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Carbonization of biomass wastes for solid fuel and adsorbent applications

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Abstract. Biomass waste treatment via carbonization has drawn considerable attention due to its applications such as a solid fuel and an adsorbents for wastewater. The characteristics of carbonized products can be influenced by various factors including selection of biomass waste, carbonization temperature, duration, and pretreatment technologies adopted during the process. Indeed, the conversion of biomass waste into the carbonized product presents the sustainable approach to deal with increasing biomass waste responding to the growing energy demands and the need for emerging contaminant removal. This paper provides a brief review of current re-search trends and advancements in biomass carbonization, along with proposed carbonization system design for a sustainable approach. Emphasis is placed on the value-added products through carbonized biomass waste, highlighting its significance towards a sustainable society along with the carbon-neutral system.

Keywords: adsorbent; biomass; carbonization; energy; solid fuel

1. Introduction

Waste is among the growing renewable energy sources and recyclable materials, with significant impacts on climate change, circular economy, and sustainability. With the continuous global population increase, the food consumption and the resultant waste generation are gradually increasing (Thyberg and Tonjes 2016). Especially, due to the expansion of western diet style, the meat consumption has been significantly increased leading to the drastic increase in the livestock waste (González and Manyà 2020). Indeed, finding solutions to not only dealing with such increasing waste but also responding to the energy demand and sustainable world are critical in this era. Regarding the organic waste management practices aiming at renewable energy and resources, it is imperative to adopt a perspective that considers waste in a more productive manner.

Considering the total amount of biomass on Earth (~2 trillion T) and the total energy content (~27,500 billion GJ), it is inevitable to focus on the biomass waste as an energy source (Kulikova *et al*. 2022). Also, biomass wastes can be converted to the value-added products such as biochar (Hoyos-Sebá *et al*. 2024). Biomass, from agricultural wastes in the cropland to sludge in the wastewater treatment, have become one of the significant concerns for the sustainable world (Chew *et al*. 2019). Due to the carbon-rich property, the proper handling of biomass wastes is re-quested to achieve the carbon neutrality (Chen *et al*. 2020).

Conventional biomass waste treatment primarily falls on the composting, incineration, landfill, etc. However, such a treatment brings the atmospheric pollution against the carbon-neutral society (Kataya *et al*. 2023). With the increasing threat of climate change, the urgent need to treat biomass waste in a sustainable fashion brings more attention to the carbonization (Liu *et al*. 2018). Considering the coalization under higher pressure and temperature for a long-term period, the carbonization of biomass waste (that is, biochar production) is a quick process to bring back the carbon (which might be released into the atmosphere) into the ground from which they are originated (Rhodes 2012). Though the carbonization is an energy intensive process which requires carbon emission for the energy supply, further investigation to optimize the process might be a game-changer to balance carbon distribution between atmosphere and lithosphere (Matovic 2011).

In this paper, the carbonization of various biomass wastes and their applications in terms of solid fuel and biochar adsorbent are reviewed for the appropriate treatment operation to generate desirable form of the carbonized products. In addition, the idea to gain economic feasibility to disseminate carbonization process for the practical application is also addressed as a way of moving toward carbon-neutral society responding to climate change.

2. Biochar production

Carbonization is the thermochemical process to convert complex carbonaceous substances into elemental carbon and some carbon-containing compounds. Actually, carbonization generates its products in three phase, coke, coal tar, and syngas. However, the focus on the carbonization is in the solid product which is stable and inert for a long time. Due to the heating at high temperature, the carbonized products are sterilized free of pathogens. In the context of safe carbon storage, maintaining a pathogen-free environment is crucial. For instance, while the

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materials utilized for carbonization are organic in nature, from a resource circulation perspective, organic waste materials like livestock manure and sludge are predominantly employed. Ensuring proper sterilization of these substances is advantageous for safe handling and storage. Therefore, carbonization draws more attention as one of the fascinating carbon storage methods. Though the slow conversion of dead animals or vegetation into coal mineral is also ongoing under high pressure and temperature, the quick conversion of biomass wastes into fixed carbon forms is desirable to respond to the increasing organic wastes. The fast version of carbonization is classified into two types – dry carbonization (DC) and hydrothermal carbonization (HTC). Also, another classification of carbonization depending on the temperature is torrefaction (below 300℃) and pyrolysis (above 300℃). Since the temperature can be relatively simple variable, the comparison of DC and HTC is highlighted in this review.

Dry carbonization necessitates high temperatures and, preferably, minimal to no oxygen contact. Consequently, it necessitates a closed system with an intensely heating process. Although such a system is still perceived as energy-intensive, its carbon-generating process and easy-to-handle product form garner increased attention in the biomass waste treatment sector. Given the desirability of low water content in biomass, the drying process is commonly employed as a pretreatment step. Not to lose the carbon content in the biomass is also important in the carbonization, the probable drying plus carbonization process should be carried out in the quick manner. In fact, the quality of the carbonized products is heavily dependent on the selection of the temperature and the carbonization time. Higher temperature and longer processing time result in the less carbon content with higher porosity, which are good qualities of activated carbon. On the other hand, the good quality for solid fuel comes from the lower temperature and shorter processing time. As a solid fuel production process, dry carbonization shows higher heating value and energy condensation than simple drying, however, considering the overall energy yield, it is hard to mention that dry carbonization is superior to simple drying depending on the raw materials (Hong *et al*. 2023). Therefore, the dry carbonization should be favored for the biomass with little water content which requires no drying for the carbonization process.

Hydrothermal carbonization was introduced to overcome the drawbacks of dry carbonization. It works with water, therefore, the raw material with high water content is good to go with hydrothermal carbonization. However, it requests a certain amount of pressure as well as the high temperature (which is relatively low compared to dry carbonization), therefore, the carbonization system should be in a form of high-pressure vessel. That means the process is more complex and difficult to handle compared to dry carbonization, as a result, the actual application in the field is less favored than dry carbonization so far. Nevertheless, hydrothermal carbonization can be carried out as soon as the biomass is generated minimizing the carbon loss in the process of carbonization, and the final product normally contains higher heating value. Therefore, hydrothermal carbonization is considered as a promising option in solid fuel generation. Also, co-hydrothermal carbonization draws attention in terms of treating multiple types of wastes, such as biomass-biomass, biomass-coal, and biomass-PVC fuel mixtures, simultaneously (Fakudze and Chen 2023).

To save the energy in dry carbonization, the carbonization temperature can be lowered to less than 300℃, which is called torrefaction. Many torrefied products are aligned with the hydrothermally carbonized products since their temperature range is comparable. The decomposition of biomass is greater in hydrothermal carbonization than dry carbonization (Babinszki *et al*. 2020), showing the powerful destruction with the presence of high pressure and temperature. Due to the potent and destructive power, hydrothermal carbonization consumes plastics together with biomass (Shen 2020). Therefore, hydrothermal carbonization can serve as an extended treatment option for not only biomass, but also other organic wastes such as plastics.

Depending on the desirable form of final product, the selection of the carbonization can be determined. So far, two representative carbonized products are solid fuel as an energy source and adsorbent (that is, activated carbon) for contaminants removal. The following sections review the literatures related to the two products.

3. Waste-to-energy: Energy recovery as a solid fuel

As an indicator to evaluate the quality of solid fuel, the heating value is frequently measured, and efforts to enhance it have been continued by varying raw materials, carbonization temperature and time, and so on. As shown in Table 1, many studies have reported the heating value of solid fuels derived from biomass wastes to be above 4,000 kcal/kg which is in the range of moderate to high quality bituminous coal.

In general, as the temperature and the duration increase, volatile content and mass yield decrease, while fixed carbon and ash content increase, leading to an improvement in heating value. To account for the feasibility of the biomass waste-derived solid fuel production, the energy yield which includes both heating value and mass yield, is often adopted as an indicator (for example, at least 70% (Park and Jang 2013)) for the economic and quality solid fuel production. Therefore, the carbonization conditions should be selected carefully, considering the tradeoff between mass yield and heating value. Though higher energy yield is preferentially targeted, there are more factors to consider to ensure the qualification of solid fuel.

To evaluate the applicability of solid fuel, the combustibility index can also be employed to determine suitability for thermal power plant application as co-combustion with coal, with appropriate value of around 5,500 kcal/kg (Singh *et al*. 2020). Although additional considerations such as coal type, co-combustion system, and desired outcome are included to determine the combustibility index, biomass waste-derived solid fuel quality close to coal consumed in thermal power plant would be satisfactory. This can be optimized by controlling

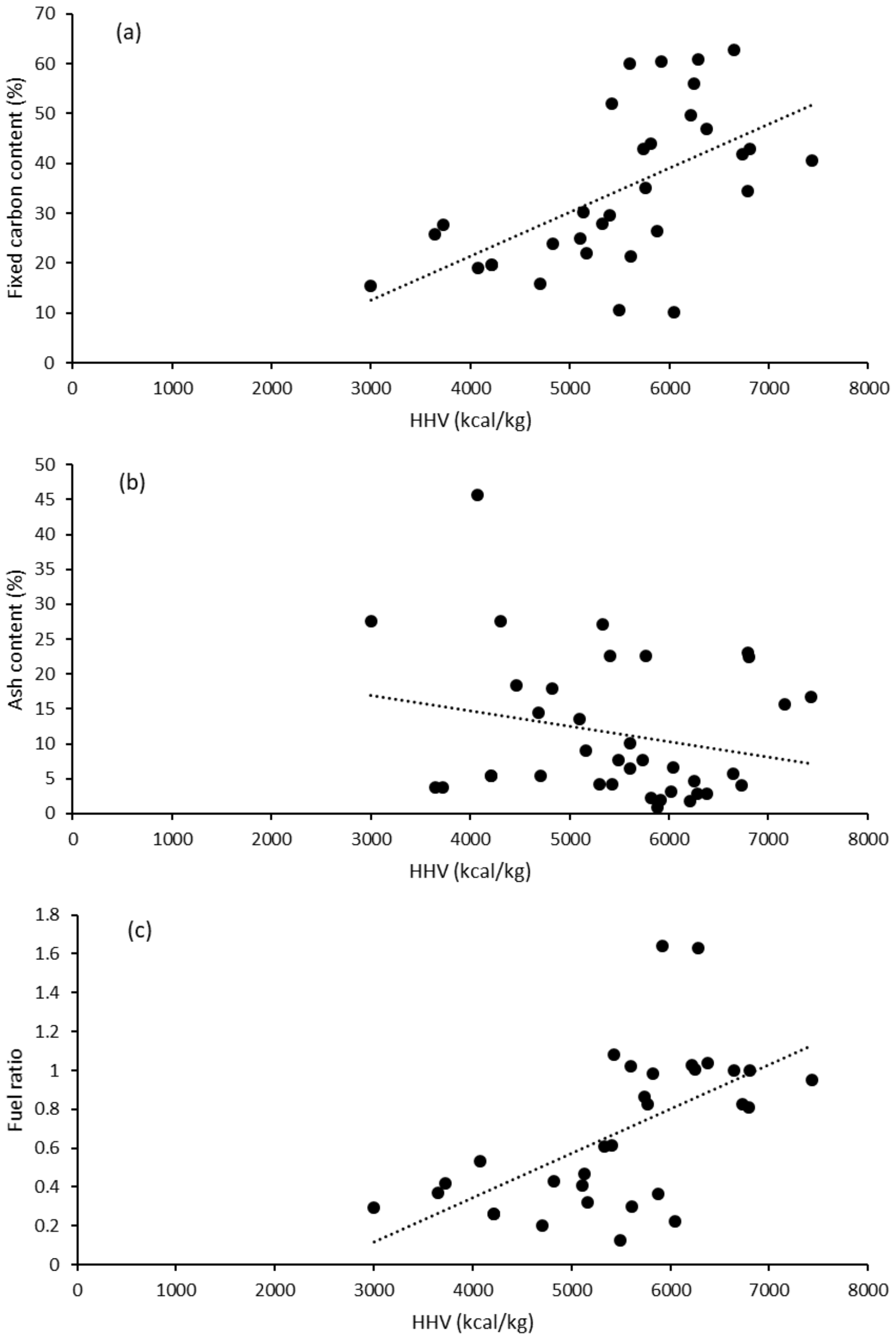

Fig. 1 Correlation between (a) higher heating value and fixed carbon content, (b) higher heating value and ash content, and (c) higher heating value and fuel ratio (data from the literatures in Table 1)

carbonization temperature and duration.

Considering post treatment, low ash content is desirable since the presence of ash in solid fuel reduces its energy content. The heat energy that would have been released by burning the ash-forming components of the solid fuel is lost as it is absorbed by the non-combustible ash. Resulting in lower net heat output compared to fuel with lower ash content (Fig. 1(a)). Additionally, the accumulation of ash in combustion equipment can cause fouling, slagging, and increased maintenance requirements, affecting the efficiency of energy production processes. Therefore, selecting raw materials such as wood or purified biomass which have low mineral content or are carbon-rich, is desirable (Peterson and Brown 2020). An inert atmosphere during carbonization is critical in minimizing reactions between minerals and oxygen, which might otherwise lead to ash formation. A slower heating rate during carbonization can allow more time for volatile components, including some mineral compounds, to escape before they have an opportunity to react and contribute to ash formation. Moreover, a longer carbonization temperature allows for the gradual release of volatiles and the transformation of organic materials into

Table 1 Higher heating values and energy yields obtained from the biomass waste-derived solid fuel via torrefaction

Raw material	Country	Temp. [℃]	Retention time [min]	Higher heating value [kcal/kg]	Energy yield [%]	References
Agricultural waste	Pakistan	300	60	5738.39	80.32	Kanwal *et al*. 2019
Waste wood chips	Poland	300	60	6285.70	54.03	Mokrzycki *et al*. 2020
Camel dung	China	300	30	5764.68	48.91	Wang *et al*. 2023
Cattle manure with sawdust	Korea	300	30	4823.30	63.90	Hong *et al*. 2023
Coffee residue	Taiwan	270	30	6022.60	90.79	Chen *et al*. 2012
Food waste	UK	225	60	4072.56	45.88	Banaget, Check, and Watson, 2023
Food waste	Malaysia	330	30	6792.38	78.18	Abdul Samad, Jamin, and Saleh, 2017
Food waste	Russia	300	30	6214.00	80.18	Khuong and Aleksandrovna, 2023
Granulated organic manure	Russia	300	60	4302.00	58.06	Krysanova *et al*. 2020
Leaf litter	Indonesia	225	30	5105.04	72.24	Triyono *et al*. 2018
[1]MSW	Slovenia	300	90	6046.70	68.51	Ivanovski, Goričanec, and Urbancl, 2023
MSW	Malaysia	280	60	6378.91	83.61	Abdulyekeen *et al*. 2022
MSW	Brazil	275	60	5131.33	86.52	Santanna *et al*. 2020
Oil palm waste	Malaysia	300	30	5298.63	59.30	Uemura *et al*. 2011
Olive mill waste	Spain	300	120	7170.00	39.77	Benavente and Fullana, 2015
Organic waste + plastic mixture	Indonesia	225	30	4703.52	67.88	Triyono *et al*. 2019
Rice husk	Taiwan	270	30	4684.40	95.08	Chen *et al*. 2012
Sawdust	Taiwan	270	30	4469.30	92.94	Chen *et al*. 2012
Sludge	Estonia	300	60	5403.79	71.61	Doddapaneni, Pärn, and Kikas, 2022
Vegetable w aste	indonesia	225	30	5611.72	49.22	Triyono *et al*. 2019
Wood waste	Malaysia	330	30	7430.51	74.22	Abdul Samad, Jamin and Saleh, 2017
Wood + MSW	Sweden	310	90	5162.40	91.26	Edo *et al*. 2017
Woody biomass	India	280	40	5917.64	45.37	Singh, Chakraborty and Mondal, 2020

[*] Municipal solid waste

carbon while minimizing the incorporation of minerals.

Additionally, other parameters such as fixed carbon and fuel ratio index can affect the higher heating value of solid fuel. The fixed carbon content of solid fuel is directly

Table 2 Types of activators to enhance the adsorption capacity of biomass waste-derived solid fuel in wastewater

Activator	Activator :biochar ratio	Raw material	Country	Temp. [°C]	Retention time [min]	Target pollutant	Adsorption capacity [mg/g]	Surface area [m^2/g]	References
[1]CTAB	N.A	peanut shell	Pakistan	600	120	Cr(VI)	27.05	14.04	Murad *et al.* 2022
H_3PO_4	3 mL H_3PO_4 : 1 g Char	tree seed hull	India	600	150	Cr(VI)	41.92	246.23	Nawaz *et al.* 2023
H_3PO_4	1 g H_3PO_4 : 2 g Char	hay pellet	Poland	550	30	Cu(II)	81.81	217.00	Szewczuk-Karpisz *et al.* 2020
H_3PO_4	N.A.	corn straw	China	600	150	[2]TC	612.38	563.93	Tan *et al.* 2020
H_3PO_4	N.A.	inonotus obliquus	China	547	240	TC	1515.46	2014.51	Guo *et al.* 2023
K_3PO_4	0.05 g K_3PO_4 : 1 g Char	apple tree branch	China	500	120	Cd(II)	116.00	37.80	Wang *et al.* 2022
$KHCO_3$	2 g $KHCO_3$: 1 g Char	bamboo	China	700	120	Phenol	169.00	1328.00	Li *et al.* 2020
$KMNO_4$	100mL 5%$KMNO_4$: 1 g Char	vermi-compost	China	500	120	Cd(II)	123.69	17.92	Zhang *et al.* 2020b
KOH	100 mL 7M KOH : 11.22 Char	bamboo	China	675	120	Cr(VI)	48.90	1555.00	He *et al.* 2019
KOH	10 mL 1M KOH : 1 g Char	starfish	South Korea	500	120	Cu(II)	28.50	5.74	Jang and Moon 2022
KOH	1 g KOH : 1 g Char	blue algae	China	800	120	Ni(II)	2.26	1657.80	Wang *et al.* 2020
KOH	2 g KOH : 1 g Char	sewage sludge	China	700	60	Pb(II)	57.48	907.95	Zhang *et al.* 2019
KOH	4 g KOH : 1 g Char	douglas fir	U.S.A.	700	60	Pb(II)	140.00	1050.00	Herath *et al.* 2021
KOH	1 g 1M KOH : 1 g Char	sugarcane bagasse	China	500	120	TC	1.22	156.38	Wang *et al.* 2023
$MgCl_2$	100 mL 1M $MgCl_2$: 10 g Char	plant straw	China	500	120	Cd(II)	763.12	202.75	Yin *et al.* 2021
$MgCl_2$	50 mL 1M $MgCl_2$: 10 g Char	crayfish shell	China	600	120	Cd(II)	72.10	32.20	Zhang *et al.* 2021
$MgCl_2$	2500 mL 1M $MgCl_2$: 500 g Char	rice husk	Iran	600	120	Cd(II)	98.40	231.00	Abolfazli Behrooz *et al.* 2023
$MgCl_2$	2.5 mL 1M $MgCl_2$: 1 g Char	crayfish	China	600	120	Pb(II)	152.30	103.30	Zhang *et al.* 2020a
NaOH	2 g NaOH : 1 g Char	cladode	India	500	120	Cu(II)	49.36	32.07	Choudhary, Kumar, and Neogi, 2020
$ZnCl_2$	1 g $ZnCl_2$: 1 g Char	coffee grounds	South Korea	600	120	[3]AMX	178.57	491.28	Choi, *et al.* 2023
$ZnCl_2$	3 g $ZnCl_2$: 1 g Char	sea buckthorn stones	China	500	180	Cr(VI)	19.29	1031.00	Guo *et al.* 2021
$ZnCl_2$	1 g $ZnCl_2$: 1 g Char	sugarcane bagasse	China	700	120	Cr(VI)	264.03	1031.41	Jiang *et al.* 2023

1Cetrimonium bromide, 2Tetracycline, 3Amoxicillin

related to its higher heating value (Fig. 1(b)). Generally, solid fuels with higher fixed carbon content tend to have higher heating values Because fixed carbon is the primary source of heat energy released during combustion. While fixed carbon content is an important factor in determining higher heating value, the hydrogen content also contributes additional heat energy as hydrogen reacts with oxygen during combustion. Furthermore, the presence of impurities such as sulfur and ash can affect the overall heating value by producing heat-absorbing reactions and reducing the net energy output.

The fuel ratio, which is the ratio of fixed carbon to volatile matter, can provide insights into the composition and behavior of solid fuels. As shown in Fig. 1(c), a higher fuel ratio indicates a higher heating value derived from a higher proportion of fixed carbon compared to volatile matter, which might suggest better combustion stability. While the direct relationship between fuel ratio and higher

Table 3 Adsorption of CO_2 and odor using biochar derived from biomass

Target pollutant	Raw material	Country	Activator	Activator: biochar ratio	Temp. [℃]	Retention time [min]	Adsorption capacity [mg/g]	References
CO_2	Almond shell	Spain	Physical activation by CO_2, NH_3	N.A.	700	120	605	Plaza *et al.* 2011
CO_2	Coconut shell	China	KOH	6 g KOH : 2 g Char	500	120	221.2	Chen *et al.* 2016
CO_2	Rice husk	China	KOH	3 g KOH : 1 g Char	710	60	274.56	Li *et al.* 2015
CO_2	Water chestnut shell	China	$NaNH_2$	3 g $NaNH_2$: 1 g Char	500	120	265.76	Rao *et al.* 2019
CO_2	Olive mill	Spain	KOH	5 g KOH : 1 g Char	350	60	154.92	González and Manyà, 2020
CO_2	Wood residue	Iran	H_3PO_4	2 g H_3PO_4 : 1 g Char	450	60	131.12	Heidari *et al.* 2014
CO_2	Palm kernel shell	Malaysia	CO_2	N.A.	700	120	322.08	Nasri *et al.* 2014
H_2S	Palm shell	Malaysia	H_2SO_4	200 mL 40% H_2SO_4 : 10 g Char	700	120	76	Guo *et al.* 2007
H_2S	Swine manure	China	No activator	N.A.	500	240	65.4	Xu *et al.* 2014
Benzene	Date palm pits	Saudi Arabia	KH_2PO_4	1.6 mL 60% KH_2PO_4 : 1 g Char	500	120	76	Vohra 2015
Toluene	Cotton stalks	China	H_3PO_4	20 mL 80% H_3PO_4 : 1.2 g Char	400	60	328	Hu *et al.* 2017
Toluene	Bovine bone	China	K_2CO_3	1 g K_2CO_3 : 2.5 g Char	450	240	274.72	Yang *et al.* 2020
Toluene	Pistachio shells	China	K_2CO_3	1 g K_2CO_3 : 2 g Char	700	120	123.01	Cheng *et al.* 2023
p-Xylene	Sawdust	China	Citric acid, KOH	50 mL 2M KOH : 10 g Char	800	60	110.774	Yuan *et al.* 2022
Acetone	Soybean straw	China	Sodium lignosulfonate	15 g Activator : 1 g Char	600	180	80.99	Zhang *et al.* 2022
Chloroform	Biosludge	Taiwan	$ZnCl_2$	N.A.	500	30	244	Tsai *et al.* 2008

heating value is unassured, higher fuel ratio tend to have more consistent and stable combustion behavior, contributing to better utilization of the energy content present in the fuel.

Overall, the selection of raw materials is as critical as optimized carbonization conditions for producing a quality solid fuel. Higher fixed carbon content and low moisture content are apparently necessary to enhance energy content as well as carbonization efficiency. Lower nitrogen and sulfur content is desirable to prevent emissions of nitrogen oxides and sulfur oxides during carbonization. Additionally, pre-treatments such as drying, grinding, or pelletizing to enhance the suitability of raw materials for carbonization are also desirable. Therefore, certain types of wood and agricultural wastes are favorable materials for solid fuel via carbonization. Typically, the quality of solid fuels via carbonization has been often evaluated using the van Krevelen diagram, where points located in the left-down side indicate better quality as solid fuel. However, since van Krevelen focuses on the carbon content, other factors affecting quality solid fuel generation should also be considered for comprehensive evaluation.

Synthesis gas (syngas) produced during carbonization process is a mixture of hydrogen, carbon monoxide, and sometimes small amounts of methane and other gases, maintaining elevated temperature. Therefore, syngas recirculation back to the carbonization system can help manage and control the temperature within the carbonization reactor, acting as a heat carrier. Unlike the inert gas provided outside the system, a higher flowrate of syngas recirculation is not expected to sweep heated air inside the system. However, increased gas flow rate in the carbonization process can decrease solid fuel generation by removing volatile products from carbonized product surfaces and reducing the secondary reactions such as repolymerization and recondensation (Özçimen and Ersoy-Meriçboyu 2008). The main obstacle in syngas recirculation is installing hardware (e.g., recirculating pump) capable of enduring high temperatures. In most cases, lower moisture content of raw materials is desirable for efficient carbonization, as moisture consumes energy during heating, reducing overall energy available for the carbonization process. As a rule of thumb, moisture content levels below 10~15% are often considered suitable for efficient carbonization. However, specific moisture content should be determined through experimentation and testing based on the characteristics of the raw material, carbonization process parameters, and desired qualities of the final carbonized product.

Table 4 The yield variation with increasing flow rate

Flow rate (mL/min)	Yield (%)	Temperature (°C)	Time (h)	Material	Country	References
20	58.34	N.A.	1	Coal	China	Song *et al*. 2008
100	56.78					
200	56.65					
0	54	300	0.75	Sugar cane bagasse	Australia	Katyal *et al*. 2003
50	45					
350	42.5					
700	39					
0	31	500	0.75			
50	27					
350	23					
700	20					
0	52.8	449.85	0.5	Chestnut	Türkiye	Özçimen and Ersoy-Meriçboyu, 2008
250	52.7					
500	51.9					
750	50.5					
1000	49.7					
0	59			Grapeseed		
250	59					
500	58.6					
750	58					
1000	56.5					
50	32.5	500	N.A.	Olive bagasse	Türkiye	Şensöz *et al*. 2006
100	31.9					
150	31.88					
200	31.8					
5	24.5	500	1	Spruce	Norway	Babinszki *et al*. 2021
400	24					
5	23.8			Birch		
400	22					
0	23.25	449.85	N.A.	Hybrid poplar	Türkiye	Özyurtkan *et al*. 2008
40	19.52					
50	43	500	N.A.	Green algae	USA	Campanella and Harold, 2012
150	41.6					
250	41.2					
350	40.4					

4. Waste-to-adsorbent for contaminant removal

If the carbonization is carried out at higher temperature and longer retention time, the carbonized product can be utilized as biochar adsorbent achieving higher surface area. As a contaminant adsorbent, the adsorption capacity can be dependent on the surface area generated during the carbonization as well as activation process. In fact, various activators have been applied to produce the quality biochar which can adsorb the target contaminant as much as possible. The physical and chemical activations are typical classification in the biochar activation, and the various ctivation methods in the chemical activation have been developed (Table 2).

The acid and base activation processes of biochar determine the surface acid-base characteristics, altering its hydrophilicity. Strong acids (HNO_3, $KMnO_4$, H_2O_2, or H_3PO_4) can introduce functional groups rich in oxygen, such as hydroxyl and carboxyl, onto the surface of biochar (Sánchez-Sánchez *et al.* 2015). These oxygen-containing functional groups contribute to an increase in polarity and cation exchange capacity, enhancing hydrogen bonding and π-π interactions (Luo *et al.* 2022). The detachment of oxygen functional groups can result in the negatively charged biochar surface binding with positively charged contaminants (Fan *et al*. 2018). Additionally, the increased surface acidity leads to a lower pH of the biochar surface, promoting the adsorption of anionic organic pollutants (Sufri 2019).

Base activators (KOH, NaOH) increase the surface area of biochar through their corrosive action, providing more sites for chemical reactions and physical adsorption (Bamdad *et al*. 2018). The enhanced surface area contributes to increased chemical re-activity and adsorption capacity (Li *et al*. 2014). The alkalinization of biochar alters its pH, promoting the adsorption of acidic contaminants (Mu *et al*.). Moreover, attaching hydroxyl groups to the biochar surface enhances adsorption through increased hydrogen bonding and electrostatic interactions (Liu *et al*. 2020).

Various activation treatments can enhance the adsorption capacity of biochar and induce the adsorption of specific substances. Phosphoric acid treatment enhances the adsorption of F (fluoride), while mineral treatments (calcite, silicate, $Mg(OH)_2$) accelerate the oxidation of Fe^{2+} and the formation of Fe^{3+} hydroxide precipitates (Usman *et al*. 2013). Amino modification efficiently forms complexes with heavy metals through amino functional groups (Yang and Jiang 2014). Polyethyleneimine treatment promotes the chemical reduction of Cr^{6+} and increases adsorption capacity through the intro-duction of amino groups (Ma *et al*. 2014). Fe(III) coating enhances adsorption capacity through interactions with FeOH and $FeOH^{2+}$ groups (Samsuri *et al*. 2013). Ammonia activation increases nitrogen functional groups, aiding in CO_2 adsorption (Qiao and Wu 2022). These treatment methods contribute to the adjustment of the physical and chemical properties of biochar, enabling the design of biochar adsorbents suitable for specific applications.

Numerous studies have highlighted the effectiveness of biochar in terms of the adsorption capacity and specific surface area. Most target compounds were heavy metals and organic pollutants such as antibiotics. The adsorption kinetics (pseudo-first, pseudo-second, intraparticle model, etc.) and adsorption isotherm (representatively, Langmuir and Freundlich model) are frequently used to explain the adsorption mechanism and behavior. The characteristics of the biochar are usually analyzed by microscopic observation (e.g., SEM images) along with the surface area analysis (e.g., BET, porosimeter, etc.). In addition, the functional groups on the biochar surface can be analyzed by Fourier Transform Infrared Spectrometer (FTIR), providing hydroxyl groups, carbonyl groups, aliphatic groups, carboxylic groups, and so on.

The relationship between carbonization temperature and surface area is a crucial aspect of carbon material's formation and properties. During the carbonization process, organic materials undergo various chemical and physical transformations. As the temperature increases, volatile components are driven off, leaving behind a solid carbonaceous residue. At higher temperatures, the carbon atoms rearrange and bond to form a more ordered structure. This restructuring leads to the generation of pores in the biochar. The pores formed during carbonization and activation can be classified into two main categories: micropores and mesopores. Micropores are very small pores with diameters typically less than 2 nm, while mesopores are very small pores ranging from 2 to 50 nm. The activation process tends to generate a higher proportion of micropores due to the complex chemical reactions taking place. The carbonization temperature and activation process significantly influence the distribution and size of these pores. Higher carbonization temperatures tend to result in more ordered and compact carbon structures with fewer defects and larger pore sizes. On the other hand, lower temperatures can lead to disordered structures with smaller pores (Grioui *et al*. 2007). The activation process further refines the pore structure, increasing surface area by generating more micropores and mesopores. These surface area characteristics play a crucial role in determining the biochar's suitability for various applications such as energy storage and adsorption. As shown in Table 2, the biochar adsorbents were generated at least 500℃ or higher, while the solid fuel conversion is desirable around 300℃ or less.

The application of biochar adsorbent for the adsorption of contaminants offers a cost-effective means of removing a wide range of water contaminants. Especially, in the regions where traditional wastewater treatment process might be expensive or less accessible, the utilization of biomass wastes can contribute to the region's public health. Also, the biochar adsorbent implies the potential for biomass wastes as a valuable product contributing to resource recycling. Despite the technically promising potential of biochar adsorbents, the variability of biomass feedstock, carbonization conditions, and adsorbent performance necessitates standardized protocols for characterization and testing. In addition, the long-term stability and regeneration of biochar need further investigation to ensure sustainable applications. Above all, the cost for producing biochar should be outweighed by the benefits from using the biochar. One of the main obstacles in disseminating the carbonization application is the economic feasibility which has not been assured in the field (Lohri *et al*. 2016).

The carbonization process is unfavorable in terms of economic feasibility. However, as more attention is given to the carbon capture, storage, and utilization, the carbonization process is gaining more rooms to expand its profits. Especially, biochar, itself, can be used as an adsorbent for the direct CO_2 capture (Plaza *et al*. 2011). The mechanisms of CO_2 adsorption onto biochar involve physical and chemical processes that occur at the surface of the biochar. In terms of physical adsorption, higher surface area as well as greater formation of micropores and mesopores provides the opportunities to adsorb more CO_2 through van der Waals force (Heidari *et al*. 2014, Tsai *et al*. 2008). Regarding chemical adsorption, surface functional groups such as hydroxyl, carboxyl, and carbonyl groups can interact with CO_2 via hydrogen bonding (Li *et al*. 2015, Rao *et al*. 2019). Especially with N-doped biochar, CO_2 can be adsorbed via carbamate formation (Wang *et al*. 2023). The charged nature of certain functional groups on biochar can induce electrostatic interaction with negatively charged part of CO_2 molecules (Li *et al*. 2023). Also, CO_2, being a nonpolar molecule, can be attracted to the hydrophobic sites of biochar through hydrophobic interactions. Furthermore, other greenhouse gases (CH_4, N_2O, etc.) and odor (VOCs,

Table 5 BET surface area with increasing flow rate

Flow rate (mL/min)	Temperature (°C)	Time (h)	Material	Country	Reference
200	500	2	Bamboo	Japan	Yamashita and Machida, 2011
500					
100	850	3.5	Oil palm fibre	Malaysia	Lua and Guo, 1998
150					
200					
250					
100	600	2	Wine stone	Turkye	Arslanoğlu, 2019
200					
300					
400					
500					
600					
50	750	3	Zeolite	India	Konwar and De, 2013
100					
80	700	1	KOH: anthracite (2:1)	Spain	Lozano-Castello *et al.* 2001
200					
400					
800					
100	900	1	Elaeis guineensis frond fiber	Malaysia	Low *et al*. 2015
500					
50	800	1	Waste tire	Columbia	Betancur *et al*. 2009
150					
50	900	1			
150					
50	800	1.5			
150					
50	900	1.5			
150					
50	800	2			
150					
50	900	2			
150					
50	800	2.5			
150					
50	900	2.5			
150					
50	800	3			
150					
50	900	3			
150					
20	500	N.A.	Silica gel	Poland	(Gierak and Leboda, 1988
50					
100					

H_2S, etc.) can be removed using biochar adsorption (Table 3).

In the process of carbonization aimed at producing solid residues, volatile by-products emerge as byproducts, a

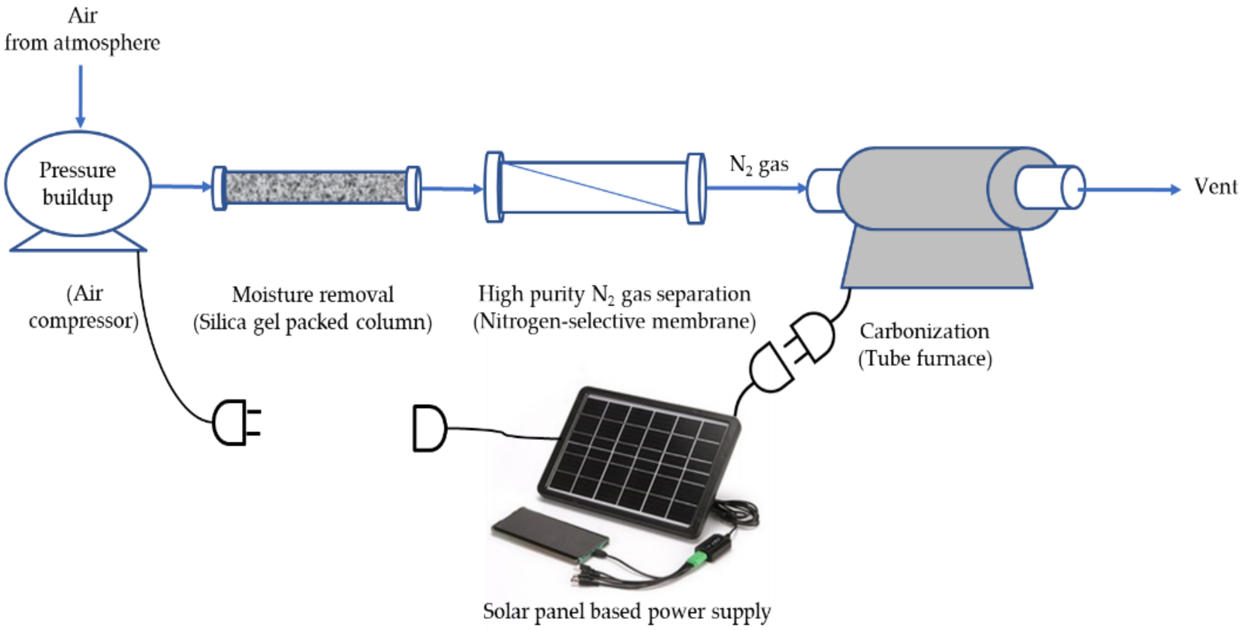

Fig. 2 Proposed design of energy self-sufficient carbonization system

result of the fracture or disruption of functional groups in the corresponding moieties of volatile intermediates (e.g., CH4 formation through the breakdown of methyl and methylene groups) (Fu *et al*. 2013). The volatile by-products can induce secondary reactions, such as repolymerization and recondensation, potentially diminishing the porosity of the resulting solid residues. To address this challenge, it is imperative to eliminate volatile by-products generated during carbonization, often accomplished by employing inert gas, such as nitrogen, as a sweep gas. Sweep gas, introduced at a controlled flow rate, enhances porosity of solid char (Arslanoğlu 2019, Konwar and De 2013, Yamashita and Machida 2011) thereby increasing the adsorption performance for contaminants (Zhang *et al*. 2022). However, a consequential reduction in the yield of the resulting material occurs when the sweep gas flow rate is low, causing a slow removal of volatile compounds. This can lead to the induction of solid char formation and secondary reactions, resulting in adverse effects on BET surface area and porosity (Kataya *et al*. 2023, Özçimen and Ersoy-Meriçboyu 2008, Song *et al*. 2008). The Brunauer–Emmett–Teller (BET) surface area represents the surface area per unit mass of the solid. BET adsorption isotherms are routinely used to determine the specific surface areas of porous materials, either amorphous like activated carbons or crystalline like metal organic frameworks (MOFs) and covalent organic frameworks (COFs) (Tian and Wu 2017).

Research findings, which observe the impact of increasing inert gas flow rates during carbonization on the yield and BET surface area of solid residues, are presented in Tables 4 and 5. While there were instances where the correlation between flow rate and yield was not significant (Nakason *et al*. 2021, Pathomrotsakun *et al*. 2020), a common trend emerged, showing a reduction in yield with increasing flow rates. Similarly, BET surface area exhibited varying trends, with some cases showing a decrease or no significant change with increasing flow rates (Dizbay-Onat *et al*. 2017, Guo and Lua 2000). Nevertheless, there was a general inclination for BET surface area to increase with rising flow rates, although specific literature reported a decrease in BET surface area when injecting nitrogen at flow rates exceeding 200 mL/min at carbonization temperatures between 850 and 900 ℃ (Lua and Guo 1998, Low *et al*. 2015). This suggests that excessively high flow rates may remove excess heat from the char surface, lowering sample temperature and reducing BET surface area.

5. Challenges and suggestions for sustainability

With regard to sustainability, considerations include resource cycling, reduction in energy consumption, and mitigation of carbon emissions. In the carbonization process, the most significant expenditure is attributed to energy consumption. Also, a substantial cost can be expended to maintain oxygen-free conditions, ensuring operational stability for fire prevention and improving the quality of carbonized products (Lucian and Fiori 2017, González-Arias *et al*. 2021). The energy self-sufficient carbonization system aligns with the principles of sustainability and circular economy by minimizing external energy inputs, reducing greenhouse gas emissions, and potentially utilizing waste materials or by-products as feedstock.

This type of system typically employs innovative design principles and engineering techniques to capture and utilize the heat generated during the carbonization process. However, the design and implementation of such a system can be complex and require careful consideration of engineering and process optimization. To ensure the economic feasibility, the utilization of nitrogen gas in the atmosphere and the sunlight is desirable to design an energy self-sufficient carbonization system. Therefore, nitrogen-selective membrane and solar panel equipped power supply device are proposed in a small-scale application (Fig. 2).

In this system, the energy captured from solar panel is stored in the power supply device and is utilized for 0.5~2 hr heating for carbonization process. The nitrogen gas separated from atmosphere is suppled as an inert gas for carbonization process. To ensure the gas separating performance and the long-term gas operation of the nitro-gen-selective membrane, an air compressor and a moisture removal device are installed in advance to the membrane. As long as the operation of the membrane (in terms of the appropriate flow rate and pressure) as well as the solar panel-based power supply is optimized, such a design is expected to enable independent operation of small-scale carbonization processes, and further technical advances will bring the scaled-up carbonization feasible in the near future. Therefore, it is anticipated that achieving sustainability is feasible by reducing energy consumption through the utilization of solar energy and atmospheric resources (such as power and inert gases) required for the carbonization process.

6. Conclusions

In the carbonization process, the most significant expenditure is attributed to energy consumption. Also, a substantial cost can be expended to maintain oxygen-free conditions, Biomass wastes have been widely investigated in terms of converting to solid fuel or adsorbent. As more research outcomes are anticipated continuously, more efforts to enhance practical applicability are required in research and development. For the high-quality solid fuel production, the careful selection of raw material is critical in terms of possessing higher heating value and minimizing the emission of air pollutants. For the high-quality biochar adsorbent production, the selection of activator can enhance the surface area of biochar, allowing further contaminant removal. However, the evaluation of such a carbonized product should encompass a comprehensive assessment beyond just higher heating value or adsorption capacity, including factors such as energy consumption and potential environmental pollution.

Carbonization is gaining significant attention not only for its sustainable treatment of waste, promoting circular economy, but also as a burgeoning venture that yields value-added products such as energy resources and adsorbents. With a foundation built upon continuous research advancements, it is anticipated that the development of optimized and economically viable carbonization processes will contribute to achieving carbon neutral society. Since carbonization is an alternative process to carbon storage, carbonization of biomass wastes will receive more attention. Coupled with energy self-sufficient system, the efforts to gain economic feasibility should be invested. Also, in the realm of research and development, there is a need to establish standard protocol for material supply as well as carbonization performance evaluation. It is recommended to leverage these foundations to effectively address research gaps.

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