

Article

Conversion of Oil Palm Kernel Shell Wastes into Active Biocarbons by N₂ Pyrolysis and CO₂ Activation

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Abstract

Oil palm kernel shell is an abundant agricultural waste generated by the palm oil industry. To achieve sustainable use of this waste, oil palm kernel shells were converted into valuable resources as active biocarbons. A two-stage preparation method involving N₂ pyrolysis, followed by CO₂ activation, was used to produce the active biocarbon. The optimum pyrolysis conditions that produced the largest BET surface area of 519.1 m²/g were a temperature of 600 °C, a hold time of 2 h, a nitrogen flow rate of 150 cm³/min, and a heating rate of 10 °C/min. The optimum activation conditions to prepare the active biocarbon with the largest micropore surface area or the best micropore/BET surface area combination were a temperature of 950 °C, a CO₂ flow rate of 300 cm³/min, a heating rate of 10 °C/min, and a hold time of 3 h, yielding BET and micropore surface areas of 1232.3 and 941.0 m²/g, respectively, and consisting of 76.36% of micropores for the experimental optimisation technique adopted here. This study underscores the importance of optimising both the pyrolysis and activation conditions to produce an active biocarbon with a maximum micropore surface area for gaseous adsorption applications, especially to capture CO₂ greenhouse gas, to mitigate global warming and climate change. Such a comprehensive and detailed study on the conversion of oil palm kernel shell into active biocarbon is lacking in the open literature. The research results provide a practical blueprint on the process parameters and technical know-how for the industrial production of highly microporous active biocarbons prepared from oil palm kernel shells.



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Keywords: oil palm (*Elaeis guineensis*) kernel shell; pyrolysis; physical activation; biochar; active biocarbon

1. Introduction

Activated carbon is commonly used as an adsorbent in many applications such as air pollution control, gas purification and separation, water purification and wastewater treatment, and more recently studies have shown that it can be used for carbon dioxide capture and storage, as a catalyst support, and energy carrier as a battery and supercapacitor electrode material [1,2]. Traditionally, the precursors for the commercial production of activated carbons come from wood, coal, lignite, and peat. However, these activated carbon precursors are not cheap, and therefore, there is a need to find other cheaper carbonaceous materials such as agricultural biomass wastes. Generally, the starting materials for the preparation of activated carbons are those with high carbon but low inorganic contents. The high volatile contents associated with these lignocellulosic agricultural biomasses are ideal for creating highly porous structures within the active biocarbon matrix. Rice straw, wheat straw, corn straw, soybean root, spent coffee ground, sugarcane bagasse, rice husk, peanut

shell, coconut shell, walnut shell, castor shell, corncob, olive seed, jujube pit, sunflower head, and cotton seed are some of the agricultural wastes that have been used to prepare active biocarbons [1,2].

Active biocarbon can be prepared by a physical or chemical activation process. The physical process usually involves two stages: pyrolysis or carbonisation followed by activation. During pyrolysis, the biomass is heated in an inert atmosphere of N_2 flow at a moderate temperature of usually 600 to 800 °C for a period of 1 to 3 h to remove water moisture, and volatile matters within the carbon matrix. For a lignocellulosic biomass, the types of volatiles that are evolved from cellulose, hemicellulose, and lignin at various temperatures during pyrolysis for the temperature range of 150 to 800 °C are given later in Section 3.2. The purpose of pyrolysis is to produce biochars with rudimentary pore structures, which will facilitate the diffusion of the activating agent, such as CO_2 , into the interior carbon structure during activation. The pore surface area of biochar is low; for example, the highest BET surface area of biochar prepared from rice straw was only 78.17 m^2/g [3]. The biomass can also undergo vacuum pyrolysis, which eliminates the use of N_2 flow [4]. It was suggested that the evolution of volatiles from the carbon matrix for vacuum pyrolysis was more complete, resulting in a better adsorbent, with less tar present in the biochar than that pyrolysed in N_2 flow [4]. Subsequently, in the physical activation process, the resulting biochar is subjected to a partial gasification at a higher temperature, i.e., 850 to 950 °C, with carbon dioxide (CO_2) or steam (H_2O) to enlarge the pores already formed during pyrolysis and to form new porosities, therein to produce an active biocarbon with well-developed and accessible internal porosities, resulting in a very significant increase in the BET surface area than that for the biochar.

In chemical activation, the starting materials are impregnated with a chemical reagent, such as acids (phosphoric acid, H_3PO_4 and sulphuric acid, H_2SO_4), bases (potassium hydroxide, KOH and sodium hydroxide, NaOH) and salts (zinc chloride, $ZnCl_2$; potassium carbonate, K_2CO_3 and potassium chloride, KCl) and then activated in an inert atmosphere, such as N_2 , to produce the final active biocarbon [1,2,4]. This chemical is a dehydrating agent that can influence the pyrolytic decomposition and retard the formation of tars during the carbonisation process. Besides enhancing the pore development, these activation agents are supposed to modify the chemical properties of the resulting active biocarbons. Impregnation with different agents has limited effects on the inorganic components but significant effects on their surface organic functional groups, which are closely related to the adsorptive capacity of these chemically active biocarbons. Typically, active biocarbons with acidic surface chemical properties are favourable for basic gas adsorption, such as ammonia, while active biocarbons with basic surface chemical properties are suitable for acidic gas adsorption, such as sulphur dioxide. If the biomass is impregnated with one of those chemical agents mentioned earlier and is subjected to CO_2 or steam during activation, the final product, physical–chemical active biocarbon, generally has a higher pore surface area than its physically activated counterpart [4].

One of the major agricultural wastes is oil palm kernel shell. Oil palm (*Elaeis guineensis*) is a main agricultural crop in Malaysia with a planted area of 5.613 million hectares in 2024 [5]. Malaysia is the second largest producer of crude palm oil in the world, amounting to 19.338 million tonnes in 2024 [5], whilst Indonesia is the largest world producer of crude palm oil with 48.164 million tonnes in 2024 [6]. Crude palm oil is obtained from the yellowish fibrous flesh, which is called mesocarp, whilst palm kernel oil is produced using the white kernel. The oil palm industry generates vast quantities of biomass wastes, which are disposed of from the oil palm plantations and palm oil mills. The wastes in the plantations constitute oil palm trunks (OPTs) and oil palm fronds (OPFs). The OPTs are discarded during tree replanting, while the OPFs are left when the palm trees are

pruned during fruit harvesting. The solid wastes from the palm oil mills consist of empty fruit bunches, mesocarp fibres, and palm kernel shells. The liquid waste in the mills is generated from an extraction of palm oil for a wet process in a decanter. This liquid waste, combined with the wastes from the cooling water and steriliser, contributes to the palm oil mill effluent. An empty fruit bunch is the woody fibrous remnants after the removal of the fruits from the bunch in the stripper. The mesocarp fibre is the fibrous matter in the press cake (after the extraction of crude palm oil from the mesocarp), where the digested pressed fruit passes through screens to separate the fibre and nut. The kernel shell is the hard endocarp of the palm fruit that encloses the palm seed. It is recovered as part of the nut in the press cake and subsequently obtained as broken bits and pieces after threshing or crushing to remove the seed, which is used to produce palm kernel oil.

As a general guide, a fresh fruit bunch consists, by weight, of about 21% palm oil, 6–7% palm kernel, 14–15% fibre, 6–7% palm kernel shell, 23% empty fruit bunch, and 27–30% others as shown in Table 1 [7]. Based on this composition on a percent weight basis, the amounts of some oil palm wastes that were generated in Malaysia in 2024 could be estimated. Using the data available for 2024, Malaysia produced 19,338,266 tonnes of crude palm oil [5]. Hence, the estimated amounts of oil palm biomass wastes produced in Malaysia in 2024, based on 19,338,266 tonnes of palm oil and Table 1, are as follows: 21.180 million tonnes of empty fruit bunches, 13.353 million tonnes of mesocarp fibres, and 5.986 million tonnes of palm kernel shells. Based on 48.164 million tonnes of crude palm oil produced in Indonesia [6] and Table 1, Indonesia generated an estimated 14.908 million tonnes of palm kernel shells in 2024. Therefore, Indonesia and Malaysia generated an estimated combined total of 20.894 million tonnes of palm kernel shell wastes in 2024. Aside from the main traded commodities of crude palm oil, palm kernel oil, and palm kernel cake (a by-product of crushing and expelling oil from the palm kernel), these vast quantities of lignocellulosic biomass palm wastes, together with the chopped oil palm trunks and oil palm fronds, have negligible or no commercial value, except to use mesocarp fibres and palm kernel shells as fuels for boilers to generate process steam mostly to sterilise fresh fruit bunches and operate steam turbines to provide electricity to the palm oil mill complex.

Table 1. Percent weight composition of fresh fruit bunch [7].

Constituents	Percent Weight of Fresh Fruit Bunch (wt.%)
Palm oil	21
Palm kernel	6–7
Fiber	14–15
Palm kernel shell	6–7
Empty fruit bunch	23
Others	27–30

To explore the potential uses of the vast oil palm wastes as starting materials for biochar and active biocarbon production, the author and his co-author commenced research studies in 1995 to convert oil palm mesocarp fibres and palm kernel shells into chars with the first independently reported and detailed studies in 1998 in Lua and Guo [8] for mesocarp fibre waste and Guo and Lua [9] for palm kernel shell waste. Further subsequent studies by the author and his co-workers into possible industry applications of the active biocarbons prepared from oil palm wastes were directed into the adsorption of nitrogen dioxide (NO₂) [10], sulphur dioxide (SO₂) [11], ammonia (NH₃) [12], hydrogen sulphide (H₂S) [13], iodine [10], and phenol [4]. With increasing concerns and catastrophic effects arising from adverse climate changes due to global warming effects, studies have been re-

ported on the use of palm kernel shell active biocarbons to capture carbon dioxide, which is the predominant greenhouse gas constituent [14–16]. These detrimental warming phenomena occur because the absorptive properties of these greenhouse gases have overlapping wavelengths with those of the infrared radiation emissions from the Earth, and hence, heat is trapped by these greenhouse gases within the Earth's atmosphere, causing an increasing rise in global temperature with increasing amounts of greenhouse gases emitted on Earth.

There are hardly any research papers in the open literature that report on complete and comprehensive studies on all the operating parameters of the N₂ pyrolysis process and the subsequent CO₂ activation parameters for oil palm kernel shells as starting materials for preparing active biocarbons, and the optimisation of each of these parameters individually to achieve the highest microporous surface area in the resulting active biocarbons. Hence, this paper presents a thorough and detailed parametric process to prepare oil palm kernel shell active biocarbons with the largest micropore surface area or the best micropore/BET surface area combination for a two-stage physical activation using nitrogen as the inert atmosphere for pyrolysis and carbon dioxide as the activating agent. The development of such active biocarbon can be used to capture CO₂ to reduce greenhouse gas emissions and thereby mitigate global warming. At the same time, oil palm kernel shells can be economically used and valorised instead of being treated as biomass waste.

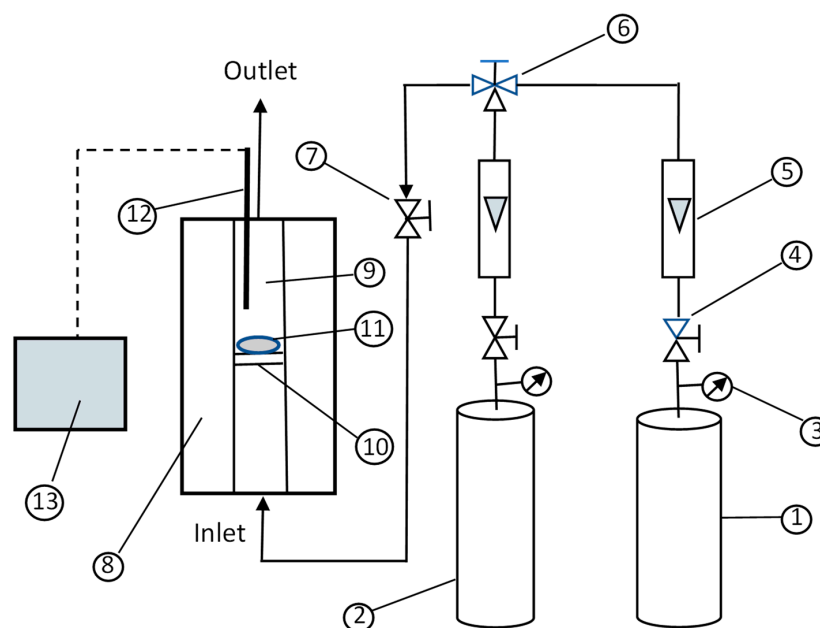
2. Materials and Methods

2.1. Material

Oil palm kernel shells were sourced from an oil palm plantation in Selangor, a state in Malaysia. The shells were initially dried at 120 °C for 6 h to remove any water moisture on the surfaces. They were then crushed and sieved to sizes ranging from 2.0 to 2.8 mm. The shells were subjected to physical activation, which consisted of a two-stage heating process involving pyrolysis and followed by activation using carbon dioxide. The pyrolysis process was carried out under a nitrogen stream. To achieve effective adsorbents, the basic requirement is to maximise the specific pore surface area of active biocarbon. In a two-stage optimisation process, the operating parameters for pyrolysis were optimised first, and subsequently, these optimum pyrolysis conditions were used to determine the optimum parameters for activation.

2.2. Pyrolysis and Activation

Pyrolysis of the shells and subsequent activation of the biochars were conducted in a vertical stainless steel reactor, which was 550 mm long and 38 mm in inside diameter. The reactor was positioned within an electrical tube furnace (818P, Lenton) with programmable controls such as ramp rate, final temperature, and dwell time. Figure 1 shows the schematic diagram of the experimental set-up. The absolute pressure of nitrogen and CO₂ gas on entering the reactor was slightly higher than the atmospheric pressure, i.e., slightly greater than 101 kPa, and their temperature was at a room temperature of 30 °C. Approximately 20 g of the shells was placed in the reactor and supported on a 120 µm metal mesh, which was mounted at the mid-point of the tube furnace. For pyrolysis under a nitrogen stream, the CO₂ gas cylinder in Figure 1 was shut off, and pure nitrogen (99.9995%) was used as the inactive gas flowing in the reactor at the commencement of pyrolysis at room temperature until the end of pyrolysis when the reactor had cooled down to room temperature. At each pre-selected pyrolysis temperature, the sample was subjected to its pre-set hold time, nitrogen flow rate, and heating rate. During optimisation, each of the pyrolysis parameters, namely, temperature, hold time, nitrogen flow rate, and heating rate, was adjusted independently while the other three parameters remained constant.



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|-----------------------------------|------------------------------------|--------------------|
| 1. Gas cylinder (N ₂) | 2. Gas cylinder (CO ₂) | 3. Pressure gauge |
| 4. Regulating valve | 5. Flowmeter | 6. Three-way valve |
| 7. On-off valve | 8. Tube furnace | 9. Reactor tube |
| 10. Metal mesh | 11. Sample | 12. Thermocouple |
| 13. Temperature controller | | |

Figure 1. Schematic diagram of experimental set-up.

With the optimisation of each pyrolysis parameter, the optimised value was used when optimising the next pyrolysis parameter until all pyrolysis parameters were optimised. Table 2 shows the optimisation process of operating parameters for pyrolysis, with 4 series of pyrolysis tests in the sequence of Series 1, 2, 3, and 4 for parameters of pyrolysis temperature, pyrolysis hold time, N₂ flow rate, and pyrolysis heating rate, respectively. The range of values for each pyrolysis parameter is also given. For this pyrolysis optimisation process, all biochars were subsequently subjected to the same activation conditions, namely, a heating rate of 10 °C/min from room temperature to 900 °C under a nitrogen flow rate of 150 cm³/min, an activation temperature of 900 °C, an activation hold time of 0.5 h, and a carbon dioxide flow rate of 100 cm³/min. After this short activation, the process was cooled to room temperature under a nitrogen flow rate of 150 cm³/min. The selection criterion for each optimum pyrolysis parameter was based on the largest BET surface area of the resulting active biocarbon, so that the largest rudimentary pore surface area formation was available for the activation optimisation. The optimised pyrolysis conditions would thus be used to prepare the biochars for the subsequent activation process when optimising the activation parameters to prepare the active biocarbons.

Table 2. Process optimisation of operating parameters for pyrolysis.

Parameter	Pyrolysis Series 1	Pyrolysis Series 2	Pyrolysis Series 3	Pyrolysis Series 4
Pyrolysis Temperature (°C)	400, 500, 600, 700, 800, and 900	Suitable pyrolysis temperature from Series 1		
Pyrolysis Hold Time (h)	2	0.5, 1.0, 1.5, 2.0, 2.5, and 3.0	Suitable pyrolysis hold time from Series 2	
Pyrolysis N ₂ Flow Rate (cm ³ /min)	150	150	50, 100, 150, 200, 250, and 300	Suitable pyrolysis N ₂ flow rate from Series 3
Pyrolysis Heating Rate (°C/min)	10	10	10	5, 10, 15, 30, 40, and 50

In the activation process, the optimised biochar was placed in the same reactor that was used for the pyrolysis process in Figure 1. Nitrogen gas with a flow rate of 150 cm³/min was used during the ramping up of temperature from room temperature to the set activation temperature, and thereafter once the activation temperature was attained, the nitrogen was replaced by carbon dioxide by shutting the valve for the nitrogen cylinder and opening the valve for the carbon dioxide cylinder to allow carbon dioxide gas to flow to the reactor via the three-way valve in Figure 1. After activation, carbon dioxide flow was stopped, and nitrogen gas of the same flow rate of 150 cm³/min was used to cool the reactor to room temperature. In these activation tests, the parameters studied were activation temperature, carbon dioxide flow rate, heating rate, and activation hold time. Likewise, to achieve the optimum activation parameters, each parameter was varied independently to obtain the optimum value while the other three parameters were held constant, and thereafter this optimised value would be used when optimising the next activation parameter until all activation parameters were optimised. Table 3 shows the optimisation process of operating parameters for activation, with 4 series of activation tests in the sequence of Series 1, 2, 3, and 4 for the parameters of activation temperature, CO₂ flow rate, activation heating rate, and activation hold time, respectively. The range of values for each activation parameter is also given. The basis of selecting each optimised value was based on the largest micropore surface area or the best micropore/BET surface area combination of the resulting active biocarbon, so that it is suitable and effective for gaseous adsorption.

Table 3. Process optimisation of operating parameters for activation.

Parameter	Activation Series 1	Activation Series 2	Activation Series 3	Activation Series 4
Activation Temperature (°C)	750, 800, 850, 900, and 950	Suitable activation temperature from Series 1		
Activation CO ₂ Flow Rate (cm ³ /min)	100	50, 100, 200, 300, 400, and 500	Suitable activation CO ₂ flow rate from Series 2	
Activation Heating Rate (°C/min)	10	10	5, 10, 20, 30, 40, and 50	Suitable activation heating rate from Series 3
Activation Hold Time (h)	3	3	3	1.0, 1.5, 2.0, 2.5, 3.0, and 4.0

In the preparation of active biocarbons, there are substantial weight losses during the pyrolysis reaction due to the release of volatile matter and water contents, as well as during the activation reaction, where there is carbon consumption due to the CO₂–carbon reaction

and further release of volatile matter. Hence, the yield of the active biocarbon is indicative of these losses and the intensities of the pyrolysis and activation reactions. The yield of active biocarbon is defined as follows:

$$\text{Yield of active biocarbon} = \frac{\text{Weight of active biocarbon}}{\text{Weight of initial raw material}} \times 100\%$$

2.3. Adsorption Isotherms and Proximate Analyses

An accelerated surface area and porosimetry system (ASAP 2010, Micromeritics Instrument Corporation, Norcross, GA, USA) was used to obtain the adsorption isotherms of the active biocarbons under N₂ adsorption at 77 K (−196 °C). These adsorption isotherms were used to calculate the BET surface area by the Brunauer–Emmett–Teller (BET) equation [17]. The micropore volume was determined by the Dubinin–Radushkevich equation, and hence the micropore surface area was then calculated [18]. The Barrett–Joyner–Halenda (BJH) model was used to determine the pore size distributions [19]. A thermogravimetric analyser (TA-50, Shimadzu Corporation, Kyoto, Japan) was used to determine the proximate analyses of the oil palm kernel shell, biochar, and active biocarbon in terms of their chemical compositions, which are expressed in percent by weight of moisture, volatile, fixed carbon, and ash contents.

3. Results and Discussion

3.1. Proximate Analyses

The proximate analysis of raw oil palm kernel shell is given in Table 4. The weight percent of volatile organic matter content of the raw oil palm kernel shell was the highest at 65.85%, followed by the fixed carbon content at 28.36%; the high contents of these two constituents in the raw material are very suitable for preparing active biocarbon with a large pore surface area. The remaining contents were moisture and ash. The proximate analyses and yields of the optimised biochar and active biocarbon in Table 4 are discussed later in this article.

Table 4. Proximate analyses and yields of oil palm kernel shell, biochar, and active biocarbon.

	Oil Palm Kernel Shell	Biochar *	Active Biocarbon +
Moisture (wt.%)	4.82	6.74	0
Volatile Organic Matter (wt.%)	65.85	11.06	11.24
Fixed Carbon (wt.%)	28.36	77.95	83.75
Ash (wt.%)	0.97	4.25	5.01
Yield (wt.%)	100	34.80	10.05

Note: * Biochar was prepared under optimum pyrolysis conditions of a temperature of 600 °C, a hold time of 2 h, a nitrogen flow rate of 150 cm³/min, and a heating rate of 10 °C/min. + Active biocarbon was prepared under optimum activation conditions of a temperature of 950 °C, a CO₂ flow rate of 300 cm³/min, a heating rate of 10 °C/min, and a hold time of 3 h.

3.2. Effects of Pyrolysis Parameters

The effects of pyrolysis parameters, namely, pyrolysis temperature, hold time, nitrogen flow rate, and heating rate, on the pore characteristics of active biocarbons with fixed activation conditions were studied experimentally. Figure 2 shows the effects of pyrolysis temperature on the BET, micropore, and non-micropore surface areas, and the micropore volume of the active biocarbons, while the rest of the pyrolysis parameters were held constant. Increasing the pyrolysis temperature from 400 to 600 °C progressively improved all the pore characteristics of the active biocarbons except for the non-micropore surface area. The purpose of pyrolysis is to release the volatiles from the shell structures and to form rudimentary pores within the biochar structures. The rudimentary pore structures

form the tortuous passages or pathways for the diffusion of CO₂ molecules into the inner pore structures of the biochar during CO₂ activation. As a result, pore development within the existing biochar structures is enhanced, and additional new pores are formed in the active biocarbons. Oil palm kernel shell is a lignocellulosic biomass whose main constituents are cellulose (40–50%), hemicellulose (15–25%), and lignin (15–30%) [20]. At the pyrolysis temperature of 400 °C, the BET, micropore, and non-micropore surface areas of the resultant active biocarbon were 407.4, 289.82, and 117.58 m²/g, respectively. At the pyrolysis temperature of 400 °C, the rudimentary pore structures in the biochar were developed due to the release of water and volatile contents from the oil palm shell biomass. Spanning the temperature range from room temperature to 400 °C, cellulose polymers underwent dehydration to water and depolymerisation of cellulose led to the formation of low molecular compounds such as glycoaldehyde, furan, hydroxyl acetaldehyde, formic acid, and CO₂ for pyrolysis temperatures from 150 to 300 °C [21,22]. For pyrolysis temperatures between 300 and 390 °C, cellulose depolymerisation resulted in the breakdown of the glycosidic bonds and the formation of levoglucosan and levoglucosenone [23]. Hemicellulose in oil palm shells exists as angiosperm hemicellulose, which contains mostly xylan, a polysaccharide. For hemicellulose pyrolysis, the release of water due to dehydration reactions within the polysaccharides became significant at 200 °C. During the early stage of xylan decomposition, the highest production of methanol, formic acid, and acetic acid occurred at 230 °C because of fragmentation reactions. At a temperature of 240 °C, the glycosidic linkages between monomer units for xylan became extremely unstable, and a rapid depolymerisation occurred. The rapid depolymerisation of the main xylopyranose chain occurred at around 290 °C, leading to the formation of H₂O, CO₂, and CO and the production of condensable volatile compounds such as anhydro-saccharides, furans, furfural, hydroxyacetaldehyde, hydroxyacetone, and 1-hydroxy-2-butanone [23]. (Depolymerisation consists in the breaking of the bonds between the monomer units of the polymers, whereas fragmentation consists in the breaking of the linkage of many covalent bonds of the polymer, even within the monomer units.) For lignin pyrolysis, the main decomposition activity of lignin occurred over a large temperature range from 200 to 450 °C, with the highest decomposition rate generally occurring between 360 and 400 °C. During this temperature range, eugenol, cresol, guaiacol, syringol, and phenol were released. The fragmentation of the methoxy groups in lignin led to an important formation of methanol at 400 °C [23].

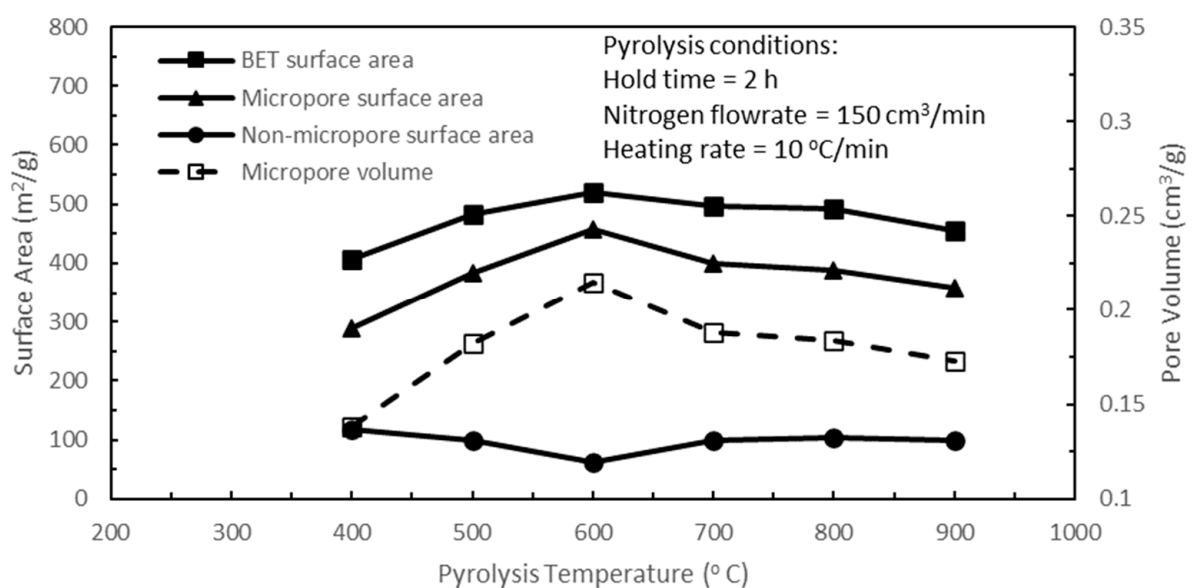


Figure 2. Effects of pyrolysis temperature on the pore characteristics of active biocarbons.

When the pyrolysis temperature was increased to 500 °C and then further to 600 °C, the continued release of the volatile contents provided more rudimentary pores in the biochar structure. The subsequent CO₂ activation of these biochars enhanced pore development and increased the formation of new pores, especially micropores, contributing to further increases in the BET and micropore surface areas and the micropore volume of the resultant active biocarbon, whilst there was a continuous slight dip in the non-micropore surface area with increasing the pyrolysis temperature from 400 to 600 °C as seen in Figure 2. This slight dip in the non-micropore surface area could probably be attributed to the increasing merging of two or more non-micropores during activation, for increasing pyrolysis temperature to form new larger non-micropores. Accompanying increasing pyrolysis temperature from 400 to 600 °C, increasing amounts of volatiles were released, resulting in more non-micropores as well as micropores being formed and in closer proximity to each other. During activation, pore widening due to the CO₂–carbon reaction and the eventual collapse of some pore walls can forge the merging of pores, with the merging of non-micropores being more predominant than that of micropores and hence resulting in gradual decreases in the non-micropore surface area with increasing pyrolysis temperature from 400 to 600 °C. Over the pyrolysis temperature span from 400 to 600 °C, methyl substituents in cellulose are converted into methane by a mechanism of demethylation for pyrolysis temperatures from 500 to 600 °C, whilst methyl substituents in hemicellulose are converted to methane by demethylation with a maximum methane production at 550 °C [23]. The fragmentation of the methoxy groups in lignin is the source of CH₄ production at 430 °C [23]. The pyrolysis of lignin releases a significant amount of CO between 500 and 800 °C, which is due to the depolymerisation of the ether bonds [23]. The depolymerisation of ether could be verified by the FTIR (Fourier transform infrared spectrometry) spectrum of the diminishing presence of the ether group in the biochar at a pyrolysis temperature of 600 °C compared to the FTIR spectrum of the biochar pyrolysed at 400 °C, which was shown in the research study of the pyrolysis of oil palm stones by Guo and Lua [24]. The release of these volatile organic compounds over the pyrolysis temperature increase from 400 to 600 °C contributed to further rudimentary pore structures in the biochar.

Subsequent increases in pyrolysis temperature from 600 to 900 °C yielded continual decreases in the BET and micropore surface areas and the micropore volume of the active biocarbons, as shown in Figure 2. However, the non-micropore surface area increased with an increase in pyrolysis temperature from 600 to 700 °C and thereafter remained almost constant up to the pyrolysis temperature of 900 °C. Increasing the pyrolysis temperature from 600 to 900 °C resulted in increasing release of more volatile organic compounds and hence increasing rudimentary pores in the biochar, which resulted in enhancing pore development and the formation of new pores in the active biocarbon. During CO₂ activation, the development of new micropores, in part due to the continual release of volatile matters, and pore widening occur concurrently due to the CO₂–carbon reaction. For these increasing pyrolysis temperatures, with the increasing rudimentary pores available in the biochar, the pore widening of micropores into non-micropores and the merger of pores to form non-micropores were more predominant than the formation of micropores, resulting in decreasing micropore surface area and decreasing BET surface area with increasing pyrolysis temperature from 600 to 900 °C, and a corresponding increase in the non-micropore surface area for the pyrolysis temperature increase from 600 to 700 °C. However, for pyrolysis temperatures from 700 to 900 °C, the non-micropore surface area remained almost constant for the following reasons. The increasing rudimentary pores available as a result of increasing the pyrolysis temperature from 700 to 900 °C and with pore widening of micropores during CO₂ activation formed non-micropores and hence

increased the non-micropore surface area with increasing pyrolysis temperature. On the other hand, the collapse of some pore walls and the merger of two or more non-micropores to form larger non-micropores decreased the non-micropore surface area with increasing pyrolysis temperature. If a net zero balance was achieved for these two opposing effects, the resulting effect would produce a constant non-micropore surface area with increasing the pyrolysis temperature from 700 to 900 °C, as seen in Figure 2. Overlapping this pyrolysis temperature span of 600 to 900 °C, CO is formed due to the conversion of the phenol rings present in lignin over the temperature range of 550 to 800 °C. The release of H₂ over the temperature range of 480 to 800 °C is mainly due to dehydrogenation reactions during the formation of a more condensed structure arising from the conversion of short substituents of the aromatic rings in xylan during hemicellulose pyrolysis [23]. Both of these conversions of the volatile contents in the biochar had also occurred in the previous pyrolysis temperature range of 400 to 600 °C. The previously stated depolymerisation of the ether bonds between 500 and 800 °C is also applicable to this pyrolysis temperature range of 600 to 900 °C. The FTIR spectrum of the biochar pyrolysed at 800 °C verified the absence of the ether group as reported by Guo and Lua [24]. At the pyrolysis temperature of 900 °C, the carbonyl group of ketones disappeared, leaving the aromatic benzene rings and the carbonyl group of quinones remaining in the biochar [24].

There are three possible end paths for the condensable volatile organic compounds released by the pyrolysis process. Most of them will be deposited and collected in the pyrolysis oil residue, whilst some of them can be redeposited on the biochar surfaces. A small remnant of the volatile contents can remain within the pore structures of the biochar. The released water due to dehydration reactions is also collected in the pyrolysis residue. However, incondensable gases such as CO₂, CO, CH₄ and H₂ are emitted to the surrounding environment. Based on the largest BET surface area in Figure 2, the optimum pyrolysis temperature was 600 °C. Hence, a pyrolysis temperature of 600 °C was used for the subsequent optimisation of the remaining pyrolysis parameters.

With the optimum pyrolysis temperature set at 600 °C, the effects of pyrolysis hold time on the pore properties of active biocarbons were studied next, while the rest of the pyrolysis parameters were held constant. In Figure 3, increasing the pyrolysis hold time from 0.5 to 2 h yielded increasing release of low-molecular-weight volatiles and resulted in increasing tiny pores in the biochar structure, which led to an increasing rudimentary pore structure within the biochar. Hence, increasing the hold time from 0.5 to 2 h resulted in increasing the BET, micropore, and non-micropore surface areas, and the micropore volume of the active biocarbons upon subsequent CO₂ activation. However, beyond a 2 h pyrolysis hold time, the textural characteristics of the active biocarbons deteriorated with increasing the hold time from 2 to 3 h. Prolonged and sustained heat treatment during pyrolysis at 600 °C for more than a 2 h hold time leads to the softening and sintering of the residual low-molecular-weight volatiles in the biochar, giving rise to the closing and sealing of part of the pore structure of the biochar. These masses of low-molecular-weight volatiles remaining in the biochar structure could impede and reduce the CO₂–carbon reaction during CO₂ activation and therefore decrease the BET and micropore surface areas and the micropore volume of the resulting active biocarbons with increasing the pyrolysis hold time from 2 to 3 h, even though these effects were much less significant for the non-micropore surface area. Based on the largest BET surface area in Figure 3, the optimum pyrolysis hold time was 2 h. Hence, a pyrolysis temperature of 600 °C and a pyrolysis hold time of 2 h were used for the subsequent optimisation of the remaining pyrolysis parameters.

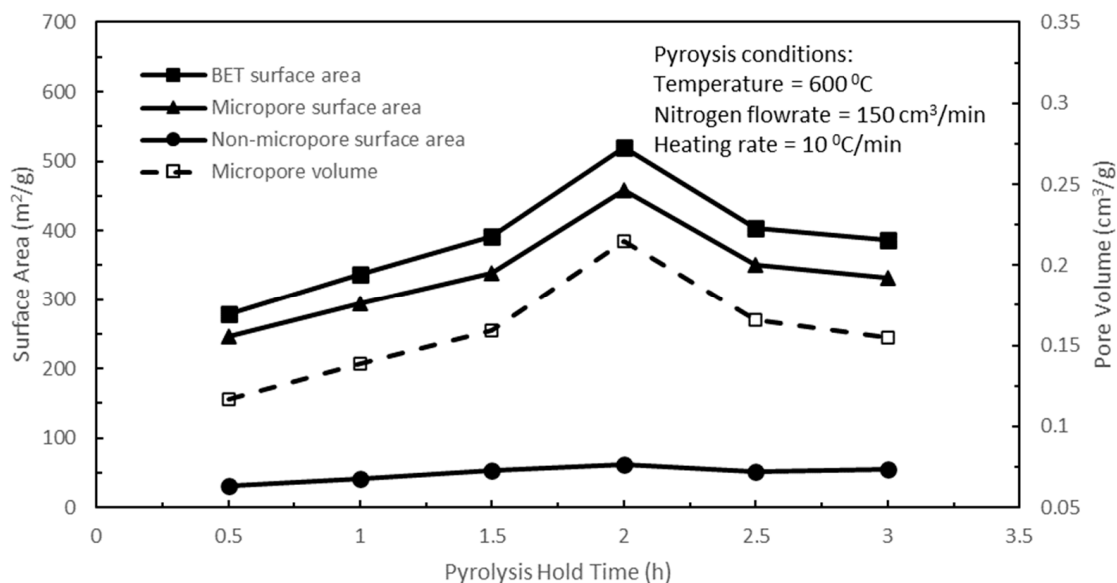


Figure 3. Effects of pyrolysis hold time on the pore characteristics of active biocarbons.

With the optimum pyrolysis temperature set at 600 °C and the pyrolysis hold time at 2 h, the effects of nitrogen flow rate during pyrolysis on the pore characteristics of active biocarbons were studied next, while the rest of the pyrolysis parameters were held constant. The functions of nitrogen flow are firstly to provide an inert atmosphere for the pyrolysis reaction and secondly to entrain the released volatiles in the nitrogen flow, thereby removing them from the reactor. In Figure 4, the results show that increasing the nitrogen flow rate during pyrolysis from 50 to 150 cm³/min (50 to 200 cm³/min for the non-micropore surface area) resulted in increasing BET and micropore surface areas, micropore volume, and non-micropore surface area of the resulting CO₂-activated biocarbons; however, further increases in the nitrogen flow rate up to 300 cm³/min had adverse effects, which resulted in continual decreases in these pore characteristics. Increasing the nitrogen flow rate from 150 to 300 cm³/min (200 to 300 cm³/min for the non-micropore surface area) had the effect of reducing the surface temperature on the biochar surfaces, resulting in a lower pyrolysis reaction rate and decrease in the release of volatiles, which led to decreasing pore development with the steepest decrease at 300 cm³/min. Hence, a nitrogen flow rate of 150 cm³/min yielded the largest BET surface area in the resulting active biocarbon. For the optimisation of the last remaining pyrolysis heating rate parameter, a pyrolysis temperature of 600 °C, a pyrolysis hold time of 2 h, and a nitrogen flow rate of 150 cm³/min during pyrolysis were used.

Figure 5 shows the effects of pyrolysis heating rate on the pore characteristics of the active biocarbons for a span of pyrolysis heating rates from 5 to 50 °C/min. Increasing the heating rate from 5 to 10 °C/min increased the BET and micropore surface areas, micropore volume, and non-micropore surface area. However, increasing the heating rates from 10 to 50 °C/min resulted in decreasing pore characteristics in the active biocarbons, with very gradual progressive reductions in these pore characteristics from 15 to 50 °C/min. The optimum pyrolysis heating rate was shown to be 10 °C/min. The pyrolysis heating rate will have a direct consequence and impact on the temperature ramp-up time from room temperature to the final pyrolysis temperature, which will ultimately affect the residence time of the biochar during pyrolysis. Increasing the heating rate shortens the temperature ramp-up time from room temperature to the final pyrolysis temperature in the reactor and vice versa. Reducing the pyrolysis heating rate from 10 °C/min to 5 °C/min was tantamount and comparable to subjecting the biochar to the detrimental effects of

prolonged hold time, as discussed earlier for the effects of an excessively long hold time on the biochar in Figure 3. Hence, the BET and micropore surface areas, micropore volume, and non-micropore surface area of the resulting active biocarbon decreased with a lower heating rate of 5 °C/min when compared to the heating rate of 10 °C/min, as seen in Figure 5. However, increasing the pyrolysis heating rate from 10 to 50 °C/min resulted in decreasing temperature ramp-up time, thereby leading to decreasing pyrolysis residence time for the biochar and hence reducing the amounts of volatiles released. This had the effect of decreasing rudimentary pore development in the biochar, and therefore, there was a small progressive decrease in the BET and micropore surface areas, micropore volume, and non-micropore surface area of the active biocarbons with increasing heating rate. For the range of pyrolysis heating rates studied, increasing the heating rate from 5 to 50 °C/min decreased the temperature ramp-up time from 1.9 to 0.19 h, respectively.

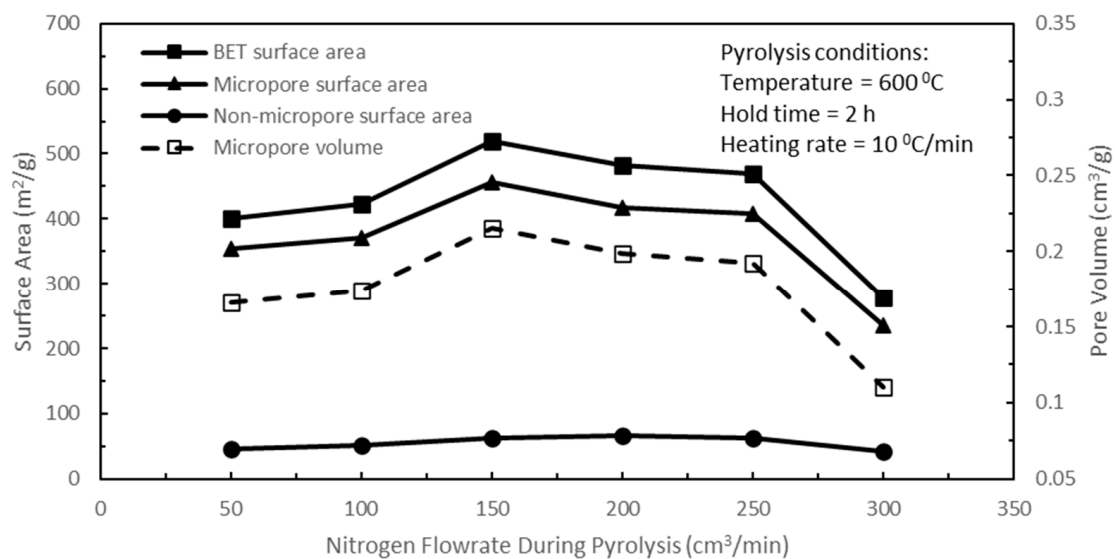


Figure 4. Effects of nitrogen flow rate during pyrolysis on the pore characteristics of active biocarbons.

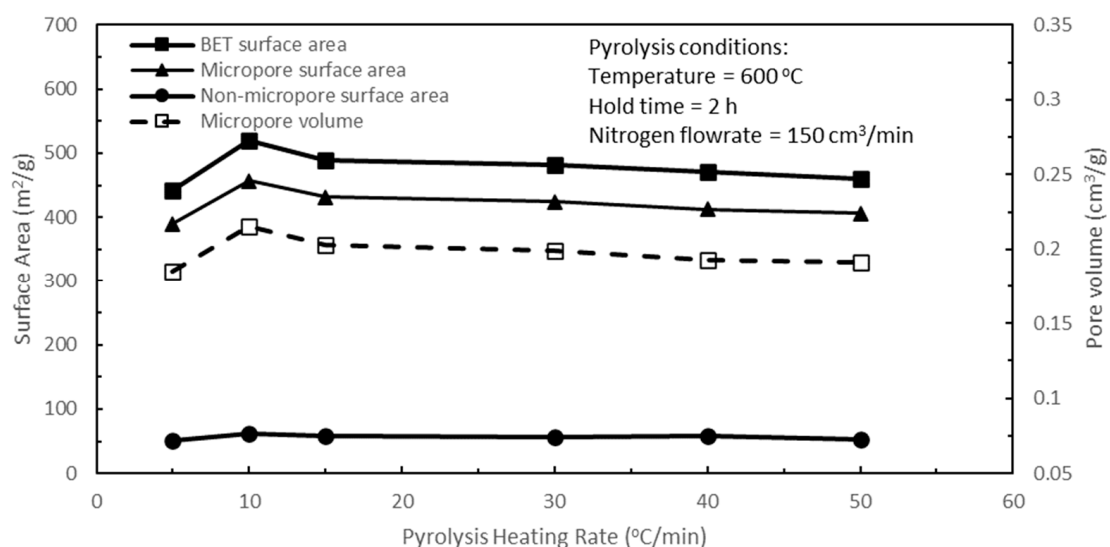


Figure 5. Effects of pyrolysis heating rate on the pore characteristics of active biocarbons.

Pore development in biochar during pyrolysis is desirable as the release of the volatile matter contents generates rudimentary pores in the biochar structure. This facilitates and enhances the BET and micropore surface areas, micropore volume, and non-micropore surface area of the active biocarbon by promoting the diffusion of CO₂ molecules into the

pores and thereby increasing the CO₂–carbon reaction, which creates more pores in the active biocarbon. For the pyrolysis parameters studied, the optimum pyrolysis conditions were a pyrolysis temperature of 600 °C, a pyrolysis hold time of 2 h, a nitrogen flow rate of 150 cm³/min during pyrolysis, and a pyrolysis heating rate of 10 °C/min to produce a resulting active biocarbon with a BET surface area of 519.1 m²/g, a micropore area of 456.94 m²/g, a non-micropore area of 62.17 m²/g, and a micropore volume of 0.215 cm³/g. The proximate analysis of this biochar is given in Table 4, which shows a large decrease in the volatile organic matter content as the volatiles were mainly released during pyrolysis and resulted in the yield of biochar at 34.80%. Pyrolysis does not consume any carbon, and hence the carbon content increased to 77.95% because of the significant reduction in weight of the biochar compared to the starting raw material. All these biochars were converted into active biocarbons under fixed activation conditions as stated in Section 2.2, which constituted part of the pyrolysis optimisation process. The above optimum pyrolysis conditions were used for the optimisation of the activation conditions for the active biocarbons.

3.3. Effects of Activation Parameters

The effects of varying activation temperature on the pore characteristics of the active biocarbons prepared from oil palm kernel shells were studied first, while the other activation parameters, namely, carbon dioxide flow rate, heating rate, and hold time were held constant at 100 cm³/min, 10 °C/min, and 3 h, respectively. Figure 6 shows the effects of activation temperature on the pore characteristics of the active biocarbons. Increasing the activation temperature from 750 to 950 °C yielded increasing BET, micropore, and non-micropore surface areas, and micropore volume. These increasing trends were attributed to the increasing CO₂–carbon reaction with increasing activation temperature, which caused increasing ‘carbon burn-offs’ within the pore structure, producing more porosities in the active biocarbon by enhancing and enlarging existing pores and the formation of new pores. At the same time, increasing activation temperature would release increasing remnant volatile matters, especially high-molecular-weight volatiles, which were still present in the starting biochars, thereby contributing to increasing new pores in the active biocarbons, namely, in the sites vacated by the volatiles. Guo and Lua [24] reported the removal of the carbonyl group of quinones when the activation temperature was increased from 900 to 950 °C, which gave credence to the continual release of volatile matters over this temperature interval. Another factor that could contribute to increasing new pores with increasing the activation temperature from 750 to 950 °C (even up to 1000 °C) was the continual release of volatile matters in the biochars during the initial temperature ramp-up time from room temperature to the final selected activation temperature with N₂ gas stream flushing through the reactor. Guo and Lua [24] reported the presence of the carbonyl group of ketones at a pyrolysis temperature of 800 °C, but it was absent at 900 °C when the pyrolysis temperature was increased from 800 to 900 °C, which therefore supported the thesis of continual release of volatile matters over this temperature interval. This volatile release could be considered as an extension to the pyrolysis process, accompanied by a longer ‘perceived hold time’ for a higher activation temperature. This ramp-up time varied from 1.20 to 1.62 h for 750 to 1000 °C activation temperatures, respectively. Thereafter, increasing the activation temperature from 950 to 1000 °C increased the BET and non-micropore surface areas but decreased the micropore surface area and the micropore volume. At this high activation temperature of 1000 °C, there were pore enlargements and specifically more pronounced pore widening of micropores into mesopores and even macropores, resulting in an increase in the BET surface area and a steep increase in the non-micropore surface area but reductions in the micropore surface area and micropore volume. On the other hand, there was the formation of new micropores for this temperature range from 950 to 1000 °C

due to the continual release of remaining high-molecular-weight volatiles, which Guo and Lua [24] reported on the presence of aromatic benzene rings in the active biocarbons at the activation temperature of 950 °C, but their increases were probably overshadowed by the significant decrease in existing micropores due to the pore widening into mesopores and macropores. Hence, there were declines in micropore surface area and micropore volume from 950 to 1000 °C, as shown in Figure 6. The yields of active biocarbons for varying activation temperatures are shown in Table 5. It shows that the yield decreased with increasing activation temperature, reaching a very low yield of 4.71% for the activation temperature of 1000 °C due to the severe CO₂–carbon reaction and the continual devolatilisation process, which persisted at this late stage as the proximate analysis of the final active biocarbon for the activation temperature at 1000 °C showed the presence of volatile contents as given in Table 5. The adsorption isotherms of the active biocarbons for the various activation temperatures from 800 to 1000 °C are shown in Figure 7. The adsorbed volume increased with increasing activation temperature from 800 to 1000 °C, which corresponded to an increase in the BET surface area for the same increasing temperature range as seen in Figure 6. The plateau of the isotherm showed the adsorption capacity limit of the mesopores, in which the isotherm for the activation temperature of 1000 °C was representative of the Type IV isotherm under the IUPAC classifications of physisorption isotherms. The supposedly linear curve at the initial low relative pressure, P/P_0 , was indicative of micropore filling, while the uptake in adsorption at high relative pressure, P/P_0 , was associated with capillary condensation occurring in mesopores. A typical adsorption–desorption isotherm of an active biocarbon prepared from oil palm kernel shell was reported by the author [4]. Figure 8 illustrates the pore size distributions of active biocarbons subjected to various activation temperatures, and their pore sizes ranged from less than 2 nm for micropores, 2 to 50 nm for mesopores, and greater than 50 nm for macropores. Figure 8 shows that the active biocarbons consisted more of micropores than mesopores, with the least amount in macropores, which were consistent with the results in Figure 6. From the results in Figure 6, the activation temperature of 950 °C resulted in the largest micropore surface area, which was ideal for gas adsorption, and hence, the optimum activation temperature of 950 °C was used to optimise the remaining activation parameters.

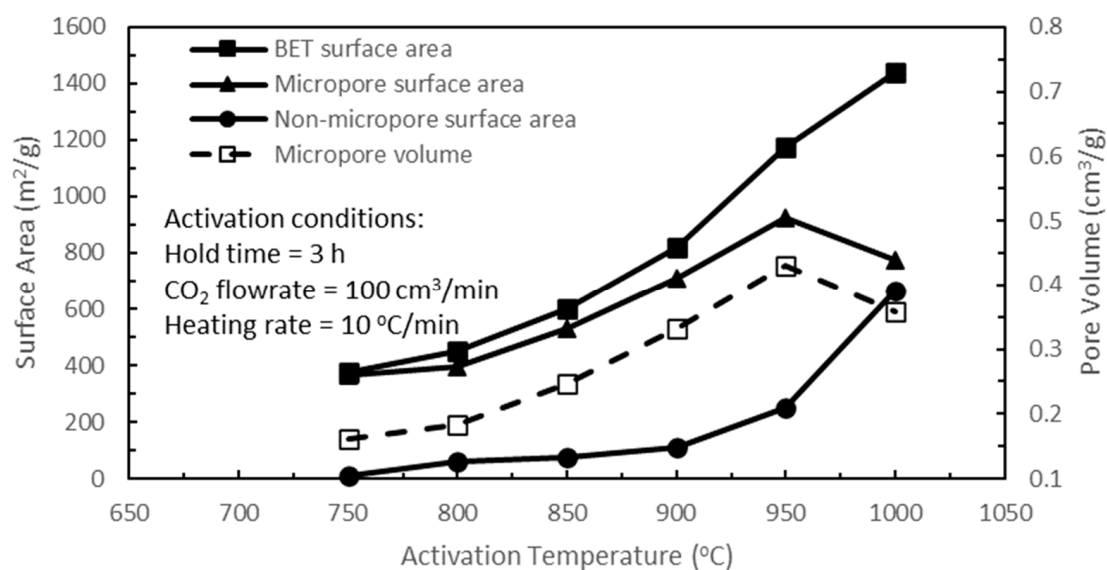


Figure 6. Effects of activation temperature on the pore characteristics of active biocarbons.

Table 5. BET surface area, micropore area, yield, and proximate analyses of active biocarbons for different activation parameters.

Activation Conditions (a-b-c-d) *	Active Biocarbon						Activation Conditions (a-b-c-d) *	Active Biocarbon					
	BET Surface Area (m ² /g)	Micro-Pore Area (m ² /g)	Yield (wt.%)	Volatile Content (wt.%)	Fixed Carbon (wt.%)	Ash (wt.%)		BET Surface Area (m ² /g)	Micro-Pore Area (m ² /g)	Yield (wt.%)	Volatile Content (wt.%)	Fixed Carbon (wt.%)	Ash (wt.%)
Effect of Activation Temperature							Effect of CO ₂ Flow Rate During Activation						
750-3-100-10	376.1	365.7	31.37	8.35	88.18	3.47	950-3-50-10	1077.7	894.0	16.84	13.09	82.53	4.38
800-3-100-10	452.2	393.6	29.12	8.29	88.65	3.06	950-3-100-10	1172.7	925.1	12.68	12.50	83.32	4.18
850-3-100-10	601.0	528.2	26.89	6.95	90.41	2.64	950-3-200-10	1180.4	931.6	11.78	8.19	88.31	3.50
900-3-100-10	819.8	709.4	21.77	10.66	86.06	3.28	950-3-300-10 +	1232.3	941.0 +	10.05	11.24	83.75	5.01
950-3-100-10 +	1172.7	925.1 +	12.68	12.50	83.32	4.18	950-3-400-10	1171.5	886.3	9.19	12.54	82.21	5.25
1000-3-100-10	1437.9	772.6	4.71	13.50	81.39	5.11	950-3-500-10	1158.1	887.2	8.60	13.58	78.36	8.06
Effect of Heating Rate During Activation							Effect of Activation Hold Time						
950-3-300-5	1242.2	920.8	7.85	11.19	83.05	5.76	950-1-300-10	753.0	648.3	22.29	7.28	88.11	4.61
950-3-300-10 +	1232.3	941.0 +	10.05	11.24	83.75	5.01	950-1.5-300-10	839.6	705.7	18.64	6.30	89.41	4.29
950-3-300-20	1239.9	922.2	8.09	11.54	83.47	4.99	950-2-300-10	989.1	822.7	15.17	5.74	90.57	3.69
950-3-300-30	1232.5	930.7	8.97	10.94	84.04	5.02	950-2.5-300-10	1042.3	827.2	15.19	6.91	89.08	4.01
950-3-300-40	1209.0	943.2	9.51	11.01	84.26	4.73	950-3-300-10 +	1232.3	941.0 +	10.05	11.24	83.75	5.01
950-3-300-50	1230.6	942.8	8.30	11.57	84.24	4.19	950-4-300-10	1381.3	883.7	4.67	12.25	82.83	4.92

Note: * a-b-c-d denotes activation temperature (°C), activation hold time (h), CO₂ flow rate during activation (cm³/min), and activation heating rate (°C/min). + Selected value for each parameter.

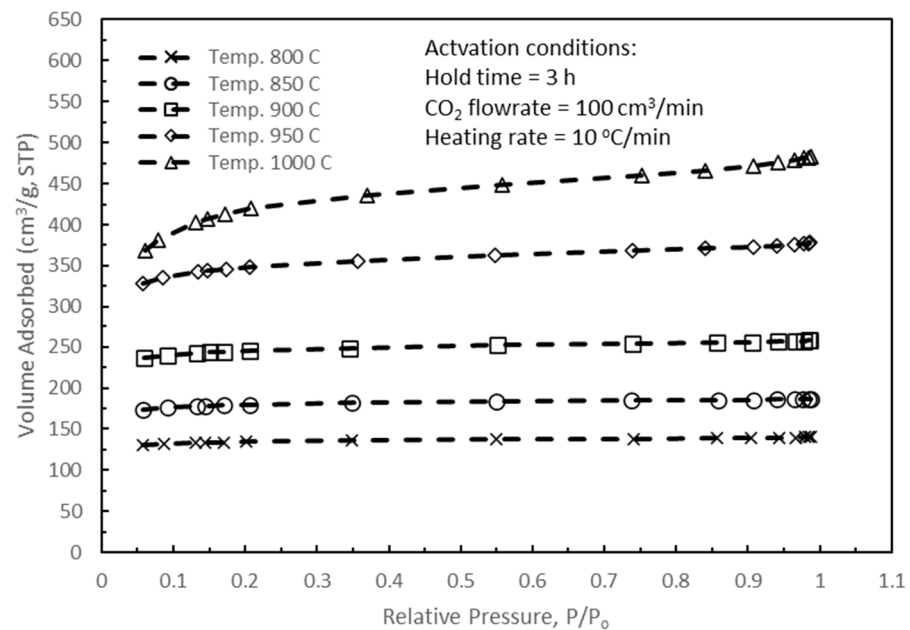


Figure 7. Adsorption isotherms of active biocarbons subjected to different activation temperatures.

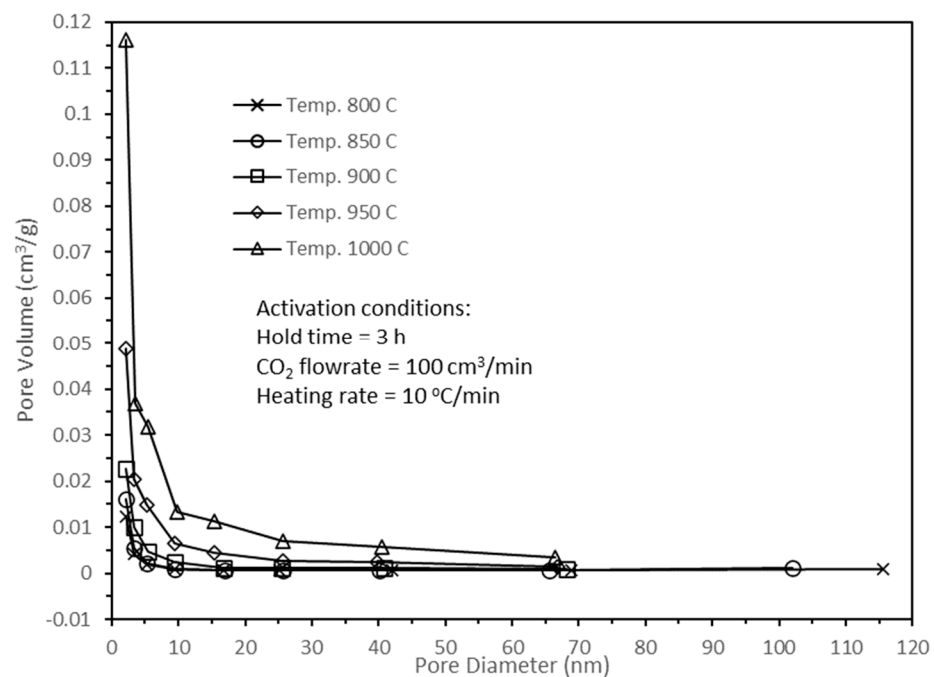


Figure 8. Pore size distributions of active biocarbons subjected to various activation temperatures.

The next activation parameter to optimise was the carbon dioxide flow rate, while the rest of the activation parameters were held constant. Figure 9 shows the effects of carbon dioxide flow rate during activation on the pore characteristics of the active biocarbons for a range of volume flow rates from 50 to 500 cm³/min. During activation, carbon dioxide reacts with carbon in the reaction $\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$ under a high temperature (such as 750 to 1000 °C used in this study) to form porosities in the physical carbon structure. Therefore, it is imperative that different CO₂ flow rates have consequences on the pore surface areas of the resulting active biocarbons. Increasing the CO₂ flow rate from 50 to 300 cm³/min increased the BET, micropore, and non-micropore surface areas, and the micropore volume of the active biocarbons due to the increasing CO₂–carbon reaction, which gave rise to new pore development, predominantly micropores, and pore widening

actions, giving rise to increases in non-micropores. After peaking at 300 cm³/min, further increases in CO₂ flow rate to 400 cm³/min and finally to 500 cm³/min resulted in decreases in these pore area formations due to excessive CO₂–carbon reactions, which caused pore enlargements, resulting in the conversion of micropores into mesopores, and mesopores into larger mesopores or even macropores. This excessive CO₂–carbon reaction was verified by the significant reductions in the fixed carbon content of the resulting active biocarbons, as shown in Table 5, especially for the CO₂ flow rate of 500 cm³/min. Figure 9 shows that a CO₂ flow rate of 300 cm³/min yielded the largest micropore surface area in the resulting active biocarbon, and therefore, this CO₂ flow rate of 300 cm³/min was used to optimise the two remaining activation parameters.

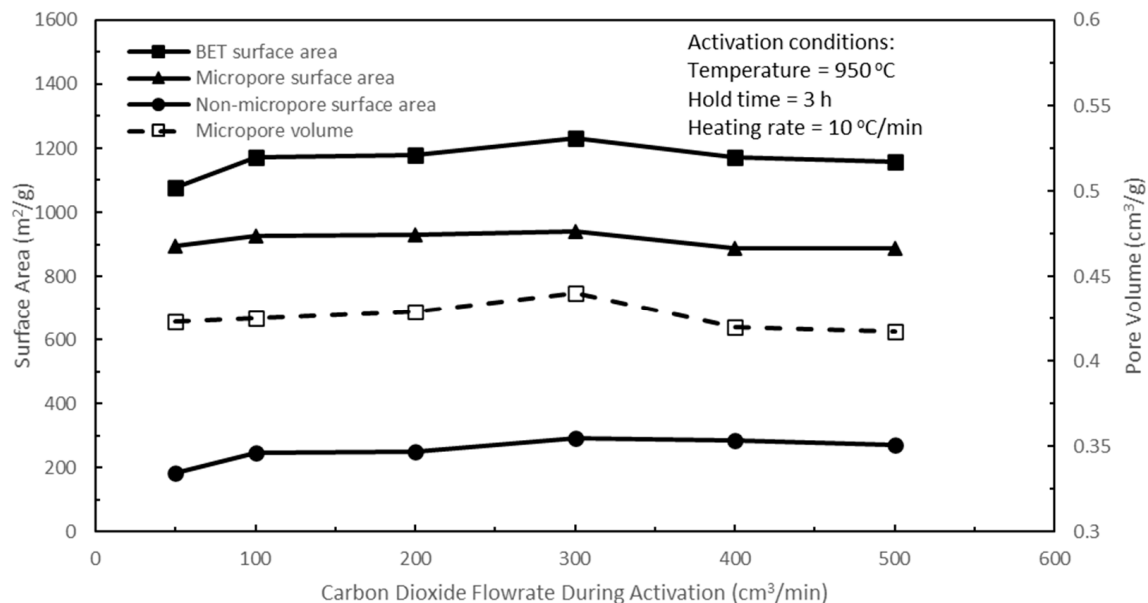


Figure 9. Effects of carbon dioxide flow rate during activation on the pore characteristics of active biocarbons.

Figure 10 shows the effects of activation heating rate on the pore characteristics of the active biocarbons for a range of heating rates from 5 to 50 °C/min. Overall, the activation heating rate had a lesser influence or weak effect on the variations in the BET, micropore, and non-micropore surface areas, and the micropore volume of the resulting active biocarbons for the heating rates used in these tests. However, in terms of micropore surface area, the heating rate of 10 °C/min had a slight lead over the heating rates of 5, 20, and 30 °C/min, and was comparable with heating rates of 40 and 50 °C/min. The temperature ramp-up time from room temperature to the activation temperature of 950 °C for the heating rate of 10 °C/min was 1.53 h compared to 0.38 and 0.31 h for the heating rates of 40 and 50 °C/min, respectively. As there were still volatile matters in the biochar, this ramp-up duration was an extension of the pyrolysis process, where there could be further release of volatile contents during this period and hence more rudimentary pore development before CO₂ activation. A closer examination of Figure 10 revealed that the best micropore/BET surface area combination is for a heating rate of 10 °C/min, and hence, the heating rate of 10 °C/min was used for optimising the last remaining activation parameter of hold time.

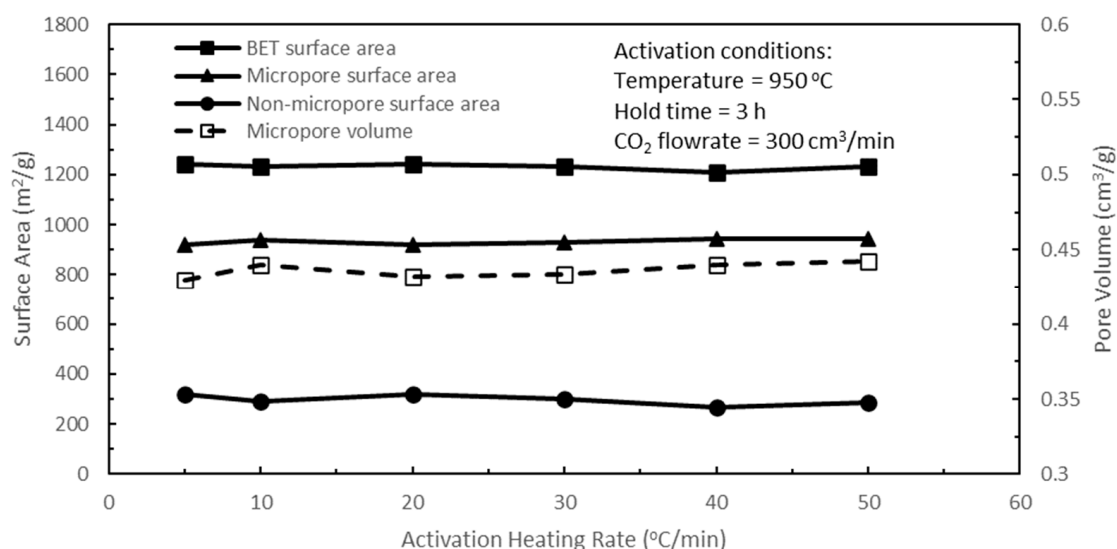


Figure 10. Effects of activation heating rate on the pore characteristics of active biocarbons.

Using the optimised activation parameters, namely, a temperature of 950 °C, a CO₂ flow rate of 300 cm³/min, and a heating rate of 10 °C/min, the effects of activation hold time on the pore characteristics of the active biocarbons were studied and presented in Figure 11. Increasing hold time increased the time duration for the release of any remaining volatile matters still present in the biochar to form more porosities, and at the same time, it also increased the residence time for the CO₂–carbon reaction, which would result in increasing pore development in the active biocarbon due to increasing carbon burn-off. These phenomena could be concurred by the reducing yield of the active biocarbons with increasing the activation hold time as shown in Table 5, reaching a very low yield of 4.67% for a hold time of 4 h. Figure 11 shows that the BET and non-micropore surface areas progressively increased with increasing the hold time from 1 to 4 h. However, the micropore surface area and the micropore volume of the active biocarbon peaked at a hold time of 3 h, and thereafter these pore characteristics decreased when the hold time was increased to 4 h. At the hold time of 4 h, it is surmised that there could be excessive carbon burn-off, which resulted in significant pore enlargements and pore wall thinning and collapse, particularly at the surfaces of the active biocarbons, converting micropores into mesopores and macropores. Hence, the BET and non-micropore surface areas continued to increase at the hold time of 4 h. Increasing the hold time from 3 to 4 h, the decreases in the micropore surface area and the micropore volume were gradual, suggesting that the excessive carbon burn-off was a surface phenomenon and the micropores in the interior of the active biocarbon were less affected. A hold time of 3 h was optimal to achieve the largest micropore surface area in the resulting active biocarbon.

To produce an active biocarbon with the largest micropore surface area or the best micropore/BET surface area combination from the pyrolysed biochar, the optimum parameters for the activation process were a temperature of 950 °C, a CO₂ flow rate of 300 cm³/min, a heating rate of 10 °C/min, and a hold time of 3 h. The largest micropore area or the best micropore/BET surface area combination of the active biocarbon selected for each activation parameter is indicated in Table 5. The biochar was prepared to yield the largest BET surface area under the optimum pyrolysis conditions, which were a pyrolysis temperature of 600 °C, a pyrolysis hold time of 2 h, a nitrogen flow rate of 150 cm³/min during pyrolysis, and a pyrolysis heating rate of 10 °C/min. The active biocarbon produced under these optimum pyrolysis and activation conditions had the following physical characteristics, namely, a BET surface area of 1232.3 m²/g, a micropore surface area of 941.0 m²/g,

a non-micropore surface area of $291.3 \text{ m}^2/\text{g}$, and a micropore volume of $0.440 \text{ cm}^3/\text{g}$. This active biocarbon consisted of 76.36% micropores, and the remaining 23.64% pores consisted of mesopores and macropores. The proximate analysis of this active biocarbon is given in Table 4, which shows its yield was 10.05% and this was a significant decrease from the 34.80% yield of its preceding biochar. This decrease in yield was due to the significant weight loss in the fixed carbon content because of the CO_2 –carbon reaction, the continual release of the remaining volatile matters within the carbon structure, and the total loss of moisture. The fixed carbon constituted the dominant species composition of the active biocarbon, thereby justifying that the precursor for active biocarbon should have high carbon content. Lastly, highly microporous active biocarbons produced from oil palm kernel shells by pyrolysis in the N_2 stream and physical activation by CO_2 are ideal and suitable for gaseous adsorption and in applications such as CO_2 capture to mitigate global warming impacts on climate change. The feasibility and viability of active biocarbons prepared by CO_2 physical activation of lignocellulosic biomasses for CO_2 capture could be seen in some research studies reported in the literature. Rashidi and Yusup [16] reported on the preparation of active biocarbon from palm kernel shell (which was the same precursor used in this study here) by one-stage CO_2 physical activation at 850°C for the uptake of CO_2 at 25°C and atmospheric pressure of 1 bar, and obtained a maximum CO_2 adsorption capacity of 2.13 mmol/g in a CO_2 environment for an active biocarbon with a BET surface area of $303.9 \text{ m}^2/\text{g}$. In another study using similar palm kernel shells as the raw materials for the preparation of active biocarbons by a two-stage process, namely, pyrolysis under N_2 flow followed by activation in CO_2 flow, Nasri et al. [14] obtained active biocarbon with a BET surface area of $167.08 \text{ m}^2/\text{g}$ under a pyrolysis temperature of 700°C and an activation temperature of 800°C . They further carried out a CO_2 adsorption test for this active biocarbon and obtained a CO_2 adsorption capacity of 1.66 mmol/g in a CO_2 environment under a room temperature of 30°C and a pressure of 1 bar. From these two studies [14,16], CO_2 adsorption by active biocarbon is directly proportional to its BET surface area (inclusive of the micropore surface area) as expected. When compared to the active biocarbons prepared in these two studies [14,16], the active biocarbon prepared in this work, with a much greater BET surface area of $1232.3 \text{ m}^2/\text{g}$ and consisting of a high 76.36% of micropore surface area, certainly surpasses the CO_2 adsorption capacities of the two former active biocarbons. This study also highlighted the importance of optimising the pyrolysis and activation conditions to obtain a maximum possible micropore surface area for the resulting active biocarbon to enhance its CO_2 adsorption capability. Some other studies using two other lignocellulosic biomasses as precursors for preparing active biocarbons by CO_2 physical activation and subsequently used in adsorbing CO_2 are briefly highlighted. Some information and results of these research studies, i.e., the type of biomass, BET surface area, and CO_2 adsorption capacity, are (i) coconut shell: BET surface area of $1327 \text{ m}^2/\text{g}$, CO_2 adsorption of 3.9 mmol/g in a CO_2 environment at 25°C and 760 mm Hg [25]; (ii) coconut shell: BET surface area of $1046 \text{ m}^2/\text{g}$, CO_2 adsorption of 5.0 mmol/g in a CO_2 environment at 0°C and 1 bar [26]; and (iii) date seed: BET surface area of $798.38 \text{ m}^2/\text{g}$, CO_2 adsorption of 141.14 mg/g (3.21 mmol/g) under a CO_2 flow at 20°C and atmospheric pressure [27]. In using other biomasses besides oil palm kernel shell, these studies [25,27] also indicated that the CO_2 adsorption capacity was directly proportional to the BET surface area of the active biocarbon under quite similar adsorption temperatures and the same adsorption pressure. It is to be noted that the active biocarbon prepared by Prauchner et al. [26] yielded a smaller BET surface area than that of Ello et al. [25] but had a higher CO_2 adsorption capacity because of its lower adsorption temperature of 0°C . In all these studies [14,16,25–27], there was no systematic optimisation of the pyrolysis parameters and their subsequent activation parameters to achieve the largest possible BET surface area for each lignocellulosic biomass.

In this study, the parameters for pyrolysis, namely, temperature, hold time, N₂ flow rate, and heating rate, and the parameters for the activation process, namely, temperature, hold time, CO₂ flow rate, and heating rate, were thoroughly and fully studied to determine the optimum operating parameters to achieve the largest possible micropore surface area for the final active biocarbons using oil palm kernel shells as the starting materials. This study also provides a blueprint of the process parameters and know-how for the commercial production of active biocarbons from oil palm kernel shells and their possible use to capture CO₂ to mitigate global warming and climate change.

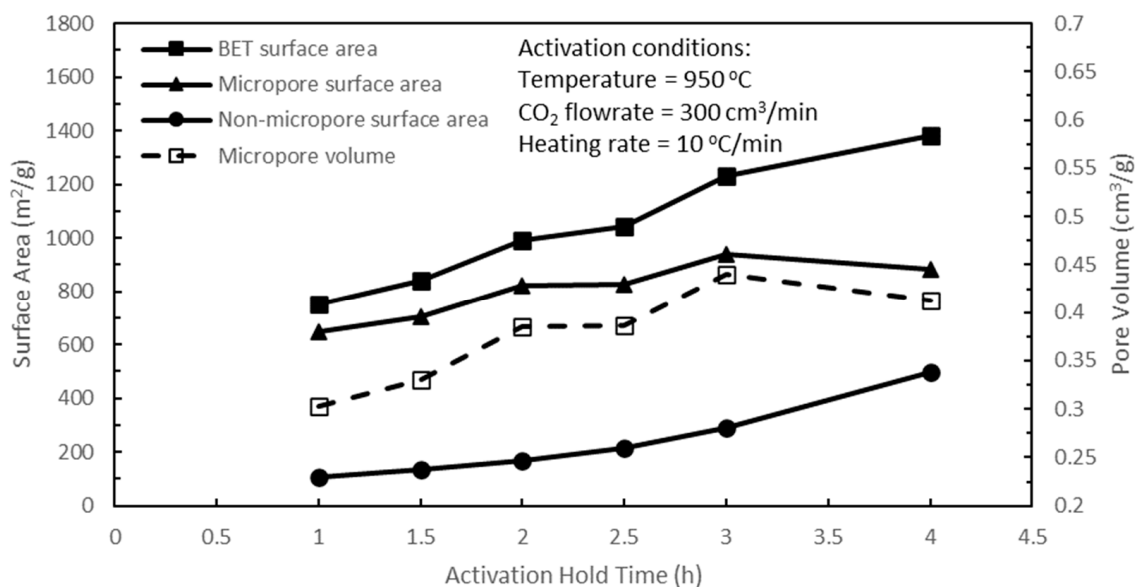


Figure 11. Effects of activation hold time on the pore characteristics of active biocarbons.

4. Conclusions

Oil palm kernel shell, which is a lignocellulosic biomass waste generated from the palm oil industry in vast amounts, was valorised as the precursor or starting material for its conversion into a valuable resource as an active biocarbon. A two-stage preparation method involving a pyrolysis process, followed by a physical activation process, was used to produce the active biocarbon. In the pyrolysis process, whereby the kernel shell was subjected to heating under a N₂ flow, the operating parameters of temperature, hold time, N₂ flow rate, and heating rate were optimised to produce the largest BET surface area in the active biocarbon. Using these optimised pyrolysis parameters, the biochars were subjected to CO₂ activation in which their operating parameters of temperature, hold time, CO₂ flow rate, and heating rate were optimised to yield the largest micropore surface area or the best micropore/BET surface area combination in the active biocarbon.

For the pyrolysis parameters studied, the optimum pyrolysis conditions were a temperature of 600 °C, a hold time of 2 h, a nitrogen flow rate of 150 cm³/min, and a heating rate of 10 °C/min, and the biochar was subjected to a short activation hold time of 30 min at 900 °C to produce a resulting active biocarbon with a BET surface area of 519.1 m²/g, a micropore surface area of 456.94 m²/g, a non-micropore surface area of 62.17 m²/g, and a micropore volume of 0.215 cm³/g. To prepare the active biocarbon with the largest micropore surface area or the best micropore/BET surface area combination from the optimised biochar, the optimum parameters for the activation process were a temperature of 950 °C, a CO₂ flow rate of 300 cm³/min, and a heating rate of 10 °C/min with a hold time of 3 h, resulting in a BET surface area of 1232.3 m²/g, a micropore surface area of 941.0 m²/g, a non-micropore surface area of 291.3 m²/g, and a micropore volume of 0.440 cm³/g for an active biocarbon that consisted of 76.36% of micropores. This study provides a very

comprehensive and detailed experimental optimisation technique to first convert oil palm kernel shells into biochars with good rudimentary pore structures and subsequently convert them into highly microporous active biocarbons through optimal N₂ pyrolysis and CO₂ activation parameters that are presently not reported in the literature. As the optimisation of the operating parameters for the N₂ pyrolysis of biochar was coupled to the fixed CO₂ activation conditions for all biochars, the history of the biochar in terms of its rudimentary pore development has a role in determining the outcome of the active biocarbon activation and its optimisation, which is a unique technique. Such active biocarbons prepared from oil palm kernel shells are ideal for gaseous adsorption applications, such as capturing CO₂ to mitigate global warming and climate change. The results of this very detailed preparation method provide a good practical blueprint of the industrial process parameters and know-how for the commercial production of active biocarbons from oil palm kernel shells by a two-stage physical N₂ pyrolysis and CO₂ activation process.

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