CHEMICAL ENGINEERING TRANSACTIONS

VOL. 105, 2023

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: David Bogle, Flavio Manenti, Piero Salatino

ISBN 979-12-81206-04-5; **ISSN** 2283-9216

DOI: 10.3303/CET23105037

Hydrothermal Gasification of Biogas Digestate: a Parametric Study using a Matlab-based Code

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In this work, effect of process parameters on hydrothermal gasification (HTG) of biogas digestate are thermodynamically investigated using a Matlab-based code, which is capable of modelling the effects of the feedstock's inorganic contents and elements. The effects of temperature (400-600 ºC), pressure (250-300 bar), and feed concentration (10-40 wt%) towards the producer gas yield and composition are evaluated while considering the influence of inorganic components in the feedstock. The result shows that temperature and feed concentration play significant roles in determining producer gas composition and yield, whereas pressure only has little influence. Hydrogen production is favored by higher temperature, lower pressure, and lower feed concentration. It was also observed that the presence of inorganic components in the feedstock reduces the production of CO_2, while H_2 and CH_4 is increased. The result of this study is essential in the future development of biogas digestate HTG.

1. Introduction

In the recent years, the increasing urgency of combatting with climate change has been accelerating the energy transition towards renewable and sustainable resources. Biogas produced from low-grade biomass materials via anaerobic digestion is an important alternative in this transition, mainly due to its flexibility to be used as transport fuel, heat, and electricity sources (Scarlat, Dallemand et al. 2018). However, the biogas technology still faces significant issues associated with complicated treatment and management of digestate (Nkoa 2014, Guilayn, Rouez et al. 2020), as well as insufficient supply of sustainable feedstock (Divya, Gopinath et al. 2015). A potential solution to overcome both problems is by integrating anaerobic digestion (AD) with hydrothermal gasification (HTG). In such an integrated system, wet digestate produced from the AD unit can be gasified, with no need of drying, in the HTG unit to reduce the load of digestate management and to recover the energy content remaining in the digestate. This integration can also widen the AD feedstock choices to include lignocellulosic biomass, which normally is not very suitable as AD feedstock due to their composition and structure complexity (Sudibyo, Pecchi et al. 2022). On the other hand, the producer gas generated from the HTG unit can be recycled back to the AD for enhancing the biogas production (Yang, Liu et al. 2020).
The implementation of AD-HTG integration with producer gas recycling requires a comprehensive understanding about the impact of process parameters on HTG performance including the yield and composition of the producer gas. Past parametric studies on HTG and producer gas using thermodynamic modelling approach have been quite active, of which several focused on investigating the effect of different types of biomass feedstock (Freitas and Guirardello 2013, Macrì, Catizzone et al. 2020, Okolie, Epelle et al. 2021). However, to the best of the authors' knowledge, the use of biogas digestate as HTG feedstock has not been studied. More importantly, attempt to investigate the effect of inorganic components of the feedstock on HTG performance was very limited, while it has been reported that the inorganic components of the feedstock could cause significant differences between modelling and experimental data (Mutlu and Zeng 2020). This suggests the importance of considering the feedstock's inorganic components and their chemistry in HTG modelling.

Paper Received: 14 February 2023; Revised: 6 April 2023; Accepted: 5 June 2023
Please cite this article as: Rahma F.N., Li T., Khalil R., Tran K.-Q., 2023, Hydrothermal Gasification of Biogas Digestate: a Parametric Study Using a Matlab-based Code, Chemical Engineering Transactions, 105, 217-222 DOI:10.3303/CET23105037

The present research aims to investigate into parametric effects on HTG performance and the behavior of producer gas from the HTG of biogas digestate while taking into account the effect of feedstock's inorganic components. For this purpose, a multiphase thermodynamic model developed in Matlab by Yakaboylu et al. (Yakaboylu, Harinck et al. 2014), which is capable of predicting compound formation over a wider range of feedstock types as well as using more updated thermodynamic data for the solute species, will be employed. The effect of key process parameters such as temperature, pressure, and feedstock dry matter content on the producer gas composition and yield is evaluated. This work would serve as a foundation for future development of an integrated AD-HTG system, considering the effect of inorganic components of the feedstock.

2. Methods

2.1 Model Description

As aforementioned, the present study is carried out, employing the multiphase thermodynamic model developed by Yakaboylu et al. The model has been validated with experimental data. Full description of the model can be found in the literature (Yakaboylu, Harinck et al. 2014). A non-stoichiometric approach based on Gibbs free energy minimization is adopted in the model. For a given temperature and pressure, the model predicts product composition at the system's equilibrium state, which is reached when the Gibbs free energy is at minimum with respect to all possible changes. The equilibrium state is mathematically defined in Equation (1).

$$(d\mathrm{G}^t)_{T,P} = 0 \tag{1}$$

The model is capable of predicting phase distribution of product components by performing multiphase thermodynamic calculations, considering both organic and inorganic components in the feedstock. In a multiphase system, the total Gibbs free energy is calculated as the sum of Gibbs free energy from each phase. Hence, in this thermodynamic model, the Gibbs free energy calculation is carried out for three phases included in the system, namely 1) gas phase, 2) pure condensed phases, and 3) aqueous solution phases. The total Gibbs free energy is presented in Equation (2), where the subscripts i and w refers to component i and water, respectively. The terms n, μ, g^o, x, and γ respectively represent the component mole amount, the gas chemical potential, the component's standard molar Gibbs free energy, the component mole fraction, and the activity coefficient based on the component mole fraction.

$$\begin{aligned} G = \sum_{\substack{\text{gas}\\ \text{phase}}} n_i \mu_i + \sum_{\substack{\text{pure}\\ \text{condensed}\\ \text{phases}}} n_i\, g_i{}^o + n_w(g_w{}^o + RT\ln x_w + RT\ln\gamma_w) \\ + \sum_{\substack{\text{aqueous}\\ \text{solution}}} n_i\,(g_i{}^o + RT\ln x_i + RT\ln\gamma_i) \end{aligned} \tag{2}$$

2.1.1. Calculations for the gas phase

The Gibbs free energy for gas phase is defined as the first term in Equation (2). As the supercritical condition of the HTG system leads to a non-ideal behavior of the gas, the Gibbs free energy calculation is based on the chemical potential of the gases. The gas phase calculation employs Peng-Robinson equation of state (EoS) with thermodynamic data acquired from the FACT53 database of the FactSage software.

2.1.2. Calculations for the pure condensed phase

The second term in Equation (2) represents the Gibbs free energy of the pure condensed phases. The required thermodynamic data for the pure condensed phases was also obtained from the FACT53 database of the FactSage software.

2.1.3. Calculations for the aqueous solution

In Equation (2), the Gibbs free energy of the aqueous solution is represented by the third term for the calculation of water in the aqueous phase, and the last term for the solute species. The thermodynamic data for the solute species were taken from the SUPCRT92 software. For the supercritical region, where the water in the aqueous phase is completely vaporized, the calculation is based on an assumption that the solute molecules interact with gases to form aqueous hydrate complexes (Chrastil 1982).

The thermodynamic model is implemented in Matlab using *fmincon* routine to minimize Equation (2) and obtain the amounts of species at the equilibrium state. A mole and charge balance constraint and non-negativity species amount constraint are applied during the minimization. The required inputs are process conditions, i.e., temperature and pressure, and the molar composition of feedstock and water. The feedstock composition is taken from biogas digestate data available on literature (Parmar and Ross 2019).

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
Ca	10.4
Cl	0.0
K	1.6
Mg	1.4
Na	0.9
P	0.7
Si	10.2

2.2 Chemical Reactions in Hydrothermal Gasification

Hydrothermal gasification of biomass includes a series of chemical reactions which produces H_2, CO, CO_2, and CH_4 as the main components in the gaseous phase. The steam reforming reaction (Equation 3), water gas shift reaction (WGSR) (Equation 4), and methanation reaction (Equation 5) are commonly considered as the main chemical reactions in HTG (Xu, Peng et al. 2021, Yang, Wang et al. 2021). The steam reforming reaction produces CO and H_2 from endothermic decomposition of biomass. The reversible WGSR produces more H_2 and CO_2 through exothermic reaction of CO and H_2O. On the other hand, the reversible methanation reaction consumes H_2 to react with CO, producing CH_4 and H_2O (Yang, Wang et al. 2021).

$$\mathrm{CH_xO_y} + (1-\mathrm{y})\mathrm{H_2O} \rightarrow \mathrm{CO} + \left(1 + \frac{\mathrm{x}}{2} - \mathrm{y}\right)\mathrm{H_2} \tag{3}$$

$$\mathrm{CO} + \mathrm{H_2O} \leftrightarrow \mathrm{CO_2} + \mathrm{H_2} \qquad \Delta\mathrm{H}(25\ ^\circ\mathrm{C}) = -41.14\ \mathrm{kJ/mol} \tag{4}$$

$$\mathrm{CO} + 3\mathrm{H_2} \leftrightarrow \mathrm{CH_4} + \mathrm{H_2O} \qquad \Delta\mathrm{H}(25\ ^\circ\mathrm{C}) = -205.89\ \mathrm{kJ/mol} \tag{5}$$

3. Results and Discussion

3.1 Effect of Temperature

Figure 1 (a) shows the effect of temperature towards the producer gas composition at different weight percentages of inorganic components. The temperature influence observed in this figure agrees well with previous studies (Tang and Kitagawa 2005, Voll, Rossi et al. 2009). Higher temperature enhances hydrogen production by promoting the endothermic steam reforming reaction (Equation 3). As the temperature increases, the methanation reaction (Equation 5) is also reversed, therefore CH_4 is consumed to produce more H_2. This also explains the decrease in methane production at higher temperature. The production of CO_2 is favored at lower temperatures, although the temperature dependence is less significant since WGSR is only slightly exothermic. The amount of CO is negligible at the investigated temperature range, indicating that CO is almost completely consumed in the WGSR and methanation reaction. On the other hand, Figure 1 (b) shows that the total gas yield is positively influenced by temperature. This result is in agreement with the literature, concerning with HTG of other biomass feedstocks (Voll, Rossi et al. 2009, Freitas and Guirardello 2014).

In addition, both figures also demonstrate the effect of inorganic contents on the producer gas yield and composition. For any temperature within the observed range, a higher inorganic content always leads to a lower production of CO_2. This might be due to the formation of inorganic salts such as $CaCO_3$, Na_2CO_3, and K_2CO_3 from the reactions between inorganic components and CO_2. As a consequence of the lower CO_2 composition, the WGSR is driven towards the forward direction to produce more H_2. This explains the higher H_2 composition at higher inorganic content. The result is consistent with the experimental observation reported by Guo et al.

(Guo, Guo et al. 2012) and Xu et al (Xu, Wang et al. 2009). Furthermore, Onwudili et al. (Onwudili and Williams 2014) argued that the presence of alkali metals promotes hydrogen production by accelerating the WGSR through the removal of CO_2 as carbonate. Su et al. (Su, Yan et al. 2022) also reported that the production of potassium salts improves the WGSR, resulting in higher H_2 production. The increased H_2 amount due to higher inorganic contents also enhances the production of CH_4 through the methanation reaction. Furthermore, Figure 1 (a) shows that the effect of inorganic contents on gas composition is more prominent at lower temperatures. This might be due to the decreasing carbonate salts forming reaction at higher temperature, which is consistent with the simulation result, although not presented in this paper.

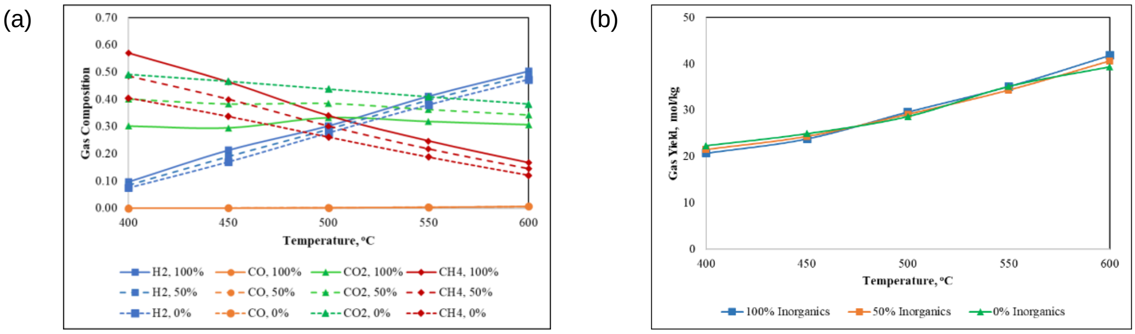

Figure 1. The effect of temperature on producer gas (a) composition and (b) yield at different inorganic contents (P = 280 bar, feedstock concentration = 10%, inorganic contents = 100%, 50%, and 0% wt.)

The effect of inorganic contents on the total gas yield is presented in Figure 1 (b). The figure indicates that at lower temperature, higher inorganic contents are associated with lower gas yields. The trend is reversed at higher temperatures, where a higher gas yields are obtained for the feedstock with higher inorganic contents.

3.2 Effect of Pressure

Figure 2 (a) and (b) demonstrate how pressure influences the producer gas composition and yield. It is observed that pressure gives minor effect on both gas composition and yield. However, a slight decrease in H_2 production and increase in CH_4 formation is observed at higher pressures. According to the Le Chatelier principle, higher HTG pressure promotes the methanation reaction (Equation 5), hence more CH_4 is produced from H_2. This result agrees well with findings from previous studies (Castello and Fiori 2011, Hantoko, Su et al. 2018).
The effect of different inorganic contents of the feedstock is also displayed in both figures. Consistent trends similar to what presented in the previous section are also observed. Higher inorganic contents negatively affect CO_2 formation, however, the production of both H_2 and CH_4 is increased. The increase in H_2 and CH_4 production is more significant than the decrease in CO_2. Overall, the total gas yield increases for higher inorganic contents, as indicated by Figure 2 (b).

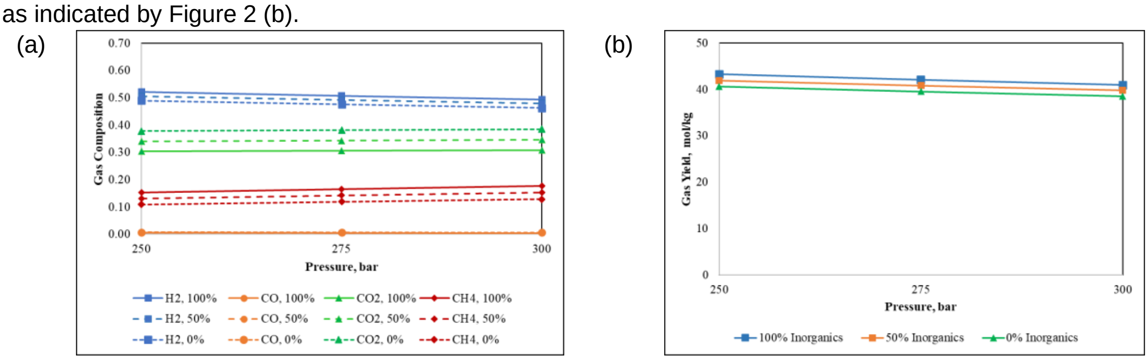

Figure 2. The effect of pressure on producer gas (a) composition and (b) yield at different inorganic contents (T = 600 °C, feedstock concentration = 10%, inorganic contents = 100%, 50%, and 0% wt.)

3.3 Effect of Feed Concentration

The effect of feed concentration on gas composition and yield is presented on Figure 3 (a) and (b), respectively. Note that, for this investigation, the total mass of feed and water was kept constant during the simulation. Therefore, a higher feed concentration represents a higher amount of feed and lower amount of water. In an HTG system, water acts as a reactant which can significantly influence the chemical reactions. Figure 3 (a) indicates that H_2 composition is significantly reduced at higher feed concentration. This is because the decreasing water amount affects the methanation reaction, pushing it towards the direction of CH_4 production

from H_2. This is also consistent with the significant increase in CH_4 composition at higher feed concentration. On the other hand, Figure 3 (b) indicates that the overall gas yield decreases notably at higher feed concentration. Similar findings were previously published in an earlier study (Hantoko, Su et al. 2018).
Both Figure 3 (a) and (b) also demonstrate the effect of inorganic contents on the producer gas yield and composition. Similar with the result presented in the previous sections, a higher inorganic content always leads to a decrease in CO_2 composition and increase in H_2 and CH_4 composition. According to the simulation result, the formation of carbonate salts is promoted at higher feed composition. Consequently, the effect of inorganic contents on gas composition is more prominent when the feed composition is higher.

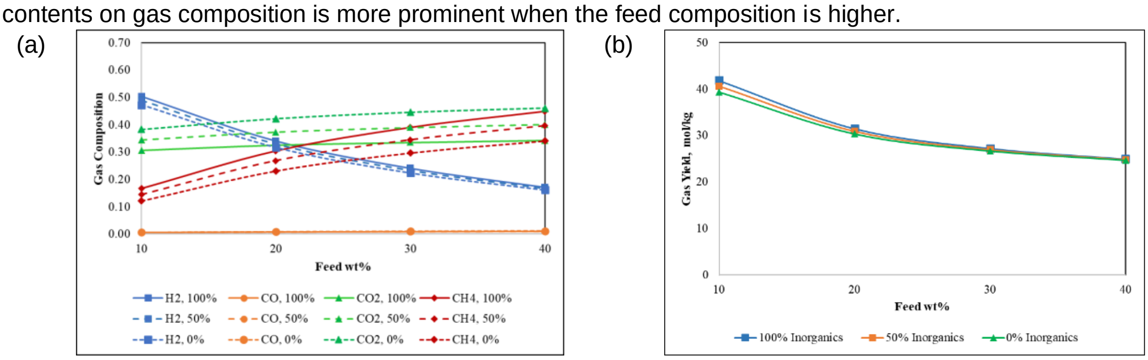

Figure 3. The effect of feedstock concentration on producer gas (a) composition and (b) yield at different inorganic contents (T = 600 °C, P = 280 bar, inorganic contents = 100%, 50%, and 0% wt.)

4. Conclusions

The present work investigated the influence of important process parameters in the HTG of biogas digestate such as temperature, pressure, and feed concentration, while taking into account the effect of inorganic contents in the feedstock. The study found that temperature rise increases H_2 composition and decreases CH_4 composition, while CO_2 composition is only slightly affected. Temperature also positively influences the total gas yield. Pressure has less significant effect, however, a slight increase in total gas yield and CH_4 composition and a slight decrease in H_2 composition is observed at higher pressure. A higher feed concentration significantly increases the production of CH_4, while H_2 composition, and overall gas yield decrease. Furthermore, it was observed that higher inorganic contents lead to a lower CO_2 composition, while H_2 and CH_4 composition are increased. These results provide a novel insight on a thermodynamic model's behavior when the feedstock inorganic content is considered.

Acknowledgement

This work was supported by the BioSynGas project partly funded by the Research Council of Norway (Project Number: 319723). The authors also want to thank Onursal Yakaboylu for developing the Matlab model used in this study, and for his valuable inputs and discussions

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