ENHANCED SYNGAS PRODUCTION FROM CO₂ GASIFICATION OF BIOMASS

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ABSTRACT

Biomass CO_2 gasification has attracted much attention as part of the CO_2 utilization and mitigation. In this study, biomass CO_2 gasification is investigated based on an equilibrium model. Parameter sensitive analysis is conducted to investigate the influence of CO_2/C ratio and gasification temperature on the gasification process. The results show that the syngas production can be enhanced by increasing the CO_2/C ratio of the biomass CO_2 gasification. Higher gasification efficiencies are also obtained under higher gasification temperatures.

Keywords: Enhanced syngas production, CO₂ gasification, Biomass, Gasification modelling.

1. INTRODUCTION

Biomass is regarded as a renewable energy source that can be expected to meet the energy demands and contribute to reducing the carbon dioxide emissions [1]. Research on biomass-to-energy conversion has been motivated in the past decades. Direct combustion and gasification are the technologies widely used to convert solid biomass resources into energy for heat and power [2]. Gasification is a thermochemical process that converts a solid fuel into a gaseous fuel by partial oxidation at temperatures around 900 °C. It produces CO, H₂ and small amounts of CH₄ as desired products with other undesired gases like N₂, CO₂ and other hydrocarbons (HC) [3-4].

Air, pure oxygen, steam and a mixture of these have all been used as biomass gasification agents in the traditional gasification processes. Recently, due to CO₂ utilization and carbon capture and storage (CCS), biomass gasification using carbon dioxide (CO₂) as the oxidizing agent has attracted much attention [5]. Biomass CO_2 gasification can be used as a compatible technology to support CO_2 mitigation. It is based on the fact that the reaction products from the gasification process mainly consists of CO and CO_2 . A high concentration of CO_2 stream can be obtained through the combustion of the produced gas with O_2 which can be easily sequestrated and/or recycled back to the gasifier as a gasifying agent. The CO_2 gasification is significant as it provides a direct role in greenhouse gas management. Further, regarding the higher production of carbon monoxide, it can be used in many chemical processes in addition to the direct use in thermal energy production.

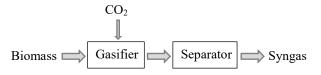


Fig 1 General schema of biomass gasification process

Additionally, exergy analysis is an interdisciplinary concept that combines energy, environment and sustainability and has been used for process evaluation and improvement [6]. Ultimately, the gasification conversion efficiency and the heating values of the produced syngas will be increased by determining the optimum operating conditions. The produced syngas with good heating values that can be used directly for different downstream applications. Therefore, understanding the energy, exergy and environmental impact of the biomass CO_2 gasification process is essential.

2. METHODOLOGY

2.1 Fuel properties

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In this study, cardboard from Ref [7] was chosen as the biomass feedstock. Its basis properties are listed in Table 1 [7].

Table 1. Ultimate analy	sis of cardboard	sample (%) [7]
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С	Н	0	Ν	S	Ash
44	5.9	44.6	0.3	0.2	5

2.2 Equilibrium model

The cardboard biomass can be described as $C_x H_y O_z$ based on the ultimate analysis, and the global gasification reaction is described as follows:

$$C_{x}H_{y}O_{z} + wH_{2}O + mCO_{2}$$

$$\rightarrow x_{1}H_{2} + x_{2}CO + x_{3}CO_{2} + x_{4}H_{2}O + x_{5}CH_{4}$$
(1)

where w and m are the amount of water and carbon dioxide per mol of biomass fuel, respectively, and x_1 , x_2 , x_3 , x_4 and x_5 are the coefficients of the gaseous products.

The three main independent equilibrium reactions that are selected for the equilibrium model are shown below:

$$C + 2H_2 \to CH_4 \tag{2}$$

 $CO + H_2O \to CO_2 + H_2 \tag{3}$

$$C + H_2 O \to CO + H_2 \tag{4}$$

Based on the mass balance and equilibrium constants, the coefficients of gaseous products could be solved.

Carbon balance:

$$x + m = x_2 + x_3 + x_5,$$
 (5)
Hydrogen balance:

$$y + 2w = 2x_1 + 2x_4 + 4x_5,$$
 (6)
Oxygen balance:

$$z + w + 2m = x_2 + 2x_3 + x_4,$$
Equilibrium constants [8]:
(7)

$$K_1 = [CH_4] / [H_2]^2 = x_5 / x_1^2, \tag{8}$$

$$K_2 = [CO_2][H_2]/[CO][H_2O] = x_1 x_3 / x_2 x_4, \tag{9}$$

$$K_3 = [CO][H_2]/[H_2O] = x_1 x_2/x_4.$$
(10)

2.3 Exergy and energy analysis

The cold gas efficiency of the gasification process is defined as [9],

$$\eta = \frac{n_{gas} LHV_{gas}}{LHV_b} \tag{11}$$

where n_{gas} is the molar amount of the product gas, LHV_{gas} and LHV_{gas} are the lower heating value of the product gas and the biomass fuel respectively. The values can be calculated by the following equations:

$$LHV_{gas} = 282993x_{CO} + 241827x_{H_2} + 802303x_{CH_4}, \quad (12)$$

$$LHV_b = (HHV_b - 219.2H)(1 - w/100) - 0.2453w, \quad (13)$$

$$HHV_b = 349.1C + 1178.3H - 103.4O.$$
(14)

where x_{CO} , x_{H_2} and x_{CH_4} represent the mole fraction of species in the product gas, *C*, *H* and *O* are the percentage weight for carbon, hydrogen and oxygen of biomass fuel.

The exergy efficiency of the gasification process is defined as [10]:

$$\varphi = \frac{E_{ch,gas} + E_{ph,gas}}{Ex_b} \tag{15}$$

where $E_{ch,gas}$ and $E_{ph,gas}$ are the chemical and physical exergy of the product gas respectively, Ex_b is the exergy of the biomass fuel. They are calculated by:

$$E_{ch,gas} = \sum_{i} n_i x_i \varepsilon_{0i} + RT_0 \sum_{i} n_i x_i ln x_i,$$
(16)

$$E_{ph,gas} = \sum_{i} n_{i} [(H_{i} - H_{0_{i}}) - T_{0}(s_{i} - s_{0_{i}})].$$
(17)

where n_i is the molar number of species i, x_i is the mole fraction of species i, R is the ideal gas constant, T_0 is the reference environmental temperature, H and s are the molar enthalpy and entropy of species i.

The energy balance of the gasification process can be written as [11]:

$$E_b + E_{CO_2} = E_{syn} + E_{sen} + E_{loss} \tag{18}$$

Thus, the energy efficiency is defined as:

$$\eta_e = 1 - E_{loss} / E_b. \tag{19}$$

here, E_b , E_{CO_2} , E_{syn} , E_{sen} and E_{loss} are the energy in biomass fuel, injected CO₂ agent, product syngas, sensible and loss, respectively.

Here, it needs to be pointed out that, as the equilibrium model focuses on the theoretical syngas production from the feedstock and the gasification temperature is fixed in the model, the calculation of efficiencies is in regardless of energy consumed by the equipment. The efficiencies considering all the factors will be investigated by the gasification system established in Aspen later.

3. VALIDATION

Figure 2 presents a comparison between the results from the experiments in Ref [7] and the data calculated from the equilibrium model. Moreover, the *GasEq* model from Ref [12] was introduced as well to compare the predictions. It can be clearly seen that the equilibrium model, proposed in this study, predicted the results well and had a better match with the experiment. Therefore, it can be concluded that the equilibrium model is valid and can support the parameter sensitive analysis.

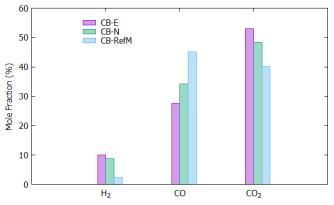


Fig 2 The compared result between the experiment and the equilibrium model. CB-E: Experiments, CB-N: Equilibrium model, CB-RefM: GasEq model referred.

4. **RESULTS AND DISCUSSION**

The syngas production and energy and exergy efficiencies under the different CO_2/C ratios and different gasification temperatures are investigated. Here, the CO_2/C ratio is defined as the mole ratio of the total amount of carbon in the biomass fuel to the total amount of CO_2 injected into the gasifier. The results are presented in Figures 3-7.

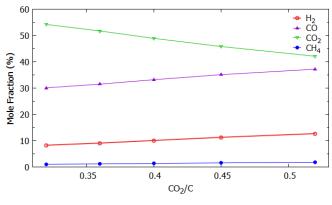


Fig 3 Effect of CO₂/C ratio on syngas production when T=1000K.

Figure 3 shows the effect of CO_2/C ratio on the composition of the producer gas when the gasifier is working at 1000K. It can be seen from the figure that the mole fraction of CH_4 is almost constant at a very low level (1%-1.8%) with the CO_2/C ratio variation. The composition of the hydrogen produced in the fuel gas continuously increases with the CO_2/C ratio from about 8% to 13%. Similarly, the increasing trend is also found in the produced carbon dioxide. The mole fraction of

carbon dioxide increases from 30.1% to 37.2%. It should be further noted that the percentage of carbon dioxide decreases with the CO₂/C ratio. The inverse changing trend of carbon dioxide and carbon monoxide can be attributed to the chemical reactions between the carbon and the gasifier agent - carbon dioxide (Boudouard reaction: $C + CO_2 \rightarrow 2CO$).

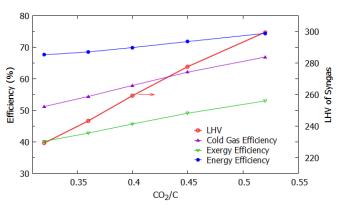


Fig 4 Effect of CO₂/C ratio on gasification efficiencies when T=1000K.

The effect of CO_2/C ratio on the lower heating value of the producer syngas, cold gas efficiency, exergy efficiency and energy efficiency at 1000K is illustrated in Figure 4. It can be seen that the lower heating value of syngas has a large rise from 229 to 300 KJ/mol with the changing CO_2/C ratios. Further, the increasing trend is observed for all the efficiencies introduced in this study. This is due to the mole fraction of syngas in the producer gas which is higher under the higher CO_2/C ratio conditions.

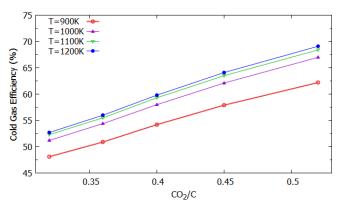


Fig 5 Effect of CO₂/C ratio on cold gas efficiency when the gasification temperature varies.

Different gasification temperatures are considered in this study. Figures 5-7 reports the effect of CO_2/C ratios on the gasification efficiencies with the gasification temperature varying from 900K to 1300K.

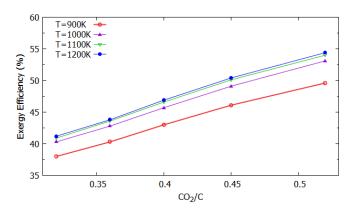


Fig 6 Effect of CO_2/C ratio on exergy efficiency when the gasification temperature varies.

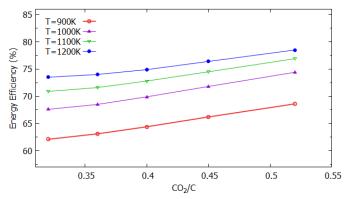


Fig 7 Effect of CO₂/C ratio on energy efficiency when the gasification temperature varies.

Overall speaking, the effect of gasification temperature on the cold gas efficiency and exergy efficiency is similar. When the gasification temperature is over 1000K, the efficiencies vary slightly. However, they are much higher than that at 900K. Further, under a specified gasification temperature, the efficiency increases with higher CO_2/C ratio.

Regarding the energy efficiency, the gasification temperature has more significant influence. The energy efficiency increases with temperature under the same CO_2/C ratio conditions, and the difference in the efficiency under different temperatures is obvious. Moreover, with higher CO_2/C ratio, the energy efficiency under different gasification temperature gets closer.

5. CONCLUSIONS

The proposed equilibrium model was validated by comparing the simulation results with the data from an existing experiment [6]. The results indicate that the mole fraction of syngas in the flue gas increases under higher CO_2/C ratio conditions. Further, the gasification efficiencies are affected by the gasification temperature. Higher temperature and higher CO_2/C

ratio result in higher gasification efficiencies. The energy efficiency is more sensitive to the gasification temperature.

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