder	240	24	-	1 g of feed and 10 mL of water	Dry	No	Doped with APTES	[265]

Corncob	230	8	-	12 g feed to 120 mL water	Dry	No	Chemically activated with 3 activating agents	[162]
Eucalyptus Sawdust, Potato Starch and Cellulose	250	2	-	320 g/L of feed in water	Dry	Doped with melamine	Chemically activated with KOH	[60]
Orange Peel	210	2	-	15 g feed and 120 mL of 10 wt% urea solution	Dry	Yes – 10 wt% solution of urea	Chemically activated using KOH	[214]
Glucose Solution	190	18	-	10 wt% glucose solution	-	No	Chemically activated using KOH	[266]
Garlic Peel	200	24	-	1 g of feed and 60 mL of 1 wt% acid solution	Dry	No	Carbonised at 400°C, 2 hours, 4°C/min ramp rate, N ₂ flow. Then chemically with KOH	[31]
Glucose	200	5	-	5 g feed and 20 mL water	Dry	Yes, up to 3 g of urea used in activation stage	Chemically activated with KHCO ₃	[267]
Loblolly Pine	260	0.5	-		Dry	Yes, choline chloride: urea (ChCl/urea) solution used (mole ratio of 1:2)	Chemically activated with KOH at 800°C	[268]
Algae and glucose mix	200	24	-	Microalgae:glucose of 1.5	-	No, but N-doped as microalgae has high N content	Chemically activated with KOH at 650-750 °C	[269]

Lignin	300 – 390	-	-		-	No	Chemically activated with KOH at 600-900 °C	[270]
Polyacrylonitrile fiber	180	20	-	-	-	Ammonium sulfide used to dope	Chemically activated using KOH at 550-650 °C	[271]
Lemon peel waste	180	1	-	-	-	No	Chemically activated using KOH, and KOH + alum at 800 °C	[54]
D-glucose	180	12	-	-	-	Yes, urea mixed with HC then carbonised at 350 °C	Chemically activated with K ₂ CO ₃ at 600-700 °C	[131]
D-glucose	180	12	-	-	-	Yes, 1:1 ratio of urea:feed before HTC	Chemically activated with KOH at 600-700 °C	[272]
Banana peel	180-220	3	-	4 g of peel to 60 mL of water	-	No	Chemically activated with KOH at 600-700 °C	[273]
Microcrystalline cellulose	200	12 - 48	-	2 g of feed and 40 mL of water	-	No	Chemically activated using NaOH or KOH at 600 °C	[177]

Banana pseudo-stem	120-280	0.09	-	20 g of feed and 300 mL of water	-	No	Chemically activated with KOH at 700 °C	[274]
Cotton straw	240	4	-	-	-	No	Chemically activated with potassium and calcium carbonate at 900 °C	[275]
Aqueous glucose solution	195	3	-	-	-	No	Freeze dried then chemically activated with potassium bicarbonate at 750-800 °C	[276]
Tea waste	200	10	-	10 g feed and 80 mL water	-	No	Physical activation at 700 °C under N ₂ . Chemical activation with potassium bicarbonate at 700°C	[277]
Lotus stalks	200	5	-	6 g of feed with 50 mL of water	-	Yes, 6 g of urea with 6 g of feed pre-HTC	Chemically activated with potassium bicarbonate at 800 °C.	[278]
Alpha-glucose	220	4	-	1g feed to 10 mL water	-	No	Some samples were produced	[279]

							with aluminium chloride added to the mixture before HTC. Chemically activated with potassium carbonate and bicarbonate at 650 °C.	
Cattail (after anaerobic digestion)	250	4	-	3 g of feed to 50 mL water	-	No	Chemically activated with sodium carbonate, bicarbonate and chloride at 900 °C	[280]
Bamboo powder	200	24	-	40 g of feed to 160 mL of HCl	-	No	Chemically activated with sodium bicarbonate and maleic anhydride at 140 °C.	[281]
Moso bamboo	180-260	1	-	100 g of feed to 1 L of potassium permanganate	-	No	-	[282]
D-glucose	180	12	-	28 g of feed to 100 mL water	-	No	Some HC's made with acrylic acid or vinyl sulfonic acid.	[283]

							HC's then mixed with solutions of potassium/sodium carbonate or hydroxide and dried (no heating)	
Microalgae	222	0.37	-	200 g feed to 1 L of water and methanol mix	-	No	Chemically activated with KOH at 525-825 °C	[284]
PVC pipes	220-280	1	-	16 g feed and 400 mL water	-	No	Chemically activated with KOH at 600-800 °C	[285]
Orange peels	150	3	-	5 g feed to 50 mL of phosphoric acid	-	No	Chemically activated with potassium carbonate at 100 °C	[216]
Sugarcane bagasse	220	12-48	-	0.5 g of feed to 20 mL water	Dry	No	Chemically activated with KOH at 800 °C	[103]
Camphor leaves and camellia leaves	180-300	5	5	3 g feed and 60 mL water	Dry	No	Chemically activated at 800 °C	[102]
Poplar and spruce wood	180-220	1.5	-	10g feed and 40 mL of water	Dry	No	Chemically activated with KOH at 800 °C	[286]

Sucrose	180	24	-	Diff solution conc.'s	Wet	No	Chemically activated with KOH at 750 °C	[287]
Sawdust and Polypyrrole	250	2	-	6.4 g feed with 20 mL water	Dry	No	Chemically activated with potassium oxalate at 600-900 °C	[288]
Glucosamine hydrochloride	200	6	-	5 g feed in 50 mL water	-	No	Chemically activated with caesium bicarbonate at 700-800 °C	[289], [290]
Loblolly pine	180-260	0.5	5	1:10 of feed to water	Dry	No	Chemically activated with KOH at 800 °C	[291]
Microalgae	160	0.17-1	-	1 g of feed, 10 mL of water and some DES	-	No	Choline chloride and formic acid used to make DES. Chemically activated with KOH at 500-800 °C	[292]
Sewage sludge	200-210	3	-	Mix	Wet	No	Chemically activated with KOH at 550-750 °C	[293]

Loblolly pine	200-260	0.5	-	20 g feed and 200 mL water	Dry	Yes, one had urea with choline chloride	Physically activated at 600 °C. Chemically activated with DES after physical activation	[101]
Orange peel	180-220	3	-	1:15 ratio of feed:water	Dry	No	Chemically activated with KOH at 700 °C	[171]
Glucose	200	6	-	5 g feed and 50 mL of water	Dry	No	Oxamic acid potassium salt used in HTC. Chemically activated with potassium salts at 700-800 °C	[294], [295]
Biogas digestate	190-250	3-6	5	15 wt% solid solution	Wet	No	Chemically activated with KOH at 600 °C	[296]
Rambutan peel	170	1.5	-		-	No	Chemically activated with KOH at 600-900 °C	[297]
Tobacco stem	230	2	-	35 g feed and 350 mL water	Dry	No	Chemically activated with NaNH ₂ at 450-550 °C.	[298]

Grape seeds	180-300	16	-	20 g of feed, and solution was altered to 10-60 wt% solids	-	No	Chemically activated with KOH, FeCl ₃ (both at 750 °C) or H ₃ PO ₄ at 500 °C	[299]
Orange peels	210	2	-	15 g feed and 120 mL 10 wt% urea solution	Dry	Yes, urea solution	Chemically activated with KOH at 800 °C	[32]
Sludge	190-220	2-24	-	60 g total sludge + water	-	No	Chemically activated with H ₃ PO ₄ at 450 °C	[300]
Sugarcane bagasse	240	10	-	3 g of feed and 60 mL of water of sulphuric acid	Dry	No	Chemically activated with KOH at 800 °C	[301]
Pomelo peel	210	2	-	30 g feed and 240 mL water	-	No	Chemically activated with KOH at 700 °C. Copper loaded onto some samples.	[302]
Mango seed shells	180-250	5	-		Dry	No	Chemically activated with KOH at 600 °C	[303]
Jute	200	4	-	7 g of feed and 70 mL of water	-	No	Chemically activated with KOH at 600-1000 °C	[304]
Glucose	190	10	-	6.75 g of feed and 50 mL water	-	No	Chemically activated with KMnO ₄ , NaOH +	[305]

							KMnO ₄ and KOH + KMnO ₄ at 800 °C	
Sucrose	190	5	-	15 mL feed solution	Wet	No	Chemically activated with KOH or K ₂ CO ₃ at 800 °C	[306]
Canola stalks	200-275	0.5-2	-	3 g feed and 15 mL water	Dry	No	Chemically activate with KOH at 700 °C	[307]
Digestate	250	5.33	-	Mix of digestate and water, some include H ₂ SO ₄ too	Wet	No	Chemically activated with KOH at 600 °C	[308]
Grape seeds	180-250	1	-	6 g feed and 20 mL water	Dry	No	Chemically activated with KOH at 600 °C	[309]
Chitosan	220	12	-	3 g feed and 18 mL water	-	No	Chemically activated with KOH at 600-800 °C	[310]
Onion peels	200	4	-	300 g/L mix of peels in water	Dry	No	Carbonised at 500 °C after HTC. Chemically activated with KOH at 600-800 °C	[311]
Alpha-d-glucose	180	5	-	Solution – no mention of conc	-	Some doped with melamine	Chemically activated with potassium	[312]

							bicarbonate at 850 °C. Comparison materials were activated using potassium carbonate and KOH	
Sewage sludge and algae	180	1	-	Mix of ratios			No activation carried out. Sodium bicarbonate included in mix.	[313]
Pine sawdust	220	4	-		-	Some doped with melamine and ammonium chloride	Physical activation carried out with CO ₂ at 875 °C. Chemical activation carried out with potassium bicarbonate at 850 °C	[314]
Glucosamine hydrochloride	200	6	-	5 g feed with 50 mL water	-	No	Chemically activated with KOH at 550-700 °C initially (first paper). Second paper – activate with	[290], [315]

							potassium acetate, bicarbonate, carbonate and oxalate monohydrate. Temp 700-900 °C.	
Glucose	200	6	-	5 g glucose, 5 mg CTAB and 50 mL water	-	Use thiourea for N and S doping	Chemically activated with thiourea and potassium bicarbonate at 700-800 °C	[267], [316]
Chitosan	180	12	-	60 mL water with 10% mass frac feed, eutectic salt also used as catalyst	Dry	No	Carbonised at 300°C for 4 hours, then chemical activation with KOH	[317]
Citrus aurantium Waste Leaves	80 – 250	4 – 24	-	3 g feed and 20 mL water	Dry	Doped with N-rich microalgae	Chemically activated with ZnCl ₂ and physically activated with CO ₂ – this was 800°C for 2 hours under CO ₂ flow	[163]

Citric Acid	800 W (microwave)	0.09	-	8.75 g feed and 20 mL water	-	Yes, 7.5 g of urea	Carbonised at 700°C then chemically activated with KOH	[318]
Delonix regia seeds	180	16	-	30g feed to 100 mL water. Citric acid inc. as acid catalyst	-	No	Physically activated with N ₂ at 450-750 °C. Then best sample was chemically activated with KOH at 650 °C	[319]
Glucosamine hydrochloride	200	6	-	5 g feed and 60 mL water	Dry	No	Chemically activated with salt (HAPS) at 900 °C	[320]
Wood sawdust and lignin	250	2	-		Dry	No	Chemically activated with KOH – mixed together, compacted then heated to 600- 650 °C	[321]
Coconut shells	220	3	-	15 g of feed with 60 g of water	Dry	No	Chemically activated with KOH at 700 °C. Chemical activation also carried out using Chlorella	[322]

							microalgae and MgO, with sonication.	
Glucose, sodium oleate and Pluronic P123	170	24	-	43.5 mg of P123, 36.5 mg of sodium oleate, 3.168 g of glucose and 40 mL of water	-	Yes, urea added after HTC and before activation	Chemically activated with potassium bicarbonate and urea at 700 °C	[323]
Textile waste	210-240	1	5	10 g of feed and 150 mL water	-	No	Chemically activated with ZnCl ₂ at 500, °C, KOH at 700 °C and physically activated with CO ₂ at 850 °C	[324]
Wastewater sludge	170-260	1	20	170 g of feed	-	No	Physically activated with CO ₂ at 900 °C. Chemically activated with KOH at 700 °C	[325]
Hazelnut shells	180	3	-	Mix of feed, water and HCl	-	No	Physically activated with N ₂ at 600 °C. Then chemically activated with KOH and H ₃ PO ₄ at 500 and 400 °C respectively.	[326]

Hogweed	200	24	-	3 g feed and 65 mL water	-	Yes, urea and/or NH ₄ Cl used and activated at 600 °C. Urea also used in HTC for one sample	Chemically activated with KOH at 400-800 °C. Chemically activated with ZnCl ₂ at 600 °C. Activation by Fenton's reagent and UV also carried out	[327]
Andiroba Shells	180	12	-	-	Dry	No	Physically activated with CO ₂ – 880°C for 1, 5 and 10 hours under 80 mL/min CO ₂ flow	[328]
Starch	190	12	-	15 g feed and 50 mL water	Dry	No	Physically activated with CO ₂ – heated under 60 mL/min N ₂ flow to 500°C, 5°C/min, 3 hours. Then heated to 1000°C and held for 2.5 hours under 100 mL/min CO ₂ flow	[148]
Pineapple Peel	160, 180, 200, 220	2, 4, 6, 8	5, 10, 20, 30	30 g of feed, unknown water	Dry	No	Carbonised at 600°C, 2 hours,	[113]

							10°C/min ramp rate and 150 mL/min N ₂	
Microalgae Mixed with Pine Sawdust	180 and 220	1	-	10 g of feed as paste, water content of this paste ranged from 73-88 wt%.	Wet	No	Conformed into pellets, then physical activation with CO ₂ – 700 and 800°C for 1 hour, 5°C/min and 50 mL/min CO ₂ flow	[329]
Spent Coffee Grounds	220	5	5	20 wt% coffee grounds, and balance water	Dry	Yes, 0.5, 1, 3 and 5 M slurries of urea used	Carbonised at 600°C	[330]
Prickly Pear Seed Waste	180, 200 and 220	1, 4, 8, 16 and 24	6	6 g feed and 100 mL water	Dry	No	Physically activated with CO ₂ – 1 hour at 800°C with 100 mL/min gas flow	[331]
Wood	N/A (carried out prior to receiving)	N/A	-	-	-	No	Some were pyrolyzed with N ₂ gas (400-900°C, 1-2 hours). Others underwent physical activation with CO ₂ – 700-850°C	[332]

							for 1, 2 and 3 hours. All heating rates were 50°C/min and gas flowrates were 0.4 mol/hour (150 mL/min). Some steam activation was also carried out	
Pine Cones	220	24	-	Mass ratio of 1:2 for solids:liquids	Dry	No	Yes, physically activated with steam	[250]
Cow manure	200	24	-	4 g feed, 112 mL water and 38 mL NaOH solution	-	No	Carbonised after at 400 °C for 1 hour	[333]
Glucose, CoSO₄·7H₂O and hexamethylenetetramine	180	6	-	5 g total feed and 50 mL of water	Dry	Yes, hexamethylenetetramine (HMT)	Physically activated at 500 °C for 2 hours then 700 °C for 1-4 hours (N ₂ then switched to CO ₂ flow)	
Olive and date pips	220	10-48	-	10 g feed and 30 mL water	Dry	No	Physically activated with CO ₂ at 750 °C	[334]

Microalgae	350	0.5	-	10 wt% algae to water	Wet	No	Physically activated with CO ₂ at 800 °C. Also, some type of oil extraction activation carried out.	[335]
Sugarcanes	180	24	-	No solvent added, just natural state	-	No	Physically activated with N ₂ at 400-800 °C	[336]
Sucrose	194	20	-	0.85 mol/L solution	Wet	No	Physically activated with CO ₂ at 750 °C.	[337]
Flax fibers and corn husks	200-220	24	-	0.1 g of feed per mL of liquid. Either 80 or 200 mL of water or milk as liquid	Dry	No	Physically activated with CO ₂ at 800 °C	[338]
Cellulose	200	24	-	6 g of feed and 30 mL water	Dry	No	Physically activated with CO ₂ at 800 °C. Doping during HTC with either silicon or iron.	[339]
Corn cob	200	20	5	1:3 ratio of feed to water	Dry	No	Physically activated with N ₂ at 900 °C	[340]
Bagasse fly ash	180-200	0.5	-	1:6 ratio of feed to water	Wet	No	Physically activated with	[341]

							steam at 700-900 °C. Biochar was also produced here, without the initial HTC step, under same conditions	
Cigarette filters	250	5	-	1 g of feed and 10 mL of water	Dry	No	Chemically activated with KOH at 700 °C. Activated HC was then used to make a MOF	[342]
Tingui shells	200	24	10	7.5 g feed and 30 mL water	-	No	Physically activated with CO ₂ at 850 °C. Biochars also produced at 550 °C, then activated in same way	[114]
Chitosan	190	14	-	6 g of feed and 30 mL water	Dry	No	Physically activated with N ₂ at 600-900 °C	[343]
Garden pruning, citrus peels, municipal solid wastes	210-215	2-4	-	-	-	No	Physically activated with CO ₂ or O ₂ at 800 °C	[344]

Apple Pomace	230	5	-	40 g feed and 350 ml water	-	No	Physically activated with CO ₂ at 800 °C	[345]
Oil palm empty fruit bunches	275	1	-	-	-	Yes, urea mixed with HC and then activated at 800 °C under CO ₂	-	[346]
Waste shrimp shells and chitosan	180	12	-	-	-	No	One sample mixed with calcium carbonate to achieve etching	[347]
Two Phase Olive Mill Waste (TPOMW)	N/A	N/A	-	-	-	No	Some physical activation with CO ₂ – 700 and 850°C, 10°C/min, 100 mL/min CO ₂ , 1 and 3 hours Chemical activation with KOH also carried out	[25]
Palm Date Seeds	200	48	-	5 g feed, 50 mL water	Dry	No	Physical activation with CO ₂ , 900°C, 5°/min, 3 hours and 50 cm ³ /min of CO ₂ . Chemical activation with KOH and H ₃ PO ₄	[348]

							was also carried out	
Pinewood sawdust	180	2	5	50 kg of feed, 150 L of water	Dry	No	Underwent pelletisation with spent mushroom substrates	[115]
Cocoa shell powder	240	24	-	1 g feed and 10 mL water	-	No	Chemically activated with other chemicals, ZnO etc, at 100 °C	[349]
Canna indica biomass	200	2	-	1:10 of feed:water	Dry	No	-	[350]
Fructose Solutions	180	0, 0.5, 1 and 2	-	Different conc.'s of fructose solution	-	Yes, at different conc.'s	No	[351]
Tobacco stalks	180-260	1-12	-	2 g feed, 15 mL water	Dry	No	No further activation	[352]
Deoiled flaxseed	180-220	3-7	-	1:5 ratio of feed to water	-	No	Some HC's made with just water, others made with HCl replacing water (form of chemical activation)	[353]
Residual sludge	100-190	1	-	Liquid to solid ratio of 5:1	Wet	No	Also made 'biochar' at 250 °C for comparison	[354]
Chinese medicine residue	200-250	4-12	-	5 g of feed to 25 mL water	Dry	No	No	[355]

Cigarette filters	180-220	4-8	-	-	Dry	No	One made with HCl instead of water	[356]
Food waste	200	1-2	10	1 kg feed and 1500 mL water	-	No	Underwent palletization after HTC	
Black liquor	190-210	0.67	-	Different ratios used, see paper	-	No	No	[357]
Corn starch and biogas slurry	160-280	3	-	Different ratios used, see paper	Wet	No	No	[358]
Poplar leaves	100-300		-	2 g feed and 50 mL water		No	No	[359]

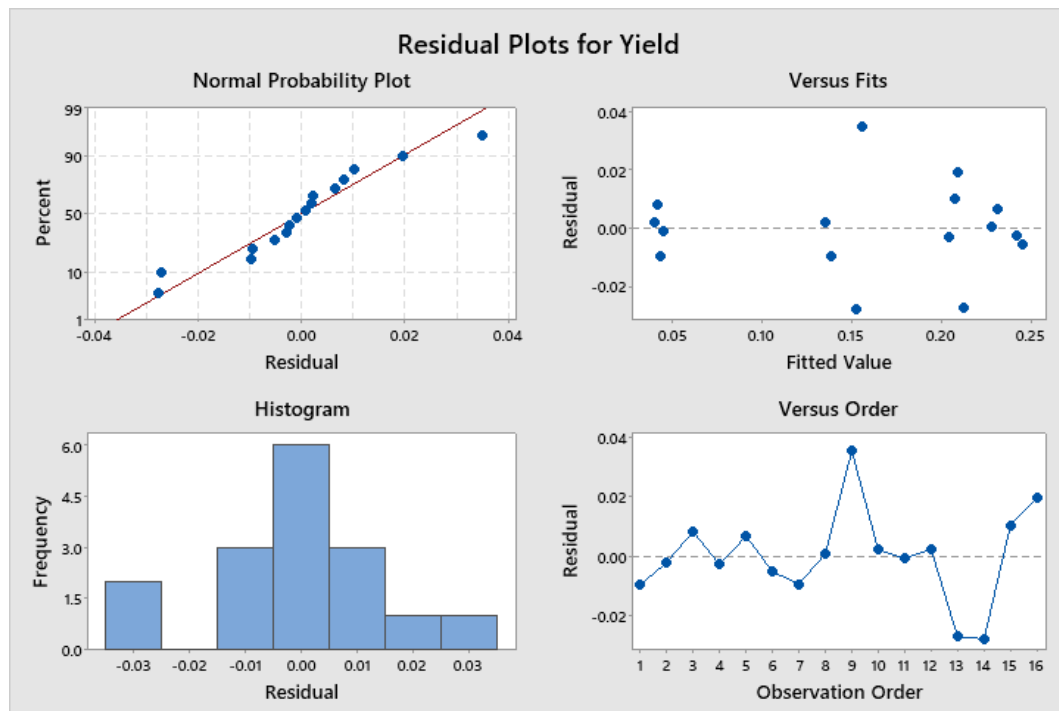
Appendix B: Screening Biochar ANOVA Results

The statistical ANOVA results and associated residual plots for the screening design models can be seen in Appendix Figure B.1 to Appendix Figure B.6. The yield model ANOVA results are present firstly, followed by the micropore area model ANOVA, and finally the carbon content model ANOVA.

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	7	0.089599	0.012800	28.93	0.000
Linear	4	0.079067	0.019767	44.67	0.000
Temp	1	0.066065	0.066065	149.30	0.000
Time	1	0.011632	0.011632	26.29	0.001
Peel Type	1	0.001321	0.001321	2.98	0.122
CO2 Flow	1	0.000049	0.000049	0.11	0.749
2-Way Interactions	3	0.010532	0.003511	7.93	0.009
Temp*Time	1	0.009731	0.009731	21.99	0.002
Temp*Peel Type	1	0.000443	0.000443	1.00	0.346
Time*Peel Type	1	0.000358	0.000358	0.81	0.395
Error	8	0.003540	0.000443		
Total	15	0.093139			

Appendix Figure B.1: Screening ANOVA for Biochar Yield as DoE Response

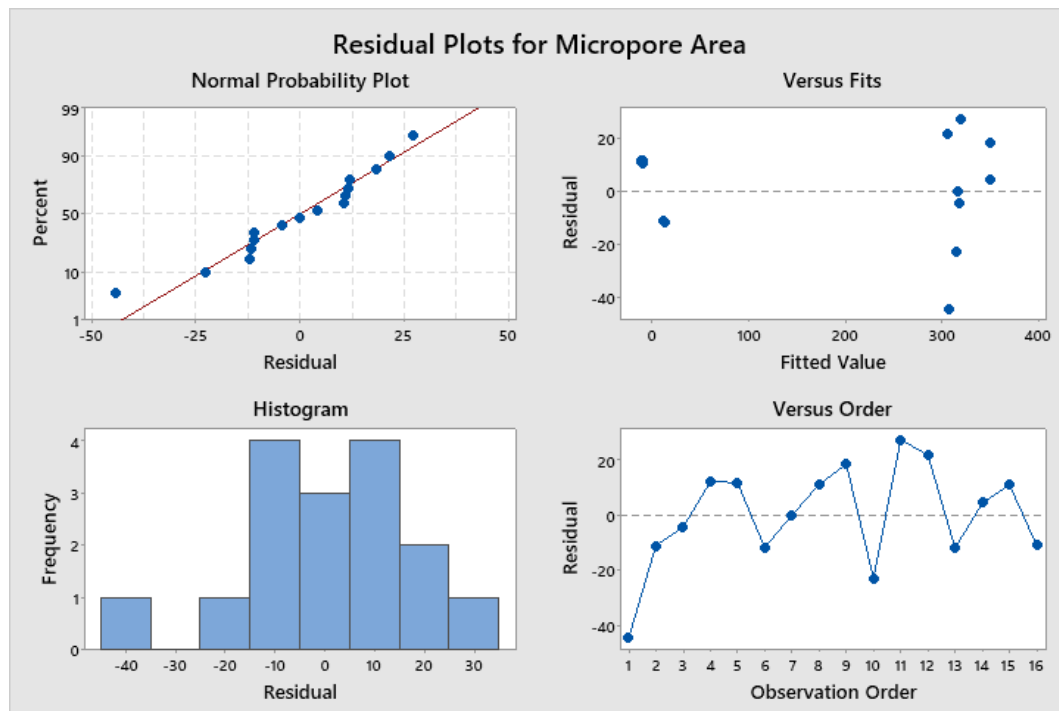


Appendix Figure B.2: Screening Residual Plots for Biochar Yield as DoE Response

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	7	417722	59675	93.82	0.000
Linear	4	415053	103763	163.14	0.000
Temp	1	414514	414514	651.73	0.000
Time	1	399	399	0.63	0.451
Peel Type	1	134	134	0.21	0.658
CO2 Flow	1	5	5	0.01	0.930
2-Way Interactions	3	2669	890	1.40	0.312
Temp*Time	1	421	421	0.66	0.439
Temp*Peel Type	1	104	104	0.16	0.697
Time*Peel Type	1	2143	2143	3.37	0.104
Error	8	5088	636		
Total	15	422810			

Appendix Figure B.3: Screening ANOVA for Biochar Micropore Area as DoE Response

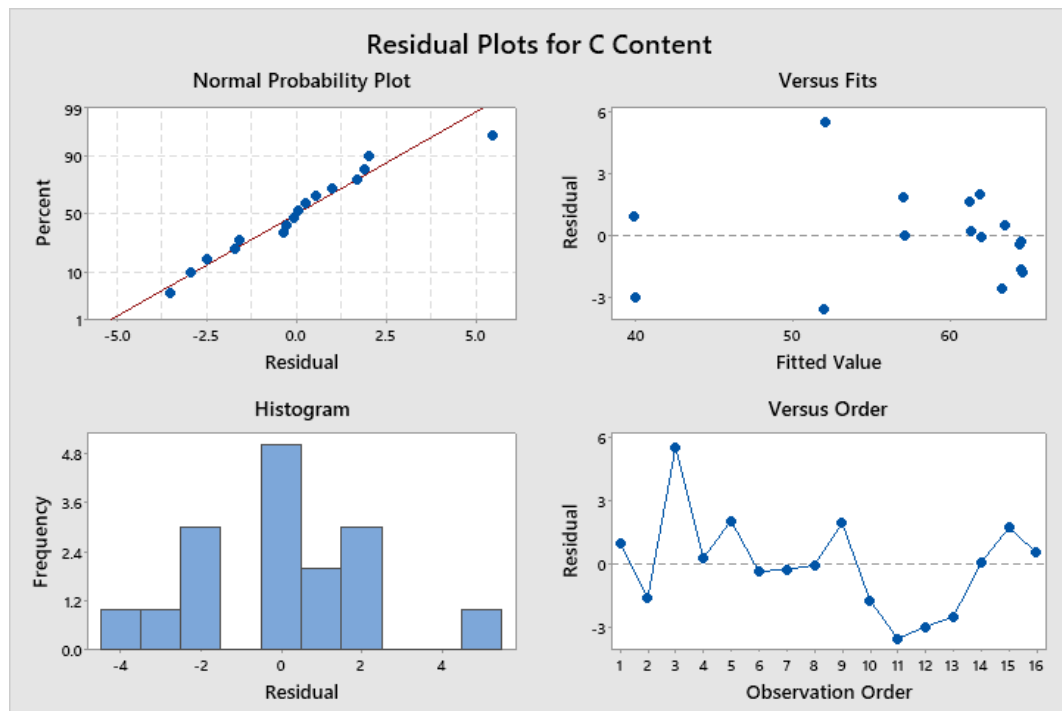


Appendix Figure B.4: Screening Residual Plots for Biochar Micropore Area as DoE Response

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	7	999.99	142.855	15.29	0.000
Linear	4	653.16	163.289	17.48	0.001
Temp	1	350.17	350.172	37.48	0.000
Time	1	224.47	224.472	24.03	0.001
Peel Type	1	78.46	78.462	8.40	0.020
CO2 Flow	1	0.05	0.049	0.01	0.944
2-Way Interactions	3	346.83	115.611	12.37	0.002
Temp*Time	1	213.34	213.335	22.83	0.001
Temp*Peel Type	1	112.22	112.220	12.01	0.008
Time*Peel Type	1	21.28	21.277	2.28	0.170
Error	8	74.74	9.343		
Total	15	1074.73			

Appendix Figure B.5: Screening ANOVA for Biochar Carbon Content as DoE Response



Appendix Figure B.6: Screening Residual Plots for Biochar Carbon Content as DoE Response

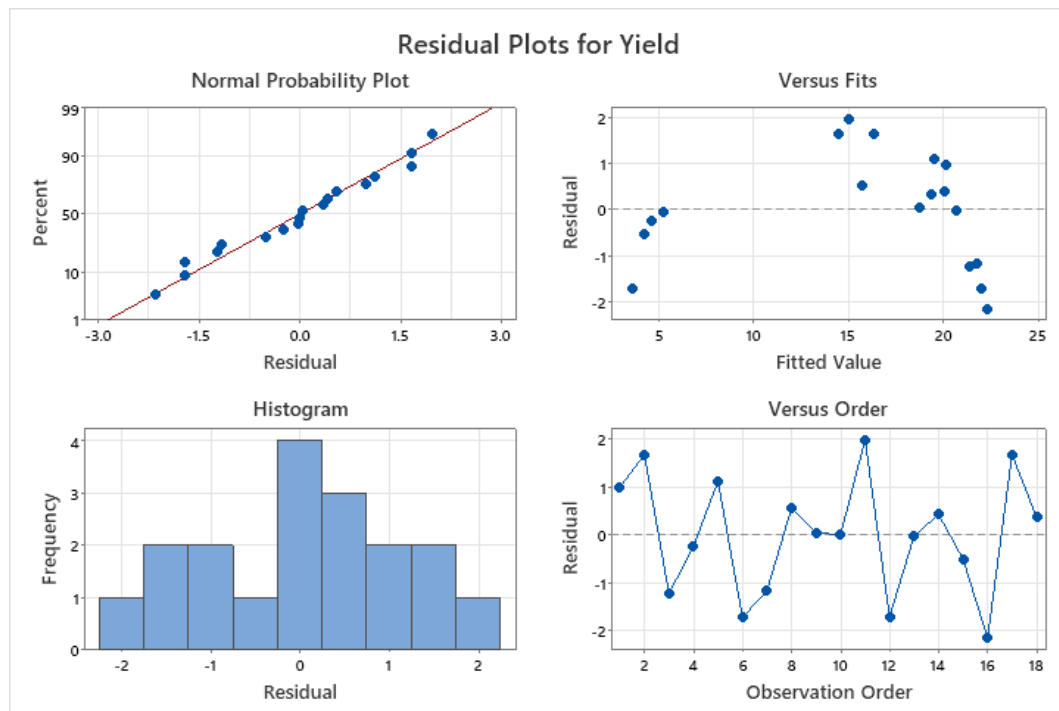
Appendix C: Optimisation Biochar ANOVA Results

The statistical ANOVA results and associated residual plots for the optimisation design models can be seen in Appendix Figure C.1 to Appendix Figure C.6. The yield model ANOVA results are present firstly, followed by the micropore area model ANOVA, and finally the carbon content model ANOVA.

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	5	766.157	153.231	71.25	0.000
Linear	3	577.832	192.611	89.56	0.000
Temperature	1	504.054	504.054	234.37	0.000
Time	1	72.218	72.218	33.58	0.000
Peel Type	1	1.561	1.561	0.73	0.411
Square	1	126.720	126.720	58.92	0.000
Temperature*Temperature	1	126.720	126.720	58.92	0.000
2-Way Interaction	1	61.605	61.605	28.64	0.000
Temperature*Time	1	61.605	61.605	28.64	0.000
Error	12	25.808	2.151		
Total	17	791.965			

Appendix Figure C.1: Optimisation ANOVA for Biochar Yield as DoE Response

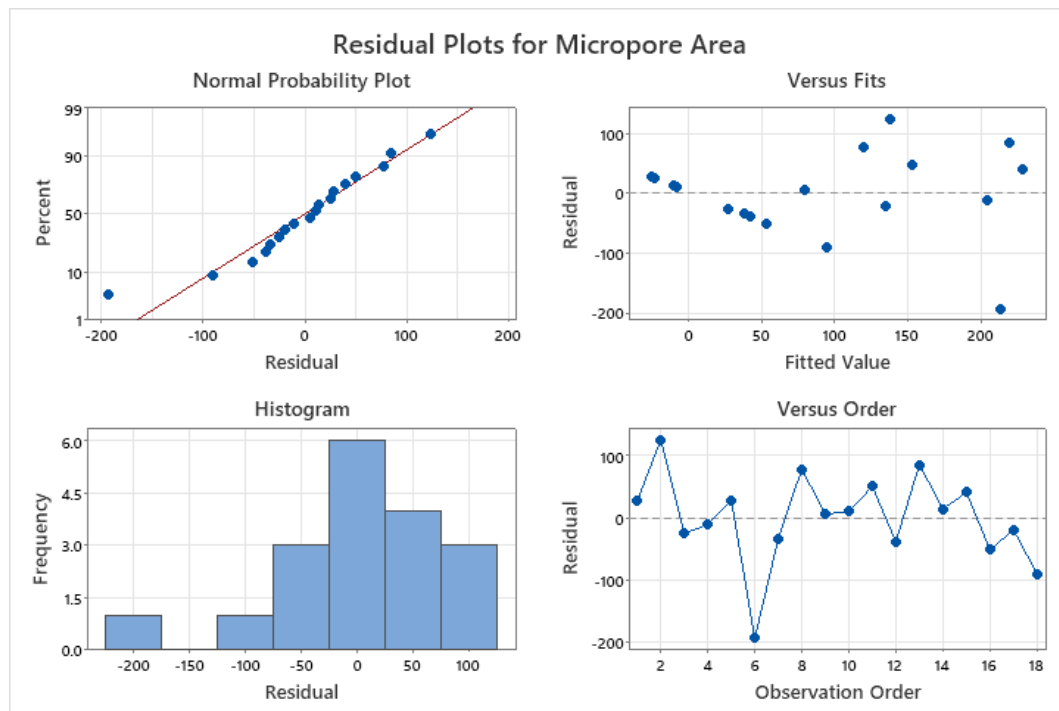


Appendix Figure C.2: Optimisation Residual Plots for Biochar Yield as DoE Response

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	5	129561	25912	3.62	0.031
Linear	3	128880	42960	6.01	0.010
Temperature	1	114536	114536	16.01	0.002
Time	1	13332	13332	1.86	0.197
Peel Type	1	1013	1013	0.14	0.713
Square	1	551	551	0.08	0.786
Temperature*Temperature	1	551	551	0.08	0.786
2-Way Interaction	1	129	129	0.02	0.895
Temperature*Time	1	129	129	0.02	0.895
Error	12	85834	7153		
Total	17	215395			

Appendix Figure C.3: Optimisation ANOVA for Biochar Micropore Area as DoE Response

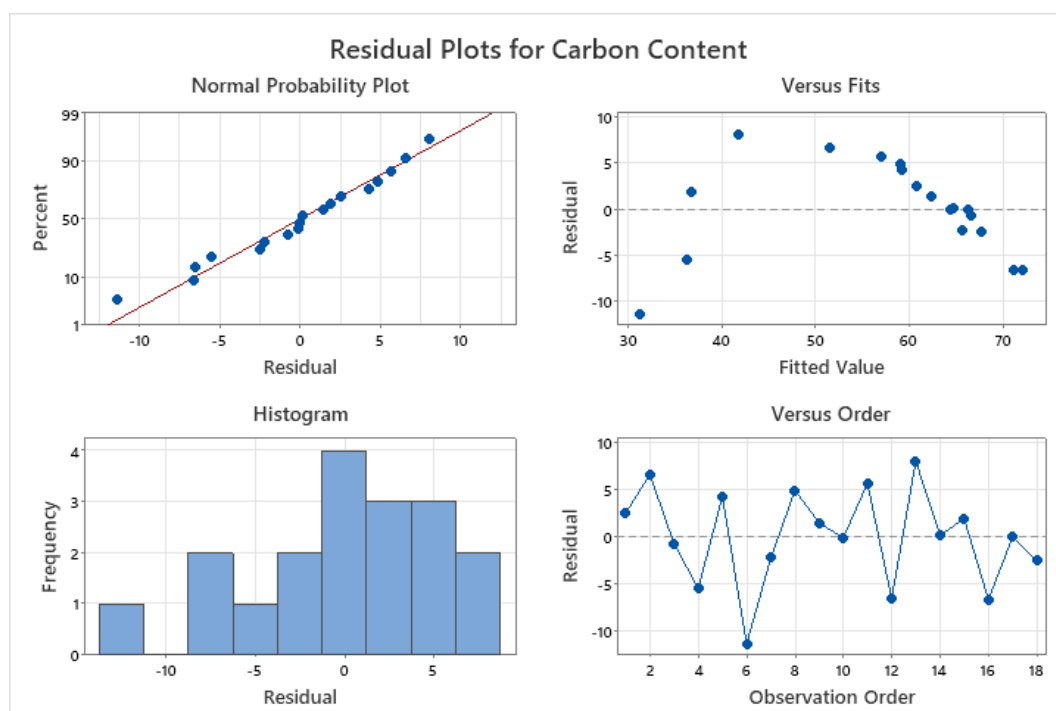


Appendix Figure C.4: Optimisation Residual Plots for Biochar Micropore Area as DoE Response

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	5	2722.20	544.44	14.49	0.000
Linear	3	1788.36	596.12	15.86	0.000
Temperature	1	1567.99	1567.99	41.72	0.000
Time	1	87.70	87.70	2.33	0.153
Peel Type	1	132.67	132.67	3.53	0.085
Square	1	711.12	711.12	18.92	0.001
Temperature*Temperature	1	711.12	711.12	18.92	0.001
2-Way Interaction	1	222.73	222.73	5.93	0.031
Temperature*Time	1	222.73	222.73	5.93	0.031
Error	12	450.98	37.58		
Total	17	3173.19			

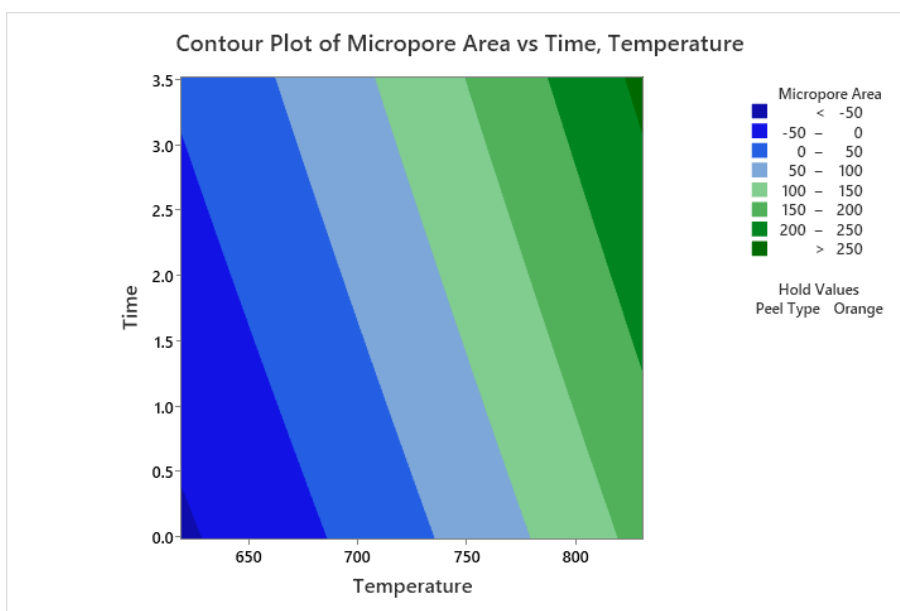
Appendix Figure C.5: Optimisation ANOVA for Biochar Carbon Content as DoE Response



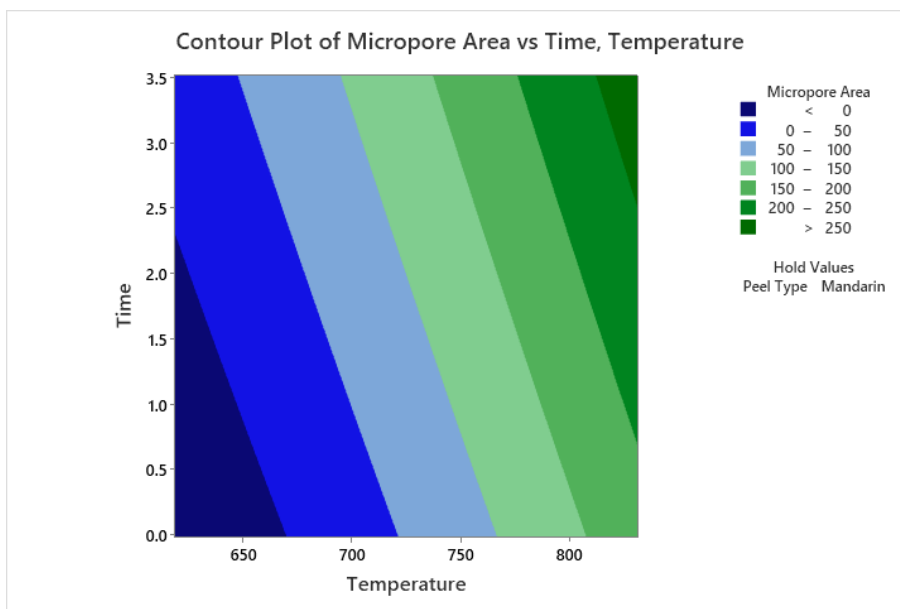
Appendix Figure C.6: Optimisation Residual Plots for Biochar Carbon Content as DoE Response

Appendix D: Biochar Micropore Area Optimisation Model Contour Plots

The original contour plot (before truncation) for the micropore area optimisation models are shown in Appendix Figure D.1 for the orange peel biochars and Appendix Figure D.2 for the mandarin peel biochars.



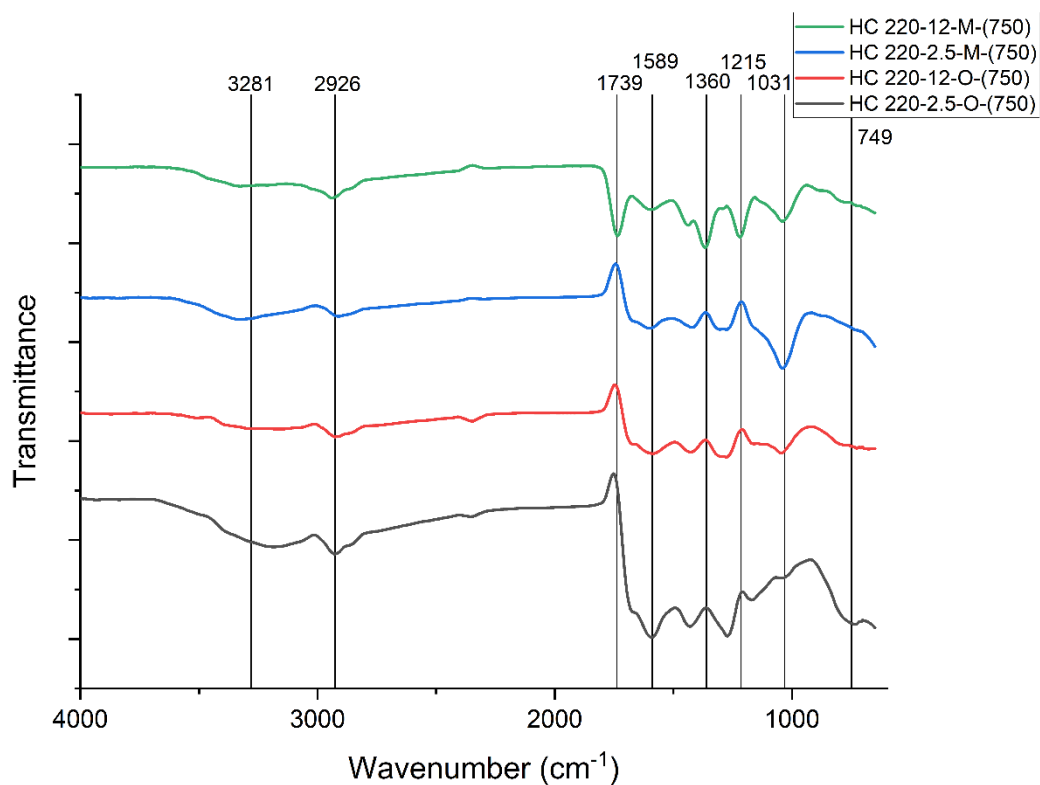
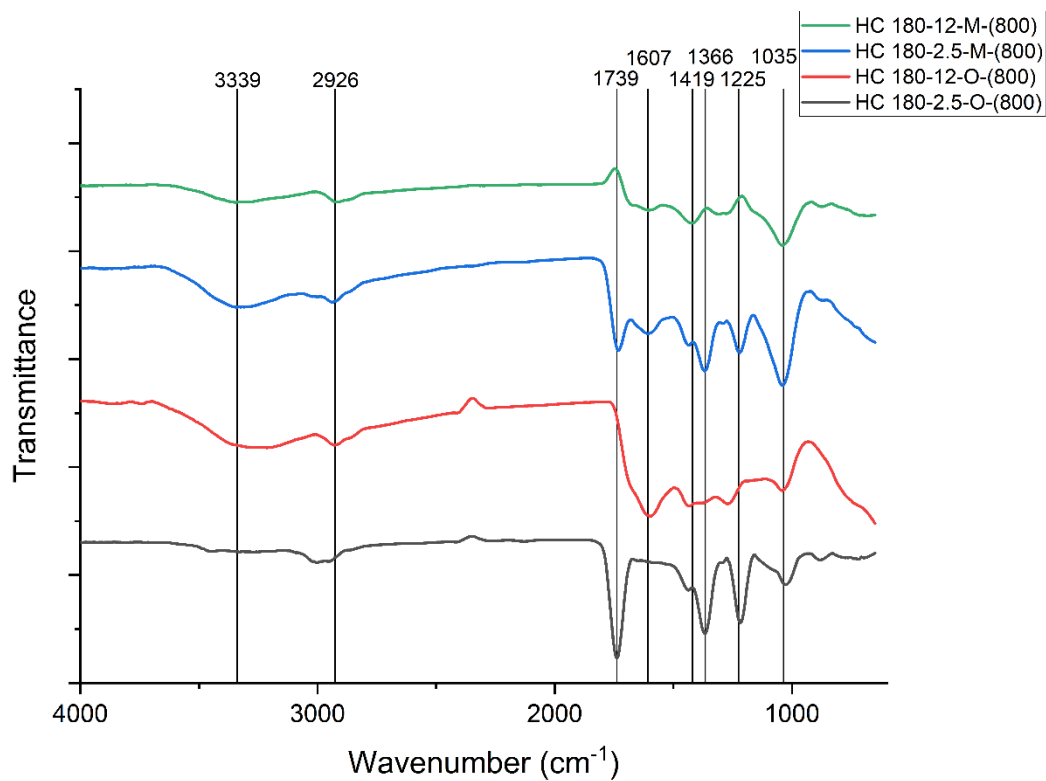
Appendix Figure D.1: Contour Plot for Optimisation of Model for Orange Peel Biochar Micropore Area (m^2/g) with Respect to Pyrolysis Temperature ($^{\circ}\text{C}$) and Residence Time (h)



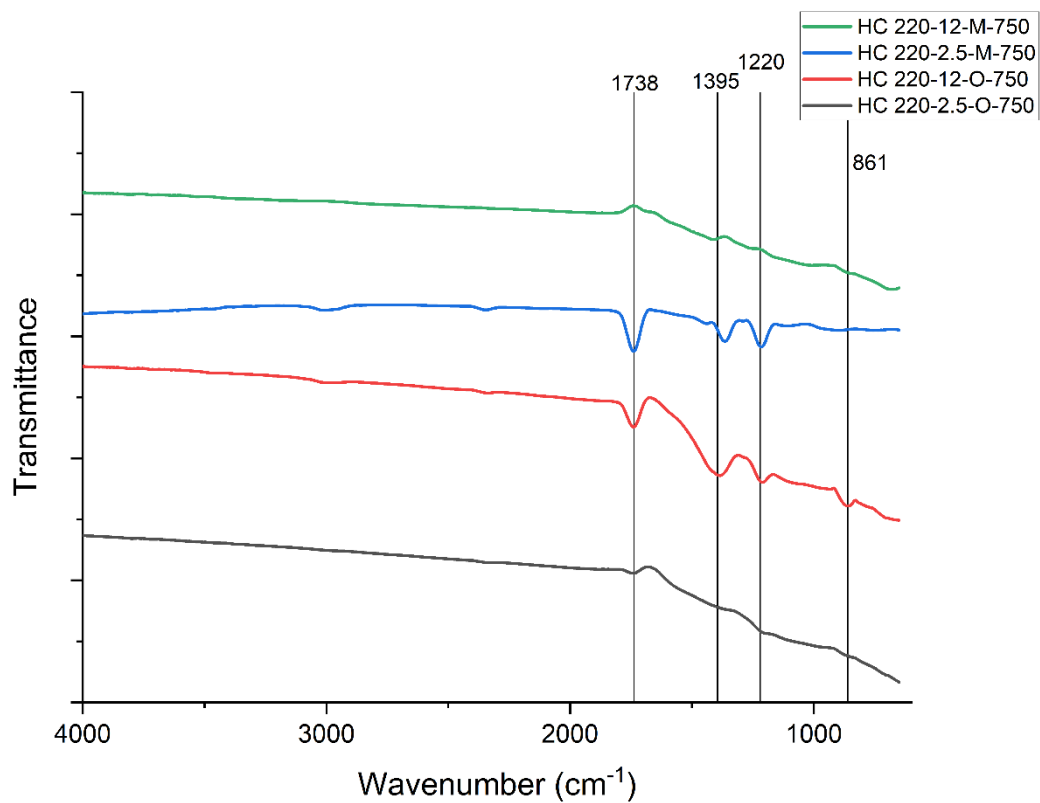
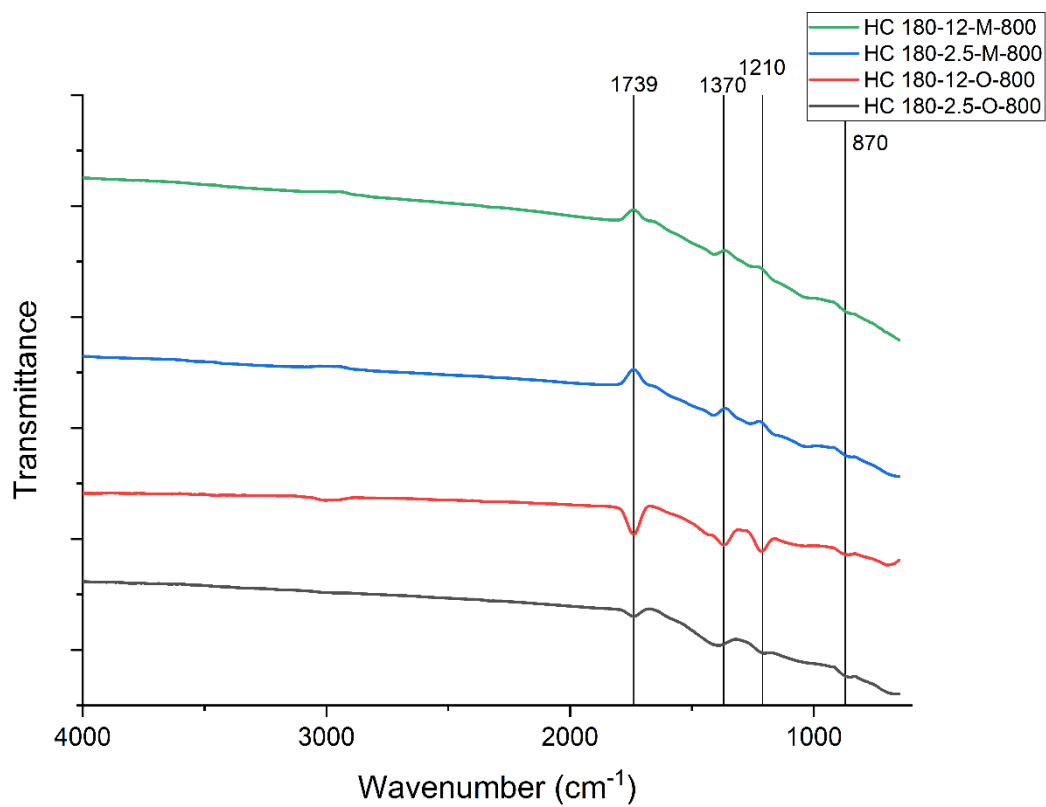
Appendix Figure D.2: Contour Plot for Optimisation of Model for Mandarin Peel Biochar Micropore Area (m^2/g) with Respect to Pyrolysis Temperature ($^{\circ}\text{C}$) and Residence Time (h)

Appendix E: Screening Hydrochar FTIR Spectra

FTIR Spectra of pre-activation screening hydrochars are shown in Appendix Figure E.1, and spectra of post-activation screening hydrochars are shown in Appendix Figure E.2.



Appendix Figure E.1: FTIR Spectra of Hydrochar Samples Produced Through HTC at 180 °C for Activation at 800 °C (top) and at 220 °C for Activation at 750 °C (bottom)



Appendix Figure E.2: FTIR Spectra of Hydrochar Samples Produced Through HTC at 180 °C and Activated at 800 °C (top) and at 220 °C and Activated at 750 °C (bottom)

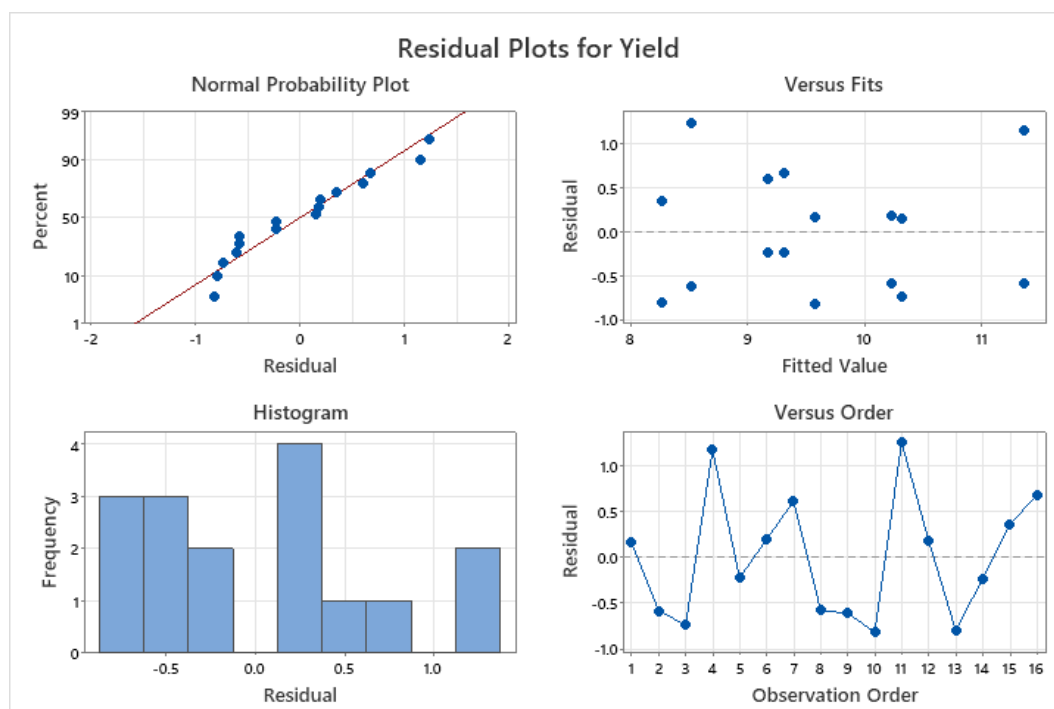
Appendix F: Screening Hydrochar ANOVA Results

The statistical ANOVA results and associated residual plots for the screening design models can be seen in Appendix Figure F.1 to Appendix Figure F.6. The yield model ANOVA results are present firstly, followed by the micropore area model ANOVA, and finally the carbon content model ANOVA.

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	4	14.3881	3.5970	5.73	0.010
Linear	3	13.6312	4.5437	7.24	0.006
HTC Temperature	1	4.3681	4.3681	6.96	0.023
Peel Type	1	1.9460	1.9460	3.10	0.106
Activation Temperature	1	7.3170	7.3170	11.67	0.006
2-Way Interactions	1	0.7569	0.7569	1.21	0.295
Peel Type*Activation Temperature	1	0.7569	0.7569	1.21	0.295
Error	11	6.8998	0.6273		
Total	15	21.2878			

Appendix Figure F.1: Screening ANOVA for Hydrochar Yield as DoE Response

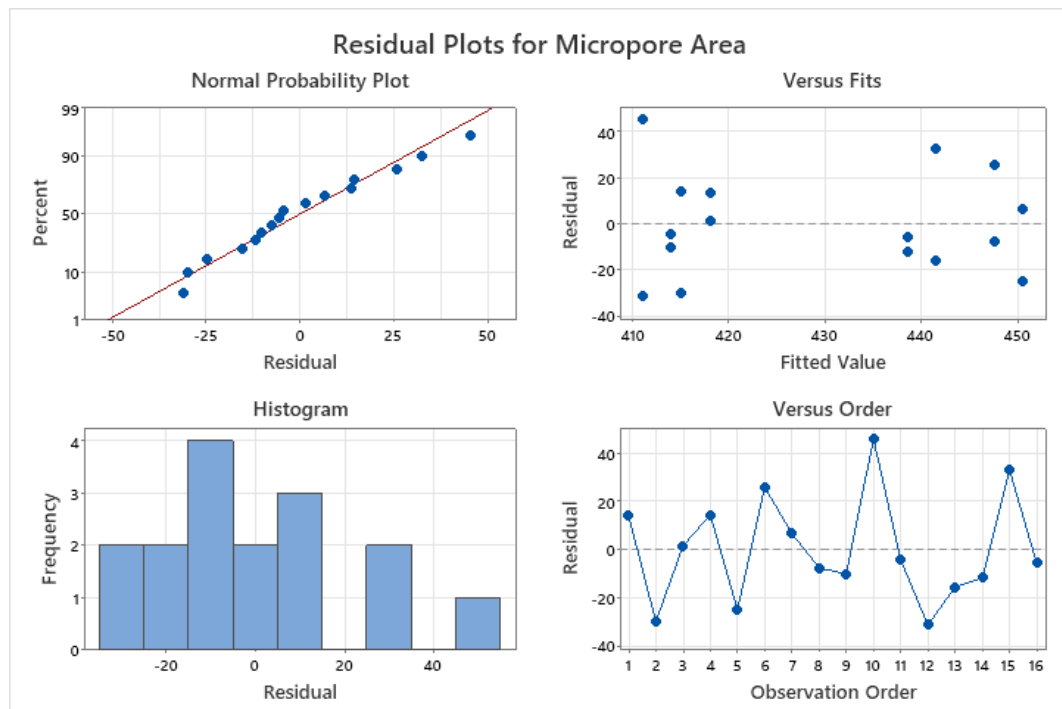


Appendix Figure F.2: Screening Residual Plots for Hydrochar Yield as DoE Response

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	4	3836.6	959.15	1.44	0.284
Linear	3	3811.8	1270.61	1.91	0.186
HTC Temperature	1	34.7	34.69	0.05	0.824
Peel Type	1	3605.9	3605.92	5.42	0.040
Activation Temperature	1	171.2	171.23	0.26	0.622
2-Way Interactions	1	24.8	24.76	0.04	0.851
Peel Type*Activation Temperature	1	24.8	24.76	0.04	0.851
Error	11	7314.5	664.96		
Total	15	11151.1			

Appendix Figure F.3: Screening ANOVA for Hydrochar Micropore Area as DoE Response

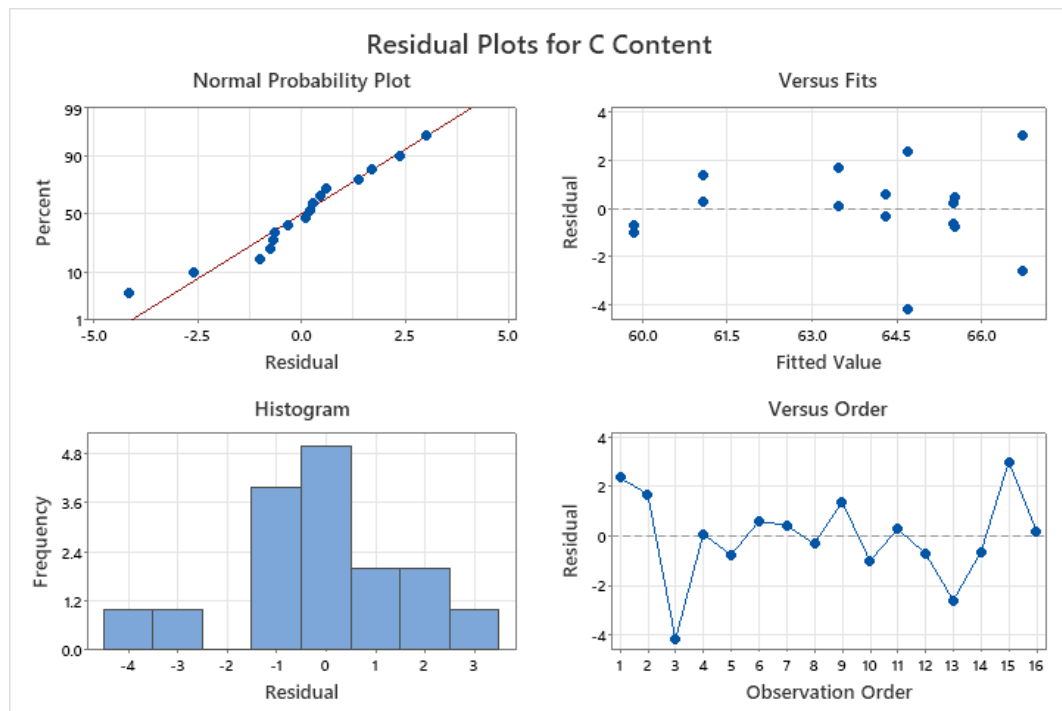


Appendix Figure F.4: Screening Residual Plots for Hydrochar Micropore Area as DoE Response

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	4	76.865	19.216	4.53	0.021
Linear	3	53.662	17.887	4.22	0.033
HTC Temperature	1	5.853	5.853	1.38	0.265
Peel Type	1	41.948	41.948	9.90	0.009
Activation Temperature	1	5.861	5.861	1.38	0.264
2-Way Interactions	1	23.203	23.203	5.47	0.039
Peel Type*Activation Temperature	1	23.203	23.203	5.47	0.039
Error	11	46.623	4.238		
Total	15	123.488			

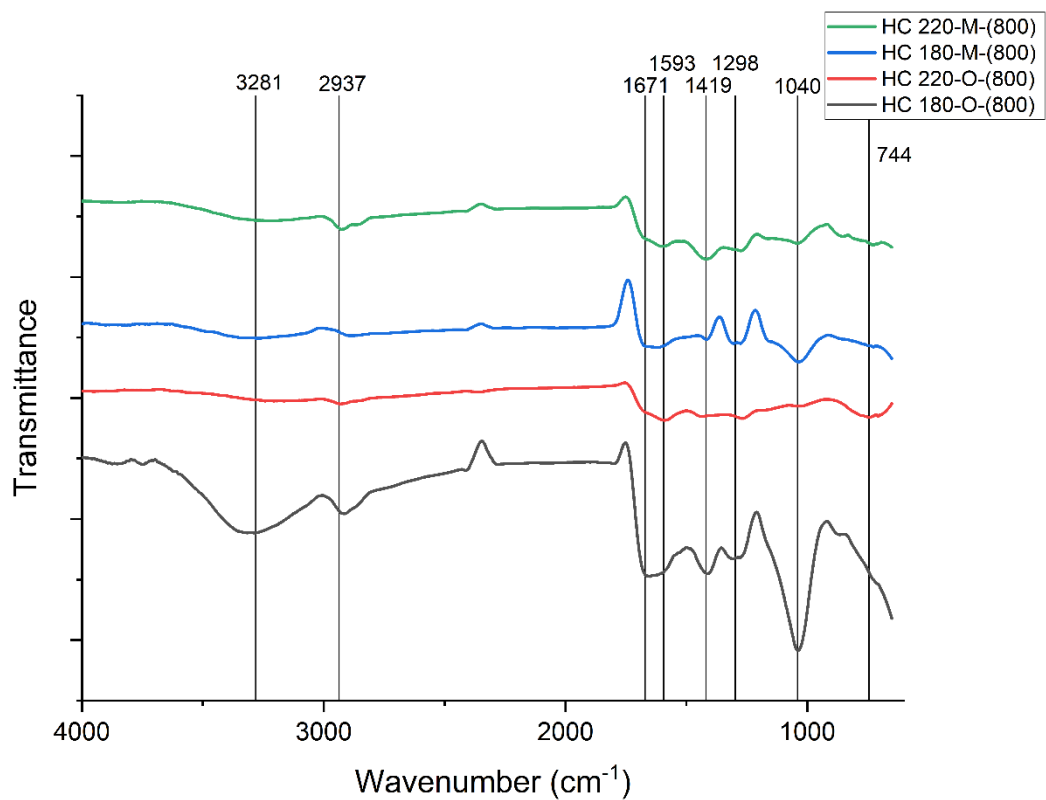
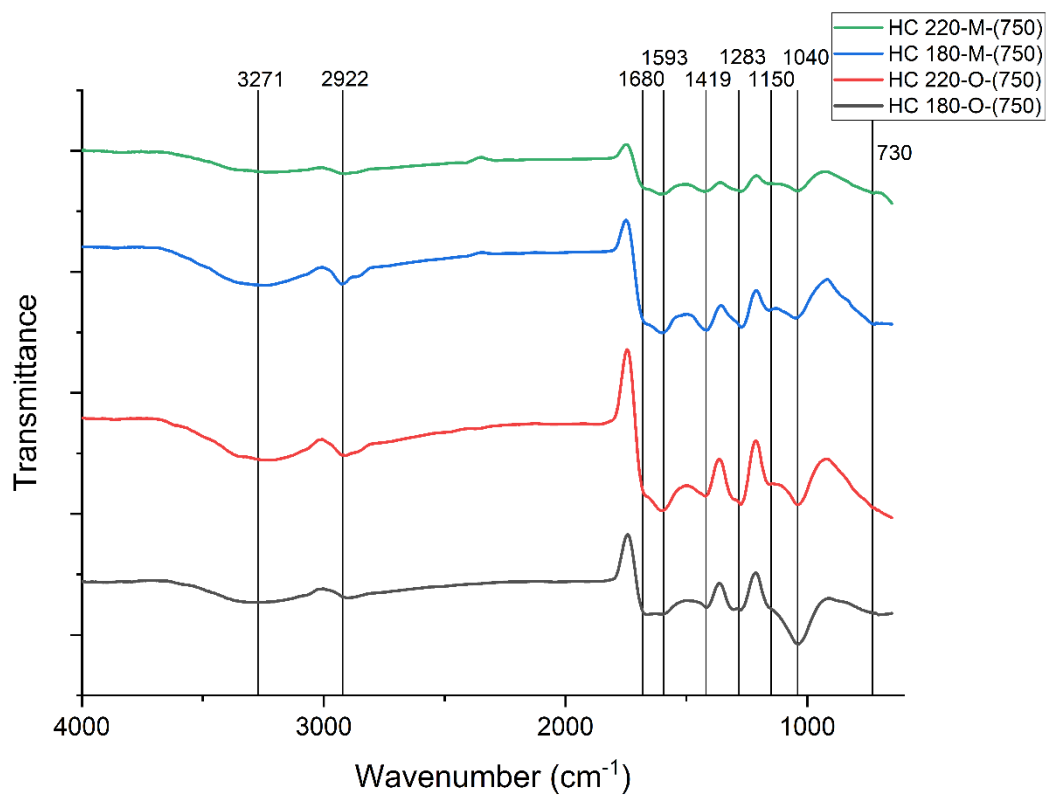
Appendix Figure F.5: Screening ANOVA for Hydrochar Carbon Content as DoE Response



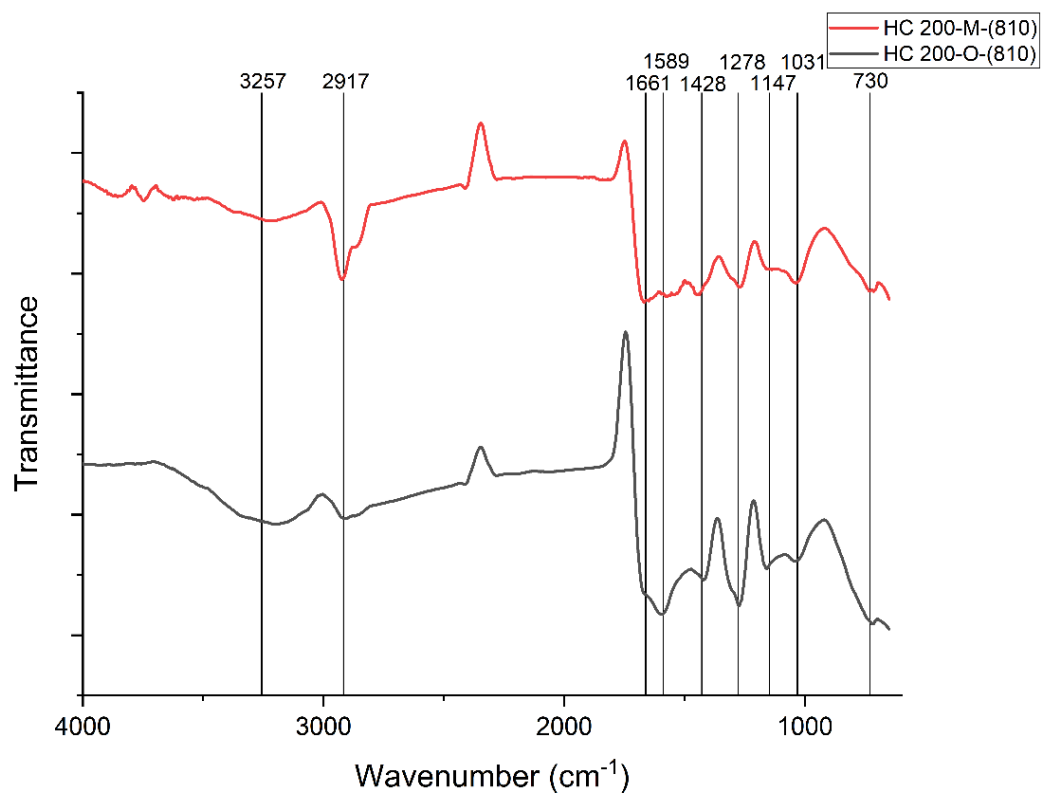
Appendix Figure F.6: Screening Residual Plots for Hydrochar Carbon Content as DoE Response

Appendix G: Optimisation Hydrochar FTIR Spectra

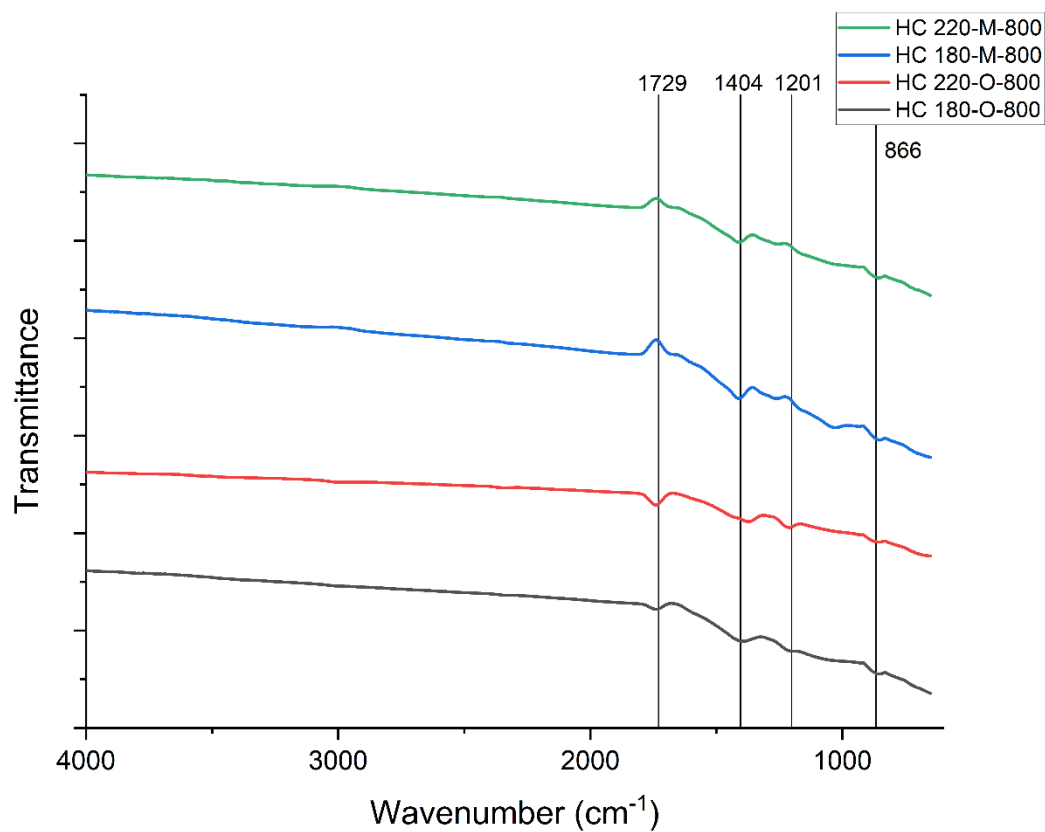
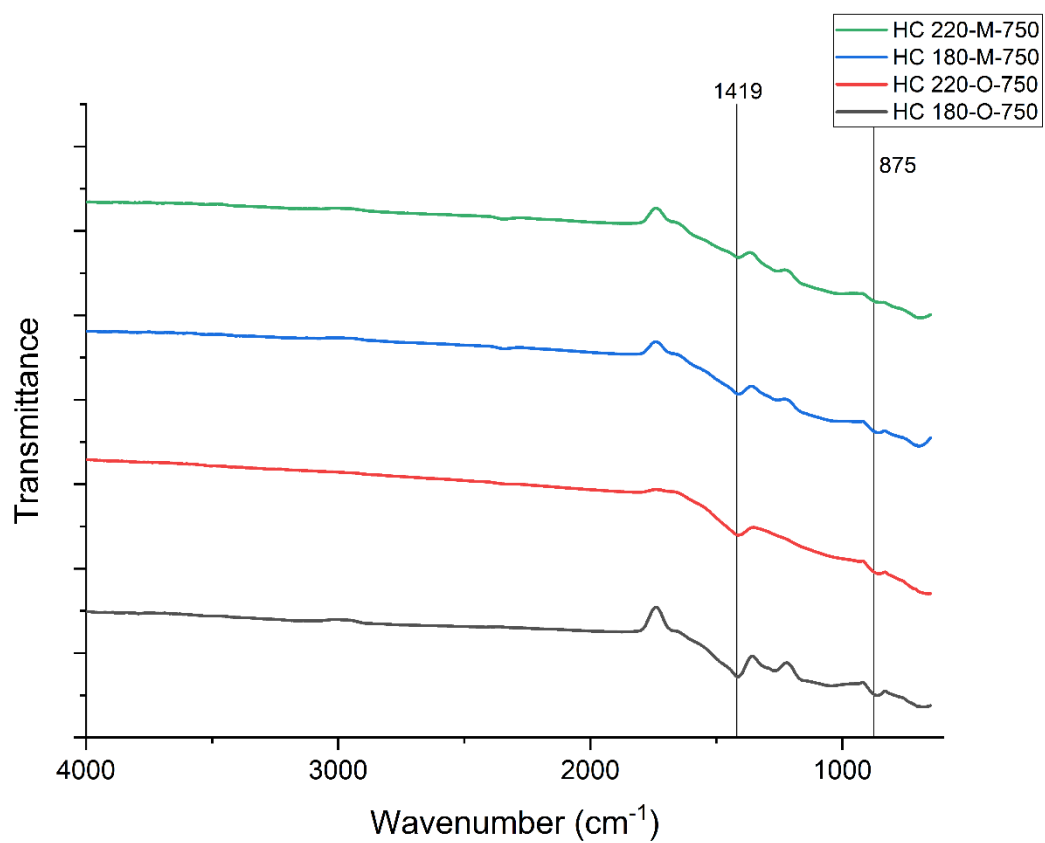
FTIR Spectra of pre-activation screening hydrochars are shown in Appendix Figure G.1 and Appendix Figure G.2, and spectra of post-activation screening hydrochars are shown in Appendix Figure G.3 and Appendix Figure G.4.



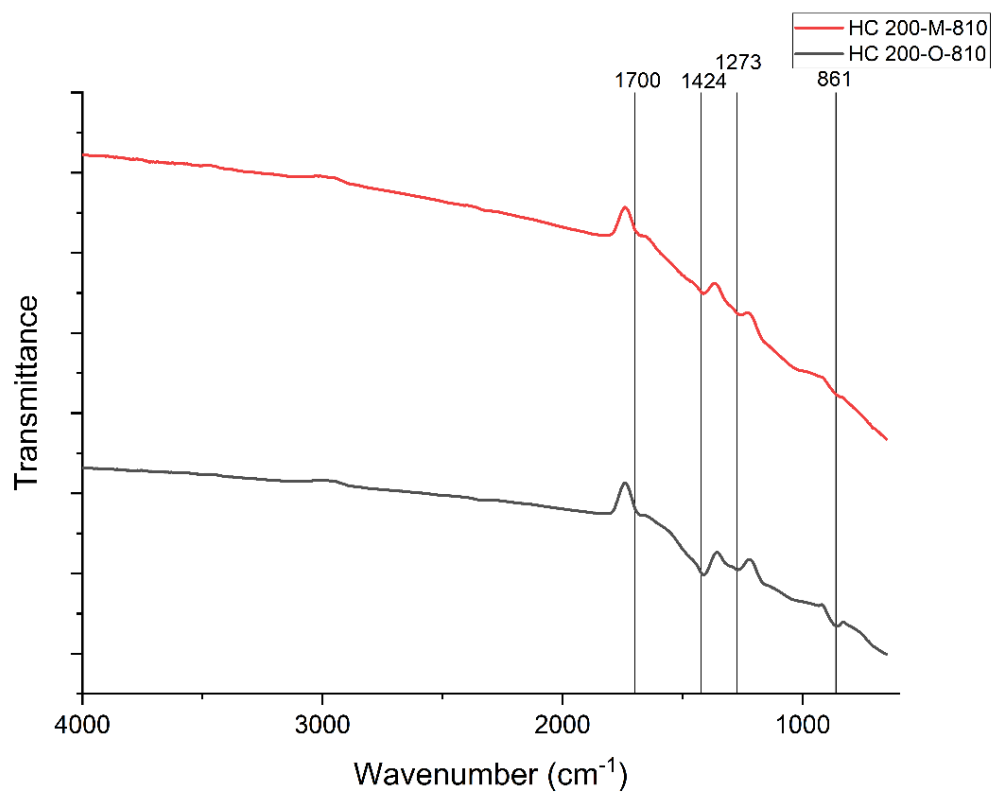
Appendix Figure G.1: FTIR Spectra of Hydrochar Samples Produced Through HTC for Activation at 750 °C (top) and 800 °C (bottom)



Appendix Figure G.2: FTIR Spectra of Hydrochar Samples Produced Through HTC for Activation at 810 °C



Appendix Figure G.3: FTIR Spectra of Hydrochar Samples Produced Through HTC and Activated at 750 °C (top) and 800 °C (bottom)



Appendix Figure G.4: FTIR Spectra of Hydrochar Samples Produced Through HTC and Activated at 810 °C

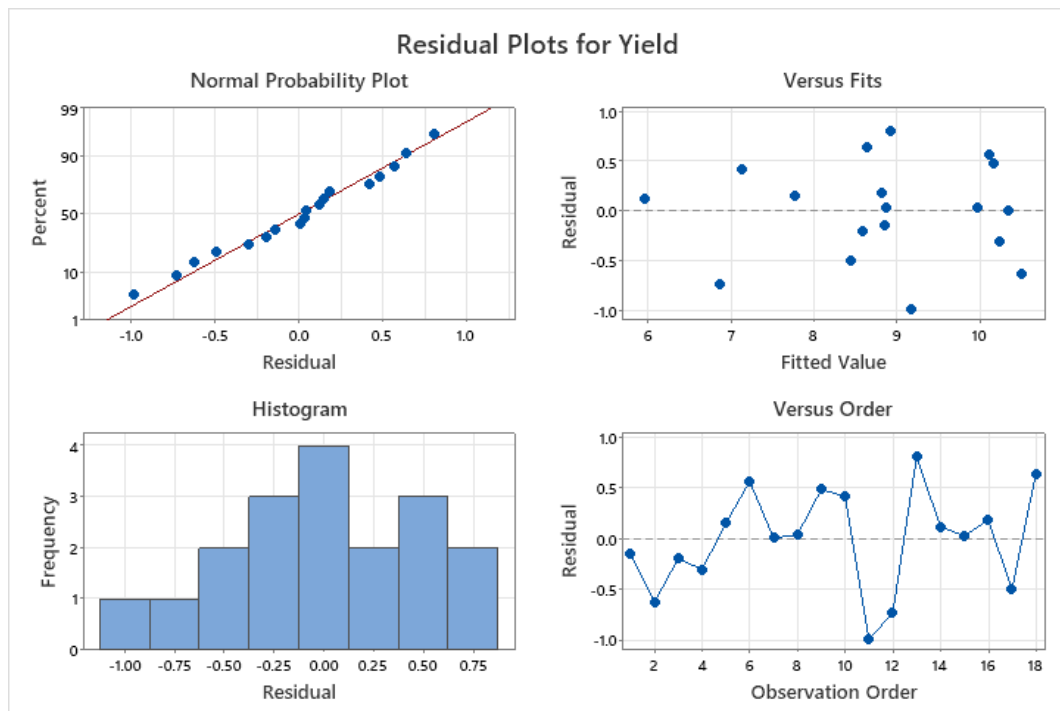
Appendix H: Optimisation Hydrochar ANOVA Results

The statistical ANOVA results and associated residual plots for the screening design models can be seen in Appendix Figure H.1 to Appendix Figure H.6. The yield model ANOVA results are present firstly, followed by the micropore area model ANOVA, and finally the carbon content model ANOVA.

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	5	28.3742	5.6748	16.41	0.000
Linear	3	24.5511	8.1837	23.66	0.000
HTC Temp	1	13.8037	13.8037	39.91	0.000
Activation Temp	1	0.2745	0.2745	0.79	0.390
Peel	1	10.4729	10.4729	30.28	0.000
Square	1	3.6641	3.6641	10.59	0.007
HTC Temp*HTC Temp	1	3.6641	3.6641	10.59	0.007
2-Way Interaction	1	0.1590	0.1590	0.46	0.511
HTC Temp*Peel	1	0.1590	0.1590	0.46	0.511
Error	12	4.1504	0.3459		
Total	17	32.5246			

Appendix Figure H.1: Optimisation ANOVA for Hydrochar Yield as DoE Response

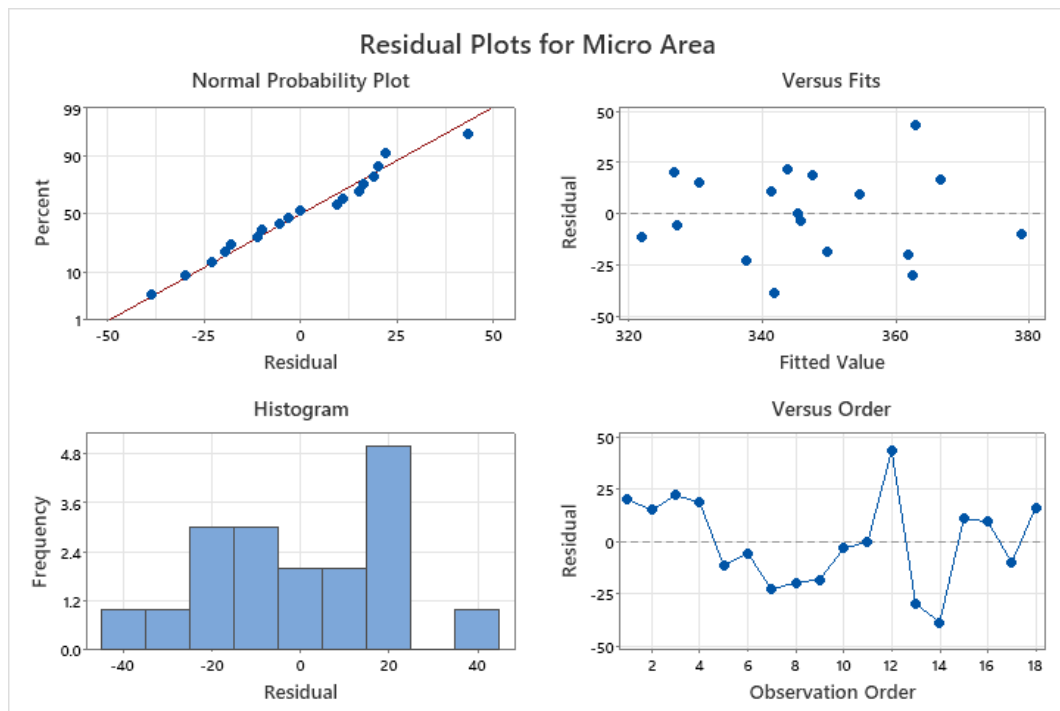


Appendix Figure H.2: Optimisation Residual Plots for Hydrochar Yield as DoE Response

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	5	4043.5	808.70	1.26	0.342
Linear	3	2480.5	826.82	1.29	0.323
HTC Temp	1	11.4	11.38	0.02	0.896
Activation Temp	1	1170.3	1170.28	1.82	0.202
Peel	1	1298.8	1298.80	2.02	0.180
Square	1	1546.4	1546.45	2.41	0.146
HTC Temp*HTC Temp	1	1546.4	1546.45	2.41	0.146
2-Way Interaction	1	16.6	16.61	0.03	0.875
HTC Temp*Peel	1	16.6	16.61	0.03	0.875
Error	12	7698.7	641.56		
Total	17	11742.3			

Appendix Figure H.3: Optimisation ANOVA for Hydrochar Micropore Area as DoE Response

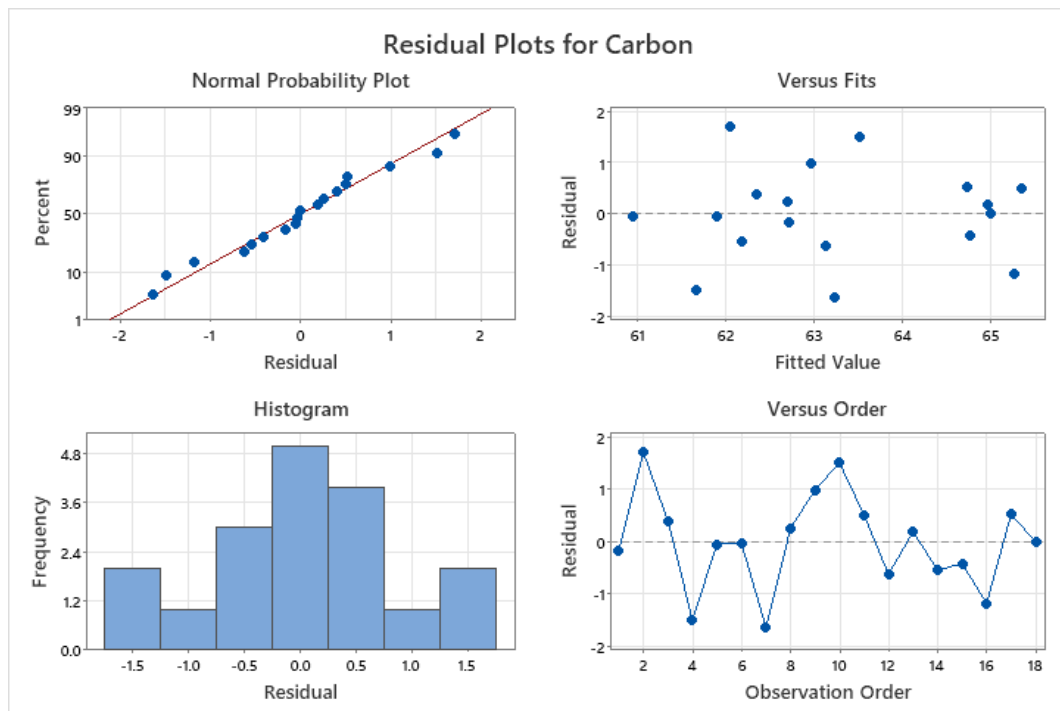


Appendix Figure H.4: Optimisation Residual Plots for Hydrochar Micropore Area as DoE Response

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	5	32.5761	6.5152	5.54	0.007
Linear	3	20.6004	6.8668	5.84	0.011
HTC Temp	1	1.3353	1.3353	1.14	0.308
Activation Temp	1	0.5711	0.5711	0.49	0.499
Peel	1	18.6940	18.6940	15.89	0.002
Square	1	5.7295	5.7295	4.87	0.048
HTC Temp*HTC Temp	1	5.7295	5.7295	4.87	0.048
2-Way Interaction	1	6.2462	6.2462	5.31	0.040
HTC Temp*Peel	1	6.2462	6.2462	5.31	0.040
Error	12	14.1142	1.1762		
Total	17	46.6904			

Appendix Figure H.5: Optimisation ANOVA for Hydrochar Carbon Content as DoE Response

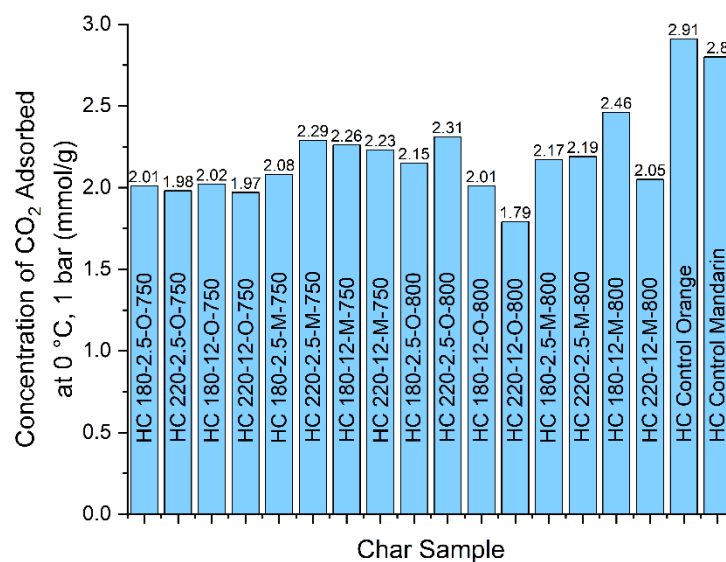


Appendix Figure H.6: Optimisation Residual Plots for Hydrochar Carbon Content as DoE Response

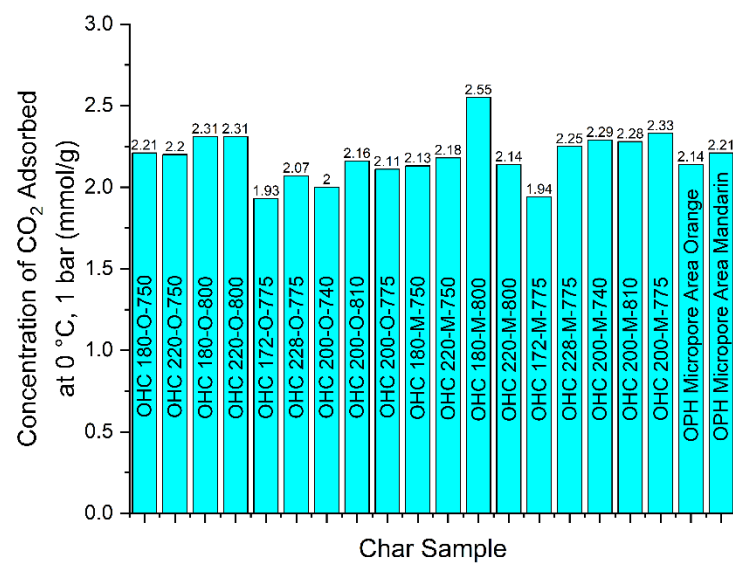
Appendix I: Volumetric Adsorption Results in Graphical Form

The volumetric CO₂ adsorption results for all samples tested can be seen in Appendix Figure

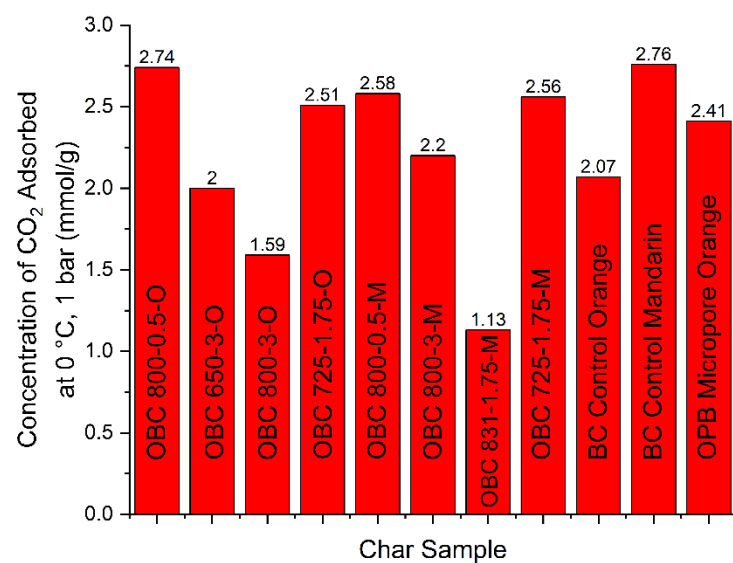
I.1 to Appendix Figure I.3.



Appendix Figure I.1: CO₂ Volumetric Adsorption Uptake Results at 0 °C, 1 bar for Screening Hydrochars Tested in This Project



Appendix Figure I.2: CO₂ Volumetric Adsorption Uptake Results at 0 °C, 1 bar for Optimisation Hydrochars Tested in This Project

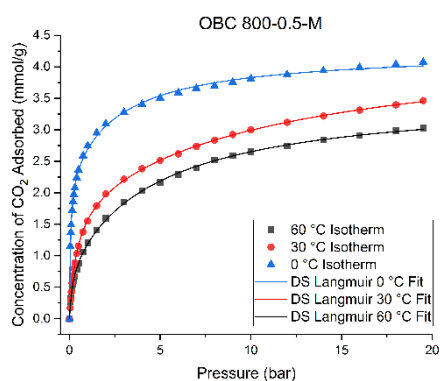


Appendix Figure I.3: CO₂ Volumetric Adsorption Uptake Results at 0 °C, 1 bar for Biochars Tested in This Project

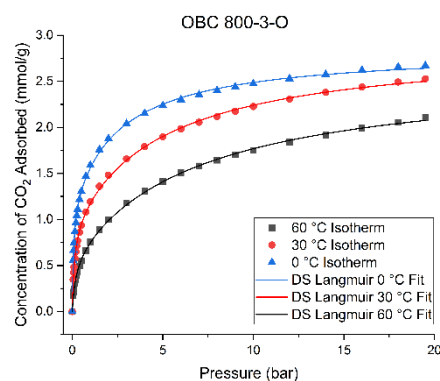
Appendix J: Gravimetric Adsorption Isotherm Fits and Associated Fittings

Parameters

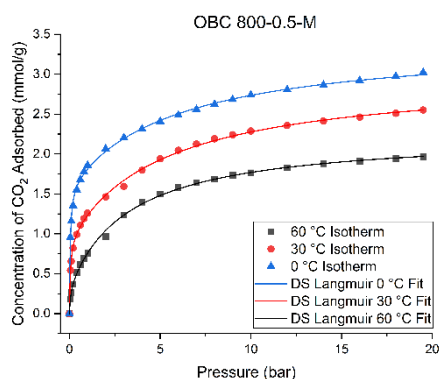
The Dual Site Langmuir fits for each gravimetric adsorption isotherm can be seen in Appendix Figure J.1 to Appendix Figure J.10. The associated fitting parameters for each of the models can be seen in Appendix Table J.1 to Appendix Table J.10.



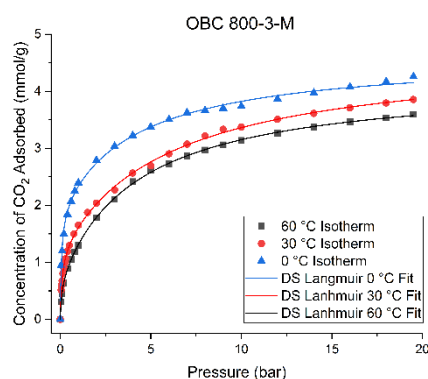
Appendix Figure J.1: Dual-Site Langmuir Isotherm Fittings for OBC 800-0.5-O



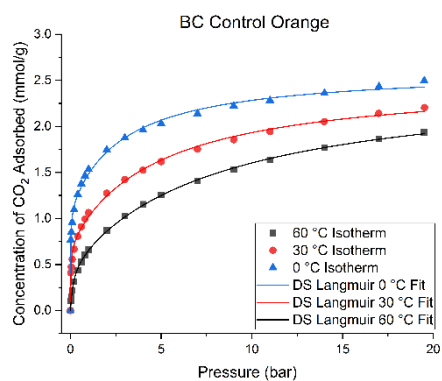
Appendix Figure J.2: Dual-Site Langmuir Isotherm Fittings for OBC 800 3-O



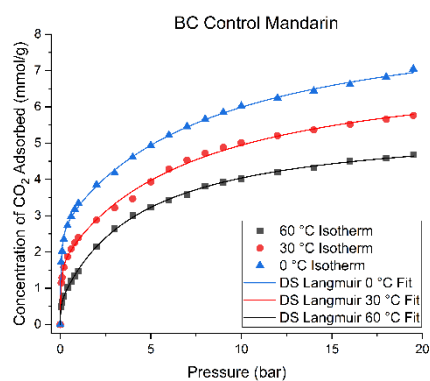
Appendix Figure J.3: Dual-Site Langmuir Isotherm Fittings for OBC 800-0.5-M



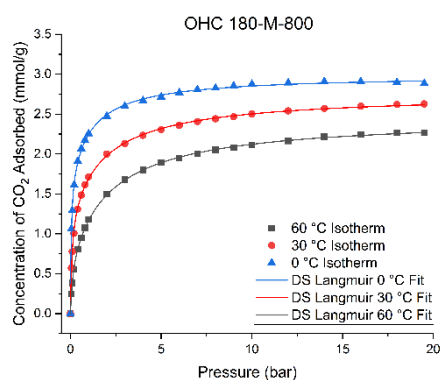
Appendix Figure J.4: Dual-Site Langmuir Isotherm Fittings for OBC 800-3-M



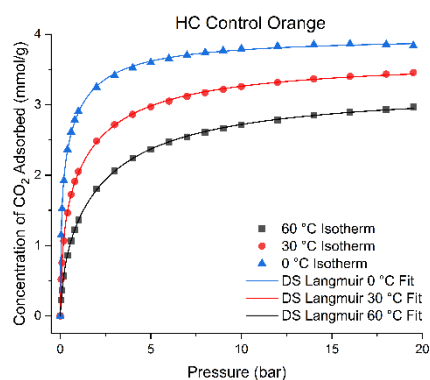
Appendix Figure J.5: Dual-Site Langmuir Isotherm Fittings for BC Control Orange



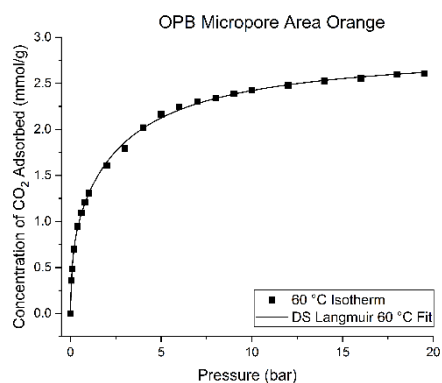
Appendix Figure J.6: Dual-Site Langmuir Isotherm Fittings for BC Control Mandarin



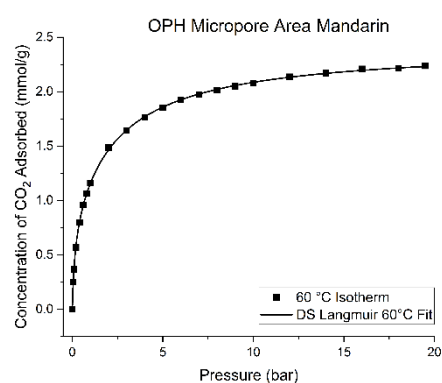
Appendix Figure J.7: Dual-Site Langmuir Isotherm Fittings for OHC 180-M-800



Appendix Figure J.8: Dual-Site Langmuir Isotherm Fittings for HC Control Orange



Appendix Figure J.9: Dual-Site Langmuir Isotherm Fittings for OPB Micropore Orange



Appendix Figure J.10: Dual-Site Langmuir Isotherm Fittings for OPH Micropore Mandarin

Appendix Table J.1: Dual Site Langmuir Model Fitting Coefficients for OBC 800-0.5-O

Isotherm	Dual Site Langmuir Model Coefficients				
	q _{max} (mmol/g)	Alpha (unitless)	K ₁ (bar ⁻¹)	K ₂ (bar ⁻¹)	R ² (unitless)
0 °C	4.26033	0.47023	17.99752	0.37685	0.99870
30 °C	4.47846	0.57137	2.50531	0.08115	0.99986
60 °C	3.56621	0.75864	5.70772	0.20072	0.99965

Appendix Table J.2: Dual Site Langmuir Model Fitting Coefficients for OBC 800-3-O

Isotherm	Dual Site Langmuir Model Coefficients				
	q _{max} (mmol/g)	Alpha (unitless)	K ₁ (bar ⁻¹)	K ₂ (bar ⁻¹)	R ² (unitless)
0 °C	2.84577	0.58291	13.9221	0.37492	0.99932
30 °C	2.91106	0.67401	8.51868	0.19739	0.99936
60 °C	2.62524	0.77522	5.31619	0.14058	0.99951

Appendix Table J.3: Dual Site Langmuir Model Fitting Coefficients for OBC 800-0.5-M

Isotherm	Dual Site Langmuir Model Coefficients				
	q _{max} (mmol/g)	Alpha (unitless)	K ₁ (bar ⁻¹)	K ₂ (bar ⁻¹)	R ² (unitless)
0 °C	3.42692	0.52743	24.9267	0.16372	0.99890
30 °C	2.99503	0.68045	20.34813	0.18522	0.99893
60 °C	2.25217	0.85018	17.19069	0.29797	0.99911

Appendix Table J.4: Dual Site Langmuir Model Fitting Coefficients for OBC 800-3-M

Isotherm	Dual Site Langmuir Model Coefficients				
	q _{max} (mmol/g)	Alpha (unitless)	K ₁ (bar ⁻¹)	K ₂ (bar ⁻¹)	R ² (unitless)
0 °C	4.64222	0.58276	14.97388	0.23560	0.99810
30 °C	4.68835	0.73663	10.05133	0.16298	0.99932
60 °C	4.20906	0.83209	11.14648	0.23303	0.99982

Appendix Table J.5: Dual Site Langmuir Model Fitting Coefficients for OHC 180-M-800

Isotherm	Dual Site Langmuir Model Coefficients				
	q _{max} (mmol/g)	Alpha (unitless)	K ₁ (bar ⁻¹)	K ₂ (bar ⁻¹)	R ² (unitless)
0 °C	2.98951	0.42379	24.79235	0.86922	0.99929
30 °C	2.75852	0.51889	11.5972	0.48509	0.99951
60 °C	2.45866	0.69566	7.26689	0.42452	0.99978

Appendix Table J.6: Dual Site Langmuir Model Fitting Coefficients for BC Control Orange

Isotherm	Dual Site Langmuir Model Coefficients				
	q _{max} (mmol/g)	Alpha (unitless)	K ₁ (bar ⁻¹)	K ₂ (bar ⁻¹)	R ² (unitless)
0 °C	2.62212	0.57718	68.78936	0.34824	0.99684
30 °C	2.51903	0.70831	35.21723	0.20508	0.99759
60 °C	2.52798	0.80112	6.38832	0.12073	0.99955

Appendix Table J.7: Dual Site Langmuir Model Fitting Coefficients for BC Control Mandarin

Isotherm	Dual Site Langmuir Model Coefficients				
	q _{max} (mmol/g)	Alpha (unitless)	K ₁ (bar ⁻¹)	K ₂ (bar ⁻¹)	R ² (unitless)
0 °C	8.79914	0.69362	28.96148	0.11792	0.99911
30 °C	7.33741	0.76578	28.40180	0.23422	0.99826
60 °C	5.56746	0.88773	45.12470	0.22319	0.99966

Appendix Table J.8: Dual Site Langmuir Model Fitting Coefficients for HC Control Orange

Isotherm	Dual Site Langmuir Model Coefficients				
	q _{max} (mmol/g)	Alpha (unitless)	K ₁ (bar ⁻¹)	K ₂ (bar ⁻¹)	R ² (unitless)
0 °C	3.97136	0.48779	20.37256	0.96168	0.99963
30 °C	3.65428	0.58785	7.83586	0.47673	0.99972
60 °C	3.25400	0.72829	4.60204	0.35953	0.99989

Appendix Table J.9: Dual Site Langmuir Model Fitting Coefficients for OPB Micropore Orange

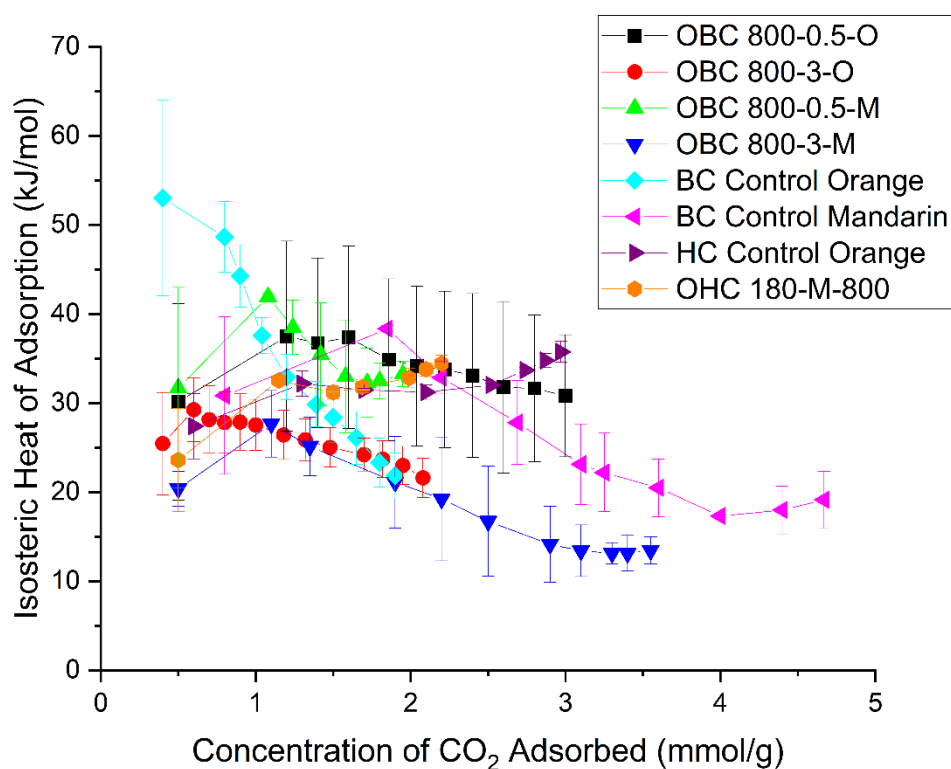
Isotherm	Dual Site Langmuir Model Coefficients				
	q _{max} (mmol/g)	Alpha (unitless)	K ₁ (bar ⁻¹)	K ₂ (bar ⁻¹)	R ² (unitless)
60 °C	2.88455	0.71107	11.1748	0.35043	0.99918

Appendix Table J.10: Dual Site Langmuir Model Fitting Coefficients for OPH Micropore Mandarin

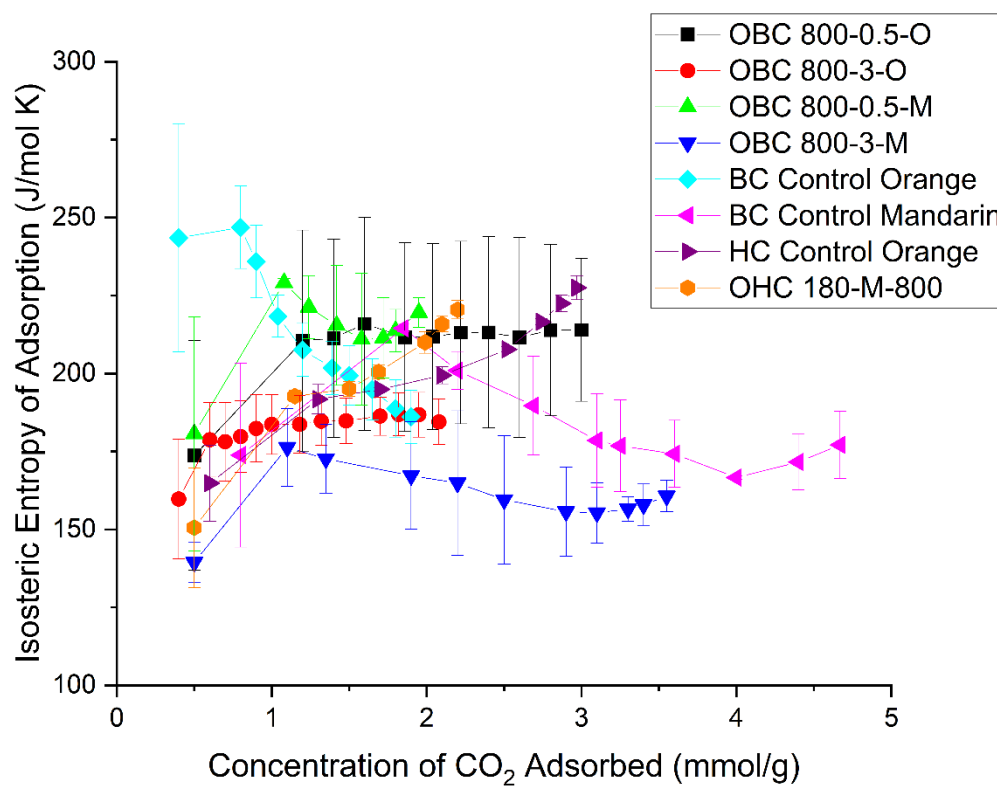
Isotherm	Dual Site Langmuir Model Coefficients				
	q _{max} (mmol/g)	Alpha (unitless)	K ₁ (bar ⁻¹)	K ₂ (bar ⁻¹)	R ² (unitless)
60 °C	2.42295	0.67000	6.57275	0.40025	0.99978

Appendix K: Isosteric Heat of Adsorption and Entropy of Adsorption Graphs

The plots of isosteric heat of adsorption against pressure, and entropy of adsorption against pressure can be seen with attached error bars in Appendix Figure K.1 and Appendix Figure K.2, respectively.



Appendix Figure K.1: Isosteric Heat of Adsorption of Selected Biochar and Hydrochar Samples Including Error Bars (Across Temperature Range of 0 – 60 °C)

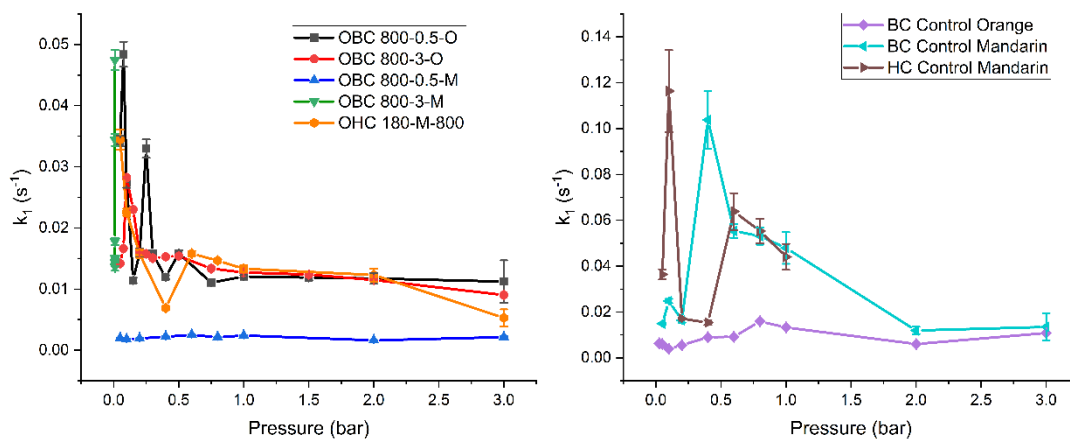


Appendix Figure K.2: Isosteric Entropy of Adsorption of Selected Biochar and Hydrochar Samples Including Error Bars (Across Temperature Range of 0 – 60 °C)

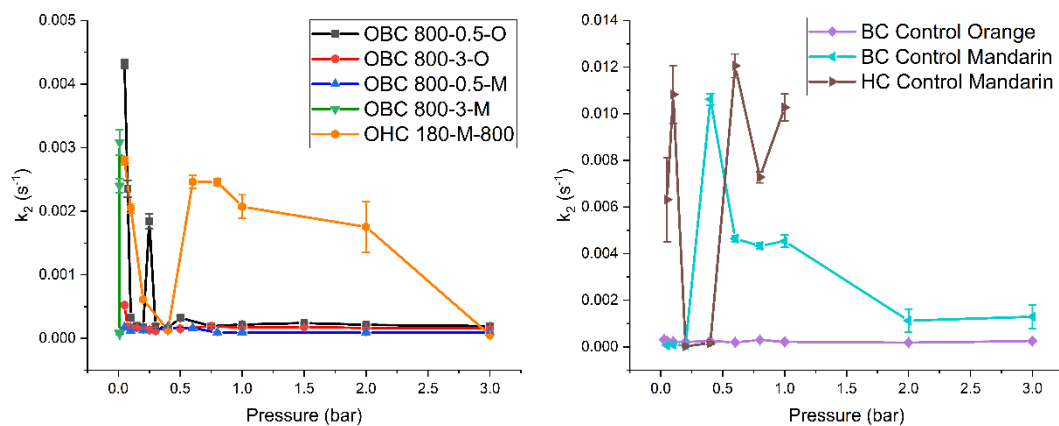
Appendix L: 0 °C and 30 °C k_1 and k_2 Plots vs Pressure

The plots of k_1 and k_2 against pressure for the 0 °C and 30 °C isotherms can be seen in

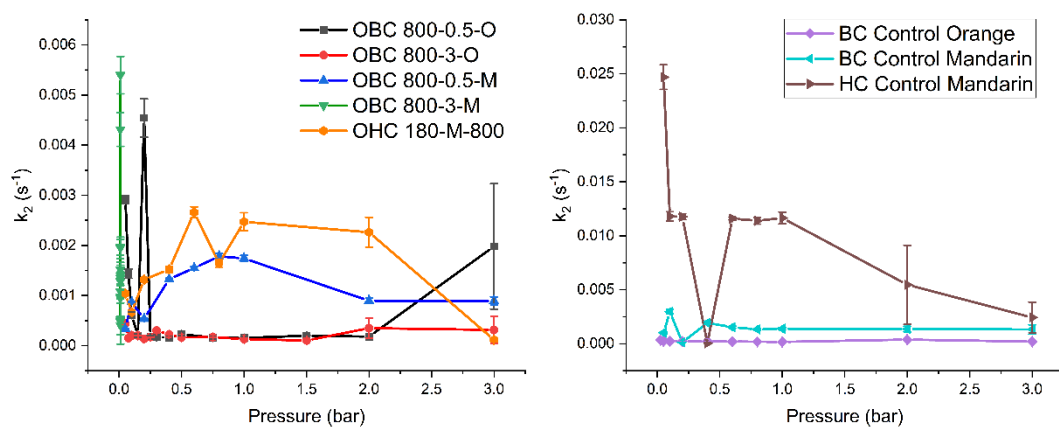
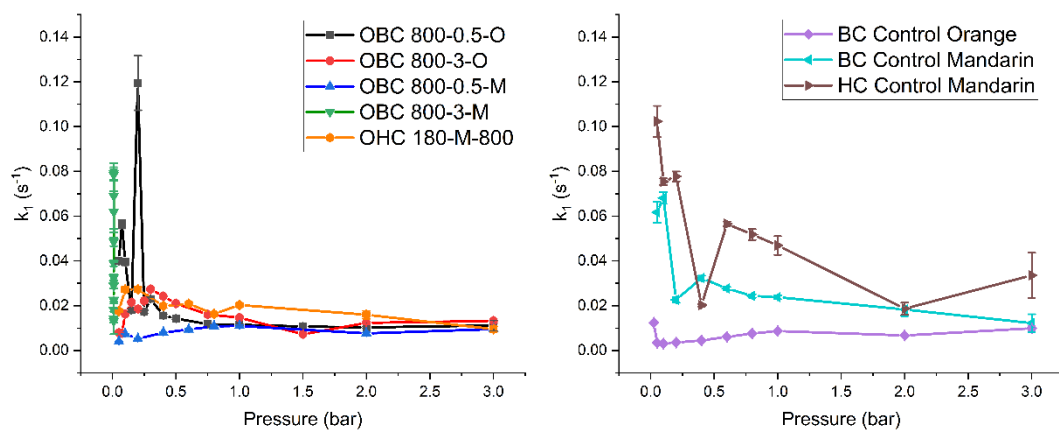
Appendix Figure L.1 to Appendix Figure L.4.



Appendix Figure L.1: k_1 Values for 0 °C CO₂ Adsorption Isotherms of Selected Chars Produced in this Study

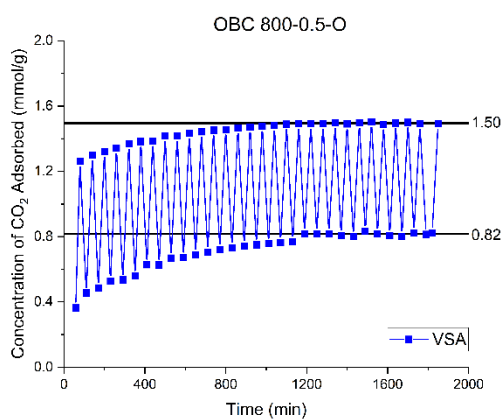


Appendix Figure L.2: k_2 Values for 0 °C CO₂ Adsorption Isotherms of Selected Chars Produced in this Study

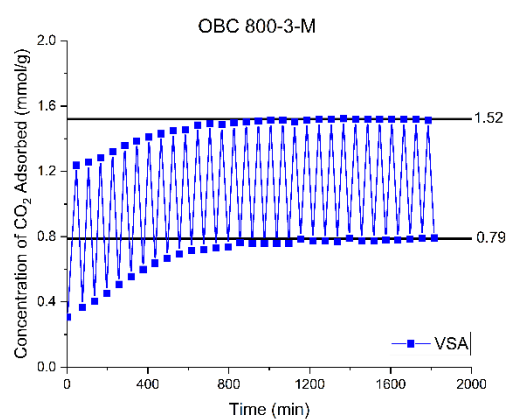


Appendix M: Vacuum Swing Adsorption Graphs

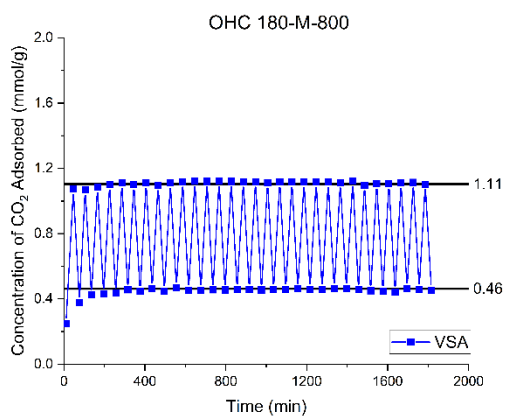
The VSA cyclic adsorption tests can be seen in Appendix Figure M.1 to Appendix Figure M.7.



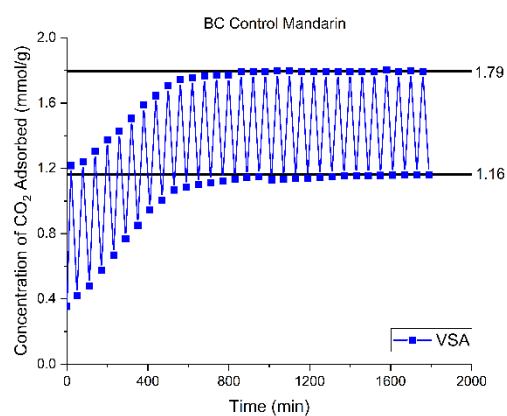
Appendix Figure M.1: Cyclic Adsorption Results for OBC 800-0.5-O (0.05 - 1 bar cycling, 60 °C, VSA)



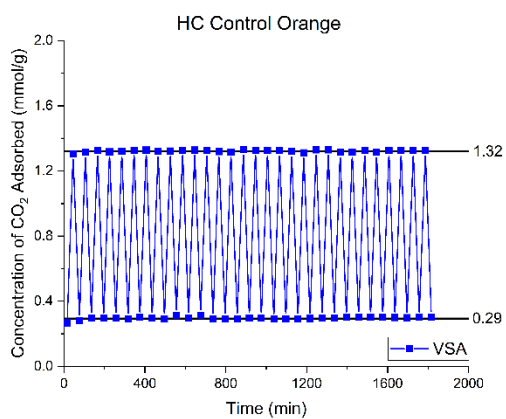
Appendix Figure M.2: Cyclic Adsorption Results for OBC 800-3-M (0.05 - 1 bar cycling, 60 °C, VSA)



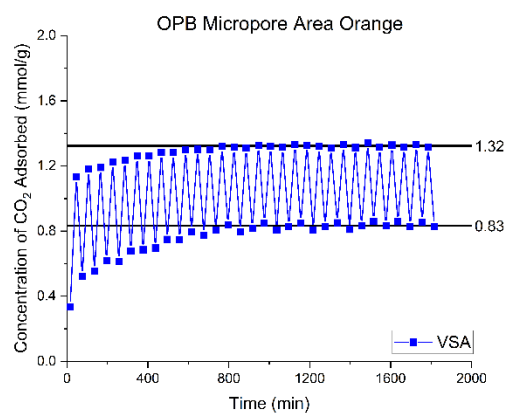
Appendix Figure M.3: Cyclic Adsorption Results for OHC 180-M-800 (0.05 - 1 bar cycling, 60 °C, VSA)



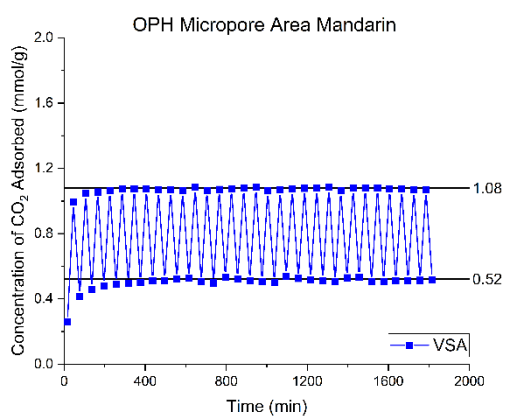
Appendix Figure M.4: Cyclic Adsorption Results for BC Control Mandarin (0.05 - 1 bar cycling, 60 °C, VSA)



Appendix Figure M.5: Cyclic Adsorption Results for HC Control Orange (0.05 - 1 bar cycling, 60 °C, VSA)



Appendix Figure M.6: Cyclic Adsorption Results for OPB Micropore Orange (0.05 - 1 bar cycling, 60 °C, VSA)



Appendix Figure M.7: Cyclic Adsorption Results for OPH Micropore Mandarin (0.05 - 1 bar cycling, 60 °C, VSA)