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CO$_2$ Gasification of Charcoals in the Context of Metallurgical Application

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Abstract

The CO$_2$ gasification reactivity of Norwegian spruce charcoals from stem wood and its forest residue produced at different pressures was investigated in the present study. The gasification behavior was analyzed thermogravimetrically at different gasification temperatures of 800, 850 and 950°C, followed by a kinetic modelling applying the random pore model (RPM) and overlapped grain model (OGM). It is found that gasification temperature has a considerable influence on the reactivity of charcoals. Higher carbonization pressures reduce the gasification reactivity of the produced charcoals towards CO$_2$. The employed kinetic models represents well the experimental data. The initial porosity computed through the OGM is found to depend on the carbonization pressure. The activation energy is found in the range of 210 to 230 kJ/mol, in line with the values reported in the literature.

Keywords: Charcoals; Flash Carbonization; Pressures; Gasification Kinetics.

1. Introduction

The iron and steel production is accounting for approx. 70% of total greenhouse gas emission from primary metal production and is also the fourth biggest industry using fossil fuels [1]. About 2.2 ton of CO$_2$ is released for the production of one ton crude steel on average [2]. An ambitious target was established by steel producers to decrease both direct and indirect CO$_2$ emission by 50% or even more by 2050 [3]. Hence, for a long-term perspective, the replacement of fossil fuel-based reductants with carbon derived from biomass such as charcoal is necessary to reduce the greenhouse gas footprint from metal production, especially from iron and steel industry, but also from the expanding silicon production industry.

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However, it is still challenging to develop and manage woody biomass resources on a sustainable basis and advance economical charcoal production technologies with lower environmental impacts [1]. Indeed, there are several potential applications of charcoal in steelmaking processes including sintering solid fuel, coke making blend component and steelmaking recarburiser [3]. In addition to this, the use of charcoal as reductant also improves the metal quality and offers a possibility of higher productivities [4]. On the other hand, charcoal is also playing an important role in silicon industry in which the silicon losses might reach 20% of the mass of silicon charged to the furnace due to the low reactivity of reductants [5]. In fact, the reactivity of reductants is a primary factor to determine the silica reduction process efficiency. A CO_2 gasification reactivity test is often conducted to select the right reductants due to its simplicity [6].

The present work aims at performing a comparison on the kinetic modelling of CO_2 gasification of charcoals produced via flash carbonization at different pressures. To our best knowledge, no investigations related to this aspect are available from open literature. Additionally, a new approach is proposed to determine the initial porosity of charcoal samples.

2. Materials and Method

The charcoals used in the present study is prepared from Norwegian spruce stem wood and forest residues containing mainly branches and tops (GROT). After cutting into small pieces and drying at 105°C for 24 h, the raw samples was subjected to flash carbonization at about 500°C and different pressures of 7.9 and 21.7 bar [7]. A thermogravimetric analyzer (TGA) "Mettler Toledo TGA/SDTA 851^e" was also used to produce charcoal at atmospheric pressure (1 bar). The proximate analysis of produced charcoals was carried out in accordance with a standard method, ASTM D 1762-84, whereas the elemental analysis was performed by employing a Eurovector EA 3000 CHNS-O Elemental Analyzer. Characteristics of produced charcoals are given in Table 1.

Table 1 Proximate and ultimate analysis of charcoal samples (dry basis, wt%)

Samples	Charcoal production pressure, bar	Proximate analysis			Ultimate analysis				
		VM	Ash	FC	C	H	N	S	O
Spruce	7.9	18.1	1.7	80.2	77.35	3.68	0.29	<0.02	18.66
	21.7	18.8	1.1	80.1	76.36	3.5	0.47	<0.02	19.55
Spruce GROT	7.9	13.1	6.1	80.7	83.49	2.65	0.56	<0.02	13.28
	21.7	28.5	3.7	67.7	77.34	3.79	0.66	<0.02	18.19

VM: Volatile matter; FC: Fixed carbon

The gasification behaviour of charcoals towards CO_2 was investigated by using the above-mentioned TGA. Approximately 2 mg of samples was used for every experimental run. The sample was heated from room temperature to different gasification temperatures of 800, 850 and 950°C with a heating rate of 13°C/min under a nitrogen flow of 100 ml/min. After reaching the gasification temperature, the nitrogen flow was replaced by a CO_2 flow with the same flow rate. The charcoal gasification was maintained until a constant weight was reached. In the present study, two kinetic models, the random pore model (RPM) and overlapped grain model (OGM), were employed for kinetic modelling and simulation. The RPM takes into account the overlapping of pore surfaces and the change of surface area available for reaction along with the progress of the reaction [8]. The reaction rate under kinetic control is mathematically described by Eq. 1 [9]

$$\frac{d\alpha}{dt} = k\,(1-\alpha)\sqrt{[1 - \psi \ln(1-\alpha)]} \qquad (1)$$

The structural parameter (ψ) related to the pore structure and surface area of initial char samples can be estimated through a non-linear least square regression method that was developed by Everson et al. and the mathematical equation is expressed in Eq. 2 in which t_α stands for the instant time at conversion of α whereas $t_{0.9}$ is the time required for 90% charcoal conversion degree [10].

$$\frac{t_\alpha}{t_{0.9}} = \frac{\sqrt{1 - \psi\ln(1 - \alpha)} - 1}{\sqrt{1 - \psi\ln(1 - 0.9)} - 1} \tag{2}$$

The OGM was introduced in 1986 by Adschiri et al. [11] to widen the validity of the grain model. Note that the OGM was developed to describe the dynamic change of surface area, which first increases to a maximum and then decreases with the further evolution of gasification. Under kinetic control, the reaction rate of the OGM is described as in Eq. 3 [11].

$$\frac{d\alpha}{dt} = k[1 - (1 - \varepsilon_0^{-1})\alpha][1 + (ln\varepsilon_0)^{-1}\ln[1 - (1 - \varepsilon_0^{-1})\alpha]]^{\frac{2}{3}} \tag{3}$$

where k is the reaction rate constant and ε_0 and α represent the initial porosity and conversion degree, respectively. The authors propose the following equation (Eq. 4) for computing the initial porosity of charcoals involved in Eq. 3. Indeed, the development of this approach is based on the procedures developed by Everson et al. [10].

$$\frac{t_\alpha}{t_{0.9}} = \frac{\left(1 + \frac{1}{ln\varepsilon_0}\ln\left(1 - \left(1 - \frac{1}{\varepsilon_0}\right)\alpha\right)\right)^{\frac{1}{3}} - 1}{\left(1 + \frac{1}{ln\varepsilon_0}\ln\left(1 - \left(1 - \frac{1}{\varepsilon_0}\right)0.9\right)\right)^{\frac{1}{3}} - 1} \tag{4}$$

where t_α and $t_{0.9}$ are the instant time and the time at 90% conversion, respectively. The curve fit quality for the kinetic modelling is evaluated by Eq. 5 in which $(\alpha_i)_{exp}$ and $(\alpha_i)_{simulated}$ are the experiment and simulated conversion rate, and N is the number of experimental points.

$$Fit\ (\%) = \left(1 - \frac{\sqrt{\frac{\sum_{i=1}^{N}[(\alpha_i)_{exp} - (\alpha_i)_{simulated}]^2}{N}}}{[(\alpha)_{exp}]_{max}}\right) \cdot 100\% \tag{5}$$

The gasification reactivity is normally quantified by a reactivity index R which is defined as $R=0.5/\tau_{0.5}$ where $\tau_{0.5}$ is the time required to reach 50% charcoal conversion [12].

3. Results and Discussion

3.1 Effect of gasification temperature on gasification reactivity

The effect of charcoal gasification temperatures on its reactivity is illustrated in Figure 1. It can be seen clearly that the reactivity index, indicating the gasification reactivity of charcoal, increases significantly with increases in gasification temperature. For example, the gasification reactivity of birch charcoal produced at 1 bar is approximately 30 times faster when the gasification temperature increases from 800°C to 950°C. Indeed, several investigations found that temperature has strong impact on gasification reactivity [13, 14]. Noticeably, the difference in gasification reactivity of charcoal produced at 1 bar compared to those produced at 7.9 and 21.7 bar becomes considerable when the gasification

temperatures increase from 800°C to 950°C. More interestingly, increasing carbonization pressure reduces the gasification reactivity of charcoals except for the case of spruce GROT charcoal produced at 21.7, exhibiting higher reactivity than that of the sample produced at 7.9 bar. This might be because of increased graphitization level or uniformity of the carbon structure as well as reduced total surface area [15].
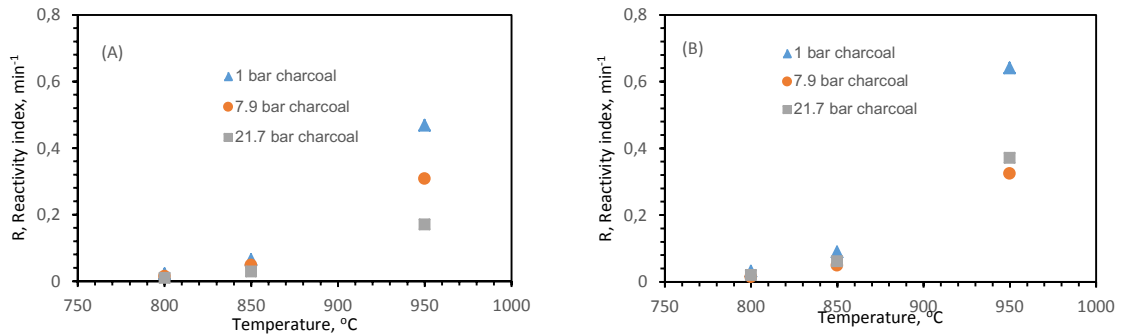

Figure 1. Effect of gasification temperature on charcoal reactivity; (A) spruce, (B) spruce GROT

3.2 Kinetic modelling

Figure 2 demonstrates an example for calculating the structural parameter and initial porosity of charcoals according to Eq. 2 and 4, respectively. The ψ and ε_o values for other samples listed in Table 2 were also determined by the same regression procedure. It appears that the ψ values of charcoals produced at 7.9 bar were the highest among the others; however, the ε_o exhibited an opposite trend. According to the definition of the RPM, the initial charcoal samples are porous and have negligible pore growth during the gasification reaction if the values of ψ is close to zero. In a contrary direction, a large value of ψ anticipates a pore growth with the evolution of the gasification reaction [9, 10]. These results are in line with other studies. Indeed, Somerville et al. investigated the effect of sample compression and pressure during pyrolysis of woody biomass on the characteristics of produced charcoals. It was found that the porosity decreased with increasing pyrolysis pressure up to about 7 bar, followed by an increasing trend up to 20 bar and it became independent from pyrolysis pressure at higher pressure [16].
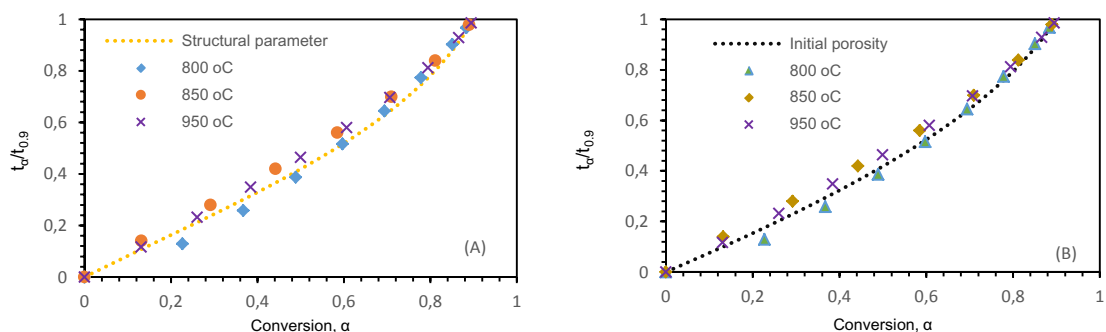

Figure 2. Computation of (A) structural parameter and (B) initial porosity of spruce charcoal produced at 1 bar

The kinetic modelling of CO_2 gasification at different temperature for spruce and spruce GROT charcoals produced at 1 bar is presented in Figure 3 whereas the extracted kinetic parameters together with fit quality at 850°C for all charcoal samples are shown in Table 2. It can be visually observed that the

two kinetic models represent well the experimental data. However, the OGM was better regarding fit quality. The extracted kinetic parameters from the two kinetic models were similar to each other and in good agreement with other studies [17, 18]. For instance, the activation energy of spruce charcoal produced at 7.9 bar was about 222 kJ/mol obtained from the RPM whereas it was about 224 kJ/mol for the OGM.
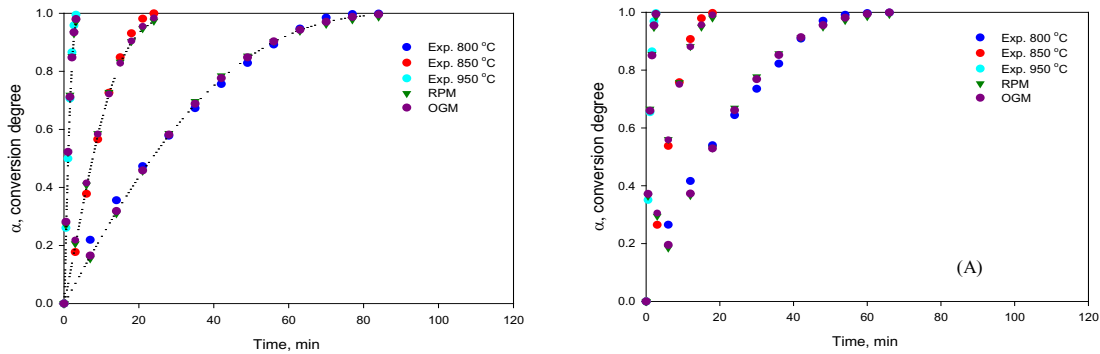

Figure 3. Kinetic simulation for (A) spruce and (B) spruce GROT charcoal gasification at 800, 850 and 950 °C (Charcoals were produced at 1 bar)

The plot of $ln(k)$ vs $1/T$ of spruce and spruce GROT charcoal produced at 1 bar is illustrated in Figure 4. A linear correlation between them indicates that the gasification reaction at temperatures of 800, 850 and 950°C was in the kinetic-controlled regime. As a matter of fact, when the gasification temperature increases to a high enough level, the gasification reaction turns to a diffusion-controlled regime. An investigation on CO_2 gasification of charcoals conducted by Yuan et al. revealed that pore diffusion acted as a rate-controlling factor at temperatures higher than 950°C [19].
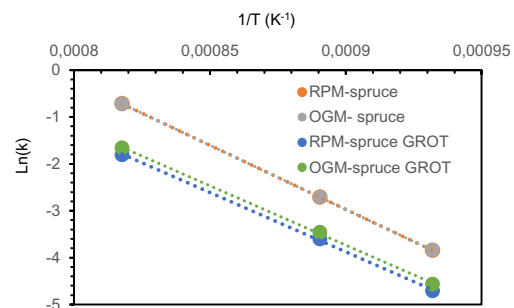

Figure 4. Arrhenius plot of gasification reaction rate of spruce and spruce GROT charcoals produced at 1 bar

Table 2 Extracted kinetic parameters from the RPM and OGM

Sample	Charcoal Production Pressure, bar	RPM				OGM			
		A (min⁻¹)	Ea (kJ/mol)	ψ	Fit (%)	A (min⁻¹)	Ea (kJ/mol)	ε_0	Fit (%)
spruce	1	2.59E+09	227.65	3.17	97.54	3.02E+09	227.91	0.64	97.41
	7.9	8.78E+08	222.21	5.37	98.62	1.06E+09	222.40	0.46	99.04
	21.7	1.63E+08	210.50	3.98	98.97	1.90E+08	210.56	0.56	99.27
spruce GROT	1	2.91E+09	225.54	2.97	97.80	3.35E+09	225.73	0.67	97.73
	7.9	2.08E+09	229.61	4.59	97.55	2.47E+09	229.76	0.50	98.01
	21.7	5.87E+08	215.15	3.79	98.58	6.97E+08	215.42	0.58	98.81

3. Conclusion

The results from the present study show that the CO_2 gasification reactivity is significantly influenced by gasification temperature. The gasification reactivity of charcoals produced at different pressures decreases with increasing carbonization pressure. The initial porosity is dependent on the carbonization pressure, and this value of charcoals prepared at atmospheric pressure is the highest. The kinetic modelling conducted by employing the RPM and OGM resulted in similar kinetic parameters regarding activation energy and pre-exponential coefficient. The activation energy is found in the range of 210 to 230 kJ/mol.

Acknowledgements

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