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Gasification char as a potential substitute of activated carbon in adsorption applications

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Abstract

This study points out the similarities between char from biomass gasification and activated carbon and reviews its successful applications in the field of adsorption. Surface area (S_{BET}) is considered as the standard parameter. Since only few data on biomass gasification char are available in the literature, in this work char residues from different commercial gasification plants were collected and characterized, reporting their S_{BET} values for comparison. The highest values for S_{BET} are associated to dual-stage gasification technologies and are highly affected by the operating temperature.

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Keywords: gasification; biomass; char; activated carbon; adsorption; surface area

1 Introduction

Gasification is a thermochemical process in which carbonaceous substances, like biomass, are converted into gas in the presence of a gasifying agent, typically air, steam, nitrogen, carbon dioxide, oxygen or a combination of these [1]. It takes place at temperatures between 500 and 1400 °C and entails several chemical reactions. The main products are syngas, tar and char and their amount and properties strictly depend on the initial composition of the feedstock. The desirable product is syngas, a mixture of gases such as CO, H_2, CH_4 and lighter hydrocarbons, that can be used in combined heat and power (CHP) engines for the cogeneration of heat and electricity or for production of fuels (e.g. F-T diesel, methanol, hydrogen, etc.). On the other hand, tar, a black and highly viscous liquid residue similar to a bituminous oil, and char, a solid carbon based material with a highly porous structure, are the undesirable byproducts of the process.

A critical aspect for the management of the existing gasification plants is the disposal of char, which, presently, has to be treated as a waste - representing thus an actual loss for the plant owner. The urgency to find alternative and innovative applications for char residues from an industrial point of view, has lead the

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scientific community to explore different viable pathways for their valorization (e.g. dye adsorption, catalyst preparation, tar cracking, soil fertilization) [2]. In particular, this study focuses on the application of char from biomass gasification as adsorbent and the assessment of its feasibility.

First, the similarities among char and activated carbons (ACs) are pointed out. Char is a low-cost product with unique, variable and tailorable surface properties (surface functional groups, porosity and surface area). ACs are highly porous materials and they have been widely and successfully applied in this field for many decades [3]. Cheaper precursors for ACs like biomass gasification char, could decrease the cost of ACs-based adsorbents and expand their utilization especially because projections show that the entire world demand for ACs will increase to 2.1 million metric tons in 2018 [4]. Subsequently, data on char and ACs surface areas are reported for comparison. Since characterizations of char from actual plants are very scarce in the literature, chars from five different gasifiers operating in South Tyrol, Italy, were collected and their surface areas were measured. Finally, successful examples of biomass gasification char used as ACs in adsorption applications are presented.

2 ACs production from biomass and their adsorption applications

ACs are amorphous carbonaceous materials characterized by high surface area, microporous structure, and high degree of surface reactivity. ACs contain 85-95% carbon but also hydrogen, nitrogen, sulfur and oxygen. Their surface area ranges from 500 to 2000 m^2/g, pore volume from 0.20 to 0.60 cm^3/g [5]. As far as this study is concerned, ACs obtained from biomass are considered. Nowadays, 50% of the ACs production involves lignocellulosic biomass as precursor (fruit shells, fruit stones, agricultural residues, wood, etc.) because of their low contents of inorganic materials and high volatile content, respectively associated to a low ash content and a high porosity [5]. During ACs production, raw materials undergo a first carbonization process. Water, methanol, carbon dioxide leave the material. The feedstock decomposes, lowers its density and increases its porosity. Since the porosity network obtained is not sufficiently developed, an activation step is needed to widen the pores and modify their surfaces. Activation can be thermal (or physical) and chemical. Thermal activation is obtained gasifying the precursor with CO_2 or H_2O, usually at 800-900°C, while chemical activation is obtained through the co-carbonization with metal oxide, alkaline metal and acid. $ZnCl_2$, H_3PO_4, KOH are the mostly used but also activations involving NaOH, $CaCl_2$, H_2SO_4, K_2CO_3, $Cu(NO_3)_2$ and NH_3 are reported in the literature [5,6].

ACs properties make them perfect for adsorption. Indeed, according to the specific application, a good adsorbent has a large surface area (200-2000 m^2/g), a micro- and meso-pore distribution compatible with the molecular dimensions of the adsorbates and a surface chemistry (e.g. presence of acid surface oxides) that does not inhibit the adsorption mechanism. Adsorption of dyes, pharmaceutical compounds, heavy metals, herbicides, air pollutants, nitrates and phosphates have been successfully demonstrated [3,7].

3 Char as activated carbon

3.1 Mechanisms of formation of ACs and char

The high content of carbon (85-90%) and high porosity of char (40-50%) are very similar to the ones of AC [1]. This paves the way to different possible applications of char as AC.

In order to compare gasification char and AC, it is fundamental to look at the analogies in the mechanisms of formation. For this purpose, only ACs from physical activation are considered.

As stated before, physical activated ACs are first carbonized under a pyrolysis process at temperature ranging from 400 to 600 °C for 1-2 hours [5]. Then, during a second step, the product is gasified usually through CO_2 and H_2O to further develop its porosity releasing tar and other decomposed products from the blocked pores. O_2 is not used since the carbon-oxygen reaction is highly exothermal and very difficult to

be controlled. The activation process can be described qualitatively through R.1 and R.2 where C atoms leave the bulk material as carbon monoxide, therefore increasing the system porosity.

$$C + CO_2 = 2CO \quad (R.1)$$

$$C + H_2O = CO + H_2 \quad (R.2)$$

A typical gasification process involves almost the same steps: drying, pyrolysis, char gasification and char combustion [1]. In the drying zone, feedstock moisture is reduced. During pyrolysis, in absence of oxygen, larger hydrocarbons molecules are broken down into smaller gas molecules, condensable and un-condensable vapors are released, and pyrolytic char and tar are formed. In the gasification zone, several reactions including R.1 and R.2, occur according to the gasifying agent used. In this case an additional step is required in which char is combusted with oxygen to provide the necessary heat for the self-sustainment of the process. As mentioned before, in ACs production, carbon-oxygen reaction is avoided in order to have a better control on the development of the porosity network.

Despite the similar mechanisms involved in the two processes, ACs for adsorption applications are synthetized on purpose to adsorb a specific adsorbate and their properties are carefully tuned through controlled carbonization and activation processes. On the other hand, chars from gasification are not developed to be adsorbents. Their properties have to be critically evaluated before choosing the most suitable adsorbate for their utilization.

3.2 Char from biomass gasification and its surface area

The properties affecting adsorption are the surface area and surface chemistry of the adsorbent. The former gives information about the space available for the adsorbate, the latter about the possible interactions between adsorbent and adsorbate. In order to assess the feasibility of the utilization of gasification char as adsorbent, both these properties should be analyzed. However, data on char residues from biomass gasification are very rare in the literature [9-16]. Only a few studies report gasification char characteristics, such as elemental and proximate analysis results, calorific value, SEM images and BET surface area (S_{BET}). In order to compare and investigate possible adsorption applications of gasification char, S_{BET} has been chosen as the standard parameter. Table 1 summarizes data on S_{BET} of biomass gasification chars. For comparison, a few examples of S_{BET} values of some ACs successfully used in adsorption applications are reported (S_{BET} values up to 1700 m^2/g [6]).

4 Surface area of chars from industrial biomass gasification plants

Due to the scarcity of data on S_{BET} of biomass gasification chars [9-16], BET analysis of chars collected from five different industrial gasification plants located in South Tyrol, Italy, was carried out by using a 3Flex Surface Characterization Analyser (Micromeritics Co., USA) operating with N_2 at 77 K [2]. Details of the five technologies (A, B, C, D, E) along with the S_{BET} results, are reported in Table 2.

Comparing Table 1 and Table 2, S_{BET} associated to char from dual-stage gasifiers are among the largest. Unlike one-stage gasifiers in which all the phases of gasification occur in the same vessel, dual-stage ones are made up of two main sections where feedstock undergoes first pyrolysis and then gasification [1]. This process is more similar to ACs production and allows for a better control of the porosity development. It reduces the production of tars and thus their probability to block and negatively affect the pore development.

Moreover, gasification temperature affects the final S_{BET} of chars. At high temperatures, a high amount of compounds volatilizes and thus porosity increases. However, too high temperatures may cause the break-down of pore walls and the consequent sintering of the material with consequent porosity reduction. The

Table 1. Data on S_{BET} values of char from biomass gasification available in the literature

Feedstock	Technology	Gasifying agent	T (°C)	S_{BET} (m^2/g)	Ref.
poplar	fluidized bed	90%H_2O/10%N_2	750	621	[8]
		10%CO_2/90%N_2	750	435	
			920	687	
dealcoholized marc of grape	entrained flow	air	1200	60	[9]
		steam	1200	35	
coal 60%/pine 40%	fluidized bed	steam/air (ER=0.2)	850	127	[10]
soft wood chips	bubbling fluidized bed	steam	850	489	[11]
soft wood pellets				1581	
switchgrass	fluidized bed	air (ER=0.28)	700-800	20.8	[12]
sorghum		air (ER=0.28)		5.6	
red cedar		air (ER=0.25)		60.8	
wheat straw	two stage gasifier	steam	1000-1200	75	[13]
pine wood chips				1027	
sieved pine wood chips				426	
switchgrass	bubbling fluidized bed	air/N_2	760	31.4	[14]
corn stover			730	23.9	
pine wood	fluidized bed	steam	800	603	[15]
		steam/air	800-850	411-147	
AC - Coconut shell				1700	[6]
AC - Apricot stones				359.40	
AC - Macadamia nut-shell				844	

Table 2. S_{BET} values of char collected from different biomass gasification plants in South Tyrol, Italy.

	Feedstock	Technology	Gasifying agent	Nominal power	T (°C)	S_{BET} (m^2/g)
A	wood chips	downdraft	air	45 kWel 120 kWth	~650	352.41
B	pellets	rising co-current	air	180-190 kWel 220-240 kWth	~700	127.67
C	wood chips	downdraft	air	100-150 kWel 200-250 kWth	~650	77.90
D	wood chips	downdraft	air	300 kWel 600 kWth	~800	281.23
E	wood chips	dual stage gasifier	air	50 kWel 80 kWth	~900	586.72

external surface area is the most affected by this phenomenon. Wide external pores are needed to let the adsorbate penetrate the material. Once they are partially occluded, they lose their functionality blocking the access to micro-pores still present inside the material and thus, limiting the adsorption capacity.

5 Gasification char in adsorption applications

This section reviews and analyzes the examples found in the literature in which gasification chars are valorized in adsorption applications. Table 3 summarizes gasification and activation technologies used in these studies and reports the relative S_{BET} values.

Kilpimaa et al. used activated char (char-AC) for removing nitrate and phosphate from aqueous solutions causing eutrophication and deterioration of water bodies. Char from a downdraft gasifier was activated both physically and chemically. Physical activation by CO_2 at high temperature was the most effective process. Although phosphates were better removed than nitrate, the overall performance of char-AC was

Table 3. S_{BET} values of biomass gasification char used as AC for adsorption applications

Application	Feedstock	Gasification		Activation			Ref.
		conditions *	S_{BET} (m^2/g)	agent	T (°C)	S_{BET} (m^2/g)	
Nitrate and phosphate removal	spruce, pine	downdraft gasifier, air, 1000 °C	52	CO_2	600 -800	152 - 590	[16,17]
				CO	600 - 800	126 - 135	
				N_2	600 - 800	145 - 160	
Fe(II), Cu(II) , Ni(II) ions removal				$ZnCl_2$	-	285	
				HCl	-	194	
				H_2SO_4	-	157	
				KOH	-	117	
				HNO_3	-	259	
Acetaminophen and caffeine adsorption	pine	fluidized bed, air, 850 °C	101	K_2CO_3	700 - 800	570 - 1509	[18]
Rhodamine B removal	mesquite wood chips	downdraft, air, -	172	CO_2	700 - 800	485 - 737	[4]
				Steam	700 - 800 - 900	538 - 737 - 776	
				N_2	700 - 800 - 900	178 - 280 - 287	

* technology, gasification agent, process temperature

satisfactory. The maximum monolayer adsorption capability (q_m) for phosphate and nitrate was 30.211-11.198 mg/g for char-AC and 8.6957-14.599 mg/g for commercial AC. The same char-AC were used by Runtti et al. as sorbent for Fe(II), Cu(II) and Ni(II) ions and were activated by $ZnCl_2$. q_m was 2-5 times greater than commercial AC. Indeed, for Fe, Cu and Ni, q_m was 20.5, 23.1 and 18.2 mg/g for char-AC and 13.9, 5.1 and 2.9 mg/g for commercial AC. Galhetas et al. activated char from a fluidized bed gasifier with K_2CO_3 for adsorption of acetaminophen and caffeine. Also in this case, a high activation temperature is associated to a large S_{BET}. The authors stated that pre-treatments can be avoided, reducing the energetic and economic cost. Char-AC are reported to be very effective and their removal efficiency proved to be superior to the one of commercial AC under the specific experimental conditions. q_m for acetaminophen and caffeine was 434.8 and 500.0 mg/g for char-AC and 169.5 and 303.0 mg/g for commercial AC. Maneerung et al. applied char-AC from a downdraft gasifier in order to absorb Rhodamine B, a cationic dye. Steam as activating agent and high temperatures promote pores development in the char matrix. q_m of char-AC was189.83 mg/g, value higher than values reported in the literature for dye adsorption on ACs prepared from different materials (23.5-180.7 mg/g).

6 Conclusions

According to preliminary practical studies and S_{BET} values, there is potential for biomass gasification char to be used as activated carbon in adsorption applications, although the literature on this topic is still scarce. By char recycling, plant owners will have the opportunity to manage it as a valuable product with tremendous synergies with industrial processes and applications.

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Biography of the presenting author

Francesco Patuzzi received his PhD in 2014 and is presently assistant professor at the Faculty of Science and Technology at the Free University of Bozen-Bolzano (Italy). His research activities are mainly related to the study of thermochemical conversion of ligno-cellulosic biomasses, with a particular focus on the process by-products valorization.