Thermodynamic analysis of supercritical water gasification of oleic acid for hydrogen production

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Abstract. In this study, the equilibrium behaviour of palmitic acid in supercritical water gasification was investigated, using the Gibbs minimum free energy employed within the HSC. The effects of concentration, temperature, and pressure on gas production were studied. The model predictions have been validated by comparing the results with published literature under identical conditions, and the agreement is generally satisfying.

1. Introduction
The shortage of fossil fuels and the growing concerns about the environment problems make hydrogen an alternative clean source for energy generation. Hydrogen is mainly obtained from natural gas and oil fractions reforming, which are abundant and economic raw materials [1]. However, the use of natural gas and oil produces large quantities of carbon dioxide. Because of this, biomass have attracted a growing interest for energy generation.

Supercritical water gasification (SCWG) is a promising technology of biomass for producing the hydrogen, methane, and the other gases. Water above its critical point (Tc = 374.15 °C, Pc = 22.12 MPa) has unique physical-chemical properties. Water is much less polar in this state and become a good solvent for nonpolar compounds and gases, chemical reactions can be conducted in a single phase, which reduce the mass transfer resistance [2]. The high density and high thermal conductivity associated with supercritical water are beneficial in developing a compact reformer system [1]. SCWG does not require the energy consumption pretreatment of dewatering or drying process that other thermochemical processes require.

Thermodynamics analysis of SCWG have been widely studied on various model compounds (such as isooctane, hexadecane, methanol, ethanol, glycerol, glucose and cellulose) [3-5] and real biomass (such as sewage sludge, wheat straw black liquor, microalgae, and cornstarch) [6-8]. For example, Adhikari et al. [9] have shown that increasing the water to carbon ratio increases the yield of hydrogen and minimizes the yield of CO at high temperature reforming glycerol. Algal and sewage sludge has attracted growing attention. They mainly consist of lipid, protein, and carbohydrates. As mentioned above, some work had been done on model compounds. However, palmitic acid (PA), the most abundant saturated fatty acid among lipid, has not been investigated of SCWG thus far.

Therefore, the present work reports a new parametric study on thermodynamic equilibrium analysis of PA of SCWG, using the HSC simulation, and employing the Gibbs minimum free energy model. The model has been validated by comparing its results with theoretical and experimental results of literature, which revealed a good agreement.
2. Methodology
PA was selected as a saturated fatty acid model compound and its SCWG process was studied by using the HSC. The model is based on the minimization of Gibbs free energy.

SCWG of PA for hydrogen production can be summarized by following reactions:

Steam reforming:

\[
\text{C}_{16}\text{H}_{32}\text{O}_2 + 14 \text{H}_2\text{O} = 16 \text{CO} + 30 \text{H}_2 \quad \Delta H(25^\circ C) = 2509.62 \text{ kJ} \cdot \text{mol}^{-1}
\]

\[
\text{C}_{16}\text{H}_{32}\text{O}_2 + 30 \text{H}_2\text{O} = 16 \text{CO}_2 + 46 \text{H}_2 \quad \Delta H(25^\circ C) = 1851.41 \text{ kJ} \cdot \text{mol}^{-1}
\]

Water gas shift reaction:

\[
\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2 \quad \Delta H(25^\circ C) = -41.14 \text{kJ} \cdot \text{mol}^{-1}
\]

Methanation of CO:

\[
\text{CO} + 3 \text{H}_2 = \text{CH}_4 + \text{H}_2\text{O} \quad \Delta H(25^\circ C) = -205.89 \text{kJ} \cdot \text{mol}^{-1}
\]

As a result, the product stream is a mixture of above gases, furthermore, the hydrogen production depends on several operating parameters, such as concentration, temperature, and pressure.

The total Gibbs free energy of a system is given as shown in the following equations [1].

\[
\mathcal{G} = \sum_{i=1}^{K} n_i \mu_i
\]

\[
\mu_i = RT \left[ \ln \left( \frac{\phi_i p}{p_0} \right) + \ln(X_i) + G_i^0(T, p_0) \right]
\]

When the system is in equilibrium at a certain temperature and pressure, \( G \) is minimum, where \( n_i \) must satisfy the mass conservation and non-negativity.

\[
\sum_{i=1}^{K} \beta_i n_i = \beta_e (e = 1, 2, 3, \ldots, M)
\]

\[
0 \leq n_i \leq n_{IT} (i = 1, 2, 3, \ldots, K)
\]

Where \( n_i \) represents the number moles of species \( i \); \( \beta_e \) represents the number moles of element \( e \) in species \( i \); \( \beta_e \) represents the total number moles of element \( e \) in the system; \( n_{IT} \) represents the possible number moles of species \( i \)

3. Results and discussion

3.1. Model validation
The predictions of the HSC were validated by comparing its results with previous published data under identical conditions. Figure 1 shows that the equilibrium dry mole fractions of gas species was in close agreement with Tang [10]. Modeling data on the SCWG of cellulose have also been modelled. As shown in Figure 2, the modelling results in this study revealed a good agreement.
3.2. Effects of concentration

Concentration is a key parameter for SCWG, which directly influence the capacity of a SCWG system. The effect of concentration was studied under isothermal conditions at a temperature of 600 °C and a pressure of 25 MPa as shown in Figure 3. It was found that the mole fraction of hydrogen was the largest and steeply decreased, from 52% to 4% as the concentration of PA increases from 5wt% to 60wt%. The decrease is connected with a significant increase of methane mole fraction from 21% to 68%. At higher concentrations of PA, the reduction of hydrogen yield is usually due to the lower water content in the reaction system, which reduces the possibility of overcoming the equilibrium limit of steam reforming reaction. Other researchers [1] have reported the similar phenomena. The increase of methane content is mainly related to the methanation reaction promoted at higher concentrations. The increase of PA content has little effect on carbon dioxide and monoxide. The yield of CO is the lowest among the gases, because it is consumed on the methanation and water gas shift reaction, this was also observed during the modelling and experiment of supercritical water reforming of different model compounds [1].

It was also observed that although hydrogen mole fraction decreases, its production first increased and then decreased. The hydrogen production increased from a concentration between 5wt% and 28wt%, then it began to decrease. The hydrogen production provides a practical approach to determine the optimum PA concentration. The maximum production of hydrogen was 0.07 mol per mol of the feed.
3.3. Effects of temperature

According to the optimization concentration (28wt%) in Section 3.2, the effects of temperature on gas equilibrium mole production of gases was investigated as shown in Figure 4. Unlike the concentration, the hydrogen production increases sharply when the temperature goes from 400 to 800 °C, along with methane reduction. It is because with the temperature increases, the steam reforming reaction is promoted, that is, the generation of hydrogen is promoted, and the methanation reaction is inhibited, reducing the generation of methane and consumption of hydrogen. Byrd [3] also reported that the water gas shift reaction, which is slightly exothermic as shown in equation (3), is possibly to cause such an increase during the methanol SCWG. It was also observed that the hydrogen production increases sharply from 600 °C, along with CO production begin to increase, similarly, Louw et al. [2] had pointed that thermodynamics play a definitive role in SCWG at temperatures greater than 600 °C.

3.4. Effects of pressure

As shown in Figure 5, when the operating pressure increased from 25 to 35 MPa, the effect on gas production was minimal. Louw [2] had also reported that an increase in the pressure did not seem to have a significant effect on the gas yields. Methane, carbon dioxide, and carbon monoxide yields barely changed, while hydrogen production decreased slightly, which are possibly because of the enhancement
of methanation. However, when the system pressure increases, the pump, pipe, heat exchanger, and reactor costs will drastically increase.

![Graph Showing Gas Production vs Pressure]

Figure 5. Effect of pressure on the gas production at 600 °C and palmitic acid concentration of 28wt%

4. Conclusion
This study investigated the equilibrium behaviour of the supercritical water gasification of palmitic acid by using Gibbs free energy method in HSC. The hydrogen yields increased before the concentration of palmitic acid reached 28wt%, and then began to decrease, however, the molar ratio of hydrogen was always decreasing. It was observed that an increase in the hydrogen yield and a decrease in the methane yield result from an increase in the operation temperature from 400 to 800 °C. In addition, increasing the operating pressure above the critical pressure of water did not seem to have a significant effect on the gas yields.

References
[1] Alshammari, Y.M. and K. Hellgardt, Thermodynamic analysis of hydrogen production via hydrothermal gasification of hexadecane. International Journal of Hydrogen Energy, 2012. 37(7): p. 5656-5664.
[2] Louw, J., et al., Thermodynamic modelling of supercritical water gasification: investigating the effect of biomass composition to aid in the selection of appropriate feedstock material. Bioresour Technol, 2014. 174: p. 11-23.
[3] Byrd, A.J., K.K. Pant, and R.B. Gupta, Hydrogen production from glycerol by reforming in supercritical water over Ru/Al2O3 catalyst. Fuel, 2008. 87(13-14): p. 2956-2960.
[4] Susanti, R.F., et al., Noncatalytic gasification of isooctane in supercritical water: A Strategy for high-yield hydrogen production. International Journal of Hydrogen Energy, 2011. 36(6): p. 3895-3906.
[5] Voll, F.A.P., et al., Thermodynamic analysis of supercritical water gasification of methanol, ethanol, glycerol, glucose and cellulose. International Journal of Hydrogen Energy, 2009. 34(24): p. 9737-9744.
[6] Cao, C., et al., High-Efficiency Gasification of Wheat Straw Black Liquor in Supercritical Water at High Temperatures for Hydrogen Production. Energy & Fuels, 2017. 31(4): p. 3970-3978.
[7] Louw, J., C.E. Schwarz, and A.J. Burger, Catalytic supercritical water gasification of primary paper sludge using a homogeneous and heterogeneous catalyst: Experimental vs thermodynamic equilibrium results. Bioresour Technol, 2016. 201: p. 111-20.
[8] Yakaboylu, O., et al., Supercritical Water Gasification of Biomass: A Detailed Process Modeling Analysis for a Microalgae Gasification Process. Industrial & Engineering Chemistry Research,
2015. 54(21): p. 5550-5562.

[9] Authayanun, S., et al., Thermodynamic study of hydrogen production from crude glycerol autothermal reforming for fuel cell applications. International Journal of Hydrogen Energy, 2010. 35(13): p. 6617-6623.

[10] Tang, H. and K. Kitagawa, Supercritical water gasification of biomass: thermodynamic analysis with direct Gibbs free energy minimization. Chemical Engineering Journal, 2005. 106(3): p. 261-267.