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Original Article

Synthesis and Characterization of Biochars and Activated Carbons Derived from Various Biomass for CO_2 Adsorption

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Abstract: Reducing CO_2 emissions is urgently needed to slow down the impacts of climate change. CO_2 capture using an amine solution has been developed and implemented on pilot and commercial scales. However, amine scrubbing, in particular, produces a lot of degraded solvent as waste and is energy intensive. Solid sorbents have been called to overcome those drawbacks. In this work, waste biomass-derived carbon materials were developed and tested for CO_2 capture and conversion. Advanced thermal chemical processes i.e., hydrothermal and pyrolysis were applied to produce materials from agri-food waste such as soybean and okara. It was found that the number of functional groups (-C=O and -OH) in activated carbon appears in the synthesized materials, implying the generation of surface oxygenated groups. Preliminary results showed that the synthesized activated carbons are obtained with good yields, and a relatively high surface area, which may be applied as CO_2 adsorption materials to solve the CO_2 emission problems.

Keywords: biomass; okara powder waste; pyrolysis; hydrothermal carbonization; activated carbon; catalysis; adsorption; CO_2 capture

1. Introduction

CO_2 emissions have become a global concern for decades [1] due to the increasing emissions into the atmosphere [2–5]. For instance, in 2022, global CO_2 emissions from fossil fuel combustion and cement production alone reached 36.1 ± 0.3 $GtCO_2$, an increase of 1.5 % compared to the global CO_2 emissions in 2021, which is 35.5 $GtCO_2$. [6]. Many countries, stakeholders, and organizations are working towards CO_2 reductions and committed to net zero targets including Vietnam. In 2022, Vietnam's CO_2 emissions were 343.61 million tons and is estimated being quadruple by 2050 if no action is taken. To combat the climate change problem, CO_2 needs to be captured and long-term stored. CO_2 capture using an amine solution has been developed and implemented on pilot and commercial scales. However, aqueous amine solutions or amine scrubbing in particular produce a lot of degraded solvent as waste, is energy-intensive, and is not very economical during the regeneration process [7]. Using solid adsorption materials is an important approach to cutting down CO_2 emissions [2] since such materials would overcome the drawbacks of aqueous amine-based solutions [1]. The most widely used solid materials for CO_2 capture are silica, zeolites, alumina, amine-based materials, metal oxides, metal-organic frameworks (MOFs), polymers, and carbon materials (activated carbon, graphite, graphene, fullerene, carbon nanotubes, biochar, and hydrochar, etc. [2,7].

Biomass is the major sustainable source for generating activated carbon, biochar, hydrochars [8,9], and biomaterials [2,10]. Popular biomass sources include rice husk, rice straw, and coffee waste.

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As it can be observed, over the last several years, there has been a substantial increase in the number of researchers working on CO_2 capture materials by those common biomass sources.

Okara, also known as soy pulp in English, and doufu zha or dou zha in Chinese, or ''bã đậu phụ'' in Vietnamese is the insoluble residue after filtering soy slurry into soy milk [11]. Therefore, it is considered to be a by-product during soy milk and tofu preparation. Yet, for every kg of dry soybeans made into soy milk or tofu, about 1 kg of okara is generated [12]. The crude fiber in okara is mainly composed of cellulose, hemicellulose, and lignin, and is used in enteral nutrition products and some bakery goods such as biscuits and snacks [13].

Most okara worldwide is used as feed for livestock — especially hogs and dairy cows [14]. Most of the rest is used as a natural fertilizer or compost, which is fairly rich in nitrogen. A small amount is used in cooking. Due to its high fiber content and low production costs, okara is a good raw material and rich source for preparing fiber and could also be used as a dietary supplement to prevent diabetes, obesity, and hyperlipidemia [15].

Pyrolysis is a thermal decomposition process in an inert i.e., N_2 environment at an elevated temperature range of 500-600 ^oC. It is commonly used for producing carbon-rich materials from organic matter, e.g., biomass. This process produces liquid (known as bio-oil, condensable volatiles), non-condensable gases (CO, CO_2, H_2, and gaseous hydrocarbons) [6,16], and solid (known as biochar). Biochar is found to be a popular adsorbent for environmental remediation, such as removing heavy metal(oids) from wastewater [17,18]. Better adoption is obtained when biochar nano adsorbent surface area is heightened [17]. The proportion of these fractions depends on the operation conditions such as heating rate, temperature [19], holding time, types of reactors [20–22], particle size, and nature of feedstock [23,24]. To maximize the solid fraction, it is found [13] that the heating rate of the pyrolysis process should be below 1.0 ^oC/min[19], the operating temperature should be around 550 ^oC [19] and residence time should be below 2 hours [19].

The hydrothermal carbonization (known as HTC) method is a thermal chemical reaction using water as a solvent in a sealed pressure vessel in a temperature range of 180 °C - 300 °C (corresponding to a pressure of 2-6 MPa for 5 to 240 min [25–27]. The hydrothermal technology is suitable for wet feedstock, eliminating the energy-intensive drying step to produce carbon-rich solids known as ''hydrochars'' [28]. Hydrochars can be used for pollutant treatment [29] and bioenergy [30] or as a precursor for activated carbon production [31]. The hydrothermal process is favorable in lowering the ash content as a significant part of inorganics is dissolved in the aqueous phase [31]. Zeolites can be mixed with inorganic compounds to increase heating value and yield in the catalytic pyrolysis processes of biomass [16] Zeolites can have distant catalytic effects on the hydrothermal carbonization of biomass [32].

Though there has been a lot of research undertaken in developing CO_2 adsorbent, no research has been done on the synthesis of okara powder waste into CO_2 absorbent. In terms of environmental implication and cost-effectiveness, it is worthy to consider okara as an ideal biomass source for activated carbon, hydrochar, and biochar production for CO_2 adsorption. This research aims to use those simple, low-cost, and environment-friendly methods to obtain activated carbon via a chemical thermal process namely slow pyrolysis and hydrothermal synthesis of okara-derived materials for CO_2 adsorption. In the context of global CO_2 emissions and sustainable development [33], this research is therefore useful since these experiments offer new insights into the application of okara powder waste to various outputs.

2. Materials and Methods

Okara powder waste was collected from local tofu producers in Hanoi. The okara powder waste collected in Hanoi is naturally in white-color, water-absorbing-powder phase and is often sold by tofu producers to livestock farmers or gardeners as animal feeds or as a supplement for flowers and ornamental plant growers. Okara powder waste is brought to the lab and dried naturally under sunlight for 7-10 days. Next, the okara powder waste is dried in a Contherm Thermotec 2000 oven at 100 ^oC for 4-6 hours while the okara powder waste is drained of water and turns into the solid-porous phase. Then, the dried biomass was ground into small particles to achieve uniform particles of 0.2-

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0.45 mm. Ethanol (C_2H_5OH 99%), KOH, and melamine ($C_3H_6N_6$) were purchased from Xilong Chemical Inc (China). Potato peels, shrimp shells, and coffee waste were collected from household uses while rice husks and rice straw were collected from rice fields in Hanoi municipal areas. All of these biomass sources were dried in sunlight and dried oven (100 °C) before they were grounded into particle sizes of 0.2-0.45 mm and went through pyrolysis or hydrothermal carbonization processes.

2.1. Preparation of Activated Carbon (AC) from Okara Powder Wastes

2.1.1. Pyrolysis Experiment Setup

In the experiment, several samples were coded OPWi, where i is the experiment conducted. Dried okara powder waste was ground into a powder. Through sieving, particles with the size of 0.2-0.45 mm were obtained, and a weight of 1.35 grams was carried out as a precursor for carbonization.

The pyrolysis is carried out in a tube furnace as shown in Figures 1 and 2. In this research, we use N_2 as inert gasses during pyrolysis experiments. A horizontal furnace (Lenton thermal) and a vertical tube furnace (Nabertherm GmbH) were used. The tube of these tow two furnaces was charged with okara powder waste in an N_2 flow. In our pyrolysis experiment, dried biomass or okara is supplied, and the high temperatures of 600 °C are used to carbonize a significant amount of feedstock, the heating rate is maintained at 3°C/min, and residence time is maintained for 1 hour. Schematic of the vertical and horizontal batch pyrolysis system setups is shown in Figures 1 and 2 below:

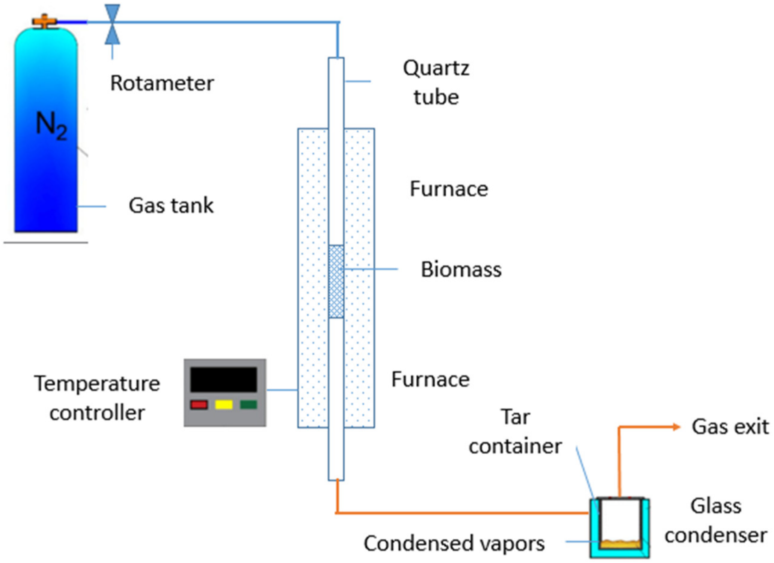


Figure 1. Schematic of the vertical batch pyrolysis system setup.

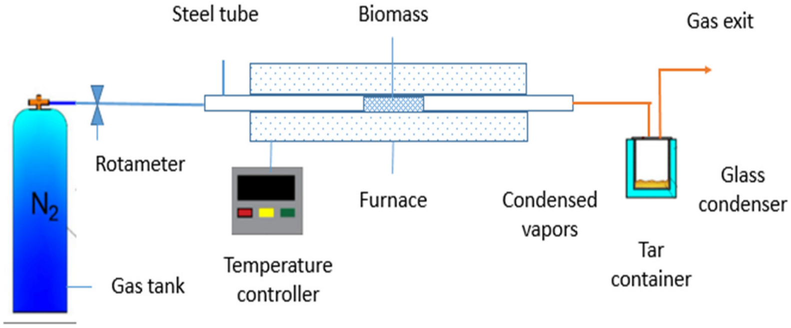


Figure 2. Schematic of the horizontal batch pyrolysis system setup.

2.1.2. Preparation of Activated Carbon via Hydrothermal Carbonization Method

In this study, HTC is performed at 200 °C, during which biomass is submerged in water and heated in a closed system (a steel autoclave) under pressure (2–6 MPa) for 240 minutes. An amount of 12.8 g okara powder waste and 40 ml of water (equivalent to 2/3 volume of a medium-sized stainless steel autoclave) was placed in a stainless steel autoclave, heated up to 200 °C, and kept at this temperature for 4 hours; then leave the stainless steel autoclave to cool down overnight. The next day the sample is filtered with filter paper, and washed with distilled water to about neutral pH. HTC method to prepare hydrochar is illustrated in Figure 3.

Figure 3. HTC method and procedure to prepare hydrochar.

2.1.3. Activate Biochar/Hydrochar

For some samples, (i.e sample OPW6), the activated carbon was prepared from the bichar/hydrochar of dried okara through physiochemical activation processes. The biochar, produced at a 600 ◦C pyrolysis temperature, or hydrochar produced at 200 ◦C hydrothermal treatment was used for further treatment, to produce a high porosity product with less tars impurity [34]. The biochar/hydrochar was mixed with KOH and water with a mass ratio of biochar: KOH: water being 1:4:5. This sample was then kept in a beaker at room temperature for 48 h. After this KOH impregnation step, the mixture was oven-dried overnight at 100 ◦C. Then, the dried mixture was again pyrolyzed at 600 ◦C temperature for 1 h with a heating rate of 25 ◦C/min under nitrogen gas (99.99% purity) flow of 1.5 L/min. After pyrolysis, the activated carbon was washed with hot and aqueous HCl to remove excess KOH and impurities until the pH value of the drained liquid was neutral. Finally, the AC was dried in the oven and stored in a zipper bag. The size of the activated carbon was less than 0.25 mm due to the biomass precursor's size. The list of the synthesized samples is presented in Table 1.

Table 1. The synthesized samples and detailed pretreatment methods.

Biomass precursor	Sample code	Pretreatment methods	Activating agent
Okara powder waste	OPW1	Carbonization, 800 ^{o}C, in an Ar flow over 1h	No activating
Okara powder waste	OPW2	Carbonization at 650 ^{o}C in a gas N2 flow for 1 hour	No activating
Okara powder waste	OPW3	Carbonization at 600 ^{o}C in a gas N2 flow for 1 hour	No activating
Okara powder waste	OPW4	Hydrothermal carbonization at 200 oC; heating rate is 60 oC/h: temperature of 200 oC is maintained in 4h; weight ratio of OPW: water is 12.8 gram: 40 ml	No activating
Okara powder waste	OPW5	Hydrothermal carbonization at 200 oC; weight ratio is 12.8-gram OPW: 6.4 gr zeolite (4 mm in size): 40 ml water; a temperature of 200 oC is maintained in 4h; the heating rate is 60 oC/h:	No activating
Okara powder waste	OPW6	Hydrothermal carbonization at 200 ^{o}C, at a heating rate of 1 60 ^{c}C/hour, kept this 200 oC temperature for 4 hours. Then Mix with KOH, and melamine with the mass ratio of hydrochar/KOH/melamine=1:4:2 and then perform the pyrolysis (two-step processes) at 600 ^{o}C; in a flow of N_2 in 1h; N_2 flow rate of 1 l/min	KOH, melamine (weight ratio of KOH: melamine = 2:1)
Okara powder waste	OPW7	Carbonization 600 ^{o}C, N_2, 1h to make biochar; after that biochar is mixed with KOH and water; then keep the sample for 48 hours in stirring, the ratio of biochar:KOH: water is 1:4:5 in weight, then filter and dry then calcined at 600 ^{o}C in N_2 for 1h	KOH
Rice husk	RH	Carbonization 600 ^{o}C, N_2, 1h	No activating
Okara powder waste	OPW8	Carbonization 600 ^{o}C, N_2, 1h; dry mixing process with KOH(ratio of biochar: KOH = 1.3) then dry at 120oC, then carbonization at 600 ^{o}C	KOH
Okara powder waste	OPW9	Carbonization 600 ^{o}C, N_2, 1h; dry mixing process with KOH (ratio of biochar: KOH = 1.4) then dry at 120 ^{o}C, then carbonization at 600 ^{o}C	KOH
Okara powder waste	OPW10	Carbonization 600 ^{o}C, N_2, 1h; then mix biochar:KOH: water ratio of 1:5:10; keep the sample for 5 days, filter, drying, calcine at 600 ^{o}C	KOH

2.2. Characterization of the Materials

The porous carbon materials were examined by scanning electron microscopy (SEM) by a Jeol, JCM-7000 microscope. The EDS analyses were performed with a 15 kV accelerating voltage. Brunauer-Emmett-Teller (BET) surface area was measured using a Micromeristics, ASAP 2060 device. TGA and DSC were performed by a NETZSCH (STA 449 F5 Jupiter) equipment. FTIR measurements were performed by a Thermal Scientific – NICONET iS5050 FTIR. All absorbance spectra were obtained in the 4000–400 cm^{-1} range by 100 scans at 1.0 cm^{-1} resolution.

2.3. Calculation of the biomass conversion

Two factors that measure the efficiency of AC production and mass loss are burn-off and carbon yield. Burn-off measures the mass lost after the activation and is calculated from Equation (1.1) [35].

$$\text{burn off (wt.\%)} = \frac{w_o - w_{AC}}{w_o} \cdot 100\% \tag{1.1}$$

where w_o is the initial weight and w_{AC} is the dry weight of the resulting activated carbon after activation (the mass of the final activated carbon).

The carbon yield of each stage is determined using Equation (1.2) [36,37]:

$$\text{Carbon}_{\text{yield}}\text{(wt.\%)} = \frac{w_C}{w_f} \cdot 100\% = \frac{\text{mass of carbon materials after pyrolysis}}{\text{mass of okara powder waste feedstock}} * 100\% \tag{1.2}$$

where wC is the weight of carbon (g), and wf is the weight of feed (g).

3. Results and Discussions

3.1. Characterizations of the Biomass Materials

3.1.1. EDX Analysis of Various Biomass

EDX analysis was used to examine the elements of the biomass. The element composition of different biomass is presented in Table 2. The table shows that the biomass consists of 18.91% to 57.35 % of carbon weight, 42% to 55 % of oxygen weight, and 1.74 to 5.77% of K weight. For okara powder waste, the okara consists of 45.73% of carbon mass, 52.53% of oxygen weight, and 1.74% of K mass. It can be seen that okara powder possesses an average carbon mass compared to other biomass but it is one of the two biomass containing K, which may help for the activation process for improving surface area and for the adsorption of CO_2. Moreover, the source of okara waste is abundant with low economic value (it is only used for planting and fodder) so it may be a good selection for a pyrolysis process.

Table 2. Chemical composition of different biomass.

Elements	**Coffee waste**		**Okara powder waste**		**Rice straw**		**Shrimp shell**		**Rice husk**		**Potato peels**	
	Mass%	Atom%	Mass%	Atom%	Mass%	Atom%	Mass%	Atom%	Mass%	Atom%	Mass%	Atom%
C	57.35	64.17	45.73	53.36	37.88	56.56	44.38	53.4	18.91	26.44	48.12	56.79
O	42.65	35.83	52.53	46.02	9.97	11.18	48.9	44.17	55.48	58.24	46.62	41.31
K			1.74	0.62	5.77	2.65					5.26	1.91
Ca							6.72	2.42				
Si					46.37	29.61			55.61	15.31		
Total	100		100		100	100	100	100	100	100	100	100

The EDX image of the okara waste is shown in Figure 4. The element concentrations suggest the presence of a high amount of different oxygenated groups on the carbon surfaces, and the presence of K, whose contents is 1.74%. According to the literature, Cl, Ca, Na, Cu, Mg, K, Ni, Si, and P contents in the different biomass are between 0.09 and 1.21 % [31,32].

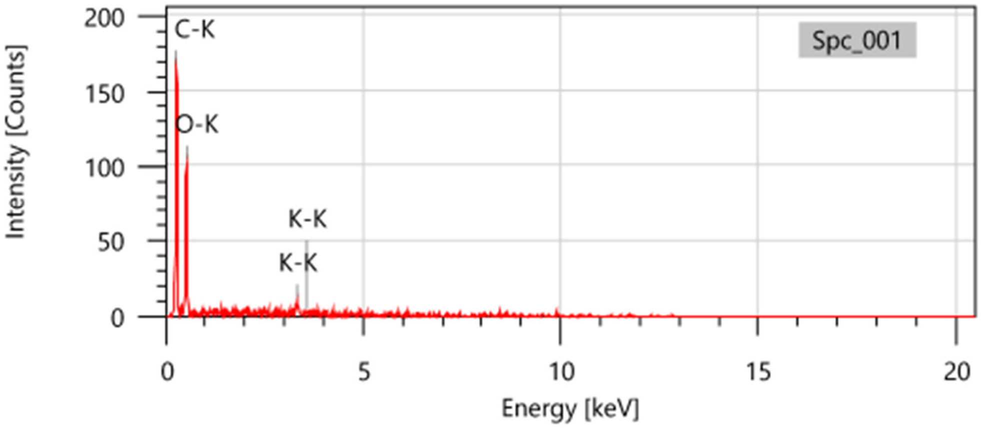
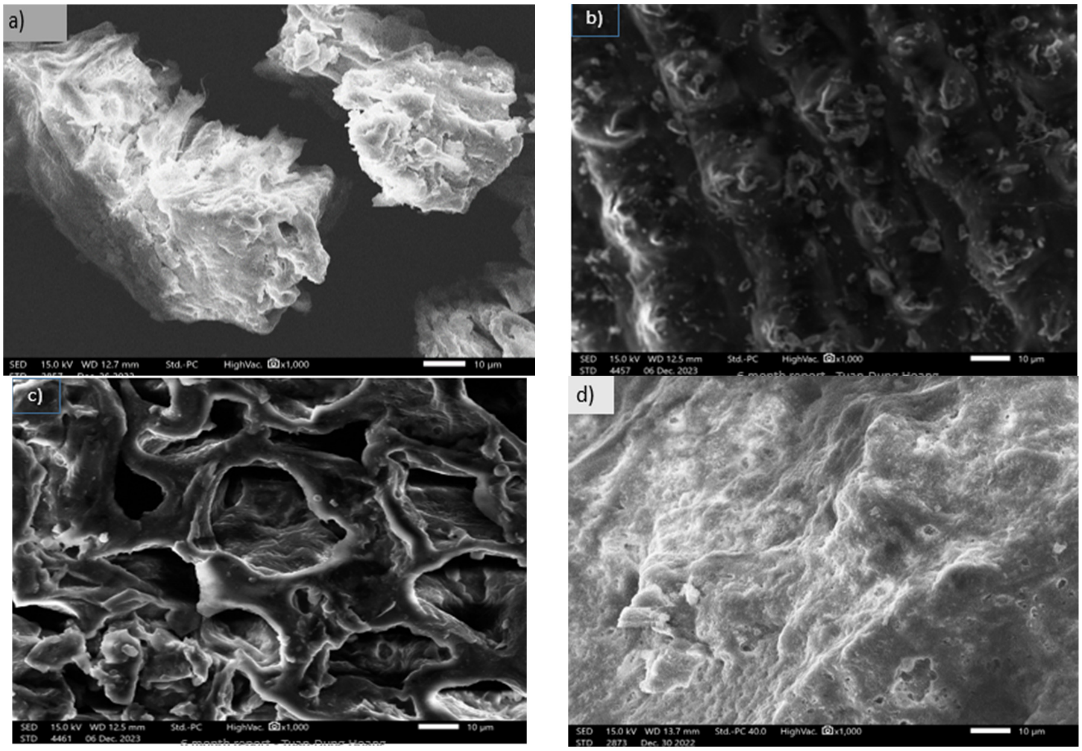


Figure 4. EDX spectra of okara powder waste.

3.1.2. SEM Images of Different Biomass

SEM was employed to investigate the surface morphology and porous structure of the precursor materials. As shown in Figure 5 SEM images, the surface morphology properties of the biomass precursors were remarkably influenced by the different types of biomass feedstock. The surface morphology of the samples b), c), and e) was intricately changed and the pores were gradually opened with deep holes while the surface morphology of the samples f), d) were relatively flat and simple. Large pores and cavities are also evident in the case of coffee waste.



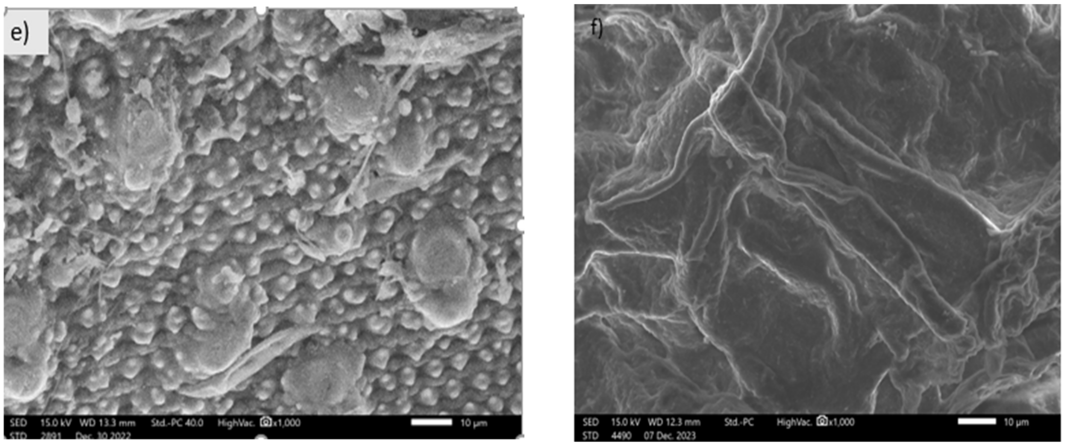
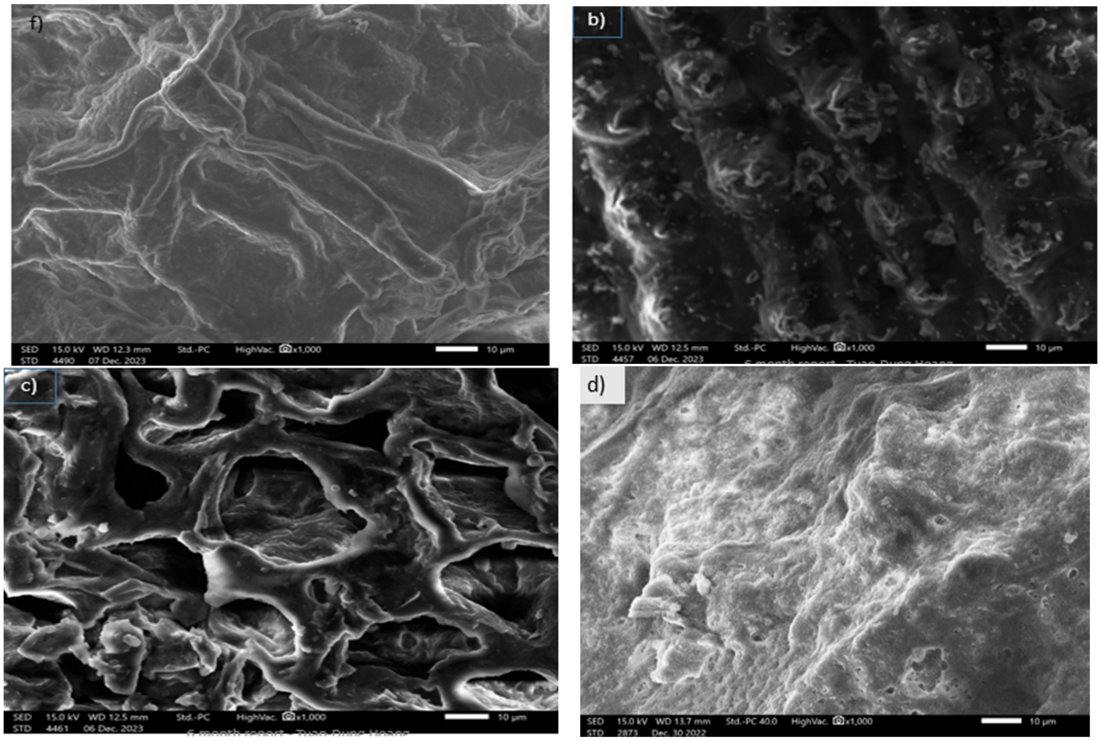


Figure 5. SEM images of a) okara powder waste; b) Rice husk; c) coffee waste; d) shrimp shell; e) Rice straw; f) potato peels.

3.1.3. SEM Images of Activated Carbon Synthesized from Okara Powder Waste

The SEM image of the activated carbon obtained after the pyrolysis process is illustrated in Figure 6.



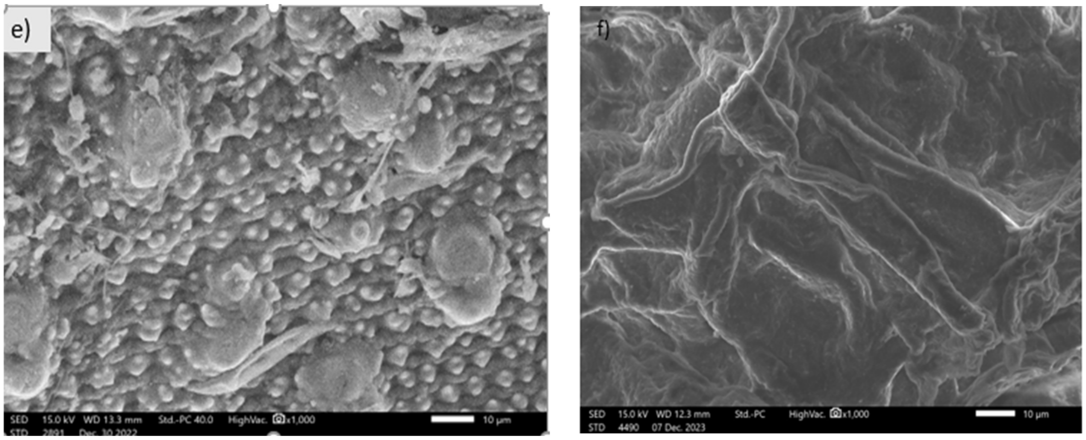


Figure 6. SEM images of the biochars synthesized at (600 °C, 1 h) (a) okara biochar (OPW3) b); rice straw; c) rice husk (RH), d) coffee ground and e) potato peels (PP) at 1000 magnifications.

The images exhibited clear pores and specific shapes on the surface of the biochar. This is possible due to the development of internal pores after tars were removed inside the biochar by the activating agents through physicochemical activation. Higher porosity is very important for the latter CO_2 uptake processes of our study and these images demonstrate a porous surface area of biochar. It could also be observed that this biochar presented as a conglomeration of spheres. The surface topology differed strongly between raw okara powder waste and biochar, which is in good agreement with the previous publication [33]. The structure of the biochar materials was shown to be porous and this creates a perfect surface environment for the CO_2 diffusion and adsorption inside the structure of the materials in the latter phase of the research.

3.1.4. FTIR Analysis

The FTIR spectroscopy technique was used to identify the functional groups on the surface of the biomass, as shown in Figure 7.

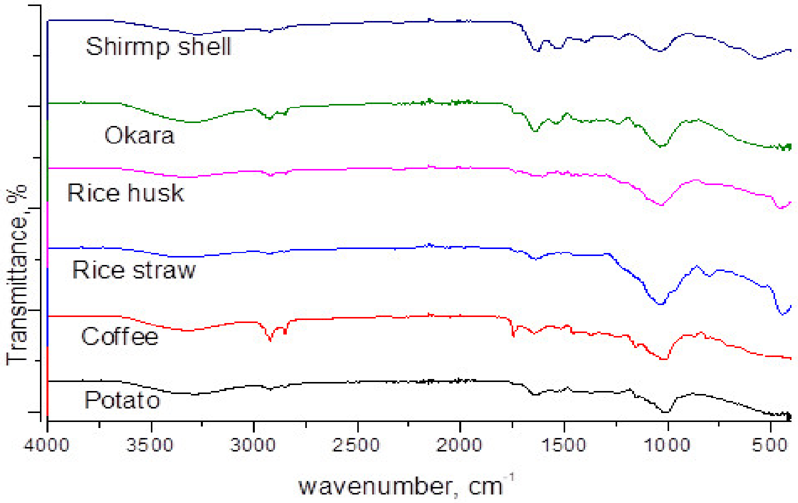


Figure 7. Fourier Transform-Infrared spectra of different biomass.

The absorption bands at 1800–1600 cm-1 (centered at 1567 cm–1) were due to the stretching vibration of νC = O and νC = C [38]. The peaks at 1000 cm-1 (centered at 1000 cm–1) were recognized as the νC–O stretching vibrations, which resulted from the hydroxyl, ester, and ether functional groups on the surface of the biomass [38]. Figure 7 displays different biomass contains some different vibrations, confirming that the chemical structures of different biomass are featured. Figure 8 illustrates the Fourier Transform-Infrared spectra of okara biomass and okara biochar.

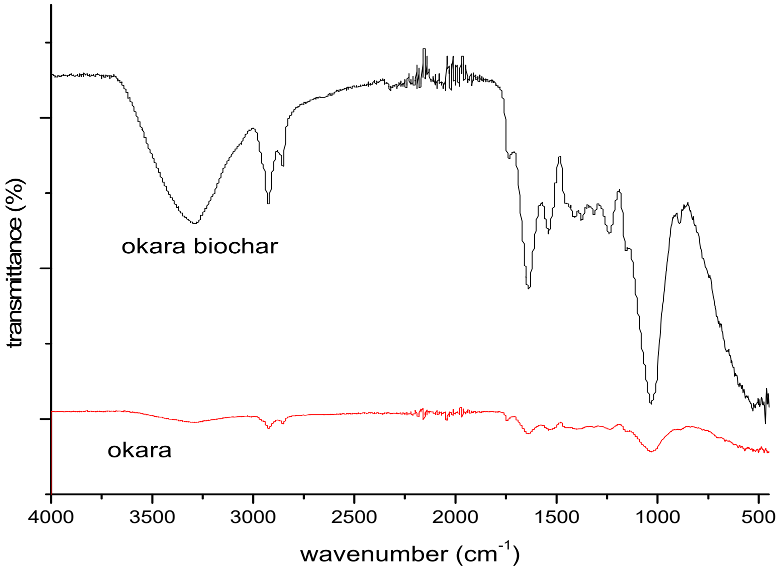


Figure 8. Fourier Transform-Infrared spectra of okara biomass and okara biochar.

3.1.5. TG-DSC Analysis

The thermogravimetry (TG) method is used to measure the mass change of an okara powder under the pyrolysis condition. A sample weighing 3–4 mg was placed into a crucible placed on a sling balance, and the parameters were set as follows: initial temperature: 25 °C; heating rate: 10 °C/min; termination temperature: 600 °C; nitrogen flow: 50 mL/min. The mass changes were recorded continuously to obtain their thermogravimetric curves. DSC measurement was performed at the same time.

The TGA-DSC profile of okara powder waste is presented in Figure 9. It can be seen that the sample mass decreases slightly during the first minutes of measurement at temperatures lower than 200 °C (the first stage), decreases significantly from the temperature of 200 °C up to 400 °C (the second stage), and again slightly decreases from the temperature of 400 °C up to 1000 °C (the 3rd stage). The 1st stage is the drying stage, where the evaporation of free water and crystal water inside the fiber of okara happens. The 2nd stage or carbonization stage happens due to the thermal decomposition or degradation of cellulose and hemicellulose of the okara. The 3rd stage or combustion stage happens when the temperature exceeds 400 °C, and the thermogravimetric curve trend becomes stable due to the gradual decomposition of the residual sample into carbon and ash [6]. Thus, at a pyrolysis temperature of 600^{o}C, the decomposition of the biomass is expected to be completed. The total mass lost if about 75%.

DSC analysis was used as a complementary and supplementary technique to TGA to determine the transition temperatures of the samples as a function of heat flow, as well as establish phase changes caused by thermal exposure as a result of blending [39]. The DSC plot in Figure 9 also indicated that okara sample displayed some endothermic peaks. The first peak appears at 319.8 °C, -0.8254 mW/mg, and a deep peak occurs at 542.8 °C, -1.665 mW/mg. The formation of the endothermic peaks and the modification temperature for the okara sample were evidence of increased burning and heat flow rates that were facilitated by auto-oxidation reactions because of the presence of oxygen-containing functional groups in the structure of the okara sample. The head flow values also indicate that before 542 °C, the heat flow reduces significantly, while from this transition temperature at 542 °C, upward), the head flow increases gradually [39].

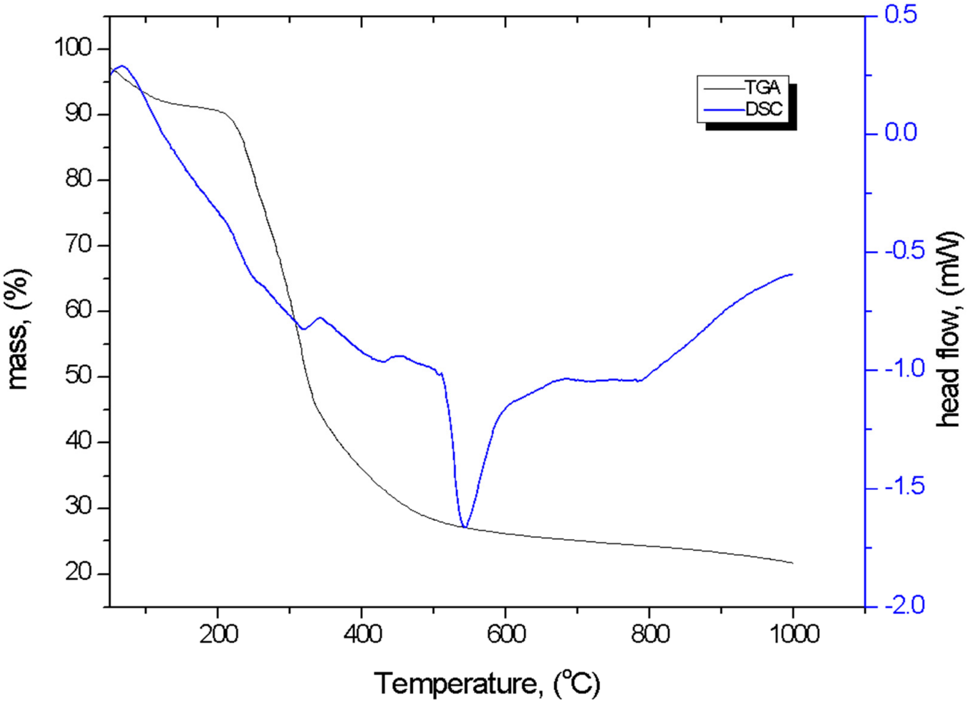


Figure 9. TGA-DSC analysis under N_2 flow of okara powder waste.

The TGA-DSC profile of hydrochar obtained from okara powder waste by the HTC method (OPW4) is presented in Figure 8. Results suggest that the DSC curves of dried okara biomass and its hydrochar samples, as shown, are significantly different.

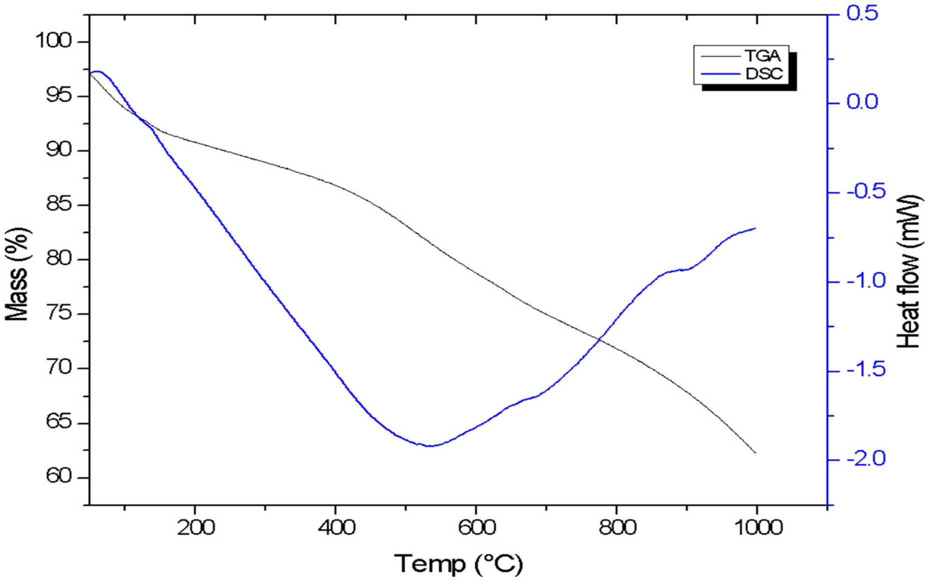


Figure 10. DSC and TGA analysis under N_2 flow of okara powder waste by HTC method (OPW 4).

Thermogravimetric experiments on okara powder waste showed that okara powder waste is a quite reactive material compared to its hydrochar obtained by HTC as the total mass lost of the decomposition of hydrochar is only 32% while it is 75% for okara waste powder. It means that during the HTC process, about 43% mass has been lost and the decomposition of the materials during the calcination at high temperatures in N_2 flow is less heavy.

3.2. Pyrolysis Products and Their Properties

Bio-oil, bio-char, and pyro-gas are essential byproducts of biomass pyrolysis [16,40]. The key constituent of pyrolysis substance is bio-oil, also known as pyrolysis oil, pyrolysis liquid, pyrolysis tar, bio-crude, wood liquid, wood oil, or wood distillate, among other names. This is often a dark brown, free-flowing liquid with a strong smoky, pungent odor. This is an intensely polar substance that is largely immiscible with nonpolar petroleum-derived fuels. The solid residue left over from the pyrolysis of carbonaceous biomass is known as biochar. The properties of biochar are primarily determined by the process and biomass used. Pyro-gas is primarily composed of CO, CH_4, CO_2, and H_2 and has a heating value of 6.4–9.8 MJ/kg. It is used internally as process heat for pyrolysis.

- Biochar and hydrochar yield and burn-off

  The carbon yield is commonly used to measure the effectiveness of a process conversion Carbon yield and burn-off of Several pyrolysis experiments are presented in Figure 11.

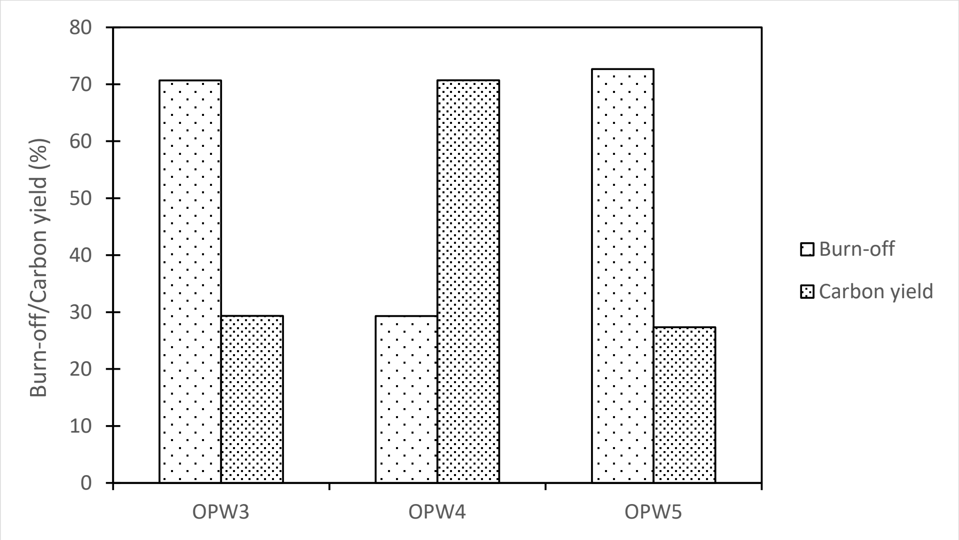


Figure 11. Carbon yields and Burn-off of different experiments.

With the samples conducted, the burn-off value is ranging from 0.29 to 0.71 %. For the OPW3 sample, the result is in good agreement with the TGA result. For the hydrothermal process without using zeolite (OPW4), the burn-off is much less, indicating that the carbonization is not yet complete. However, with the use of a zeolite catalyst, the burn-off increased significantly to the same value as the carbonization at 600 °C. Thus, the use of zeolite enhances the carbonization to help the process to occur at lower temperatures.

- Surface areas (S/BET) and pores:

Several samples have been analyzed to verify their surface areas. Table 3 is a summary of our samples tested and their S(BET) in comparison with the literature results.

Table 3. Comparative details of this experiment's specific capacitance of the okara-derived porous carbon with that of other studies in the literature.

Biomass precursor	Sample code	Pretreatment methods	Activating agent	S_{BET} (m^2/g)	References
Firewood	-	Carbonization 850 °C	Na_2CO_3/K_2CO_3	818	[41]
Banana peels	-	Hydrothermal 200 °C, 24 h	No activating agent	294.6	[42]
Elephant grass,	-	Carbonization at 600 ^{o}C, in N_2 flow; 1h	KOH	407	[34]
Lotus leaf	-	Carbonization 500 ^{o}C, N_2, 1h	Melamine and KOH	687	[43]
Lotus leaf	-	Carbonization 500 ^{o}C, N_2, 1h	No activating agent	3.82	[43]
Lotus leaf	-	Carbonization 500 ^{o}C, N_2, 1h	Melamine	4.32	[43]
Okara powder waste	OPW1	Carbonization, 800 ^{o}C, in an Ar flow over 1h	No activating	1.16	This work
Okara powder waste	OPW2	Carbonization at 650 ^{o}C in a gas N_2 flow for 1 hour	No activating	1.06	This work
Okara powder waste	OPW3	Carbonization at 600 ^{o}C in a gas N_2 flow for 1 hour	No activating	20.73	This work
Okara powder waste	OPW4	Hydrothermal carbonization at 200 ^{o}C; heating rate is 60 ^{o}C/h: temperature of 200 ^{o}C is maintained in 4h; weight ratio of OPW: water is 12.8 gram: 40 ml	No activating	7.01	This work
Okara powder waste	OPW5	Hydrothermal carbonization at 200 ^{o}C; weight ratio is 12.8-gram OPW: 6.4 gr zeolite 4 mm: 40 ml water; temperature of 200 ^{o}C is maintained in 4h; heating rate is 60 ^{o}C/h:	Zeolite (4 mm in size)	14.0	This work
Okara powder waste	OPW6	Hydrothermal carbonization 200 ^{o}C and then pyrolysis (two-step processes) at 600 ^{o}C; in a low of N_2 in 1h; N2 flow rate of 1 l/m	KOH, melamine	22.04	This work
Okara powder waste	OPW7	Carbonization 600 ^{o}C, N_2, 1h to make biochar; after that biochar is mixed with KOH and water; then keep the sample for 48 hours, then dry at 120^{o}C and calcine at 600^{o}C in N_2 flow (1l/min)	KOH (ratio of biochar:KOH: water is 1:4:5 in weight)	104.32	This work
Rice husk	RH	Carbonization 600 ^{o}C, N_2, 1h	No activating	175.48	This work
Okara powder waste	OPW8	Carbonization 600 ^{o}C, N_2, 1h; dry mixing process with KOH	KOH (mass ratio of OPW: KOH = 1/3)	212.60	This work
Okara powder waste	OPW9	Carbonization 600 ^{o}C, N_2, 1h; dry mixing process with KOH	KOH (mass ratio of OPW: KOH = 1/4)	147.85	This work

Okara powder waste	OPW10	Carbonization 600 °C, N_2, 1h; then mix with KOH, biochar:KOH: water mass ratio of 1:5:10; keep the sample for 5 days	KOH (with biochar:KOH: water ratio of 1:5:10; keep the sample for 5 days)	594.08	This work

The results show that the pyrolysis temperature influences the surface area of biochar, when the temperature exceeds 600 °C, the surface area is very small (about 1m^2/g). A surface area of 20.73 m^2/g is obtained for the sample carbonized at 600 °C, however, it is still small to be used as an adsorbent.

The surface area of hydrochar is a little higher than that of biochar obtained at high temperatures (above 650 °C), especially when zeolite and KOH melamine is used to catalyze the decomposition but the surface area is only 14 m^2/g.

The addition of KOH into biochar has possibly created small holes deep into the activated carbon surface. Thus, the S_{BET} result of the porous ACs after activation has enlarged up to 104. m^2 g -1 (OPW7) compared to the pre-activated carbon process which is only 14 and 20 m^2 g^{-1}. When the ratio of KOH increases, the surface area increases (OPW10) since KOH reacted with C to form CO_2 [44] and results more pores for the AC so with a suitable amount of KOH, the surface area can reach almost 600 m^2/g:

$$2KOH \rightarrow K_2O + H_2O \quad (1)$$

$$C + H_2O \rightarrow H_2 + CO \quad (2)$$

$$CO + H_2O \rightarrow H_2 + CO_2 \quad (3)$$

$$K_2O + CO_2 \rightarrow K_2CO_3 \quad (4)$$

$$\text{Overal reaction: } 4KOH + C \rightarrow K_2CO_3 + K_2O + 2H_2 \quad (5)$$

KOH was also mixed with okara biochar without using water and stabilized for a few days (OPW8 and OPW9). In that case, the surface area of Acs was also improved but only reached to around 200 m^2/g, thefore the stabilize of the biochar and KOH for some days is important for KOH to interact homogenously with the whole carbon sample to make it convenient for the following reaction during the next calcination at 600 °C.

For comparison, rice husk and potato peel were also simply carbonized at 600 °C (without activating with KOH). These samples showed much higher surface areas compared to the okara sample at the same carbonization process. It revealed that okara waste is possible to produce AC with a suitable surface area to serve as an adsorbent but may not be an excellent candidate to produce extremely high surface area adsorbents.

4. Conclusions and Outlooks

In the context of global warming, sustainable development, and NetZero targets [45], agricultural residues are promising sources of potential materials for various applications, ranging from energy storage, aqueous environmental treatment, biofuels, and CO_2 capture [2,10,17,46]. This study used biomass sources to obtain useful products, namely porous carbon materials - a CO_2 adsorbent by using the slow pyrolysis and hydrothermal processes. More importantly, okara powder waste was chosen to be focused on because they are cheap, abundant in Asian countries, and easy to harvest.

The adsorbent synthesized from the pyrolysis and hydrothermal processes in this study provide porous characteristics. To investigate the adsorption of the activated carbon the thermal chemical activation was performed. While with no activating agent, the surface areas of the adsorbent were small, but when activated agents were added in a combined pyrolysis and chemical activation method, the S_{BET} of the adsorbent significantly increased. Carbon yields range from 30% to 70 % for slow pyrolysis processes. Pyro-gas is primarily composed of CO, CH_4, CO_2, and H_2. Regarding the pyrolysis and HTC, we conclude that the HTC is not sufficient, solid acid catalysts (zeolite) could accelerate the carbonization in HTC (evidenced in the TGA analysis). The pyrolysis without an activating agent (or activator) shows a low surface area. And activator addition (wet vs dry thermal chemical process increases the surface area). Wet activator addition (KOH amount) increases the BET surface area.

While the current results on activated carbons synthesized from okara and other biomasses have been done, future research should continue on CO_2 uptake in these materials. Okara waste, which has never been studied previously, is possible to produce AC with a suitable surface area (about 600 m^2/g) to serve as an adsorbent but may not be an excellent candidate to produce extremely high surface area adsorbents. Further studies on CO_2 capture using the activated carbon materials developed are needed.

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