Influence of Inherent Alkali Content and Surface Area of Biomass Char on its CO_2 Gasification Reactivity

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A B S T R A C T

In this work, isothermal gasification reactivity of pistachio nut shell (PNS) char and oil palm shell (OPS) char was studied under CO_2 using Thermogravimetric analysis (TGA). The effects of temperature, inherent alkali content and surface area of each biomass char on promotion of CO_2 gasification reactivity were investigated. The achieved results revealed the profound catalytic effect of alkali, alkaline and transition metals including K, Na and Fe available in the ash of biomass on enhancing the gasification reactivity of the char at temperatures below 900 °C. However, at elevated temperatures the pore diffusion was dominant and controlled the gasification reactivity. It was found that at temperatures below 900 °C, PNS char demonstrated high gasification reactivity because of its high alkali index, while at any temperature above 900 °C, conversion of OPS char was faster due to its high porosity and larger surface area.

INTRODUCTION

In biomass gasification reaction, char gasification is known as the rate controlling step and affects the overall attainable carbon conversion [1, 2]. This knowledge has become the subject of extensive researches to investigate the intrinsic reaction rate of carbonaceous materials during gasification. The overall gasification reaction rate is closely associated with the mineral content of the char and its surface area which facilitates the diffusion of reactant gas into the char pores [1, 3].

A deep understanding of the structural features of char in terms of pore surface area, carbon crystalline structure and inherent alkali and alkaline earth metal (AAEM) content provides useful information for development of gasification systems. Tancredi et al. [4] studied the isothermal gasification reactivity of eucalyptus wood char under CO_2 using TGA. They found that the reactivity was very low at temperatures under 700 °C and was attributed to the enlargement of surface area, where CO_2 reaction led to the widening of pores and

provided accessible surface area. Increase in reactivity at high conversions was mostly attributed to the catalytic effects offered by potassium and sodium, whose proportion in the solid residue increased with burn-off. Similar observation and discussion regarding the development of surface area and catalytic activity of inherent inorganic matter with progress of CO_2 gasification of grapefruit skin char were also reported by Marquez-Montesions et al. [5]. In another study conducted by Dupont et al., [6] gasification reaction rate of 21 different woody biomass chars with various ash contents were examined. They found that the inorganic elements such as potassium played a noticeable catalytic effect and increased the reactivity up to a factor of 3.5 on char gasification, while silicium imposed an inhibitory role. In another work, Zhu et al. [7] studied the catalytic influence of metals available in the biomass on co-gasification reactivity of biomass char and coal and found that wheat straw/coal depicted higher reactivity than that of coal char. For chars from different sources, several physicochemical properties of char take part in CO_2 gasification reactivity [8]. The physicochemical

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properties of char depend deeply on the utilized carbonaceous feedstock [9].

Knowing this, the gasification reactivity of oil palm shell (OPS) char and pistachio nut shell (PNS) char was studied under CO_2 environment. The effect of inherent minerals as well as porous structure on the gasification reactivity of two biomass chars was considered and the results were discussed.

MATERIAL AND METHODS

Raw material

Oil palm shell (OPS) char and pistachio nut shell (PNS) were obtained from a palm oil mill, Penang, Malaysia and local market, Iran, respectively. The shells were washed several times with tap water and dried at 105 °C for 48 h in oven. The ultimate analysis of the shells were determined using an elemental analyzer (Perkin-Elmer 2400 Series II CHNS/O). Proximate analysis was performed to determine the fixed carbon, volatile mater, moisture and ash content of the shells using Thermogravimetric analyzer (TGA, SDTQ-600) [10]. The ash composition of the shells was determined by X-Ray Fluorescence (XRF) analysis (Rigaku RIX3000, Japan). The results of ultimate and proximate analyses as well as ash composition are summarized in Table 1.

Char preparation and characterization

In order to find the suitable pyrolysis temperature (900 °C) to prepare char, some preliminary pyrolysis experiments were carried out in TGA using 15 mg of shell sample. The sample was heated under a N_2 flow of 400 ml/min to 900 °C and kept at this temperature for 90 min. The so prepared chars were cooled to room temperature under N_2. Figure 1 shows the normalized weight loss profiles of OPS and PNS pyrolyzed at 900 °C as obtained from TGA analysis. Based on the degradation profiles of biomass samples, the weight loss of both samples was insignificant at the temperature of 900 °C. This temperature was high enough to ensure that most of the volatilematters were removed from the biomass samples and considered as the suitable temperature for carbonization and char preparation. As shown in Figure 1, thermal degradation of biomass samples initiates with the weight loss due to water evaporation, followed by the decomposition of cellulose and hemicelluloses in a narrow temperature
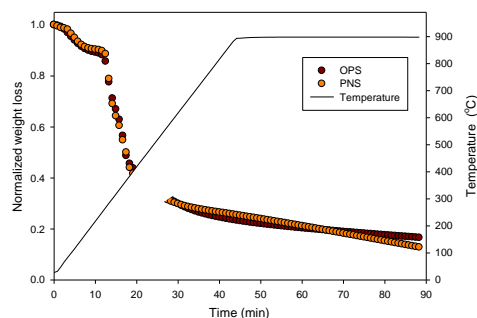

Figure 1. The weight loss profiles of OPS and PNS pyrolyzed at 900 °C in TGA

range of 200 to 400 °C and decomposition of lignin which continued to 900 °C. Based on preliminary tests performed in TGA, a carbonization rig was operated to obtain biomass char for gasification experiments. The char preparation set-up consisted of a vertical 4 cm diameter and 80 cm length stainless steel reactor surrounded by a tubular furnace. The pyrolysis experiments were carried out by loading 100 g of the raw shell in the reactor followed by heating under a N_2 flow of 400 ml/min. The temperature of the reactor was increased at a rate of 15 ºC/min until reached to 900 ºC and kept at this temperature for 90 min. The carbonized sample was cooled down to room temperature under the N_2 flow. Prepared chars were ground to a particle size of less than 75 μm and kept in a desiccator for the gasification experiments.

The study the intrinsic carbon structure of the OPS and PNS chars, Raman analysis was carried out using Renishawin Via Raman spectrometer. The morphology of the chars was studied through SEM-EDAX analysis carried out in a Hitachi S-3400N Scanning Electron Microscope. Dynamic CO_2 adsorption and desorption behavior of biomass chars was measured in Thermogravimetric analyzer (SDTQ-600). In each experiment, about 10 mg of fine char powder was heated to 850 °C at the heating rate of 30 °C /min under N_2 atmosphere. In order to remove any oxygen that could be adsorbed by char after pyrolysis, the sample was stabilized at this temperature for 60 min. The sample was then equilibrated at 300 °C and maintained at this temperature for another 30 min. Then, N_2 was switched to CO_2 to initiate CO_2 adsorption for 30 min. Finally, the gas was switched back to N_2 for 30 min for desorption

Table 1: Characteristics of the OPS and PNS.

	Proximate analysis (wt%)						Ultimate analysis (wt%)			
	Moisture	Fixed carbon	Volatile matter	Ash	HHV (MJ/kg)		C	H	N	O*
OPS	7.0	21.3	69.9	1.8	18.3		49.65	6.43	8.25	35.67
PNS	2.8	16.3	79.8	1.1	18.6		58.23	4.06	1.04	36.67

									Ash composition (wt%)		
	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	Fe_2O_3	Na_2O	SO_3	Cl	Trace elements
OPS	6.9	7.7	49.7	8.4	12.2	10.2	2.7	-	-	-	2.2
PNS	10.0	2.7	12.8	3.2	22.6	31.1	6.7	2.5	3.6	3.0	1.8

of CO_2. Total run time for chemisorption experiment was about 170 min and all gas flow rates were set at 50 ml/min. Weight changes were recorded online and normalized with the net char weight at the beginning of the chemisorption cycle.

CO_2 gasification experiments

Gasification reactivity of OPS and PNS chars was studied under iso-thermal conditions in a Thermogravimetric analyzer (TGA, SDTQ-600). In a typical experiment, 7-8 mg of OPS or PNS char was loaded in a ceramic pan and heated to the pre-set temperature at a rate of 40 °C/min under N_2 atmosphere. At the onset of gasification, nitrogen was switched to CO_2 with the flow rate of 100 ml/min for isothermal gasification. The weight loss of the char sample as a function of time was recorded continuously and conversion (X) was calculated using the following equation:

$$X = \frac{m_0 - m_t}{m_0 - m_{ash}} \times 100 \qquad (1)$$

where m_0 represents the initial mass of the sample, m_t is the instantaneous mass of the sample at time t and m_{Ash} is the remaining mass of ash after completion of the gasification.

RESULTS AND DISCUSSION

Characterization of biomass chars

Figure 2 depicts the Raman spectra of the samples of OPS and PNS chars prepared at three carbonization temperatures of 500, 700 and 900 °C. Due to the significant effect of carbonization temperature on the structure of carbonaceous materials, dissimilar Raman spectra revealed from chars pyrolyzed at different temperatures. The intensity of both the D band (representing the amorphous carbon) and G band (indicating graphite crystal) decreased with increase of the carbonization temperature. However, the ratio of I_D/I_G increased from 0.774 to 0.871 for PNS char and from 0.787 to 0.849 for OPS char along with increase of the carbonization temperature from 500 to 900 °C which indicates the increase of the share of disordered carbon in the char and breakdown of symmetry of atoms.

Char- CO_2 gasification experiments

One of the most important parameters in controlling the gasification reaction rate is the temperature. The effect of temperature on the gasification reactivity of PNS and OPS chars was studied at temperatures 800 to 1000 °C by intervals of 50 °C and the results were illustrated in Figure 3.
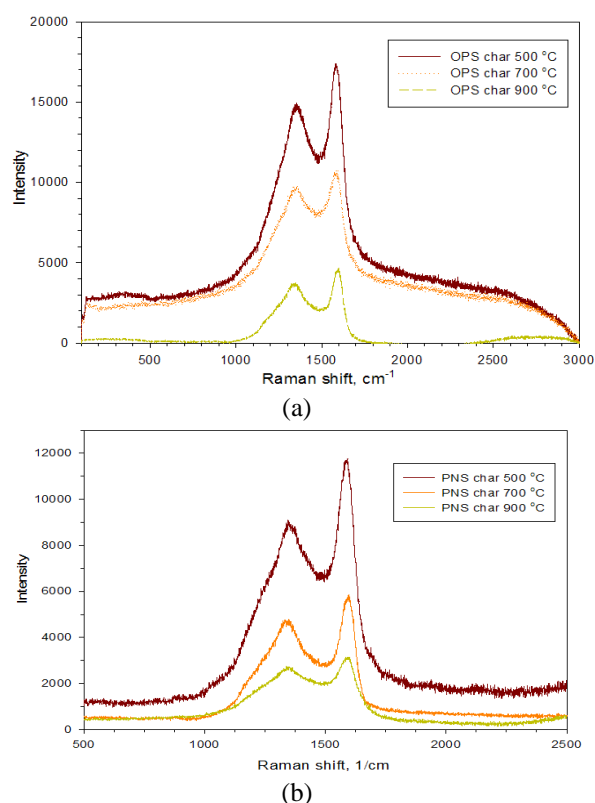

(a)

(b)

Figure 2. Raman spectra of the (a) OPS and (b) PNS chars pyrolyzed at 500, 700 and 900 °C
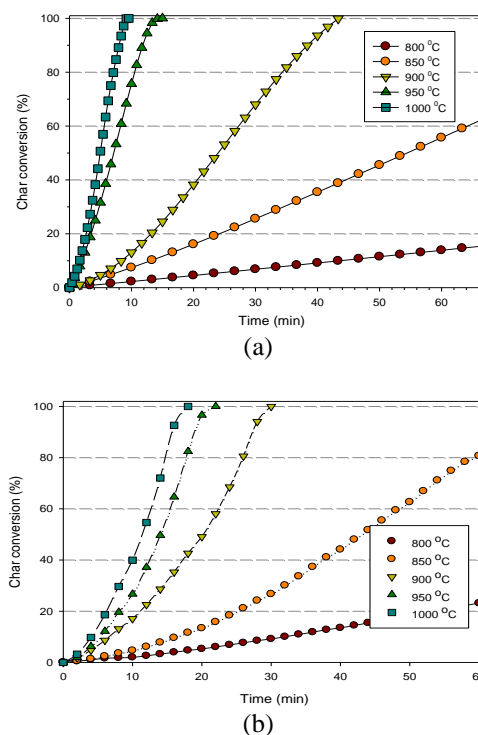

(a)

(b)

Figure 3. Char conversion of the OPS and PNS chars at different gasification temperatures

The results signify that the char conversion was significantly influenced by the temperature for both chars. The complete conversion of OPS char was achieved in 44 min at 900 °C and only 9.6 min at 1000 °C, whereas this time was prolonged to 390 min at 800 °C. Thus that carbon conversion at 900 °C was almost 9.75 times faster than that of 800 °C. Similar to the OPS char, results of gasification of PNS char confirmed the pronounced effect of temperature on promotion of char gasification reactivity. The complete carbon conversion was achieved in almost 18 min at 1000 °C, whereas this time was prolonged to 30 min at 900 °C and 210 min at 800 °C, corresponding to an increase by a factor of 1.7 and 11.7, respectively. The higher reactivity of the PNS char in the CO_2 gasification reaction compared to the OPS char from 800 to 900 °C can be implied by comparison of Figures 3(a) and 3(b). For instance, the time required to achieve the complete conversion at 900 °C was 44 min for the OPS char, whereas this time was shortened to 30 min in the case of PNS char. However, complete conversion of PNS char at 1000 °C was achieved within 18 min which was clearly slower than OPS char (9.6 min). The high reactivity of the PNS char at temperatures below 900 °C was confidently attributed to its high alkali index and the effective contribution of the alkali contents to the enhancement of char reaction rate. Most of alkali and alkaline earth metals are exclusively known as good catalysts for char gasification; whereas, Si and Al play an inhibiting role [10]. The presence of SiO_2 and Al_2O_3 in the ash of biomass char reduces the reactivity, as they react with elements in the ash and create various complex silicates including K, Na, Ca, Mg and Fe elements [11]. To quantify the catalytic effect of minerals available in the ash of carbonaceous material on enhancement of char reactivity, the alkali index is defined by following expression [12]:

$$Alkali\ index = ash(wt\%)\ \frac{Fe_2O_3 + CaO + MgO + Na_2O + K_2O}{SiO_2 + Al_2O_3} \quad (2)$$

The alkali index is defined as the sum of the mass fractions of alkali compounds in the ash divided to the sum of the mass fraction of acid compounds, multiplied by the ash content of the carbon-based material. The mostly encountered pattern reported by many researchers is the presence of good correlation between gasification reactivity and alkali index; where, the gasification reactivity of char improves with increase of the alkali index [12]. The results of ash composition of the raw PNS shows that its ash was rich in alkaline earth metal (31% CaO) and alkali metal (23% K_2O), while OPS ash was mainly composed of SiO_2 with minor amounts of metal oxides such as K_2O, CaO and MgO. Considering that the alkali index of the PNS, $(Alkali\ index)_{PNS} = 5.17$, calculated from Equation (2), was considerably higher than that of OPS, $(Alkali\ index)_{OPS} = 1.01$; it could be

expected that PNS presents higher reactivity than OPS at low gasification temperatures.

CO_2 chemisorption of PNS and OPS chars are presented in Figure 4. It is worth to note that any weakly adsorbed CO_2 molecule is removed during desorption time, while the strong chemisorbed CO_2 remain attached to the active sites. The higher irreversible CO_2 chemisorption (C_{strong}) of the PNS char compared to the OPS char revealed the higher concentration of active sites on the PNS char resulting higher conversion activity during CO_2 gasification.
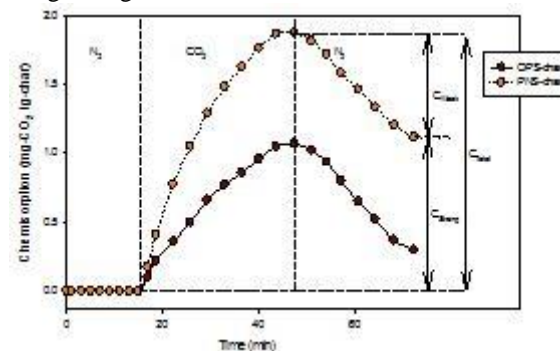

Figure 4. CO_2 chemisorption of PNS and OPS chars at 300 °C

As mentioned before, the most influential parameter in controlling the gasification reaction rate is temperature. At low gasification temperatures, the reaction rate is under chemically or kinetically controlled condition which requires high activation energy. By increasing the temperature, diffusion mechanism becomes dominant and controls the reaction rate [13]. In the current study, the reactivity of OPS char was higher than that of PNS char as the temperature increased to beyond 900 °C. In this case, the reaction turned to the diffusion controlled regime at the gasification temperature of 950-1000 °C. As can be deduced from the results, the conversion was very fast at high temperatures and rate of the reaction was influenced by diffusional resistance and diffusion of CO_2 through the pores was the dominant rate controlling mechanism at temperatures above 950 °C. It could be concluded that higher porosity of the char can conclude to higher reactivity at very high temperature; this was further approved by some structural analyses.

The SEM micrographs of OPS and PNS chars are depicted in Figure 5. As observed in the figure, OPS char presented more homogeneous and porous structure than PNS char. The high porosity of OPS char was further confirmed by surface area and porosity analysis. Table 2 summarizes the BET surface area and pore volume of OPS and PNS chars. The BET surface area of the OPS char was 266.30 m^2/g which was higher than PNS char (187.48 m^2/g). The SEM and BET results also confirm the higher reactivity of OPS char over PNS char.

Table 2. Surface area and porosity of OPS and PNS chars

Sample	BET surface area (m²/g)	Total pore volume (cm³/g)	Micropore volume (cm³/g)
OPS char	266.3	0.134	0.105
PNS char	187.48	0.090	0.069

(a)

(b)
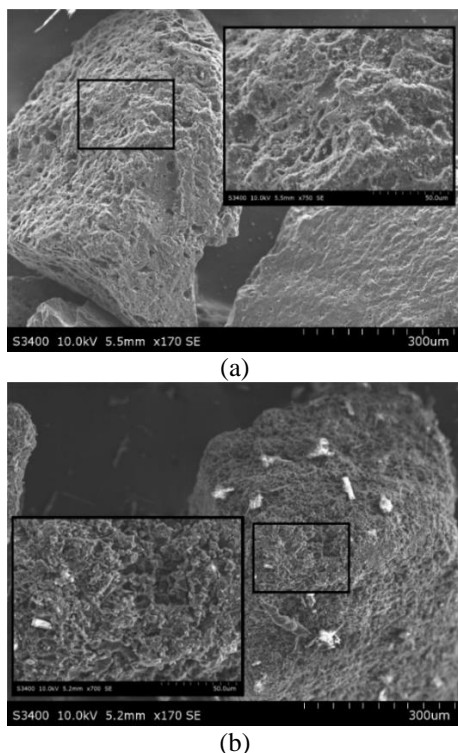
Figure 5. SEM micrographs of (a) OPS char, (b) PNS char

CONCLUSION

In this work, the influence of inherent alkali composition and surface area on the gasification reactivity of OPS char and PNS char under CO_2 was investigated. Gasification experiments were performed under isothermal condition using TGA. The effect of various temperatures as well as the catalytic influence of ash content of each biomass char was investigated. From the results, it was found that the gasification reactivity increases by increasing the temperature. However, the reactivity of PNS char was higher at temperatures below 900 ºC because of the catalytic influence of alkali, alkaline and transition metals, while at temperatures above 900 ºC, the reactivity of OPS was superior for its higher porosity and surface area.

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Persian Abstract

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چکیده

در این پژوهش، میزان واکنش‌پذیری ذغال پوسته پسته (PNS) و ذغال پوسته پالم (OPS) در واکنش گازی‌سازی با دی‌اکسیدکربن در شرایط ایزوترمال مورد بررسی قرار گرفت. اثرات دما، محتوای ترکیبات قلیائی ذاتی ذغال و مساحت سطح هر کدام از ذغال‌ها روی بهبود واکنش گازی‌سازی با دی‌اکسیدکربن مورد بررسی قرار گرفت. نتایج حاصل حاکی از اثرات کاتالیستی بسیار زیاد فلزات قلیائی، قلیائی خاکی و انتقالی مانند پتاسیم، سدیم، کلسیم و آهن که در خاکستر بیومس حضور داشتند، روی پیشرفت واکنش‌پذیری ذغال در واکنش گازی‌سازی در دماهای زیر ۹۰۰ درجه سانتی‌گراد بود. هرچند، در دماهای بالا مکانیزم نفوذ در حفرات غالب شده و کنترل کننده سرعت واکنش بود. با توجه به نتایج، در دماهای زیر ۹۰۰ درجه سانتی‌گراد، ذغال PNS به خاطر شاخص قلیائیت بالا واکنش‌پذیری زیادی با CO2 داشت، در حالی که در دمای بالاتر از ۹۰۰ درجه سانتی‌گراد، واکنش‌پذیری ذغال OPS با توجه به تخلخل بالا و مساحت سطح بزرگتر بیشتر بود.