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Hydrothermal Gasification of Biogas Digestate: a Thermodynamic Study on Effects of Process Parameters Using Aspen Plus

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In this work, effects of process parameters on hydrothermal gasification (HTG) of biogas digestate are investigated using Aspen Plus software with an assumption that the inorganic contents of feedstock are lumped together as a single input parameter. The investigated parameters are temperature (400-600 °C), pressure (250-300 bar), feedstock concentration (10-50 wt%), and feedstock ash content (0-40%), while the performance indicators are producer gas yield and composition. According to the modelling results, significant effects on the producer gas yield and composition were observed for temperature and feed concentration changes. On the other hand, pressure only had slight effects on the gas production. Hydrogen composition can be enhanced by keeping the pressure and feedstock composition low while increasing the reaction temperature. Furthermore, higher ash content leads to higher H_2 composition, lower CO_2 and CH_4 composition, and higher gas yield. However, the trends captured in this study does not represent any chemical activities of the ash components.

1. Introduction

Among the rapidly growing interests towards renewable and sustainable energy alternatives, biogas has received significant attention as one of the most promising biofuels. Biogas, primarily consisting of CH_4 and CO_2, is a versatile energy source for transport fuel as well as heat and electricity generation. It has a significant potential as a renewable energy source for both domestic and industrial applications. Biogas energy has accounted for 16,915 MW of global energy production in 2017, 71% of which is contributed by European countries (Herbes, Roth et al. 2020).

Despite its potentials, the implementation of biogas technology is still hindered by significant key challenges. Biogas is mainly produced through anaerobic digestion, a biological process that decomposes organic materials in the absence of oxygen (Surendra, Takara et al. 2014). During the biogas production, the anaerobic digestion simultaneously generates a solid-liquid digestate stream, typically consists of 30-60% fraction of the feed (Romio, Kofoed et al. 2021). Due to its rich nutrient content, biogas digestate is commonly used as bio-fertilizer and soil improver (Lu and Xu 2021). However, this practice recently raises some environmental concerns due to the risk of ammonia emission and the presence of pathogens, organic micropollutants, and heavy metal contents (Nkoa 2014). This leads to more stringent control on digestate-based fertilizer, creating disposal problems for biogas plants (Dahlin, Herbes et al. 2015). In addition, there is another major issue related to the inadequate availability of suitable feedstock to meet the biogas production target (Divya, Gopinath et al. 2015).

Process integration of anaerobic digestion (AD) and hydrothermal gasification (HTG) is a potential answer to both challenges. The idea of the integration is to process the digestate through HTG to generate producer gas, with a possibility of recycling the producer gas back into the AD. Previous experimental studies have confirmed that biomethane production can be improved through producer gas recycle into the AD (Li, Chen et al. 2019). Therefore, the integration provides simultaneous benefits: 1) reducing the amount of material disposal; 2) enabling the AD to utilize a wider feedstock selection, including materials containing non-digestible fractions; and 3) enhancing biogas production through producer gas recycling.

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The implementation of AD-HTG integration with producer gas recycling requires comprehensive understanding about the impact of important operating parameters on the behavior of producer gas from the HTG. Studies about the effects of process parameters on HTG has been carried out previously (Yakaboylu, Harinck et al. 2013, Okolie, Nanda et al. 2020), however, the use of biogas digestate as a feedstock has not been investigated. In addition, the effect of feedstock ash content has not been reported.

In this paper, an HTG Aspen Plus model with Gibbs free energy minimization is developed to study the effect of process parameters in biogas digestate HTG. The effect of temperature, pressure, feed concentration, and feedstock ash content on the producer gas yield and composition is thermodynamically evaluated. The result of this research provides an important insight for the future development of AD-HTG integration.

2. Methods

2.1 Model Description

An HTG process model is developed in Aspen Plus to represent the typical experimental setup used in previous HTG studies (Byrd, Pant et al. 2007, Byrd, Pant et al. 2008). The same setup, as presented in Figure 1, has also been repeatedly adopted in numerous HTG modelling works utilizing Aspen Plus (Hantoko, Su et al. 2018, Okolie, Nanda et al. 2020). In the Aspen Plus model, the biogas digestate feedstock is regarded as non-conventional component specified by its proximate and ultimate composition. The composition is obtained from biogas digestate data available in literature (Parmar and Ross 2019) and summarized in Table 1 and Table 2. The inorganic contents of the feedstock are lumped together as a single ash input. The PUMP and HEATER blocks are used to adjust the pressure and temperature of the feedstock to the reaction condition. The HTG reactor is represented by integrating two blocks of reactors (RYIELD and RGIBBS). The RYIELD is employed to break down the non-conventional feedstock component into its elements (C, H, O, N, S, and ash) based on the ultimate composition. For this purpose, a Fortran statement is written on a calculator block embedded in the RYIELD reactor. The output from the RYIELD flows into RGIBBS, where the Gibbs free energy minimization occurs. Following HTG, the reaction products are cooled in COOLER and brought to SEP block for separation of producer gas from the liquid product. The Peng-Robinson EoS (equation of state) is chosen for the Aspen Plus model. The process conditions range used for parametric investigation is summarized in Table 3.

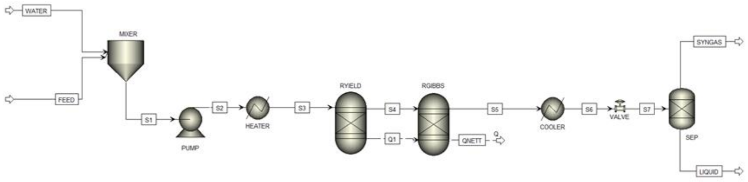

Figure 1: Flowsheet of Aspen Plus Model

Table 1: Proximate Analysis of Feedstock Materials (Parmar and Ross 2019)

Proximate Analysis (wt%)	Value (db)
Fixed Carbon	8.3
Volatile Matters	36.2
Ash	55.5

Table 2. Ultimate Analysis of Feedstock Materials (Parmar and Ross 2019)

Ultimate Analysis (wt%)	Value (db)
C	24.1
H	1.7
O	16.9
N	1.5
S	0.2

Table 3. Process Conditions for Parametric Investigation

Parameters	Value
Temperature	400-600 ^{o}C
Pressure	250-300 bar
Feedstock concentration wt%	10-50%

2.2 Chemical Reactions in Hydrothermal Gasification

HTG of biomass involves a complex combination of chemical reactions. Equation (1) to (3) are commonly recognized as the main chemical reactions in HTG, generating H_2, CO, CO_2, and CH_4 as the major components in the gaseous phase (Yang, Wang et al. 2021). The steam reforming reaction (Equation 1) is an irreversible and highly endothermic reaction responsible for producing CO and H_2 (Yang, Wang et al. 2021). Following the production of CO, two subsequent reactions take place. The water-gas shift reaction (WGSR) converts CO and water from the hydrothermal environment into CO_2 and more H_2 (Equation 2), whereas the methanation reaction (Equation 3) produces CH_4 from H_2 and CO. Both WGSR and methanation reaction are reversible reactions with exothermic nature (Xu, Peng et al. 2021). Additionally, the methanation reaction (Equation 3) is pressure-dependent based on Le Chatelier’s principle. According to the principle, increasing pressure will push the equilibrium reaction towards the side with smaller total reaction coefficients (Susanti, Kim et al. 2014).

$$\mathrm{CH_xO_y} + (1-\mathrm{y})\mathrm{H_2O} \rightarrow \mathrm{CO} + \left(1+\frac{\mathrm{x}}{2}-\mathrm{y}\right)\mathrm{H_2} \tag{1}$$

$$\mathrm{CO} + \mathrm{H_2O} \leftrightarrow \mathrm{CO_2} + \mathrm{H_2} \qquad \Delta\mathrm{H}(25\ ℃) = -41.14\ \mathrm{kJ/mol} \tag{2}$$

$$\mathrm{CO} + 3\mathrm{H_2} \leftrightarrow \mathrm{CH_4} + \mathrm{H_2O} \qquad \Delta\mathrm{H}(25\ ℃) = -205.89\ \mathrm{kJ/mol} \tag{3}$$

3. Results and Discussion

3.1 Model Validation

Figure 2 displays the comparison of modelling result against experimental data from the HTG of cornstarch (Antal Jr, Allen et al. 2000). It shows that the model predicts H_2, CO, CO_2, and CH_4 composition in the producer gas with a high accuracy. This result suggests a good reliability of the Aspen Plus model.

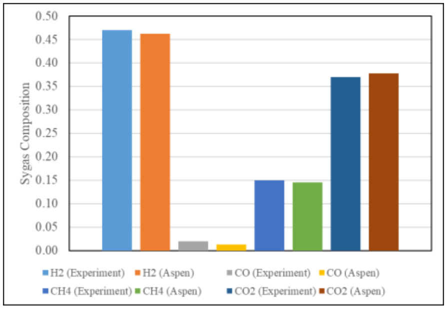

Figure 2. Validation Result of Aspen Plus Model

3.2 Effect of Temperature of Gas Composition and Yield

The effect of temperature on the gas product composition is presented in Figure 3 (a). This result was obtained at the pressure of 280 bar and feedstock concentration of 10 wt%, with temperature ranging within 400-600 ºC. An increase in temperature enhances the endothermic steam reforming reaction (Equation 1). Accordingly, H_2 production is promoted at higher temperature. Additionally, as the temperature increases, the highly exothermic methanation reaction (Equation 3) is pushed towards the backward direction, therefore converting CH_4 into H_2. This consequently leads to lower CH_4 concentrations at higher temperatures. For the entire temperature range of the investigation, only negligibly small amounts of CO are present in the product gas mixture. This indicates that CO is almost completely consumed during the HTG process via the WGSR and methanation reactions. The result also suggests that the temperature influence on CO_2 concentration is not prominent. A possible contributing factor for this is the slightly exothermic nature of the WGSR reaction (Equation 2) which can be translated to a relatively weak temperature dependence of CO_2 production. Similar results were reported in previous studies involving hydrothermal gasification of other biomass feedstocks (Tang and Kitagawa 2005, Voll, Rossi et al. 2009). Figure 3 (b) displays the effect of temperature on the overall gas yield. It is evident from the figure that temperature has a positive effect on the total gas production. This result agrees well with an earlier study which also found that temperature positively influences the overall gas yield in the HTG of almond shells, algae, and sludge (Macrì, Catizzone et al. 2020).

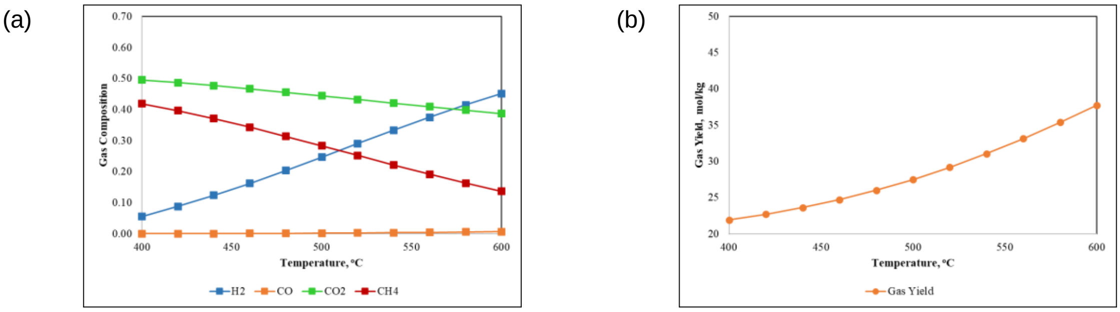

Figure 3. Effect of Temperature on (a) Gas Composition and (b) Gas Yield

3.3 Effect of Pressure on Gas Composition and Yield

The effect of pressure towards gas composition is displayed in Figure 4 (a). This figure was obtained at the reaction temperature of 600 ^{o}C, feedstock concentration of 10 wt%, and pressure range of 250-300 bar. The figure clearly indicates that pressure gives minor influence towards the gas composition in biogas digestate HTG. It can be observed, however, that a rise in pressure slightly decreases H_2 and increases CH_4 content. This trend is consistent with the Le Chatelier principle, which suggests that HTG pressure only affects the methanation reaction, where higher pressure promotes the production of CH_4 from H_2. Similar findings were reported in the HTG studies of other feedstocks (Castello and Fiori 2011, Hantoko, Su et al. 2018). However, the absolute value of total gas yield is negatively affected by the change of pressure, as indicated by Figure 4 (b).

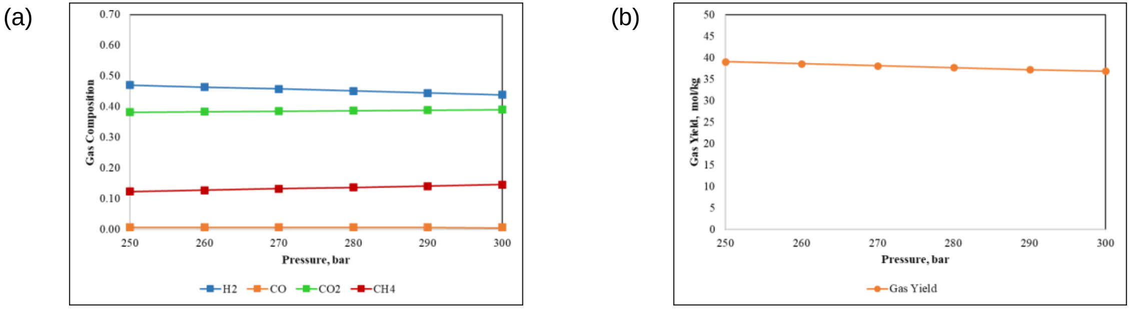

Figure 4. Effect of Pressure on (a) Gas Composition and (a) Gas Yield

3.4 Effect of Feed Concentration on Gas Composition and Yield

The influence of feedstock concentration towards gas composition is presented in Figure 5 (a). The feedstock concentration is defined as mass percentage of feedstock over the total mass of feedstock and water. The parametric investigation was performed by keeping the total mass constant; therefore, a higher feed ratio or percentage represents more feedstock and less water in the reaction system. The feedstock concentration was varied from 10 to 50 wt%, whereas the temperature and pressure were set at 600 ^{o}C and 280 bar, respectively. The presence of water strongly affects the yield and composition of HTG products since the water acts as reactant in the HTG reactions as presented earlier.

As the feedstock concentration increases, H_2 composition drops notably. There are two possible factors responsible for this. First, the decreasing amount of water shifts the WGSR (Equation 2) backward. Second, the methanation reaction (Equation 3) is pushed forward. These actions result in less H_2 present in the product gas mixture. However, CO_2, which is consumed in the backward direction of the WGSR, is only slightly affected by the change in feedstock concentration. This implies that the influence of feedstock concentration towards the WGSR is not prominent, and the decrease in H_2 concentration is mainly contributed by the methanation reaction. This is consistent with the observation that CH_4 production is promoted with the increase in feedstock concentration. Similar observation was reported for a HTG simulation study of dewatered sewage sludge (Hantoko, Su et al. 2018), where the concentration of H_2 was found decreased and the concentration of CH_4 was increased with higher feedstock concentrations. On the other hand, the effect of feedstock concentration on the producer gas yield is displayed on Figure 5 (b). The result shows that a higher feedstock concentration results in lower overall gas yield, as also reported in an earlier study (Onwudili and Williams 2014).

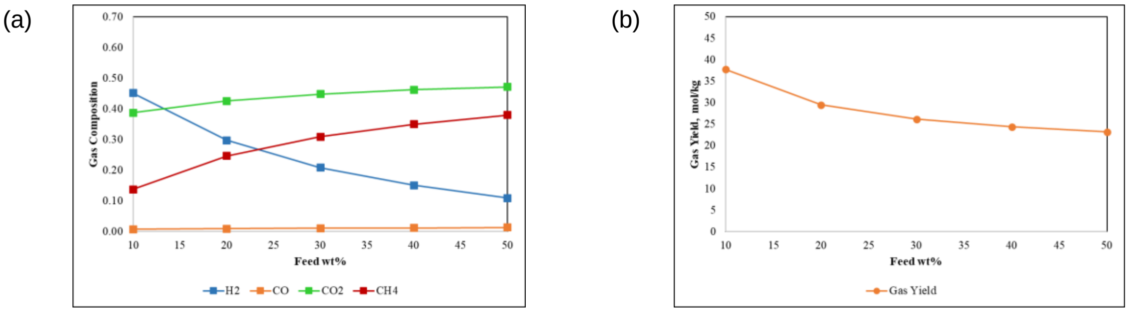

Figure 5. Effect of Feedstock Concentration on (a) Composition and (a) Yield of Product Gas

3.5 Effect of Ash Content on Gas Composition and Yield

The influence of ash content on the composition and yield of product gas is presented in Figure 6. It is important to note that the ash content of biomass feedstock was defined as a non-conventional lumped component. This is due to the limitation in the Aspen Plus database. Non-conventional components in Aspen Plus are not characterized by molecular formula and not considered as chemical components. The only properties calculated for non-conventional components are enthalpy and density, using empirical correlations. Consequently, no thermodynamic or transport properties are available for the non-conventional components, and they are excluded from any phase or chemical equilibrium calculations (Onarheim, Solantausta et al. 2015). The trend demonstrated in Figure 6, therefore, does not account for any chemical activities of ash components in the feedstock. Indeed, Figures 6a and 6b indicate that ash content affects both the gas composition and the gas yield. However, this effect is attributed to the change in organic components content, i.e., C, H, O, N, and S, with respect to the ash content. As the ash content increases, the organic content decreases accordingly, while the amount of water was kept constant. Hence, a higher ash content can be translated to a lower concentration of organic components in the water. This trend is therefore related to the effect of feedstock concentration, as previously discussed in section 3.4. Higher ash contents or lower combustibles lead to higher H_2 contents, lower CO_2 and CH_4 contents in the product gas, and higher overall gas yields.

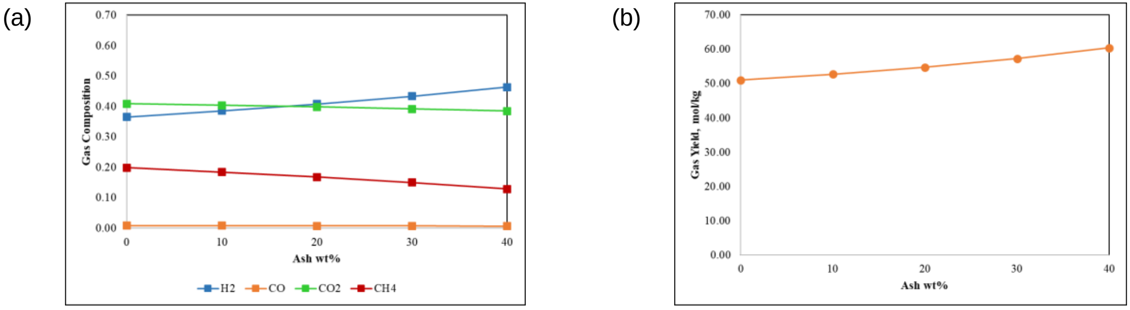

Figure 6. Effect of Ash Content on (a) Gas Composition and (a) Gas Yield

4. Conclusions

The influences of the important process parameters including temperature, pressure, feed concentration, and feedstock's ash content on HTG of biogas digestate were thermodynamically evaluated using Aspen Plus software. It was observed that temperature effect was positive on the H_2 yield, but negative on the CH_4 yield, and only slightly affected the CO_2 yield. Temperature also had a positive effect on the total producer gas yield. The influence of pressure was less significant, although a rise in pressure slightly decreased the H_2 yield, increased the CH_4 yield, and lowered the total yield of the gaseous product. On the other hand, higher feedstock concentration had a significant effect on increasing the CH_4 and decreasing the H_2 yield and the overall product gas yield. It was also found that higher ash contents led to increased H_2 yield, lower CO_2 and CH_4 contents, and higher total product gas yield. However, the influence of ash content captured in this study does not represent any chemical activities of the ash components.

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