

BIOMASS GASIFICATION CHAR AS A LOW-COST ADSORBENT FOR CO₂ CAPTURE

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ABSTRACT: This study wants to investigate a possible valorization route for char from biomass gasification taking advantage of its similarities to biomass-derived activated carbon in terms of properties and mechanisms of formation and assess its suitability for CO₂ adsorption. Char was collected from a commercial gasifier operating in South Tyrol, Italy, and characterized through elemental analysis, X-ray diffraction technique, physisorption analysis and scanning electron microscopy. The CO₂ adsorption/desorption capacity of the char was investigated through thermogravimetric analysis at different adsorption temperatures (T_{ads} = 50 - 100 °C) and CO₂ concentrations (CO₂:N₂ = 1:1 - 0.8:0.2). CO₂ adsorption capacity of char decreases with temperature and increases with CO₂:N₂ ratio. The highest CO₂ uptake of 3.4 % resulted for T_{ads} = 50 °C and CO₂:N₂ = 1:1.

Keywords: biomass, gasification, char, adsorbent, carbon dioxide, CO₂ capture.

1 INTRODUCTION

During the Paris Climate Agreement at COP21 (2015), 191 countries have committed to reducing their greenhouse gas (GHG) emissions to limit global warming to well below 2°C above pre-industrial levels and the temperature increase to 1.5 °C above pre-industrial level [1]. In particular, CO₂ is the major anthropogenic contributor to GHG emissions. Therefore, in order to pursue these goals, it is urgent to develop technologies such as Carbon Capture and Storage (CCS) to reduce CO₂ emissions and mitigate the risks and impacts of climate change [2]. CO₂ capture is the first and most consuming stage of CCS accounting for the 70–80% of CCS total cost [2]. There are different methods to capture CO₂ i.e. chemical absorption (amine scrubbing), solid adsorption, cryogenic distillation and membrane separation process [3]. Amine-based solvent such as MEA (monoethanolamine) has been applied in industries and nowadays, is the most common method [4,5]. However, there are many disadvantages associated to it [4,5]. On the other hand, adsorption on highly porous materials such as zeolite, molecular sieves, polymers, silica and activated carbon (AC) is a very promising technique. It is easier to handle, good in terms of moisture removal and requires lower energy than MEA [5]. In order to decrease the cost of CO₂ capture by adsorption, it is essential to consider adsorbents with high capture capacity and selectivity at different temperatures, adequate adsorption-desorption kinetics, high stability after regeneration cycles, good reusability and adequate mechanical strength [6]. In this framework, AC proved to have a tremendous potential as CO₂ adsorbents [7]. ACs are amorphous carbonaceous materials characterized by high surface area, microporous structure, and high degree of surface reactivity [8]. AC is quite cheap, stable at high temperatures, resistant to radiation and alkaline and acidic solution [4]. Its CO₂ adsorption capacity at ambient pressure is high and the material can be regenerated at lower temperatures than zeolites [9]. This facilitate the desorption process and strengthens cyclic operations.

It is worth pointing out that ACs derived from biomass have strong similarities to char from biomass gasification, a solid carbon based material with a highly porous structure [10]. Along with tar, char is an undesirable product of the gasification process. It is usually treated as a waste that have to be disposed of, representing an actual loss for plant owners. Therefore, it

is crucial to valorize residual char to increase the overall efficiency of the gasification plants from an energetic and economic perspective. The peculiar properties of char, its variable and tailorable surface and its low cost, make it an interesting option for several applications e.g. dye adsorption, catalyst preparation, tar cracking, soil fertilization, etc. [11].

Particularly, given the great interest towards CCS, the urgency to reduce CO₂ emissions in the atmosphere and the similarities between AC and char in terms of properties and mechanisms of formation, this study wants to assess the applicability of char from biomass gasification as CO₂ adsorbent.

At first, char was collected from a commercial biomass gasifier operating in South Tyrol, Italy and characterized through different techniques. Subsequently, its adsorption capacity was evaluated at different temperatures and CO₂ concentrations.

Considering char from actual commercial gasifiers allows for a better understanding of the impacts of this promising application on an industrial scale. This innovative way to exploit char would be beneficial from both an environmental and economic point of view. In the literature, there are several examples reporting the successful utilization of biomass-derived ACs and pyrolytic char for CO₂ adsorption [12–14]. However, there are not studies considering chars derived from biomass gasification. While pyrolytic char and ACs are synthesized on purpose for specific adsorption applications and their properties are carefully tuned accordingly through controlled pyrolysis and activation processes, chars from gasification are by-products that are not developed to be adsorbents. Therefore, their properties have to be studied in detail in order to understand their hidden potential.

2 MATERIALS AND METHODS

2.1 Char collection

Char residues were collected from a small-scale biomass gasifier currently in operation in South Tyrol, Italy, with a nominal electrical output of 50 kW and thermal output of 80 kW. The biomass gasification plant is based on a dual stage technology operating at ambient pressure.

The dried material (wood chips) enters the pyrolysis reactor, a rotating feeding auger surrounded by pipelines containing the hot gas that exits from the gasifier

downstream of the process. The residence time is 20 min ca. and temperature ranges from 200 to 700 °C. Here, the material is uplifted to the following gasification reactor. The gasifying agent (air) is fed in the center of the oxidation zone where temperature is kept at 900 - 950 °C. The producer gas exits from the top of the gasifier and by-products and impurities are removed downwards by gravity.

2.2 Char characterization

The elemental composition (C, H, N, S) and the ash content of the char were determined by using an elemental analyzer (Vario MACRO cube, Elementar) and according to UNI EN 14775:2010 [15], respectively.

Structural features of char were investigated by X-ray diffraction technique. X-ray powder diffraction (XRPD) patterns were collected at room temperature using a Philips X'Pert powder diffractometer (Bragg-Brentano parafocusing geometry) equipped with a focusing graphite monochromator on the diffracted beam and with a proportional counter with electronic pulse height discrimination. A divergence slit of 0.5°, a receiving slit of 0.2 mm, an antiscatter slit of 0.5° and Ni-filtered CuK α radiation (30 mA, 40 kV, generating CuK α 1,2 radiations at $\lambda_1 = 0.154059$ nm and $\lambda_2 = 0.154442$ nm) were used. A nickel-filtered Cu K α 1 radiation ($\lambda = 0.15406$ nm) and a step-by-step technique (step of 0.05° for 20 s) with collection times of 10 s/step were employed.

Surface area, pore volume and pore size of char were measured using a 3Flex Surface Characterization Analyser (Micromeritics Co.) operating with N₂ at 77 K. Before analysis, samples were vacuum degassed at 350°C for 3 h. The specific area was determined by the Brunauer-Emmett-Teller (BET) method while the pore size distribution was obtained by Barret-Joyner-Halenda (BJH) desorption analysis.

Char particle structure and surface topography were investigated by Scanning Electron Microscopy using a Phenom ProX, Phenom World.

2.3 CO₂ adsorption tests

Fossil-fueled based thermal power plants are the major contributors to the anthropogenic CO₂ released in the atmosphere (37 %) and thus, they have been proposed as important locations for CO₂ capture [16]. Among all the approaches for CCS (mainly pre/post-combustion capture and oxyfuel combustion systems) post-combustion capture is usually the easiest to implement since it does not require substantial adjustment to existing technologies [3].

However, the primary challenges that hinder CO₂ capture are the large volumetric flow rates of flue gas at essentially atmospheric pressure with large amounts of CO₂ at low partial pressures and the temperature range of ~ 100 - 150 °C [17].

Indeed, in combustion gases, CO₂ represents ordinarily between 5 % and 20 % of the volume [18]. Also, 5 – 9 % O₂ and a small amount of components such as H₂O, SO₂, NO_x and particulate matter is present and N₂ is the diluent. Due to the low content of other gases, dry flue gas can be treated as a binary mixture of CO₂ and N₂.

To assess the adsorption behavior of char under conditions that are more representative of post-combustion processes, experiments were carried out with CO₂ concentration of 50 % and 20 % and at adsorption temperature (T_{ads}) of 50 and 100 °C. The utilization of

100 % CO₂ would lead to high adsorption uptakes of little significance for the post-combustion capture [18].

The CO₂ capture capacity of char at atmospheric pressure was evaluated in a Jupiter STA449-F3 (Netzsch) thermo-gravimetric analyzer following the procedure reported by Rashidi et al. [18]. Fig.1 shows the test program. About 10 mg of char was loaded into an alumina sample pan. At first, the sample was dried at 120 °C in pure N₂ (40 ml/min) for 1h to purge the volatile components out. Then, the temperature was cooled to the desired adsorption temperature ($T_{ads} = 50 - 100$ °C) at a cooling rate of 10 °C/min and a CO₂:N₂ gas mixture (total flow 40 ml/min) was fed into the analyzer for 2h. In order to study the effect of the CO₂ concentration in the fed gas, experiments were carried out using CO₂:N₂ of 1:1 and 0.2:0.8. After 2 h, the gas flow was switched again to pure N₂ and temperature was increased to 120 °C at a heating rate of 10 °C/min to investigate the desorption process.

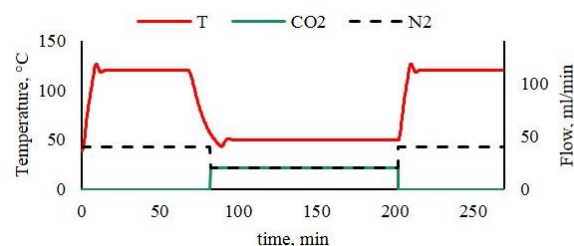


Figure 1: CO₂ adsorption test program.

The equilibrium sorption capacity was calculated from the weight change of the sample during the test and the mass uptake was expressed in weight percentage.

$$\text{Mass uptake \%} = \frac{(W_{eq} - W_0) \cdot 100}{W_0}$$

3 RESULTS AND DISCUSSION

3.1 Char properties

3.1.1 Elemental analysis

According to the elemental analysis results (see Tab. I), the char investigated has a low carbon and high ash content in comparison to other chars from biomass gasification [19–27].

Table I: Elemental analysis results on dry basis.

C	H	N	S	Ash
wt %	wt %	wt %	wt %	wt %
dry	dry	dry	dry	dry
78.97	0.68	0.20	0.31	22.20

This could be disadvantageous since high carbon content favor CO₂ adsorption enhancing the London dispersion forces among the CO₂ molecules and the carbonaceous material [5].

Ash is the inorganic part of biomass left as solid residue after the thermal conversion of the fuel. Ash is primarily made of compounds of silica, aluminum, iron, and calcium but also small amounts of magnesium, titanium, sodium, and potassium may be present [28].

Since the structure of these compounds is crystalline, a significant presence of crystalline phases is expected in the XRD pattern.

3.1.2 X-ray diffraction

Fig. 2 illustrates the XRD pattern obtained for the char sample. In general, two phases can be distinguished: an amorphous phase related to the carbon structure and a crystalline phase related to the presence of other compounds (i.e. calcite, quartz and lime). As stated above, the crystalline phase is correlated to the amount of ashes present in the sample.

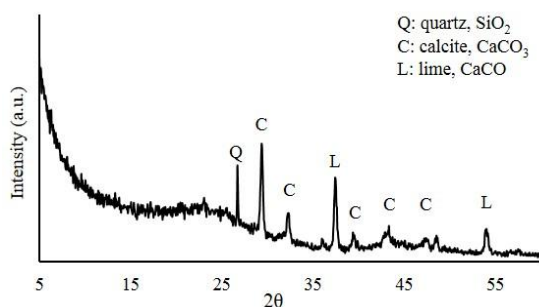


Figure 2: XRD pattern.

3.1.3 Physisorption analysis

Tab. II reports data from the surface characterization of the char.

The sample exhibits a large surface area compared to what reported in the literature, where S_{BET} values for char from biomass gasification ranging from 20 to 1000 m^2/g are found [10]. This is an optimal feature when assessing char suitability as CO_2 adsorbent. Indeed, the surface area is strictly correlated to the space available in the material to accommodate the adsorbate and is considered one of the most important parameters for characterizing the adsorption behavior of a material[29].

Pore volume and pore diameter resemble the ones reported in the literature [19–27].

It should be pointed out that pore diameter larger than 1 nm (as in this case where pore diameter is 3.88 nm) could cause the co-adsorption of N_2 with CO_2 on the material. In order to make CO_2 molecules ($d = 0.209$ nm) to be adsorbed and block N_2 molecules ($d = 0.364$ nm), pore size should be limit to 1 nm [18].

Fig. 3 shows the adsorption/desorption isotherm that gives a qualitative assessment of the porous structure of the sample. The trend matches the one reported in the literature for carbonaceous materials. According to the BDDT (Brunnauer-Deming-Deming-Teller) classification the isotherms display a type IV behavior typical of mesoporous structures where capillary condensation occurs. For relative pressure higher than 0.45, a type IV hysteresis loop, associated to slit-pores, is shown.

Table II: Physisorption analysis results

S_{BET} $m^2 g^{-1}$	Pore volume $cm^3 g^{-1}$	Pore diameter nm
603	0.30	3.88

3.1.4 SEM images

The SEM images of the char are shown in Fig. 4.

The material shows a very heterogeneous structure where the woody part is well recognizable, and a relevant porosity.

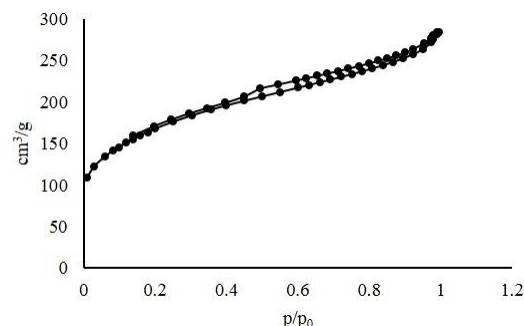


Figure 3: Adsorption isotherm (N_2 at 77 K).

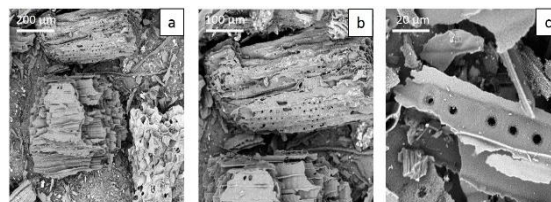


Figure 4: SEM images. a) 200 μm , b) 100 μm , c) 20 μm .

3.2 CO_2 adsorption

Comparing CO_2 adsorption capacity of char derived from biomass gasification and other activated carbons, CO_2 uptake resulted from this study complies with values reported in the literature (see Tab. III).

Fig. 5 shows the profile of CO_2 adsorption on char for $T_{ads} = 50$ °C and $CO_2:N_2 = 1:1$.

Char exhibits high adsorption and desorption rates implying that the material is easy to regenerate, as an optimal adsorbent should be. The adsorption profile quickly reaches the equilibrium as the temperature is stabilized and thus, the adsorbate loading could be controlled by the sorbent temperature.

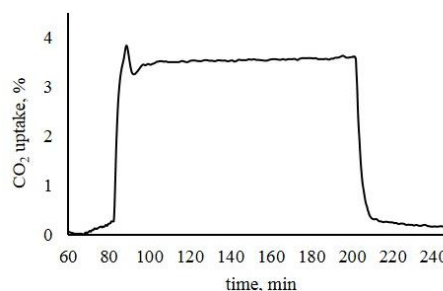


Figure 5: CO_2 adsorption on char for $T_{ads} = 50$ °C and $CO_2:N_2 = 1:1$.

CO_2 uptake on char has been evaluated at different temperatures and $CO_2:N_2$ ratios. Fig. 6 summarizes the results.

For fixed T_{ads} , higher $CO_2:N_2$ ratios are associated to lower CO_2 adsorption capacity because of the lower partial pressure of CO_2 [30].

The CO_2 uptake for both concentrations decreases with temperature (from 3.54 % to 1.84 % and from 1.86 % to 0.74 %).

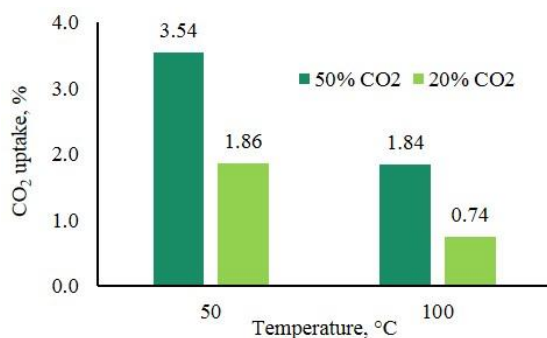
Table III: CO₂ uptake for different carbonaceous materials under different conditions.

Reference	T °C	CO ₂ conc %	CO ₂ uptake %
Rashidi et al. [18]	25	20	2.7-3.1
	50	20	1.5-1.9
Fiuza et al. [30]	40	50	2.3-6.3
Plaza et al. [31]	25	100	5.8-10.7
	100	100	1.5-3.2
Plaza et al. [32]	50	100	7.3
	50	10	2.4
Zaho et al. [33]	50	100	2.5-12.0
	50	15	1.0-4.0
This study	50	50	3.54
	50	20	1.86
	100	50	1.84
	100	20	0.74

This is due to the physical adsorption of CO₂ molecules on the adsorbent. Physisorption is an exothermic process that is favored at low temperature. Indeed, surface adsorption energy and molecule diffusion increase with temperature resulting in the instability of the adsorbed gas that is consequently desorbed [18].

High adsorption capacity at relative high temperature is desirable, as the cooling of flue gas exiting the plant can be reduced with consequent energetic and economic savings.

According to ref. [33], T = 40 – 50 °C may be a suitable temperature for sorbent from a practical point of view. Indeed, although the CO₂ uptake increased at lower temperature, at lower temperature adsorption requires more energy or time.

**Figure 6:** CO₂ uptake (%) at different T_{ads} and CO₂ concentrations.

4 CONCLUSIONS

Char residues collected from a commercial biomass gasifier operating in South Tyrol, Italy, showed many similarities to AC not only in terms of mechanisms of formation, but also in terms of carbon content and porosity. Char CO₂ adsorption capacity was tested in a thermogravimetric analyzer under different operating conditions. The uptake decreased with the adsorption temperature, due to physisorption mechanisms involved and increased with the CO₂:N₂ ratio, due to the lower partial pressure of CO₂ at higher concentration. An uptake of 3.54 % was obtained at T_{ads} = 50 °C and

CO₂:N₂ = 1:1. This value is in line with data reported in the literature.

Given the promising studies of CO₂ adsorption on AC and other carbonaceous materials found in the literature and the preliminary results of this study, char from biomass gasification plants has the potential to be valorized as a low-cost adsorbent for CO₂.

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