Potential use of residues from thermal conversion processes for CO_2 capture

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Abstract. Economic development in many developing countries is leading to a significant increase in atmospheric CO_2 in recent decades, exacerbating global climate change. One of the solutions being vigorously researched is the use of cheap and environmentally friendly CO_2 adsorbents. In this study, solid residues from gasification of bagasse, and pyrolysis of macadamia nut shells were used for CO_2 adsorption. The N_2 adsorption/desorption results showed that the post-gasification residue was much more porous compared to the post-pyrolysis residue. The CO_2 adsorption experiments were carried out in laboratory conditions (100 % CO_2, 25 °C) and flue gas conditions (15 % CO_2, 40 °C). The bagasse residue achieved a high and stable CO_2 adsorption value at 2.3 mmol/g, 2.5 times more than that of macadamia nut shells residue. This result showed that residues from thermal conversion processes could be re-used as cheap and environmentally friendly materials for CO_2 capture.

1. INTRODUCTION

The release of greenhouse gases such as carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (NO_2) into the atmosphere is a serious problem because they can cause climate change. CO_2 is the most concerned of the greenhouse gases because it is the gas that causes global warming [1], leading to enormous impacts on the terrestrial environment, causing severe droughts, altered rain patterns, extreme heat waves, melting glaciers and rising sea levels [2]. Thermal power plants or combustion installations are the main sources of CO_2 emissions because they burn large amounts of fossil fuels to generate energy for human activities.

In order to reduce CO_2 emissions into the atmosphere, many studies are aimed at finding new and modern methods to efficiently capture CO_2. In industry, CO_2 is adsorbed in solutions

with amines such as monoethanolamine (MEA), diethanolamine (DEA), or methyl diethanolamine (MDEA) [3]. However, these methods present various disadvantages such as high risks of equipment corrosion, additional energy required to regenerate the sorbent, and additional sludge generation from the process. This requires finding new materials that are more affordable and more environmentally friendly.

Recently, some studies on biochar derived from agricultural by-products showed that this material could achieve a high CO$_2$ adsorption ability, and the technology can be easily scaled-up [4, 5]. However, despite being cheaper than industrial adsorbents and taking advantage of the abundant agricultural by-products found in most countries, the biochar-making process itself is still very energy-intensive, i.e. high production cost. For that reason, the practical application of this material is not yet widespread. A new research direction that has appeared in the last few years is to make use of residues from thermochemical conversion processes [6, 7] as adsorbents for CO$_2$ capture. In these processes, agricultural residues are first used for energy production. Then, the solid residues are produced after the process, sometimes in large quantities due to the nature of the biomass used and the low efficiency of the technology. These residues are often disposed, which is expensive to handle and pollutes the environment. So being able to reuse these materials can help increase the value of the entire production process. Up to now, studies in this direction are still very few and scarce.

Therefore, in this study, solid residues from gasification of bagasse and pyrolysis of macadamia nut shells were used for CO$_2$ adsorption. These biomass feedstocks are abundantly present in Viet Nam and are being used for thermochemical conversion processes to produce energy.

2. MATERIALS AND METHODS

2.1. Biomass sample

The macadamia nut shell was sampled from factories in Dak Lak province, while the bagasse was sampled from factories in the Red River Delta of Viet Nam. To determine the characteristics of the biomass, a series of proximate analyses was performed. Important characteristics of the biomass samples, i.e. volatile matter V (ASTM D-3175), ash content A (ASTM D-3174) and fixed-carbon content FC (FC = 100 - V - A) were determined.

2.2. Analysis of biomass residues

The solid residues were collected from two pilot systems, installed at the University of Science and Technology of Hanoi (USTH). Bagasse was gasified in a gasification system at 900 °C in the presence of water as a reacting agent (20 % H$_2$O in N$_2$). Meanwhile, the pyrolysis system operated at 600 °C with the macadamia nut shell as the input fuel, in an inert environment (100 % N$_2$). The solid residues were obtained from the two most common biomass technologies: pyrolysis and gasification, thus the applicability of these residues in practice would be highly feasible. After the conversion process was finished, the solid residues were collected and stored for further analysis.

The SEM (Hitachi TM4000Plus) coupled with an EDS detector was used to observe the surface morphology and elemental compositions of the residues. As the SEM-EDS is a semi-quantitative method that only allows local observation, each sample was observed at several locations to obtain more precise information about the samples. The surface functional groups of the residues were analysed using an Elmer Perkins Spectrum Two analyser. The corresponding

FT-IR spectra of the two samples were recorded in a wavenumber range between 4000 cm^{-1} and 700 cm^{-1}. Meanwhile, the porosity and specific surface areas of the samples were determined using an ASAP2060 Micromeritics analyser. N_2 adsorption/desorption analysis was conducted at – 196 °C and the data were recorded over the range $0 < p/p_o < 0.99$. Based on this analysis, the BET method was applied to assess the total specific surface area (S_{Total}) and total pore volume (V_{Total}) of the residues. Meanwhile, the t-plot was applied to estimate the micropore volume of the samples.

2.3. CO$_2$ sorption capacity analysis

A Macro-thermogravimetric system (Macro-TGA) (Figure 1) was used to assess the CO$_2$ adsorption ability of the residues.
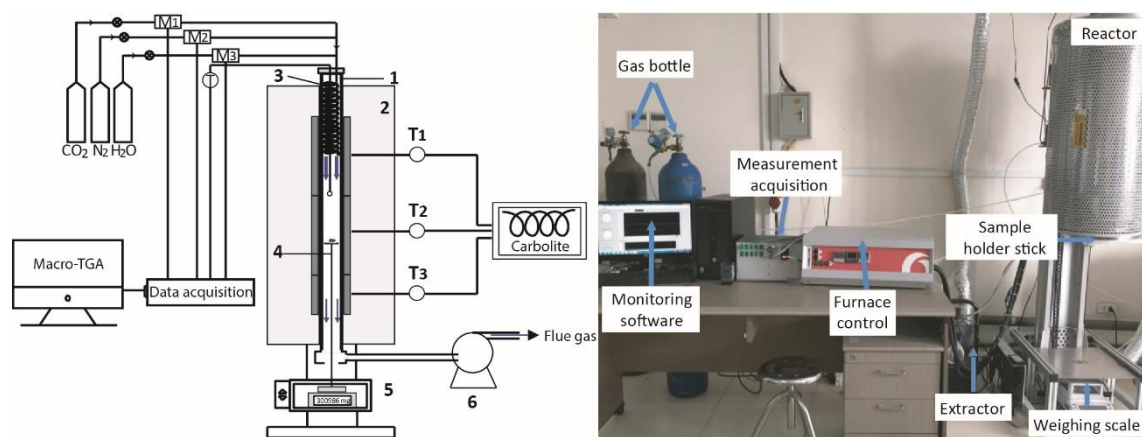

Figure 1. The macro-thermogravimetric reactor.

The reactor contains a ceramic tube (**1**) (111 cm in length and 7.5 cm in internal diameter), placed in an electrical furnace (**2**) with 03 independent heating zones (**T$_i$**) to maintain a uniform temperature. The experiment atmosphere was generated by different gas flows (N_2, CO_2) in selected concentrations, precisely controlled by mass flow meters (**M$_i$**). The gas mixture was moved across a coiled tube (**3**) before reaching the sample. For each experiment, the sample holder (**4**) containing the sample was lifted from the bottom to the desired position inside the reactor. The CO_2 stream was adjusted so that an ambient pressure was obtained for adsorption experiments. As the CO_2 adsorption occurred, the mass was gradually changed and was continuously recorded by the weight scale (**5**). The flue gas was extracted from the system by an extractor (**6**). The CO_2 capture capacity (expressed as wt% of dry adsorbent) was determined by measuring the mass uptake of the residues when exposed to laboratory conditions (100 % CO_2 at 25 °C) and more realistic conditions for CO_2 capture in flue gases (15 % CO_2 at 40 °C).

3. RESULTS AND DISCUSSIONS

3.1. Characteristics of biomass samples

The characteristics of macadamia nut shell and bagasse samples are shown in Table 1. It can be seen that the moisture content of both samples was quite high, exceeding 15 %. High moisture usually makes thermochemical conversion more unfavourable, therefore the

recommended biomass moisture content for thermochemical conversion is less than 10 % by weight [8]. Therefore, a drying process is highly recommended before putting these feedstocks to the reactor. The ash content in macadamia nut shell was 3.42 %, while that of bagasse was only 0.85 %. These values are relatively low compared to that of other types of agricultural residues, such as cashew nut shell (5 %) and coffee bean pod (11.2 %) [9]. The low ash content will reduce concerns about equipment clogging and corrosion in an industrial system, highlighting the suitability of these biomass types for large-scale energy production. The higher heating value *HHV* of macadamia nut shells and bagasse was recorded as 17.47 MJ/kg and 16.5 MJ/kg, respectively. High *HHV* make the thermochemical conversion process more energy efficient. Moreover, high fixed-carbon content was observed for both biomass samples. This is directly related to the characteristics of the residues collected after the process: one can expect that these residues contain low ash content and a complex carbon matrix, which is suitable for usage as adsorbents.

Table 1. Proximate analysis of samples.

Biomass	M_{as} (%)	A_{db} (%)	V_{db} (%)	FC_{db} (%)	HHV_{db} (MJ/kg)
Macadamia	15.72	3.42	70.48	26.10	17.47
Bagasse	20.22	0.85	72.15	27.00	16.50

M: moisture, A: ash content, V: Volatile content, FC: fixed carbon content, HHV: Higher heating value; as: as received, db: dry basis.
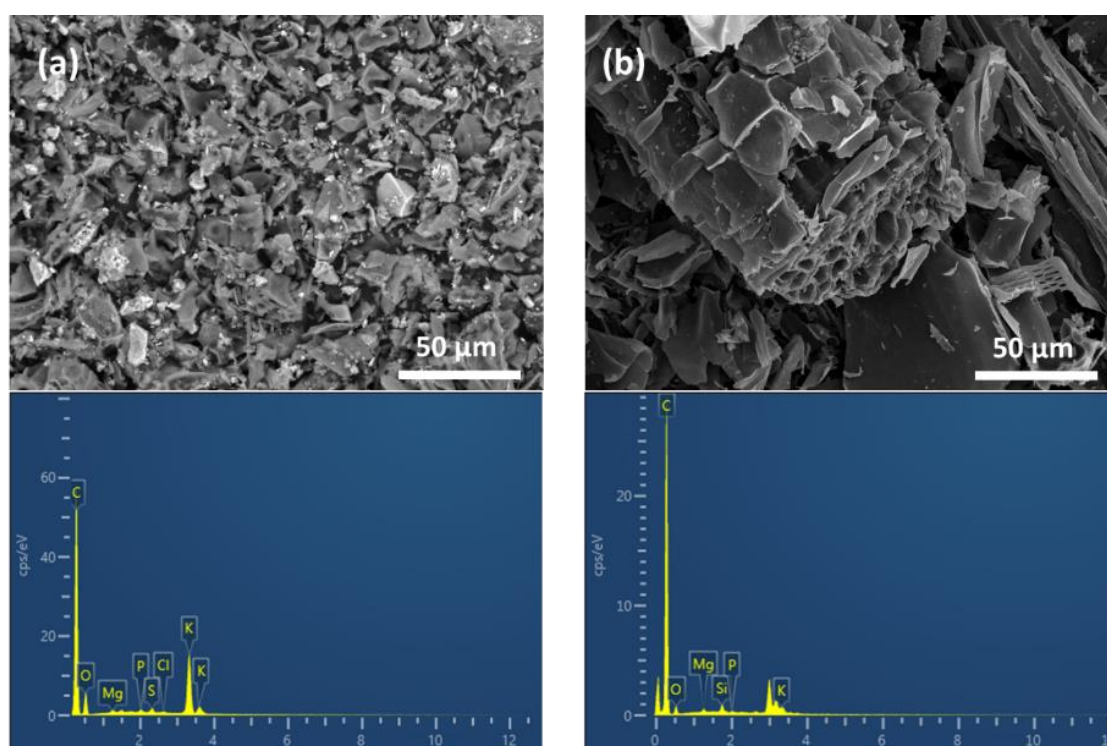
3.2. Surface morphology

Figure 2. SEM-EDS of macadamia (a) and bagasse (b) residues.

Table 2. Surface element on residues.

Sample	Surface element (Atomic %)								
	C	Si	Mg	P	K	O	S	Cl	Total
Bagasse	92.37	0.35	0.18	0.08	0.25	6.77	-	-	100
Macadamia	82.99	0.10	-	1.18	6.24	9.10	0.12	0.27	100

The SEM-EDS results of the two residues are shown in Figure 2. The SEM images allowed direct visualization of the surface morphology and macroscopic porosity of the residues. A heterogeneous morphology with rough surface interspersed between large and small particles was observed in the case of macadamia residue. Some particles were reflected brighter on the surface, possibly inorganic particles present on the surface of the residue. In the case of bagasse residue, various overlapped char layers were observed forming macroscopic porous structures.

The EDS results (Table 2) showed that the predominant element on the surface of both residues were carbon, followed by oxygen, accounting for more than 90 %. Some other elements were also found on the surface of the residues, but in very small quantities, except for the potassium content on the macadamia residue.

3.3. Surface chemistry

Figure 3 shows the results of the FTIR analysis of the two residues. Some functional groups were detected on both bagasse and macadamia residues, such as the O-H stretching at around 3700 cm^{-1}, the C≡C stretching at 2200 cm^{-1}, the C=C stretching at 1500 cm^{-1} and C-O stretching at 1100 cm^{-1}. These peaks are characteristic of biochar with the possibility to connect with adsorbates during the adsorption process. Moreover, some O-H and N-H stretching bonds were detected only on bagasse chars. As CO_2 has a high quadrupole moment and acidity, this gas is strongly adsorbed on basic and polar groups. Therefore, some functional groups with high basicity and polarity of the two residues might participate in determining the adsorption strength of CO_2.
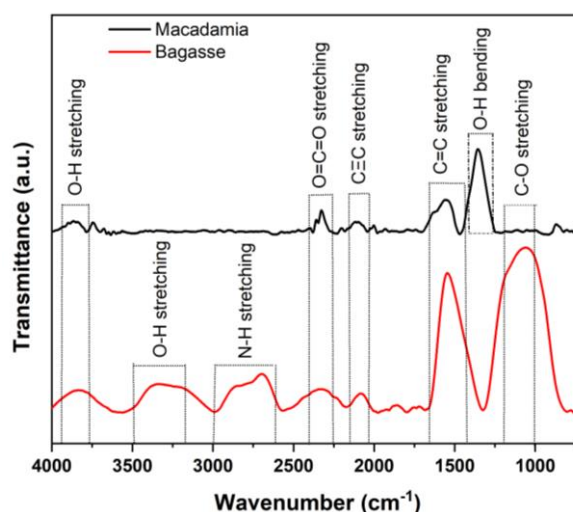

Figure 3. FTIR spectra of two residues.

3.4. Porosity

The porosity of the two residues was analysed from the N_2 adsorption-desorption isotherms, as shown in Figure 4.
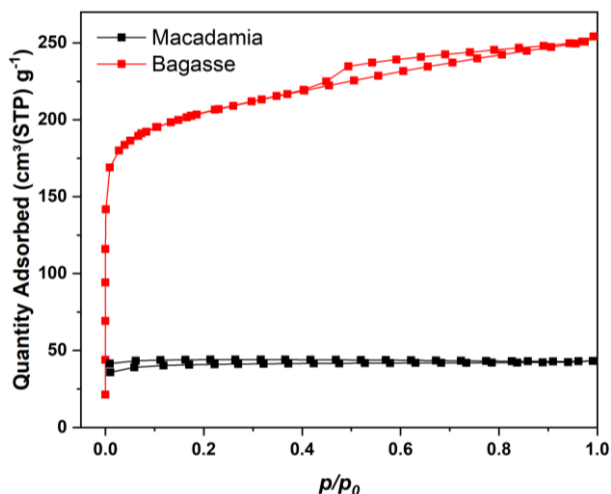

Figure 4. N_2 adsorption-desorption isotherms of two residues.

The macadamia residue showed a lower amount of N_2 adsorbed in the pores compared to that of bagasse residue, as expressed by the lower position of the N_2 isotherms. The N_2 adsorption-desorption isotherms of the macadamia residue exhibited type I in the IUPAC classification [10], which is given by microporous materials having mainly narrow micropores. Meanwhile, the N_2 adsorption-desorption isotherms of bagasse residue exhibited type IV isotherms with a steep uptake at very low relative pressures and a large-range hysteresis loop. This result suggests that both micropores and mesopores are present in this residue. The total surface area (S_{total}) and total pore volume (V_{total}), estimated by the BET method, as well as the micropore volume (V_{micro}) and mesopore volume (V_{meso}) estimated by the t-plot and BJH methods are presented in Table 3.

Table 3. Specific surface area and pore volumes of residues.

Residues	S_{total} (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)
Macadamia	127	0.06	0.05	0
Bagasse	654	0.43	0.28	0.20

The specific surface area of bagasse residue is much higher than that of macadamia residue and is comparable to that of commercial active carbons (> 500 m^2 g^{-1}) [11], showing great potential in using this residue as an adsorbent. The pore volumes of the two residues confirmed that macadamia residue was mostly composed of micropores, while the bagasse was composed of micro-mesoporous structures.

3.5. CO_2 adsorption capacity

Figure 5 shows the results of CO_2 adsorption when using the two residues as adsorbents at laboratory conditions (100 % CO_2, 25 °C) and at flue gas conditions (15 % CO_2, 40 °C). At laboratory conditions, the macadamia residue increased by 4.5 % (1.1 mmol/g), and the bagasse residue increased 9.7 % (2.3 mmol/g) compared to the initial mass. Hence, the bagasse residue has a much higher CO_2 adsorption capacity than that of macadamia residue. As there are little differences in surface functional groups and surface elements between the two residues, the gap in CO_2 uptake of the two materials is mostly due to the higher micropore volume of the bagasse residue compared to that of the macadamia residue. Previous studies also highlighted that the CO_2 uptake is more dependent on the micropore volume of the material than other factors [12 - 14]. At the flue gas conditions, the two samples still achieved a good adsorption capacity, estimated at 2 % (0.5 mmol/g) for macadamia residue, and 5.7 % (1.3 mmol/g) for bagasse residue. These values are comparable to some other materials found in previous studies [15].

In addition, the maximum adsorption capacity was obtained after a very short time, less than 2 minutes in all cases. When switching to N_2 to regenerate the sample, the time for the residues to release CO_2 was also very fast (under 5 minutes to completely release the adsorbed CO_2), meaning the two materials could achieve one adsorption cycle in a very short time. These results highlighted a big advantage in practice when using these residues, as it is possible to separate CO_2 from the exhaust gas stream and store it somewhere else very quickly. The CO_2 absorbed can be used in-situ in some specific applications, e.g. in gasification systems where an enhancement of CO_2 in the reacting atmosphere is highly recommended to increase the CO content in the syngas.
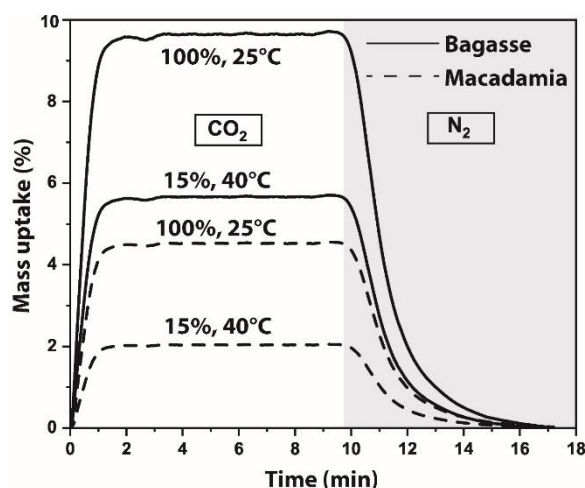

Figure 5. Mass uptake of residues during CO_2 adsorption.

The CO_2 uptake of these solid materials was compared to that of different biomass-derived activated carbons from previous studies as well as the solid residues obtained from the pyrolysis system using bagasse, and from the gasification system using macadamia nut shell, as shown in Table 4.

It can be seen that the CO_2 adsorption capacity of our solid residues are in range with that of other activated carbons. Moreover, it should be noted that some activated carbons were obtained from quite complicated and expensive processes. This highlights the advantage of using our solid residues as efficient and cheap CO_2 adsorbents.

Table 4. CO_2 adsorption uptake of different biomass-derived activated carbons.

Material	Production condition	CO_2 adsorption (mmol g^{-1})
Bamboo [16]	CO_2 activation, 800 °C, **0 – 10 – 15 – 25 – 30 min**	3.2 – 2.4 – 3.3 – 2.9 – 2.0
	Hydrothermal carbonization, 200 °C, 2.5 h, followed by CO_2 activation, 800 °C, **0 – 2 – 3 – 4 – 5 – 6 h**	2.9 – 3.2 – 3.3 – 3.4 -3.4 – 3.3 – 2.9
Pomegranate peels [17]	KOH activation, ratio 1:1, 700 °C	4.11
Kernel shell [18]	CO_2 activation, 60 min, 850 °C	2.134
Empty fruit punch [19]	KOH activation, ratio 1:5, 600 °C	1.12
Olive stone [20]	CO_2 activation, 800 °C, **0.5 – 1.0 – 1.5 – 2.0 – 4.0 – 6.0 – 8.0 h**	2.4 – 2.5 – 2.7 – 2.7 – 2.9 – 3.1 – 3.1
Bagasse	Obtained from our pyrolysis system	1.8
Macadamia nut shells	Obtained from our gasification system	2.8

4. CONCLUSION

The bagasse residue from the gasification process and macadamia residue from the pyrolysis process had a complex carbon matrix with high porosity. Bagasse residue achieved a much higher CO_2 adsorption capacity compared to that of macadamia residue, at 2.3 mmol/g in laboratory conditions, and 1.3 mmol/g in flue gas conditions. The gap in the CO_2 adsorption capacity between the two materials is mainly due to the difference in the micropore volume present in the samples. In addition, both the residues have the ability to quickly absorb and desorb CO_2 gas, bringing some advantages when applied on an industrial scale. Hence, the results of this study confirmed that the residues from thermochemical conversion processes have great potential to become cheap and environmentally friendly CO_2 adsorbents.

Credit authorship contribution statement. Nguyen Hong Nam: Methodology, Formal analysis, Funding acquisition, Supervision, Dao Thanh Duong: Investigation, Trinh Bich Ngoc: Investigation, Le Phuong Thu: Formal analysis, Dinh Thi Mai Thanh: Methodology, Nguyen Van Dong: Investigation, Nguyen Thu Phuong: Methodology, Formal analysis.

Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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