Supercritical Water Gasification on Three Types of Microalgae in the Presence and Absence of Catalyst and Salt

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Abstract

Supercritical water gasification is an efficient technique for gasifying biomass in particular with high moisture content. Therefore, it is a promising technology that allows gasification of microalgae. Supercritical water gasification (SCWG) of three microalgae was conducted at 673 K and 25 MPa, which produces various gas products such as carbon monoxide, carbon dioxide, methane, ethane, ethylene, and hydrogen gas. SCWG was conducted in the presence and absence of nickel catalyst and sodium chloride salt. In the presence of nickel catalyst, microalgae were gasified more efficiently relative to non-catalytic SCWG. Surprisingly, addition of salt to the SCWG seems to increase the carbon gasification efficiency. Also a new approach was studied by addition of catalyst and salt which reveals lower carbon gasification efficiency. SCWG of marine microalgae seems to be more efficient than freshwater microalgae as higher amount of carbon dioxide and hydrogen gas was produced.

1. Introduction

Microalgae is a potential biomass for biomass energy source as microalgae are the fastest growing photosynthetic organism. The growth rates of algae can reach up to ten times higher than terrestrial plants [1]. Microalgae are mostly in the wet or slurry form, in which is unfavourable for conversion technologies like pyrolysis and dry gasification [1]. At temperature above the critical point (temperature: 374 °C, pressure: 22.1 MPa), water undergoes significant changes in its physical properties with a drastic decrease in dielectric constant, density, ionic product, viscosity, and thermal conductivity. At such conditions, water acts as a benign solvent with good transport properties that has a strong ability to break down hydrocarbons resulting in high production of gases such as H\textsubscript{2}, CO, CO\textsubscript{2}, and CH\textsubscript{4} [2]. At higher temperature above 600 °C, supercritical water becomes a very powerful oxidant and free radical reactions prevail. The need for catalyst arises to achieve higher gasification efficiency and equilibrium gas yields at lower temperature. An effective catalyst for the production of H\textsubscript{2} in supercritical water gasification (SCWG) of biomass should facilitate the

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scissoring of C-C and C-H bonds and preferably favour the water-gas shift reaction. However, wet biomass is regarded as a non-suitable feedstock for conventional thermochemical conversion processes due to high cost associated to the drying process [3].

In conventional gasification technologies vaporization of water from biomass is needed, in which vaporization leads to energy consumption thus offsetting energy gained by producing the gaseous products [4]. On the other hand, SCWG does not require a dry feedstock, so it is more realistic for gasifying microalgae. Water as a reaction medium obviates the need to dry the microalgae and reduces the energy consumption. SCWG also lead to low tar and char formation compared to pyrolysis and torrefaction, as water serves as both reaction medium and reactant of reforming reaction [4].

Nickel catalyst naturally promotes water-gas shift reaction, methanation, and hydrogenation reaction. Water-gas shift reaction also can be enhanced by high water density. Yoshida et al. [5] expected that by increasing the amount of nickel catalyst, water-gas shift reaction, hydrogenation, and methanation are enhanced, thus leading to higher yield of gas product especially hydrogen and methane [5]. The existence of large amount of water inside the reactor swiftly converts carbon monoxide into carbon dioxide by the water-gas shift reaction (Eq.1). However, accumulation of carbon on nickel catalyst reduces the catalytic reaction.

\[2CO + H_2O \rightarrow CO_2 + H_2\]  \hspace{1cm} (Eq. 1)

This research is undertaken to study the gas product composition of SCWG of freshwater and marine microalgae, besides evaluating the carbon gasification efficiency of the microalgae.

2. Materials and method

2.1 Biomass

Three types of microalgae were used in this research of which are *Botryococcus braunii*, *Nannochloropsis oculata* and *Tetraselmis chuui*. Supercritical water gasification of freshwater microalgae was compared to seawater microalgae in term of their gasification efficiency. Freshwater microalgae used in this research is *B. braunii*, meanwhile seawater microalgae used are *N. oculata* and *T. chuui*. Seawater microalgae were grown in F2 medium for 14 days and harvested [9]. Whereby, freshwater microalgae were grown in BG-11 medium for 28 days prior to harvest [10]. All microalgae were grown in 5.0 L glass bottle under continuous illuminations with fluorescent lamp for 24 hrs. CHN elemental analysis was conducted for all three types of microalgae prior to SCWG.

2.2 Supercritical water gasification reaction

Supercritical water gasification was conducted in a batch type reactor made of 316 stainless steel tubing with an outer diameter of 9.53 mm and inner diameter of 6.53 mm. The reactor was added with 0.15 g biomass, 0.0035 g salt (if necessary), and 0.15 g catalyst (if necessary). The reactor was also loaded with 3.5 mL deionised water and mixed well prior to reaction. The amount of water required was predetermined in order to achieve the partial pressure of supercritical water 25.0 MPa. The reactor was tightly sealed and immersed into salt bath at 400 °C to initiate the reaction. The reaction temperature reaches 400 °C in approximately 60 seconds. The reactor was taken out after 10 min and immersed into water bath at room temperature to stop the reaction. The reaction temperature reaches ambient temperature in approximately 60 seconds. The reaction pressure was measured by pressure gauge attached to the reactor. Product gas was collected in a glass bottle by displacement method. Product gas was analysed by gas chromatography-thermal conductivity detector (GC-TCD) (shimadzu-GC-14B) to determine the composition of gases present in the product. Liquid in the reactor was also sampled for analysis with TOC (total organic carbon) analyser. The solid product was transferred onto filter paper Whatman number 1, by rinsing the reactor onto the filter paper. Hydrogen gas analysis was performed using nitrogen carrier gas with a column temperature starting at 343 K, followed by a 10K/min ramp to 423 K, another ramp at 25 K/min to 573 K and a 23 min hold at 573 K.

3. Results and discussion

3.1 Non-catalytic SCWG of microalgae

Microalgae consisted of carbohydrates, lipids, and proteins. Therefore, different reaction mechanism may take place out of microalgae biomass during the SCWG. Chakinala et al. [1] described that the presence of certain amino acids such as L-proline decreases the gasification efficiency. Kruse et al. [6] also noticed a reduction in glucose gasification efficiency in the presence of amino acids. This reduction is expected to occur due to free radical scavenging effect.

Supercritical water gasification of microalgae produces gas, liquid, and solid product. Gas chromatography analysis revealed the presence of carbon monoxide, carbon dioxide, methane, ethane, ethylene and hydrogen gas as presented in Figure 1. However, the composition of these gases varied according to the type of microalgae. *Tetraselmis chuui* produced significantly high volume of carbon dioxide and hydrogen gas. Meanwhile, *N. oculata* produced the least gas product. In the non-catalytic SCWG of three
microalgae, *N. oculata* showed the lowest carbon gasification efficiency (CGE) as shown in Table 2. Regardless of microalgae type, the predominant gas formed is carbon dioxide. Similarly, Tiong et al. [7] reported that in non-catalytic SCWG of *Chlorella vulgaris* and *Scedesmos quadricauda* the predominant gas produced is carbon dioxide which could be formed via decarboxylation of microalgae biomass. On the other hand, Sivasangar et al. [8] mentioned that carbon monoxide and carbon dioxide may be formed via decarbonylation and decarboxylation of oil palm in SCWG. Similarly, glucose and phenol also decompose by both decarbonylation and decarboxylation [11].

3.2 Catalytic SCWG of microalgae

Some researchers showed that high temperature favours higher gas production [1]. However, it is important to note that increasing the temperature will raise the energy consumption and therefore reduces overall energy efficiency of the reaction. On the other hand, influence of nickel catalyst was investigated in this research. As shown in Figure 2, *B. braunii* produced very small volume of carbon dioxide and negligible volume of hydrogen. However, *N. oculata* exhibited tremendous increase in all of the gas produced. Methane production by *N. oculata* is significantly higher in comparison to *T. chuui*. Generally, catalytic SCWG of microalgae showed decrease in hydrogen gas production and also increased methane production in comparison to non-catalyzed SCWG. This suggests that nickel catalyst enhances microalgal degradation and methanation reaction [8]. Amount of catalyst also influence the SCWG [5], whereby methanation reaction does not occur with the small amount of nickel catalyst (0.04 g) when most of the catalyst is expected to be poisoned by carbon formation. Although, *N. oculata* produces higher amount of lipid than *T. chuui* (Data not shown), the SCWG of both the marine microalgae does not significantly changes the CGE. Tiong et al. [7] explained that gas products are formed through steam reforming and decomposition reactions (Eq. 2) followed by shift reaction (Eq. 3) and methanation (Eq. 4 and Eq. 5).

![Chemical equations](eq-2-5)

3.3 Salt effect on SCWG of microalgae

Few researchers [1,4,7] indicated that the presence of alkali salts such as NaOH, KOH and K$_2$CO$_3$ may enhance gasification by promoting water-gas shift reaction. Hence, sodium chloride was utilized in this research to study the gas production. Result in Figure 3 show lower gas production from SCWG of *B. braunii* in comparison to *N. oculata* and *T. chuui*. SCWG of microalgae in the presence of sodium chloride salt exhibited similar methane and hydrogen gas production as catalytic SCWG. Meanwhile carbon dioxide gas production increases tremendously. This indicates that alkali salt enhances the microalgal decarboxylation and degradation reactions similar to Onwudili et al. [12].

However, Guan et al. [4] reported that the yield of carbon dioxide was decreased by addition of NaOH and KOH, as NaOH and KOH captures carbon dioxide to form metal carbonates. Based on Table 2, the CGE of microalgae SCWG in the presence of alkali salt is higher than nickel catalyzed SCWG because alkali salt enhances water-gas shift reaction, which increases the carbon dioxide and hydrogen gas production [12,13].

3.4 Addition of salt and catalyst to SCWG of microalgae

Figure 4 summarizes product gas formed due to addition of catalyst and alkali salt in SCWG of microalgae. Throughout the literatures on SCWG, no researcher has attempted similar experiment to this. Addition of catalyst and salt to the SCWG of *T. chuui* shows increase in carbon dioxide and hydrogen gas in comparison to addition of alkali salt solely. On the other hand, *N. oculata* exhibit reduced carbon dioxide, methane and hydrogen gas in comparison to catalytic SCWG. Generally, addition of alkali salt and catalyst seems to gasify microalgae less efficiently than addition of alkali salt alone in regard to CGE. This suggests that combination of alkali salt and catalyst in SCWG perform weak degradation and shift reaction. However, different combination of alkali salt and catalyst can be investigated in future.

4. Conclusion

The SCWG of freshwater and marine microalgae produces mainly carbon dioxide, methane, and hydrogen gases. It was found that non-catalyzed reaction yield very low carbon gasification efficiency. SCWG with the addition of nickel catalyst shows increased carbon gasification efficiency. However, addition of alkali salt into the SCWG, exhibit highest carbon gasification efficiency for
marine microalgae. On the other hand, addition of alkali salt and nickel catalyst into SCWG suppresses the carbon gasification efficiency. In general, SCWG of marine microalgae reveals higher carbon gasification efficiency.

Acknowledgements

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Figures and Tables

Table 1: CHN elemental analyses of microalgae

<table>
<thead>
<tr>
<th>Microalgae</th>
<th>C (wt%)</th>
<th>H (wt%)</th>
<th>N (wt%)</th>
<th>S (wt%)</th>
<th>O (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>B. braunii</em></td>
<td>48.41</td>
<td>7.42</td>
<td>6.33</td>
<td>0.81</td>
<td>37.03</td>
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<tr>
<td><em>N. oculata</em></td>
<td>53.90</td>
<td>8.44</td>
<td>2.65</td>
<td>0.66</td>
<td>34.35</td>
</tr>
<tr>
<td><em>T. chuui</em></td>
<td>45.05</td>
<td>7.02</td>
<td>2.15</td>
<td>0.83</td>
<td>44.95</td>
</tr>
</tbody>
</table>

Figure 1: Product gas composition from non-catalytic supercritical water gasification of microalgae
Figure 2: Product gas composition from catalytic supercritical water gasification of microalgae

![Graph showing gas composition from catalytic supercritical water gasification of microalgae.]

Figure 3: Product gas composition from addition of alkali salt in supercritical water gasification of microalgae

![Graph showing gas composition from addition of alkali salt.]

Figure 4: Product gas composition from addition of catalyst and alkali salt in supercritical water gasification of microalgae.

![Graph showing gas composition from addition of catalyst and alkali salt.]

Table 2: Carbon gasification efficiency of microalgae in various conditions

<table>
<thead>
<tr>
<th>CGE</th>
<th>B. braunii</th>
<th>N. oculata</th>
<th>T. chuui</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>3.964</td>
<td>0.809</td>
<td>5.964</td>
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<tr>
<td>BC</td>
<td>0.856</td>
<td>8.196</td>
<td>8.258</td>
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<tr>
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<td>0.435</td>
<td>9.143</td>
<td>15.459</td>
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<tr>
<td>BSC</td>
<td>2.131</td>
<td>6.066</td>
<td>9.599</td>
</tr>
</tbody>
</table>

Legend: B: Biomass only; BC: Biomass and catalyst; BS: Biomass and salt; BSC: Biomass, salt and catalyst
References


