Methanol production from algae biomass gasification derived syngas: A modeling study

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Abstract

Methanol is known as an alternative energy for transportation fuels and precursors in many industrial processes. Conventionally, coal and methane are used as feedstock for methanol synthesis but its combustion generates CO\textsubscript{2} emission, one of the main sources of global warming. The purpose of this study is to analyze through an analytical model the methanol production from algae biomass gasification from air-steam biomass gasification process. The model aims to investigate: 1) the influences of the gasifier temperature and gasifying agent on syngas production and 2) the operating conditions for methanol production. The results show that higher gasifier temperature and steam to algae ratio increased the syngas yield. The gasifier temperature and steam to algae ratio of 800\textdegree C and 0.5 respectively result in the maximum yield of syngas. In the methanol analysis, the operation at high pressure and low temperature enhances the methanol production. The temperature and pressure of 200\textdegree C and 80 bar respectively result in the maximum yield of methanol (76.56\%).

Keywords: Methanol, gasification, syngas, algae

1. Introduction

Fossil fuel still plays important role in everyday life and has a tendency to be used in a large quantity despite the oil price crisis, its non-renewable stock that will phase out in the near future, as well as the environmental problems emerged from its use. In these regards, many countries around the world have paid attention and invented alternatives to replace the conventional fossil fuel such as energy from plants, well known as clean energy. Among alternatives, methanol is a promising source because of it wide range applications including the production of fuel and raw material for chemical synthesis.

Methanol can be produced traditionally from natural gas and coal through methane reforming and gasification processes. However, this process also contributes to the global warming issue. Thus, production of methanol from biomass which is known as a renewable and a carbon-neutral energy sources \cite{1} have been considered though the challenges are round about its quantity and affordability to meet the energy demand.

The previous research has suggested that algae could also be used to produce alternative energy because algae as a raw material does not affect the food chain, have high yield production, able to grow fast, easy to propagate \cite{2}, and exists in various water sources from freshwater, saltwater, or even wastewater. However, there are still few studies about methanol production from algae biomass. Therefore, the purpose of this study is to investigate through an analytical model the methanol production from algae biomass gasification using air and steam as gasifying agent. A modeling tool, Aspen Plus Simulator, was used in this study to investigate: 1) the proper condition of gasifier temperature and steam...
to algae biomass ratio on the syngas composition for methanol synthesis and 2) the effect of reaction
temperature and pressure on the methanol yield, CO, CO₂, and H₂ conversions.

2. Process Description

Fig. 1. illustrates the flowsheet of Aspen Plus Simulator for methanol production using the mixture of
air-steam algae biomass gasification. The concept referred to a setup of methanol production using syngas
production, water shift reactor, and methanol synthesis unit. The overall process started from the
feedstock which is dry form of algae being fed into the gasifier and run through three main processes:
pyrolysis, oxidation, and gasification. After the syngas leaving the gasifier, the water gas shift reactor was
used to adjust the syngas ratio to meet requirement for methanol synthesis. The syngas was then
compressed and preheated before being fed for the methanol synthesis using bed reactor.

The assumptions used for simulating the syngas and methanol productions are: (1) the process
occurred in a steady state and isothermal conditions; (2) the syngas component leaving the gasifier
consists of H₂, CO, CO₂, CH₄, and H₂O, respectively; and (3) the methanol reactor is operated in
isothermal condition. The ultimate and proximate analyses of the algae are presented in Table 1.

Table 1. Proximate and ultimate analysis of algae biomass.

| Proximate analysis (wt%) | Ultimate analysis (wt%) |
|--------------------------|-------------------------|
| Fixed carbon             | 16.39                   |
| Volatile                 | 80.10                   |
| Moist content            | -                       |
| Ash                      | 9.02                    |
| Ash                      | 9.02                    |

The reaction from syngas are expressed as the carbon dioxide hydrogenation (Eq. 1) and reverse water
gas shift (Eq. 2). The Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic model for two reactions
was used in the model.

\[
CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \quad \Delta H^\circ_{298} = -49.40 \text{ kJ/mol} \quad (1)
\]

\[
CO_2 + H_2 \rightarrow CO + H_2O \quad \Delta H^\circ_{298} = 41.2 \text{ kJ/mol} \quad (2)
\]
The rate of reaction and parameters for the kinetic rate model were taken from the literature of Van den Bussche and Froment [3] as expressed in Eq. 3 and Eq. 4, where $ \dot{k} $ is the kinetic constant, $ P $ is partial pressure, and $ K $ is equilibrium constant, respectively.

$$ r_{\text{CH,OH}} = \frac{k_1 P_{\text{CO}_2} P_{\text{H}_2} (1 - \frac{1}{K_1})}{(1 + K_1 P_{\text{H}_2} + K_2 P_{\text{H}_2}^{0.5} + K_3 P_{\text{H}_2})^3} $$  

(3)

$$ r_{\text{RWGS}} = \frac{k_2 P_{\text{CO}_2} (1 - K_2 P_{\text{H}_2} P_{\text{CO}_2})}{(1 + K_1 P_{\text{H}_2} + K_2 P_{\text{H}_2}^{0.5} + K_3 P_{\text{H}_2})} $$  

(4)

The parameter of the kinetic model for CO$_2$ hydrogenation and reverse water gas shift reactions are summarized in Table 2.

| Parameter       | $ A \exp(B_i / RT) $ |
|-----------------|---------------------|
| $ k_1 $ (mol kg$^{-1}$ s$^{-1}$ bar$^{-2}$) | 1.07 36696 |
| $ k_2 $ (mol kg$^{-1}$ s$^{-1}$ bar$^{-1}$) | $1.22 \times 10^{10}$ -94.765 |
| $ K_1 $ (-)     | 3453.38 |
| $ K_2 $ (bar$^{0.5}$) | 0.499 17197 |
| $ K_3 $ (bar$^{-1}$) | $6.62 \times 10^{-11}$ 12411 |

$ K_{\text{eq1}} $ and $ K_{\text{eq2}} $ are equilibrium constant that were taken from Graaf et al. [4] based on the following equations (Eq. 5 and Eq. 6):

$$ \log_{10} K_{\text{eq1}} = \frac{3066}{T} - 10.592 $$  

(5)

$$ \log_{10} \frac{1}{K_{\text{eq2}}} = \frac{2073}{T} + 2.029 $$  

(6)

The conversion of CO, CO$_2$, and H$_2$ was calculated with the following equations (Eq. 7 – Eq. 9) where $ F_{\text{in},i} $ and $ F_{\text{out},i} $ are the molar flowrates of the component i at the input and output the methanol reactor.

$$ \text{CO conversion} (%) = \frac{F_{\text{CO, in}} - F_{\text{CO, out}}}{F_{\text{CO, in}}} \times 100 $$  

(7)

$$ \text{CO$_2$ conversion} (%) = \frac{F_{\text{CO}_2, \text{in}} - F_{\text{CO}_2, \text{out}}}{F_{\text{CO}_2, \text{in}}} \times 100 $$  

(8)

$$ \text{H}_2 \text{ conversion} (%) = \frac{F_{\text{H}_2, \text{in}} - F_{\text{H}_2, \text{out}}}{F_{\text{H}_2, \text{in}}} \times 100 $$  

(9)

The methanol yield was calculated with the following equation (Eq. 10):
\[ Y_{\text{Methanol}} = \frac{F_{\text{Methanol, out}}}{(F_{\text{CO}} + F_{\text{CO}_2})} \times 100 \] (10)

3. Verification of the Model

The experiment data of Lv et al. [5] and Van den Bussche and Froment [3] were used to verify the simulated value of algae biomass gasification and methanol synthesis respectively as presented in Fig. 2. The simulation and experiment results for both of syngas production and methanol synthesis are in good agreement. Therefore, these models can be used to predict the performance of the process.

Fig. 2. Validation of the model for (a) algae biomass gasification (b) methanol synthesis (dash line refers to simulated value and symbol refers to experimental data).

4. Results and Discussion

4.1. Algae biomass gasification

4.1.1 Effect of gasifier temperature on syngas composition

It is well known that the temperature plays an important role in the syngas production from algae biomass gasification. The gasifier temperature used in the study ranged from 500 to 1000 °C. The effect of the temperature on syngas compositions is shown in Fig. 3. It shows that the increase in gasifier temperature results in the increase in the hydrogen and carbon monoxide. This is because a higher gasifier temperature could promote the Char gasification, Boudourd reaction, and methane shift reaction respectively as expressed in Eq 11, Eq. 12, and Eq. 13.

\[ \text{Char gasification} \quad C + H_2O \rightarrow CO + H_2 \quad 131 \] (11)
\[ \text{Boudourd} \quad CO + CO_2 \rightarrow 2CO \quad +172 \] (12)
\[ \text{CH}_4 \text{ shift} \quad CH_4 + H_2O \rightarrow CO + 3H_2 \quad +206 \] (13)

On the other hand, the higher gasified temperature results in the decrease of methane and carbon dioxide that is due to the reaction being exothermic. In addition, the increase in gasifier temperature over 700 °C results in the decrease of hydrogen because of the hydrogen partial oxidation reaction. These
results are consistent with the research of Lucas et al. (2004) which concluded that the increase in the gasifier temperature results in the decrease of the proportion of gas composition.

Fig. 3. Effect of the gasifier temperature on syngas compositions.

4.1.2. Effect of steam to algae biomass ratio (S/B) on syngas composition

In this study, the gasifier temperature was kept constant at 800 °C with the ratio of steam to biomass of 1. Biomass flowrates was adjusted for the steam to biomass ratio ranged from 0 to 2.0. Fig. 4. shows the effect of the steam to biomass ratio on the syngas composition. It shows that the composition of the H₂ and CO₂ increase from 31.55 to 33.20% and 2.38 to 10.38% when the S/B ratio is increased from 0 to 0.5 respectively. On the other hand, the concentration of CO dramatically decreases from 37.42 % at S/B of 0 to 6.85 % at S/B of 2.0. The higher S/B ratio favors the water gas shift reaction and steam methane reforming as expressed in Eq. 14 and Eq. 15.

\[
\text{CO + H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \tag{14}
\]

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \tag{15}
\]

In the water gas shift reaction, The H₂ concentration slightly decreases when the S/B ratio is raised from 0.5 to 2.0 because the high flow rate of steam can dilute the H₂ composition. The maximum yield of H₂ is 33.20 %mol at S/B and gasifier temperature of 0.5 and 800 °C.

Fig. 4. Effect of the steam to biomass ratio on syngas compositions.
4.2. Methanol Synthesis

4.2.1. Effect of reaction temperature and pressure on methanol yield

The reaction temperature and pressure were varied from 200 to 300 °C and 50 to 100 bar, respectively. The H₂/CO and CO₂/CO molar ratio to be fed in the methanol reactor are 2.0 and 0.2. The methanol yield was calculated using Eq. 10 while the CO, CO₂ and H₂ conversions were calculated using Eq. 7 - 9. The effects of the reaction temperature and pressure on the methanol yield, CO, CO₂ and H₂ conversions are shown in Fig. 5. The results show that the methanol yield, CO H₂, CO₂ conversions are favourable at both high and low pressure because the CO₂ hydrogenation is exothermic reaction. Thus, the conversion of CO increases when the temperature is decreased, resulting in the increase of the methanol yield. In addition, the operation at higher pressure in the methanol reactor also enhances the CO and H₂ conversions and thereby increasing the methanol yield. This is in line with Le Chatelier's principle.

The maximum yield of methanol and CO conversion are 76.56% and 99.59% at the temperature and pressure of 200 °C and 100 bar. However, since the energy supply is needed to drive the methanol synthesis at high pressure (90-100 bar) therefore the proper conditions for producing the methanol from algae biomass gasification should be at temperature and pressure of 200 °C and 80 bar.

Fig. 5. Effect of reaction temperature and pressure on (a) methanol yield; (b) CO conversion; (c) H₂ conversion; and (d) CO₂ conversion.
5. Conclusion

This study was able to investigate the methanol production from syngas derived algae biomass gasification through an analytical model. The simulation results revealed that higher gasifier temperature and S/B ratio of 800 °C and 0.5 will result in the maximum yield of syngas because of the occurrence of the Char gasification, Boudourd reaction, and methane shift reactions. The results also showed that at reaction temperature and pressure of 200 °C and 80 bar will enhance the CO, H\textsubscript{2} and CO\textsubscript{2} conversions and methanol yield.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Mattana Santasnachok and Ekkachai Sutheerasak concluded the research; Charoen Chinwanitcharoen analyzed the data; Mattana Santasnachok and Wirogana Ruengprathungsuka wrote the paper and all authors helped drafting and reviewing the paper.

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References

[1] Gustavsson L, Borjesson P, Johansson B, Svenningsson P. Reducing CO\textsubscript{2} emissions by substituting biomass for fossil fuels. Energy, 1995;20(11):1097-1113.
[2] Aziz M, Zaini IN. Production of hydrogen from algae: Integrated gasification and chemical looping. Energy Procedia, 2017; 142:210-5.
[3] Van den Bussche KM and Froment GF. A steady-state kinetic model for methanol synthesis and the water gas shift Reaction on a commercial Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} catalyst. Journal of Catalysis, 1996; 161:1.
[4] Graaf GH, Sijtsema PJJM, Stahnhuys EJ, Joosten GEH. Chemical Equilibria in Methanol Synthesis. Chemical Engineering Science, 1986;41:2883.
[5] Lv PM, Xiong ZH, Chang J, Wu CZ, Chen Y, and Zhu JX. An experimental study on biomass air-Steam gasification in a fluidized bed. Bioresource Technology, 2004;95:95-101.

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