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Pore structure development during steam gasification of woody char residues at different temperatures

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ABSTRACT
The present study aims at investigating the development of porous structure during steam gasification of woody char and its effect on macroscopic reactivity. The experiments were conducted in a temperature range of 600–800 °C using biochar, derived from entrained flow gasification of biomass. The results show that the gasification temperature has minor effect on porous structure development. The total surface area of char as well as the specific total pore volume increase significantly until a certain conversion at all temperatures.

Keywords: Steam gasification; Char residues; Characterization, Pore structure

NONMENCLATURE

Abbreviations	
Total BET surface area S_{BET} (m^2/g)	Total pore volume V_{total} (STP cm^3/g)
Micropore surface area S_{micro} (m^2/g)	Micropore volume V_{micro} (STP cm^3/g)
Treated charA Tchar A	Treated charB Tchar B

1. INTRODUCTION

With the increasing energy demand and the environmental impact from use of fossil fuel, biomass waste, such as forestry residue and agricultural waste, become an attractive resource for energy recovery. Gasification is an effective way to convert biomass into valuable gaseous products [1]. Char conversion is the rate determining step in the efficient conversion of biomass into a producer gas. Additionally, the use of steam as gasification agent, enables the effective conversion of biochar to H_2 rich gas, which is considered as a clean, zero carbon source of energy and fuels [2]. Understanding the relation between char carbon structure and its reactivity with steam is of primary importance. At present, the relation between char carbon structure and its reactivity with steam is largely based on coal derived chars. Chars derived from biomass have different structure, as well as ash content and composition compared to coal chars [3]. This affects the char gasification rates, for example, Keown et al. [4] verified that drastic changes in char structure occurred as soon as the cane pyrolysis char was exposed to gasifying agents. Therefore, it is critical to study the evolution of the char structure during steam gasification in order to have a better understanding of the changes in char reactivity. Nevertheless, there is little information on char structure during char steam gasification at different temperatures [3–5] especially for the wood-derived char. The present study aims at investigating the development of the porous structure during the steam gasification of char residues, produced from gasification of standard pellets (mixture of spruce and pine). The study considers the evolution of biochar surface area, pore volume as well as different pore sizes while synergies with the presence of ash on char reactivity are also considered and discussed.

2. METHODS

2.1 Material and methods

The material used in the present work was char residues (char A and char B), derived from the entrained flow gasification of standard wood pellets. Char A and char B was collected from the ash container and sedimentation tank, respectively. Fig.1 showed the two sample collecting points. Prior to use, the char residues were

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dried in the oven and then heated to 950 °C in N_2 for 2 hrs to remove any residual volatile matter. The obtained chars denoted as treated primary char and treated secondary char (TcharA and TcharB) were crushed and ground to a particle size of 85 μm. The results of ultimate and proximate analyses as well as minerals are reported in Table 1.

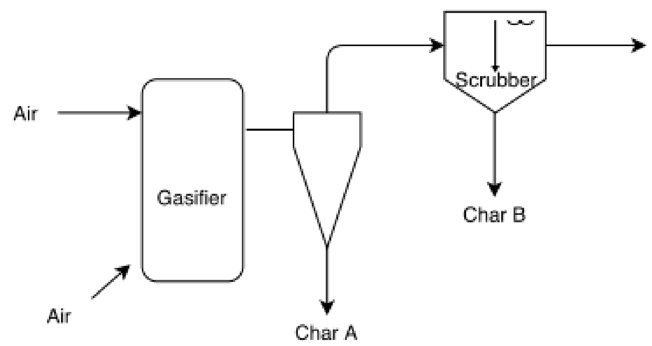


Fig. 1 Simplified layout of gasification process

Table 1 Ultimate and proximate analyses of materials used

	TcharA	TcharB
Proximate analysis (wt. %)		
Moisture	0.08	0.8
Volatile Matter (wt. %, db)	1.08	5.53
Ash(wt. %, db)	6.38	5.04
Fixed carbon(wt. %, db)	92.46	89.42
Ultimate analysis (wt. %, db)		
C	80.80	90.6
H	1.80	0.2
N	0.25	0.43
O [a]	9.35	4.27
Ash	7.80	4.5
Minerals,mg/kg		
Na	784	37
K	3770	83.1
Mg	2880	3300
Ca	17300	15300
Fe	1630	1860
Al	1740	592
Mn	2050	1980
P	945	982

[a] Calculated by difference.
db: dry basis

2.2 Experimental setup and procedures

Steam gasification experiments were carried out under isothermal conditions in a NETZCSH ST490 F3 thermogravimetric analyzer (TGA). In each gasification experiment, approximately 30 mg of char powder were loaded in ceramic crucible and heated at a rate of 10 °C /min in N_2 atmosphere (50 ml/min) to a temperature of 600-800 ℃, the sample was kept at the gasification temperature under N_2 conditions for 5 min to stabilize the stream. Thereafter, N_2 was switched to steam (1 g/h) to initiate the gasification. The char conversion (X) was calculated using the following equations:

$$X = \frac{m - m_t}{m - m_{ash}}$$

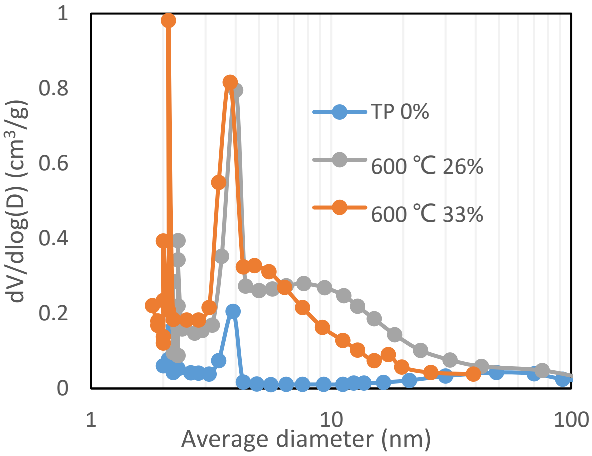
where m represents the initial mass of the char at the onset of gasification, m_t is the instantaneous mass of the char at time t and m_{ash} is the remaining mass of ash. The pore surface area and pore size distribution were analyzed by N_2 adsorption (Micromeritics ASAP 2010) based on the BET (Brunauer - Emmett - Teller) adsorption isotherm [6, 7].

2.3 Results and discussion

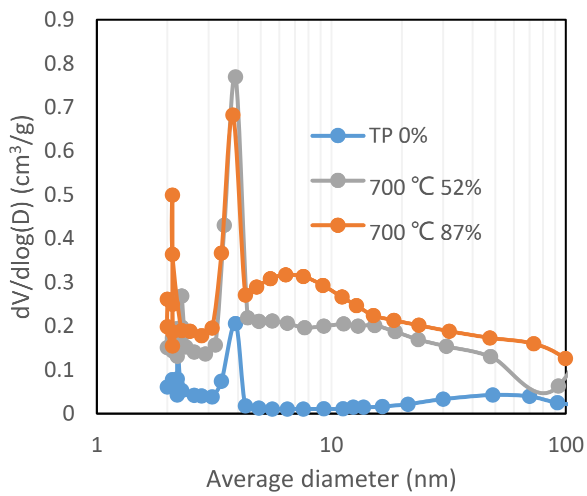
Fig. 1 shows the pore size distribution of TPchar at different conversions and temperatures. The mesopore size distributions are similar for 600 ℃ and 700 ℃. The micropore change significately with the conversion. As can be observed in Fig.1 and Table 2, the S_{total} and V_{total} increase with conversion for all temperatures, showing the formation of new pores as a result of steam carbon reaction. The micropore area exhibits an initial increase followed by a gradual decrease at increasing conversion. This indicates a faster generation of micropores pore volume at the first stages of conversion.

At 700 °C, as the char conversion increases from 0 % to 52 %, the S_{total} and S_{meso} significantly increases from 107.5 m^2/g and 51.8 m^2/g to 506.25 m^2/g and 187 m^2/g, respectively. At this stage, a large number of new pores are formed, resulting in a rapid increase of the number of mesopores. At higher conversions, the total specific surface area continuously increases contrary to the micropore area, which decreases. For micropore volume, it significantly increases from 0.19 cm^3/g to 0.50 cm^3/g with a char conversion. At this stage, a large number of micropores are formed, leading to a rapid increase of the micropore volume. The volume of micropores increases remarkably with the char conversion.

Fig. 2 shows the pore size distribution of TcharA. The mesopores pore size distributions are similar for TcharA at 700 and 800 °C.



(a)



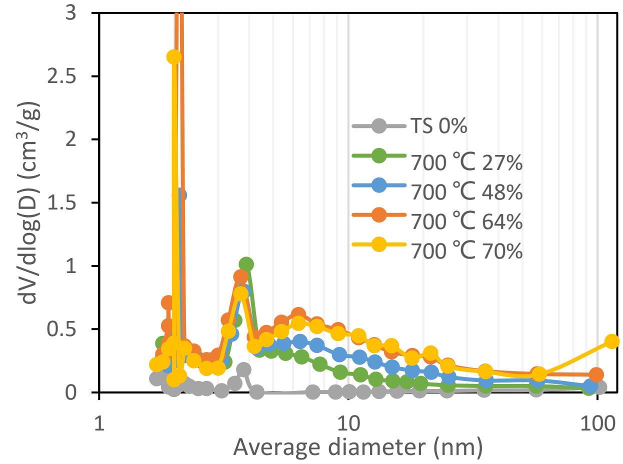
(b)

Fig. 1 Pore size distribution of TcharA at different conversions (a): 600 °C (b): 700 °C

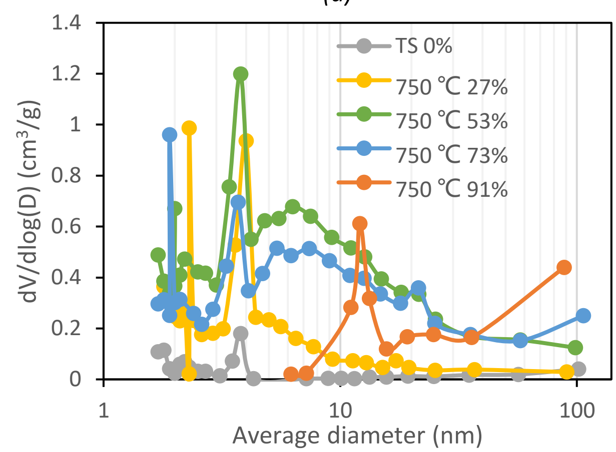
Table 2 Textural properties of the chars at different temperatures and conversions for TcharA

T (°C)	X (%)	S_{total} (m²/g)	S_{mico} (m²/g)	S_{micro}/S_{total} (%)	V_{total} (cm³/g)	V_{mico} (cm³/g)	V_{mico}/V_{total} (%)
600	0	107.50	55.70	51.81	0.09	0.024	12.85
	26	489.19	293.12	59.99	0.42	0.122	28.85
	33	524.55	289.59	55.20	0.77	0.122	15.85
700	0	107.50	55.70	51.81	0.09	0.024	12.85
	52	506.25	318.51	62.91	0.50	0.132	26.71
	87	551.11	307.05	55.71	0.57	0.131	22.82

As observed in Table 3, the surface area as well as the total pore volume increases with conversion at both temperatures, showing the formation of new pores as results of steam carbon reaction. Subsequently, the S_{total} as well as the V_{total}, start to decrease after a conversion of approximately 70%.



(a)



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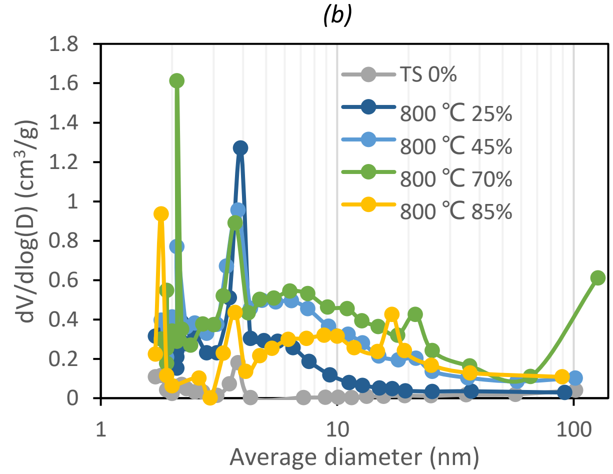

(c)

Fig. 2 Pore size distribution of TcharB at different conversions and (a): 700 °C (b): 750 °C (c): 800 °C

For all temperatures, when the char conversion increases from 0 % to 70 %, the ratio S_{micro}/S_{total} decreases from 67.8 % to around 58 %. From table 3, it shows that the S_{total} and S_{micro} increase, but the rate for S_{total} is higher than S_{micro}. So in the beginning, the mesopores are more important. When the conversion is higher than 70%, the S_{micro} /S_{total} ratio starts to increase, as similarly observed for V_{micro} /V_{total}. TcharA and TcharB samples displayed different surface area evolutions and V_{micro}/V_{total} ratio trends, possibly due to different ash components in the two char samples. Fig. 3 shows that the S_{micro} /S_{total} ratio increases to 45% when conversion reaches 70% with a subsequent decrease for all temperatures.

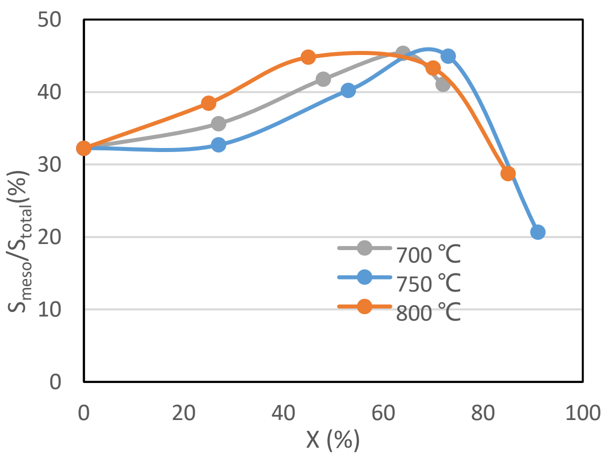

Fig. 3 S_{meso} /S_{total} ratio of TcharB at different conversions and temperatures

Table 3 Textural properties of the chars at different temperatures with different conversions for TS char

T (°C)	X (%)	S_{total} (m²/g)	Smicro (m²/g)	Smicro/Stotal (%)	Vtotal (cm³/g)	Vmicro (cm³/g)	Vmicro /Vtotal (%)
700	0	235.34	159.48	67.77	0.15	0.065	43.84
	27	763.82	491.57	64.36	0.52	0.202	38.77
	48	777.46	452.69	58.23	0.64	0.189	29.66
	64	1036.61	566.48	54.65	0.96	0.245	25.51
	72	1012.50	597.02	58.97	0.97	0.25	25.45
750	0	235.34	159.48	67.77	0.15	0.065	43.84
	27	680.27	457.89	67.31	0.43	0.289	43.88
	53	806.25	481.98	59.78	0.66	0.203	30.85
	73	888.52	489.14	55.05	0.89	0.187	23.06
	91	806.25	639.90	79.37	0.75	0.265	35.53
800	0	235.34	159.48	67.77	0.15	0.065	43.84
	25	725.63	446.54	61.54	0.48	0.184	38.34
	45	888.52	490.56	55.21	0.76	0.204	27.05
	70	967.50	548.35	56.68	1.01	0.23	22.68
	85	777.46	553.92	71.25	0.65	0.225	34.43

The pore structure development and its effect on reactivity at 750 °C is shown in fig. 4, from 0 to 70% conversion, the reactivity decrease as well as the S_{micro} /S_{total} ratio. When the S_{micro} /S_{total} starts to increase, the reactivity increases as well.

2.4 Conclusions

The evolution of char structural features and the effect of gasification temperature during steam gasification of chars, produced in an entrained flow gasifier, were

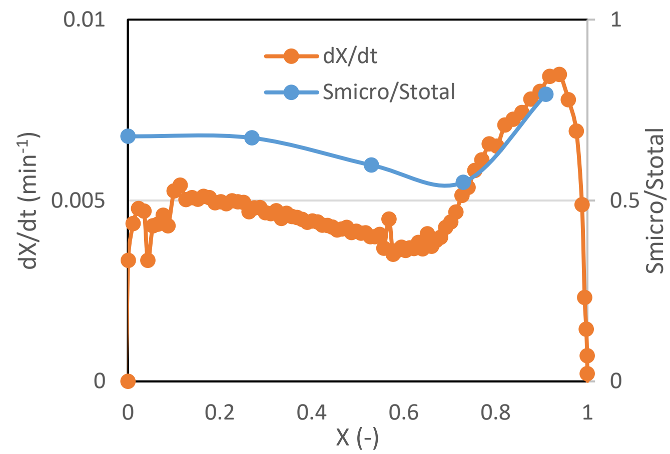

Fig. 4. Effect of microspores development and its effect of reactivity at 750℃

investigated. When the char conversion is minimal, significant changes in char structure occurred. The total surface area of char as well as the specific total pore volume increase substantially until a certain conversion at all temperatures with a subsequent decrease. Moreover, the temperature has a minor effect on TcharB pore size evolution. Furthermore, the micropore surface area has an important role in increased reactivity. TcharA and TcharB showed different surface area evolution at 700°C, this is could be attributed to different ash elements in two samples and will be further investigated.

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