Simulation of Supercritical Water Gasification of Microalgae for Hydrogen and Methane-rich Gas Production

Sherif Ishola Mustapha, Usman Aliyu Mohammed, Faizal Bux and Yusuf Makarfi Isa

Abstract— The supercritical water gasification of *Nannochloropsis* sp, *Spirulina* sp. and *Scenedesmus obliquus* microalgae was examined using Aspen plus (V11) software. The influence of temperature (400 – 700 °C) and biomass concentration (10 – 40 wt %) on the composition, yield and lower heating value (LHV) of the gaseous product was investigated. The results showed that low temperature and high biomass concentration favors the production of methane-rich gas while high temperature and low biomass concentration favors hydrogen-rich gas production. Higher CH_4 yield was observed at biomass concentration of 40 wt% which is an indication that the methanation reaction is accelerated at higher biomass concentration. The ranking order for the H_2 and CH_4 yield is Nannochloropsis sp> Scenedesmus obliquus> Spirulina sp. The highest LHV of 18.97 MJ/kg, 15.86 MJ/kg and 18.49 MJ/kg was obtained for *Nannochloropsis* sp., *Spirulina* sp. and *Scenedesmus obliquus* respectively at temperature of 400 °C and biomass concentration of 40 wt%.

Keywords— Supercritical water gasification, microalgae, methane, hydrogen.

I. Introduction

Hydrogen and methane are regarded as important components of the future world clean energy portfolio [1, 2]. Supercritical water gasification (SCWG) has the potential to produce high-quality methane-rich and hydrogen-rich gas especially from wet algal biomass without the need for drying the biomass [3]. The factors that could influence the gas yields and compositions include biomass feedstock composition, biomass concentration, gasification temperature, gasification pressure, and residence time [4, 5]. So far, this technique is seen as a more promising gasification pathway for high-moisture-containing biomasses such as microalgae. However, the effect of the factors that could influence the supercritical water gasification efficiency needs to be well understood for the development of optimal processing technique.

The experimental works on supercritical water gasification are time-consuming and expensive in terms of investment cost and consumable materials [6, 7]. Hence, it is necessary to develop a thermodynamic model to simulate the process behavior to save time and resources. Thermodynamic equilibrium model analysis is faster, economically more attractive and can be applied to determine the optimum experimental operating conditions with high accuracy [5]. Till date, only a few studies have been reported on the gasification of microalgae under supercritical water condition. There is a dearth of modelling work on supercritical water gasification of microalgae using Aspen Plus or any other simulation software. This study presents the thermodynamic modelling and simulation of the supercritical water gasification of various microalgae biomass using Aspen Plus. The effect of varying feedstock composition, temperature and biomass concentration on the composition and yield of the gaseous product were investigated and optimum conditions established.

II. Materials and Method

Fig.1 shows the Aspen flow sheet for the supercritical water gasification process. Three different microalgae biomass were considered in this study. The *Scenedesmus obliquus* microalgae was collected from the Institute of water and wastewater technology, Durban University of Technology, Durban, South Africa and characterized for its proximate and ultimate analysis. While *Nannochloropsis* sp. [11] and *Spirulina* sp. [12] were from previous work. The properties of the three microalgae biomass are presented in Table 1. The supercritical water gasification simulation model was developed based on Gibbs free energy minimization using Aspen Plus (Version 11). The simulation methodology reported by [8] was adopted. The list of components added to the simulation includes hydrogen, nitrogen, oxygen, sulfur, carbon monoxide, carbon dioxide, methane, water, ammonia, hydrogen sulfide, solid carbon, and non-conventional biomass and ash. The non-conventional components are modelled by their proximate and ultimate analyses. The Peng-Robinson with Boston-Mathias function (PR-BM) property method was considered for this simulation as it provides good accuracy for gasification simulations [6, 9, 10]. The supercritical water gasification process is simulated using the RYield and RGibbs block as shown in Fig.1. All the

Manuscript received September 10, 2020.

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https://doi.org/10.17758/EARES10.EAP1120237

assumptions made by Atikah and Harun [8] was also considered in this simulation.

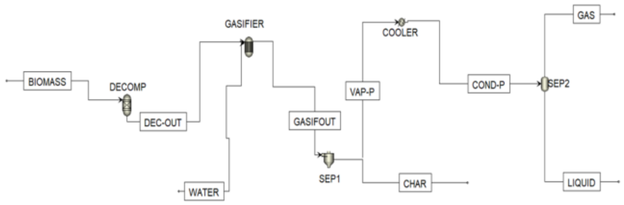

Fig 1. Aspen flow sheet for the supercritical water gasification process

TABLE 1: FEEDSTOCK COMPOSITION FOR THE HYDROTHERMAL GASIFICATION PROCESS

	Nannochloropsis sp.	*Spirulina* sp.	*Scenedesmus obliquus*
	Proximate Analysis (%)		
Moisture	5.00	8.45	4.38
Ash	5.03	13.99	10.17
Volatile matter	79.69	65.48	81.77
Fixed carbon	10.28	12.08	3.68
	Ultimate Analysis (%)		
C	49.07	39.26	45.03
H	7.59	6.11	7.50
N	6.29	6.65	3.59
S	1.42	0.57	0.98
O	35.63	47.41	42.90

III. Results and Discussion

A. *Effect of Temperature on the Composition and Yield of Gaseous Product*

Fig.2 shows the effect of temperature on the composition of hydrogen and methane gas obtained from the supercritical water gasification of *Nannochloropsis* sp., *Spirulina* sp. and *Scenedesmus obliquus* microalgae biomass. The temperature was varied between 400 °C and 700 °C at pressure of 30 MPa and biomass concentration of 10 wt%. As shown in Fig. 2, the composition of H_2 increased while the CH_4 composition decreased in all the three microalgae biomass as the temperature was increased from 400 °C to 700 °C. The three major reactions identified to be responsible for the production of gaseous products during supercritical water gasification process include steam reforming, water-gas shift reaction and methanation [1, 13]. The steam reforming and water-gas shift reactions are responsible for the H_2 production while methanation reaction is responsible for CH_4 production. Methanation and water-gas shift reaction are exothermic reaction usually favored at low temperature. On the other hand, the steam reforming reaction is endothermic favoring the production of hydrogen at higher temperature. The low H_2 composition observed at 400 °C is majorly from the water-gas shift reaction and the H_2 composition increased significantly for all the microalgae biomass as the temperature was increased due to steam reforming reactions which is favored at higher temperature. On the contrary, higher composition of CH_4 was observed at 400 °C and subsequent increase in temperature resulted in decrease of CH_4 composition possibly due to the methanation reaction favored at low temperature.

When the performance of the different microalgae biomass was compared as the temperature was increased from 400 to 700 °C, the H_2 composition increased from 4.45 to 50.235%, 5.20 to 53.845% and 4.84 to 52.60% while CH_4 composition decreased from 49.84 to 12.55%, 41.23 to 5.98% and 48.55 to 10.19% for *Nannochloropsis* sp, *Spirulina* sp. and *Scenedesmus obliquus* respectively. The ranking order for the H_2 composition is *Spirulina* sp.> *Scenedesmus obliquus*>*Nannochloropsis* sp. while the ranking order for CH_4 composition is *Nannochloropsis* sp> *Scenedesmus obliquus*> *Spirulina* sp. The difference in the H_2 and CH_4 composition could result from the variation in the microalgae biomass composition. *Nannochloropsis* sp with the higher lipid content gave the highest composition of CH_4 while H_2 composition was more favored with *Spirulina* sp. having higher carbohydrate content. Also, the degradation of the long-chain fatty acids present in lipids could be responsible for the high yield of CH_4 gas [1]. Some previous have also reported have also reported that the presence of protein and carbohydrate could favor H_2 production [13, 14].

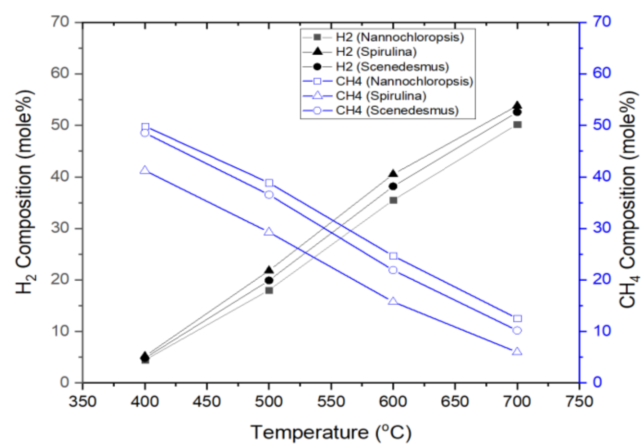

Fig. 2. Effect of temperature on H_2 and CH_4 gas composition (pressure: 30 MPa, biomass concentration: 10 wt%)

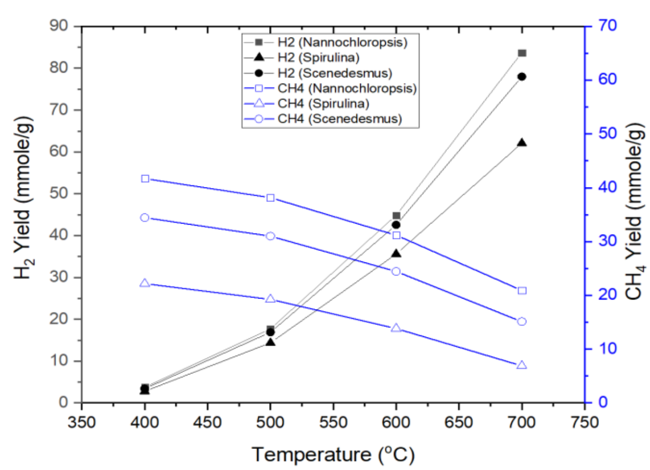

Fig. 3. Effect of temperature on H_2 and CH_4 gas yield (pressure: 30 MPa, biomass concentration: 10 wt%)

In a similar manner, the yield of H_2 produced was found to increase while CH_4 yield decreased as the temperature was increased from 400 °C to 700 °C as shown Fig. 3. The H_2 yield increased from 3.73 to 83.71 mmole/g, 2.80 to 62.09 mmol/g and 3.43 to 77.98 mmole/g while CH_4 yield decreased from 41.71 to 20.92 mmole/g, 22.18 to 6.90 mmole/g and 34.43 to 15.11 mmole/g for *Nannochloropsis* sp, *Spirulina* sp. and *Scenedesmus obliquus* respectively. The ranking order for the H_2 and CH_4 yield is *Nannochloropsis* sp> *Scenedesmus obliquus*> *Spirulina* sp. Although *Spirulina* sp. gave the highest H_2 composition of 53.84%, however, the H_2 yield (62.09 mmole/g) under the same condition was found to be the lowest when compared to *Nannochloropsis* sp. (83.71 mmole/g) and *Scenedesmus obliquus* (77.98 mmole/g). The high ash content and lower carbon content present in the *Spirulina* sp. as shown in Table 1 may be responsible for the lower H_2 yield. Not only that, *Spirulina* sp. biomass has the lowest volatile matter content when compared to *Nannochloropsis* sp. and *Scenedesmus obliquus*. This is a confirmation that biomass feedstock composition has effect on the product yield and composition under the supercritical water gasification process. Previous study by Atikah and Harun [8]) also reported that H_2 production is favored at a higher temperature whereas lower temperature favors CH_4 production.

B. Effect of Biomass Concentration on Composition and Yield of Gaseous Product

The effect of biomass concentration on the gas product yield and composition was examined. The biomass concentration was varied from 10 wt% to 40 wt% at pressure of 30 MPa and temperature of 700 °C. Fig 4 and 5 shows the effect of biomass concentration on H_2 and CH_4 composition and yield respectively. As shown in Fig. 4, the *Spirulina* sp. microalgae gave the highest composition of H_2 at biomass concentration of 10 wt% while *Nannochlopsis* sp. microalgae gave the highest CH_4 composition at biomass concentration of 40 wt%. For the microalgae biomass, the highest H_2 composition was obtained at 10 wt% and decreased as the biomass concentration was increased to 40 wt%. On the contrary, the lowest CH_4 composition was observed at 10 wt% for the microalgae biomass and increase as the biomass concentration was increased to 40 wt%. Biomass concentration could influence the supercritical water gasification process as water is a reactant for the steam reforming and water-gas shift reactions. At lower biomass concentration, more water is available which could accelerate the steam reforming and water-gas shift reactions thereby favoring more H_2 production at lower biomass concentration. In addition, the possibility of the transfer of hydrogen atoms from excess water to the gaseous product during supercritical water gasification process could contribute to the higher H_2 production observed at lower biomass concentration. Previous studies on supercritical water gasification also reported higher hydrogen gasification efficiency at lower biomass concentration [13, 15, 16].

As shown in Fig. 5, Nannochlopsis sp. gave the highest H_2 yield (83.71 mmole/g) at lower biomass concentration of 10 wt% and highest CH_4 yield (36.78 mmole/g) at higher biomass concentration of 40 wt%. The higher CH_4 yield at 40 wt% is an indication that the methanation reaction is accelerated at higher biomass concentration. These findings agree with previous study by Jiao et al. [13]. The higher H_2 yield and CH_4 observed with the *Nannochlopsis* sp. can be attributed to the cumulative effect of low ash content and high lipid content present in the microalgae.

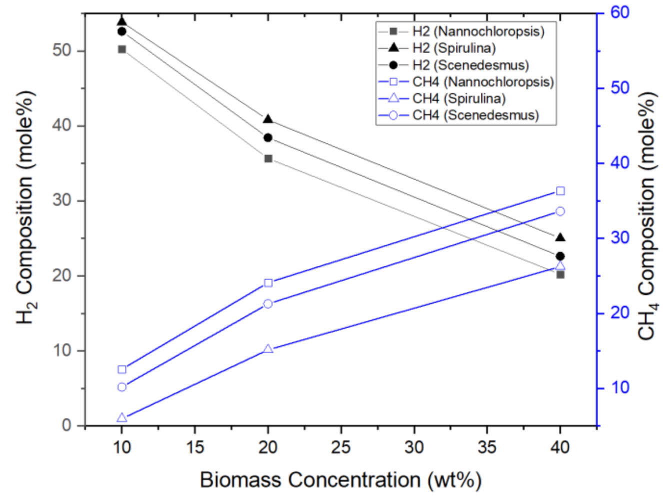

Fig. 4. Effect of biomass concentration on H_2 and CH_4 gas composition (pressure: 30 MPa, temperature: 700 °C)

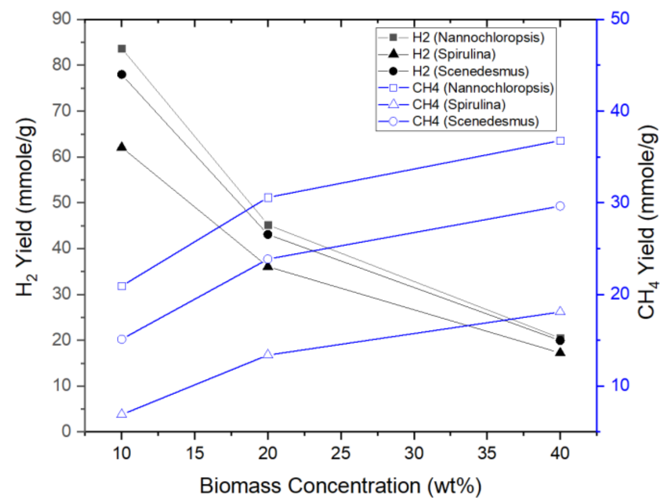

Fig. 5. Effect of biomass concentration on H_2 and CH_4 gas yield (pressure: 30 MPa, temperature: 700 °C)

C. Effect of Temperature and Biomass Concentration on Lower Heating Value of Gaseous Product

The effect of temperature and biomass concentration on the lower heating value (LHV) of the product gas was explored and results presented in Fig. 6. For all the microalgae biomass, the LHV decreases with increase in temperature and the LHV was higher at higher biomass concentration. The highest LHV was observed at temperature of 400 °C and biomass concentration of 40 wt%. Under these conditions, The LHV of 18.97 MJ/kg, 15.86 MJ/kg and 18.49 MJ/kg was observed for *Nannochloropsis* sp., *Spirulina* sp. and *Scenedesmus obliquus* respectively. In terms of ranking order, the LHV of *Nannochloropsis* sp> *Scenedesmus obliquus*> *Spirulina* sp. for all the temperature and biomass concentration considered. The high LHV observed with the *Nannochloropsis* sp. could be as a result of its high lipid content favoring more of CH_4 production which contributed significantly to the high LHV of the product gas.

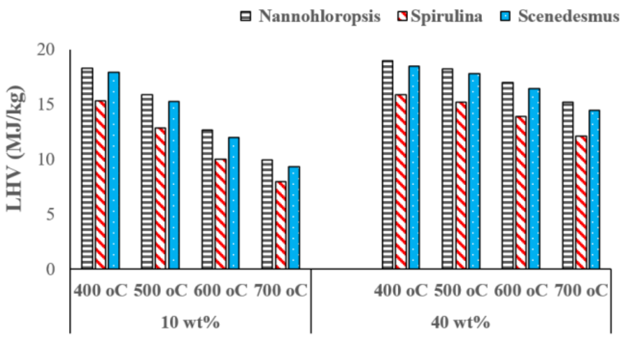

Fig. 6. Effect of temperature at different biomass concentration on the gas mixture lower heating value

IV. Conclusion

This study presents the supercritical water gasification of various microalgae biomass using thermodynamic approach based on Gibbs free energy minimization. Three microalgae biomass which include *Nannochloropsis* sp., *Spirulina* sp., and *Scenedesmus obliquus* with varying composition were considered as feedstock for the supercritical water gasification process and the simulation model was developed using Aspen plus (V11). The results show that higher temperature and lower biomass concentration favor production of hydrogen-rich gas while lower temperature and higher biomass concentration favor methane-rich gas production. *Nannochloropsis* sp. gave the highest lower heating value and also higher yield of H_2 and CH_4 was obtained when compared to *Spirulina* sp., and *Scenedesmus obliquus* microalgae. In terms of ranking order, *Nannochloropsis* sp> *Scenedesmus obliquus*> *Spirulina* sp. The findings showed that feedstock composition, temperature and biomass concentration has a great influence of the yield and composition of the product gas.

Conflict of Interest

The authors declare no competing financial interest.

Acknowledgment

The authors thankfully acknowledge the financial support of the Durban University of Technology.

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