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Production of Syngas using Entrained Flow Gasification of Pine Bark Biomass Aiming to Reduce Greenhouse Gas Emission from Power Generation

M. Shahabuddin, Sankar Bhattacharya*
Department of chemical engineering, Monash University, Wellington Rd, Clayton, 3800 VIC, Australia

ABSTRACT

In this study, CO_2 gasification characteristics of pine bark biomass have been explored using state of the art entrained flow gasifier. The effect of temperature, CO_2 concentration (gasification reagent), and particle size on carbon conversion and syngas yield have been analysed. The results show that increasing temperature and CO_2 concentration in the feed increases the carbon conversion, though the effect of CO_2 concertation is minimal. The influence of particle size on carbon conversion was also dominant. A full carbon conversion was achieved at a temperature of 1400 and 1200 °C with 20 % CO_2 using particle size 250-300 and 90-106 µm respectively. Higher conversions between 1-14%-point from smaller particle size under different operating conditions were determined. The analyses on syngas yield show that increasing temperature increases the generation of CO but decreases H_2 and CH_4. A higher gas yield and heating value from larger particle size were determined.

Keywords: Entrained flow, CO_2 gasification, Pine bark biomass, syngas, heating value

1. Introduction

Gasification is the process of converting carbonaceous solid fuels (i.e., biomass, coal, petcoke, etc.) into gaseous fuels (syngas) and chemicals. The key advantages of gasification over conventional combustion are the higher efficiency and lower emission. Furthermore, the integration of CO_2 capture and syngas cleaning system with gasification plants makes it more favourable for power generation. The by-product of gasification plant: CO_2 is potentially used for enhanced oil and methane recovery, while other pollutants such as H_2S and NH_3 are respectively be used for the production of sulfuric acid and fertiliser.

Currently, 81% of global energy and 66.7% of electricity is generated from fossil fuels such as coal, natural gas and petroleum oil [1]. These fossil fuels emit 99.4% of the world CO_2. The concern over depilation of fossil fuel reserve and greenhouse gas emissions are the driving forces to use alternative renewable sources like biomass for power generation, which has the potential to replace fossil fuel based power generation [2]. Biomass-the fourth largest source of global energy, supplies about 10% of world energy followed by three major sources of fossil fuels [3]. Currently, the syngas is predominantly generated from conventional fuel sources, for example, coal and natural gas. However, the advantages of biomass gasification over other conventional solid fuels are its renewability, availability, abundance, and higher gasification reactivity [4].

Most of the commercial gasifiers are operated in two-stages consisting of combustion and gasification. In the combustion zone, volatiles and fixed-carbon present in the biomass are oxidised (Eq.1-4) resulting in the generation of CO_2 and H_2O with a ratio of roughly 4:1. Hence, gasification reactions in reductor zone are mainly governed by the CO_2, which is a rate-limiting process. Thus, understanding of CO_2 gasification phenomena is more important than H_2O gasification. The gases (CO_2 and H_2O) generated in the combustor zone are then transferred to the reductor zone for gasification of raw biomass/char, resulting in the generation of CO and H_2 in addition to a minor amount of CH_4 and C_2H_6 [4].

$$\text{Biomass} \xrightarrow{\text{heat}} \text{Volatiles } (H_2, CO, CO_2, CH_4, \textit{etc.}) + \text{Char } (c) \quad (1)$$

$$\text{Volatiles} + O_2 \rightarrow CO_2 + H_2O \quad (2)$$

$$\text{Partial oxidation } C + \frac{1}{2}O_2 \rightarrow CO \quad (3)$$

$$\text{Complete oxidation } C + O_2 \rightarrow CO_2 \quad (4)$$

In the reductor zone, a rapid devolatilisation of biomass particles produces volatiles and solid char. This char is then gasified in the subsequent stage with the presence of CO_2 and H_2O. The key reactions those are involved in the gasification process include Boudouard reaction, steam gasification, methane reforming and water gas shift reactions as shown in Eq. 5-8.

$$\text{Boudouard reaction} = C + CO_2 \leftrightarrow 2CO \quad (5)$$

$$\text{Steam gasification} = C + H_2O \leftrightarrow CO + H_2 \quad (6)$$

$$\text{Methane reforming} = CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (7)$$

$$\text{Water gas shift reaction} = CO + H_2O \leftrightarrow CO_2 + H_2 \quad (8)$$

The gasification characteristics such as char conversion, gas yield and pollutant emission depend on the reaction rate of the aforementioned reactions. The reaction rate of these reactions are further influenced by the operating conditions, reactor configurations, and fuel properties. Kirtania and Bhattacharya [5] studied the effect of

* Corresponding author. Mob.: +61470605227
E-mail addresses: md.ahmmad@monash.edu

particle size, and temperature using the CO_2 concentrations of 5, 10 and 20% in an entrained flow gasifier for spruce and coconut shell biomass char. Three gasification temperatures of 800, 900 and 1000 °C and two particle size of 150-250 and 500-600 µm were chosen for the study. The residence times for spruce char were nine and 4.5 s, while the residence times for coconut shell char were determined to be seven and 2.5 s for lower and smaller particle size respectively. The result showed that a maximum conversion of 8 % and 50% for coconut shell and spruce chars were achieved using lower particle size under extreme operating conditions of 1000°C and 20% CO_2. The effect of CO_2 concentration was found to be dominant only for spruce char and at the highest temperature of 1000°C. It was stated that lowering the particle size did not favour the conversion for coconut shell char, though almost a double carbon conversion from lower particle size was determined in the case of spruce char. Thus, it was concluded that the conversion is independent to the particle size for the car with lower reactivity, hence increasing the temperature should be a better choice.

Sripada, et al. [6] investigated the gasification characteristics of pine bark biomass under entrained flow conditions with a residence time between 7-8 s. The results showed that operating conditions such as temperature and CO_2 concentration has a significant effect on carbon conversion and gas yield. Increasing temperature and CO_2 concentration lead to increase the carbon conversion. A maximum of 98% conversion was achieved at a temperature of 1200 °C with 40% CO_2 using particle size: 90-106 µm. The gas yield results showed that increasing CO_2 feed rate decreases the yield of syngas. In addition, increasing the temperature leads to an increase in the production of CO but decreases H_2. Moreover, the highest lower heating value (LHV) of the product gases was determined to be of 4.18 MJ/m^3 under the operating conditions of 1200°C and 10% CO_2.

From the literature, it is known that increasing temperature and CO_2 concentration increases the carbon conversion for all biomass including pine bark. However, based on the authors' knowledge, the effect of particle size on carbon conversion and syngas yield for pine bark biomass is not studied in the literature. Furthermore, most of the studies in the literature were carried out at low temperatures of up to 1000°C. However, the practical entrained flow gasifier is operated at high temperatures of above 1000°C. Hence, in this study, high-temperature CO_2 gasification study is carried out for pine bark biomass using different particle size. The result of this study will provide a better under understanding, especially the effect of particle size on gasification characteristics of pine bark biomass under CO_2 atmosphere. Moreover, the result will be applicable in the case of designing a gasification-based power plant using the substantial domestic reserve of pine bark biomass in Australia.

2. **Materials and method**

The CO_2 gasification study for pine bark biomass was carried using an electrically heated entrained flow gasifier, while a number of analytical instruments were used for the characterisation of raw pine bark sample. The following sections present the key steps those were followed to complete the experiments.

2.1 Sample preparation

Pine bark biomass studied in this study was first grounded into the desired particle sizes of 250-300 µm and 90-106 µm. The reason for selecting these size ranges are to make the study analogous to the industrial application. The grounded particles were then sieved by sieve shakers with the help of Taylor sieve shaker machine. Before conducting the experiment, the samples were oven dried overnight to ensure the particles free from moisture.

2.2 Sample characterisation

The proximate analysis was carried out using a TGA with the model number Netzsch STA 449 F3 following the standard: AS1038.1. The ultimate analysis was conducted by TruSpec CHNS analyser using ISO 29541 standard. The details of the operating conditions of TGA can be found in ref. Tanner and Bhattacharya [7]. The proximate and ultimate analyses results of pine bark biomass are shown in Table 1.

Table 1. Proximate and ultimate data for pine bark biomass

Proximate analysis (dry basis)					
Particle size (µm)	Moisture	Volatile	Fixed carbon	Ash	
90-106	2.7	69.92	22.11	5.27	
250-300	2.77	71.79	22.41	3.03	
Ultimate analysis (dry basis)					
	C	H	N	S	O
90-106	53.93	5.51	0.14	0.01	34.38

2.3 Experimental setup and operating procedures of the reactor

The entrained flow reactor used in this study is located in the chemical engineering department of Monash University, Australia. The major components of the reactor are shown in Fig. 1. This reactor imitates the reductor zone of the Mitsubishi heavy industry (MHI) commercial gasifier. The total length and internal diameter of the reactor tube are 3.80 and 0.090 m respectively. The reactor tube is made of alumina capable of sustain under high temperatures. The reactor is heated with eight independent electrical heating elements. During experiments, the sample is fed from the top of the reactor via a screw feeder with a feed rate of about one g/min. A precision balance installed in the feeder box gives a sample feed profile over time. Furthermore, the reactant gas: CO_2 is injected from the top of the reactor, which is pre-heated with a

temperature of 500°C. Different CO_2 concentrations of 10, 20 and 40% by vol. were used balancing with pure N_2. A total flow rate of 16 L/min is maintained throughout the experiment. A national instrumentation LabVIEW software is dedicated to controlling the gas and sample feed rates. The solid char/ash is collected via a series of impingers from the downstream of the reactor. The product gases (i.e., H_2, CO, CH_4) were measured using an online micro-GC. The details of the experimental setup and operating procedures can be found elsewhere [8].

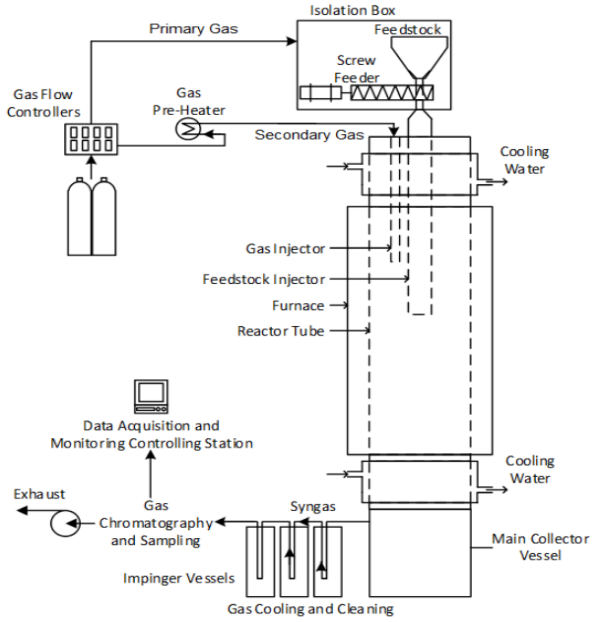

Fig. 1 Schematic diagram of the experimental setup [6]

3. Results and discussion

The carbon conversion was calculated by ash tracer method, which is verified by the gas-phase carbon conversion. The following equation (Eq. 9) was used to calculate carbon conversion by ash tracer method.

$$X\ (\%) = \left(1 - \frac{w_{c,out}}{w_{c,in}}\right) \times 100 \qquad (9)$$

Where, X is the carbon conversion, $w_{c,\,in}$ and $w_{c,\,out}$ are the weight of the carbon input and output respectively. The carbon content in the feed pine bark and post-gasified char/ash were determined by ultimate analysis.

The discrepancy between gas-phase and solid-phase carbon conversion was found to be 5-10% under different operating conditions. The sources of error in solid phase carbon conversion are incomplete char recovery from collection vessels and an error from precision balance. Whereas, the gas-phase carbon conversion might be influenced by fluctuating CO_2 feed rate and a measurement error from the Micro-GC. The quality and quantity of syngas during gasification depend on several factors including temperature, system pressure, reactant concentrations, residence time, reactor configurations and particle size. The reactor used in this study was an entrained flow reactor operated under atmospheric pressure. Based on the operating conditions the residence time for particle size 90-106 µm was calculated to be 7-8 s, which is 2.5-3.5 s for the large particle size of 250-300 µm [6, 9]. Considering the facilities available, this study predominantly tested the effects of temperature, CO_2 concentration, and particle size on syngas gas yield.

The effect of temperature, CO_2 partial pressure and particle size on carbon conversion is shown in Fig. 2. It is observed that increasing temperature and CO_2 concentration increase the carbon conversion. However, the influence of temperature is dominant as compared to that of CO_2 partial pressure. Considering equilibrium concentration, the feed of CO_2 was excess under all operating conditions. Thus, the effect of CO_2 concentration on carbon conversion was not significant. The carbon conversion using particle size 250-300 µm at 1000°C with 10% CO_2 is found to be 75%, which is increased by 2.57 %-point with 20% CO_2. However, under the same CO_2 concentration, increasing the temperature from 1000°C to 1200°C leads to increase the carbon conversion by 10%-point. The key equations those involved in gasification reaction were Boudouard and steam gasification. However, the influence of steam gasification was significantly low as compared to that of Boudouard reaction because of the low moisture content in the biomass. The reaction rate of these reactions increases with increasing temperature and CO_2 concentration. Hence, a higher conversion with increasing temperature and CO_2 was observed.

Besides, the effect of particle size on carbon conversion is significant as decreasing the particle size increases the carbon conversion. It can be seen that, decreasing the particle size from 250-300 to 90-106 µm (factor of ~2.8) increases the carbon conversion by 11, 9.43, and 8.64%-point under different CO_2 concentrations (10-40% vol.) and at a temperature of 1000°C. It is clear that 1200°C was not sufficient under any CO_2 concentrations to achieve 100% carbon conversion using the larger particle size of 250-300 µm. A temperature of 1400°C and 20% CO_2 concentration were required to reach full carbon conversion for large particle size, whereas 100% carbon conversion was achieved at a temperature of 1200°C and 20% CO_2 using smaller particle size. The diffusion limitation from large particle size prevented the reactant gas from diffusing through the micro-pores of the particle, hence a slower conversion. Furthermore, the lower residence time from larger particles led to the incomplete carbon conversion.

The production of gases during gasification is the result of devolatilisation and consumption of carbon left in the char. The devolatilisation is the first stage of gasification, resulting in the formation of H_2, CO, CO_2, CH_4 and some other minor species. In single stage gasification, both homogeneous and heterogeneous

reactions take place simultaneously under the presence of these gases and char.

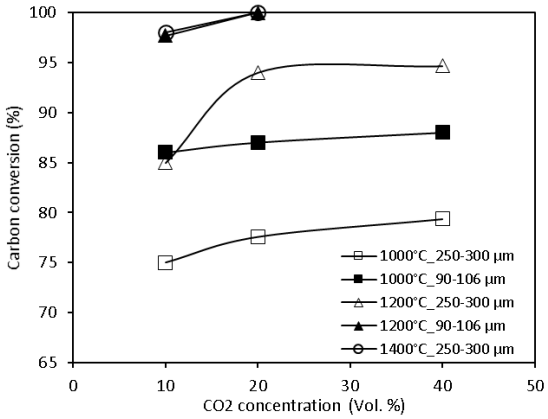

Fig. 2 The effect of CO_2 partial pressure and particle size on carbon conversion at various temperatures

The major gas components those produced during gasification is presented in Fig. 3 under various operating conditions. A significant variation in the yield of H_2 and CO were observed under different temperature, CO_2 concentrations, and particle size. However, the variation in the production of CH_4 was negligible, especially at higher CO_2 concentration. In addition, the yield of CH_4 was significantly low, particularly at 1200°C. Presumably, at a temperature above 1000°C, available CH_4 is being consumed by the Steam methane reforming reaction, which consequently decreases the yield of CH_4 [10].

The production of CO was increased with increasing temperature due to the higher carbon conversion owing to the Boudouard reaction being dominant. On the other hand, the yield of H_2 was decreased with increasing temperature and CO_2 concentration because of the water gas shift (WGS) reaction, which was favoured in the reverse direction [11].

The effect of particle size on the yield of gas species was also significant. It is observed that larger particle size results in higher syngas yield under all temperature and CO_2 concentration. The larger particles are appeared to be significantly unreacted, which resulted in the WGS reaction to be dominant as compared to those of smaller size particle. Hence, larger particle size yields more H_2 and CH_4 as compared to that of smaller particle size. However, the higher CO yield from larger particle size is not clear. It was expected that the contribution of Boudouard reaction on overall reaction would be much more significant using lower particle size consuming more carbon to produce more CO. Further analysis is therefore required to figure out the reason behind this unexpected trend.

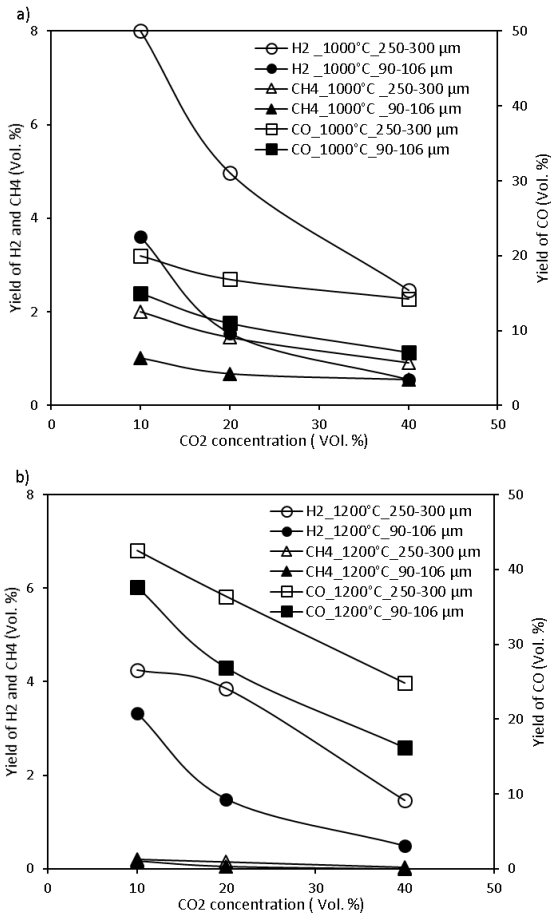

Fig. 3 Effect of temperature and CO_2 partial pressure on gas yield from two different particle sizes of 90-106 µm and 250-300 µm; a) 1000°C, b) 1200°C (N_2 and feed CO_2 free basis).

The ratio between CO and H_2 carries paramount importance, especially for chemical synthesis. Hence, gasification plants for chemical production require downstream treatment to adjust the gas composition in order to produce desired chemicals. However, this ratio does not necessarily play a pivotal role in terms of altering the heating value of the product gases, which is essential for the power generation. Table 2 and 3 show the ratio between CO and H_2 under different operating conditions for two particle sizes. It is seen that CO/H_2 ratio differs markedly under different operating conditions. As expected, the production of CO as compared to that of H_2 is higher under higher carbon conversion resulting in the ratio being higher for the corresponding condition. Furthermore, higher CO_2 concentration led to increasing the yield of CO, resulting in the higher ratio between CO and H_2.

Table 2. The ratio between CO and H_2 from two particle sizes at various temperatures and CO_2 concentrations (excluding N_2 and feed CO_2).

CO2 Concentration (Vol.%)		CO/H2 ratio		
250-300 µm		1000 °C	1200 °C	1400 °C
	10	2.50	10.01	12.75
	20	3.39	9.44	10.22
	40	5.79	16.92	-
90-106 µm				
	10	4.16	11.36	-
	20	7.10	18.10	-
	40	12.79	-	-

The lower heating value (LHV) presented in Table 3 was calculated using Eq. 10 under different operating conditions. It can be seen that increasing the temperature increases the heating value, which is opposed by the increasing CO_2 concentration. A maximum heating value under three temperatures and lowest CO_2 concentration of 10% were calculated to be 4.1, 5.9 and 6.87 MJ/m^3 for larger particle size. When LHV is compared between the particle sizes, it is depicted that, the heating values from larger particle size are higher than the smaller particle size between the range of 14 and 107%. The result can be interpreted as the fact that the yield of all gases from larger particle size was considerably higher than the smaller particle size.

$$LHV(MJ/M^3) = 10.78X_{H_2} + 12.63X_{CO} + 35.81X_{CH_4} \quad (10)$$

Table 3. The heating value of the product gases from two particle sizes under different temperatures and CO_2 concentrations (excluding N_2 and feed CO_2).

CO2 Concentration (Vol.%)		Lower Heating Value (MJ/M3)		
250-300 µm		1000°C	1200°C	1400°C
	10	4.10	5.90	6.87
	20	3.19	5.06	6.07
	40	2.39	3.30	-
90-106 µm				
	10	2.65	5.18	-
	20	1.80	3.57	-
	40	1.15	-	-

The heating value presented in the Table 3 was calculated excluding the feed N_2 and CO_2 from the outlet stream. However, calculating LHV based on CO_2 free basis results in the heating value between the range of 12-14 MJ/m^3, which are closer to the heating value of pure CO, because of the dominant concentration of CO in the outlet stream. Therefore, in order to increases the heating value of the syngas, a CO_2 separation unit should be installed. In addition, a choice of optimum CO_2 concentration in the feed can be considered without penalising the carbon conversion efficiency.

4. Conclusion

In this research, CO_2 gasification characteristics of pine bark biomass were carried out using different temperatures, CO_2 concentrations and particle sizes under entrained flow conditions. The results of this study show that increasing temperatures and CO_2 concentration increases the carbon conversion, though the effect of CO_2 concentration is not much significant, especially above 20% CO_2. Furthermore, the particle size has a strong influence on carbon conversion, gas yield and heating values. Decreasing particle increases the carbon conversion significantly. Smaller particle size (factor = ~ 2.8) resulted in a higher carbon conversion between the range of 1-12% percentage point. The gas composition results show that increasing the temperature increases the yield of CO but decreases H_2 and CH_4. In addition, larger particle size results in a higher syngas yield and heating value thereby. Further study, including solid residue characterisation by XRD, and SEM are sought for a better understanding of the pine bark gasification under CO_2 atmosphere, and these studies are in progress. The detailed analysis including solid phase characterisation and thermodynamic calculations will be published in future publications.

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