Syngas for Methanol Production from Palm Oil Biomass Residues*

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Abstract

Biodiesel is produced from palm oil and methanol; this methanol could be obtained from gasification of the raw palm oil residual. The complete process includes: pre-treatment of the biomass, gasification, cleaning and conditioning of the gas and the final synthesis of methanol. A review of the gasification stage is carried out, a classification of the existent gasification reactors is presented and the characteristics of three types of gasifiers are detailed. Furthermore, a summary of certain chemical and physical requirements of the gas obtained by the gasification process are introduced. Some conditions are highlighted: the ratio hydrogen to carbon monoxide (H₂/CO) must be close to two and, the quantities of diluted nitrogen, sulphur and water in the gas must be low. Keeping in mind these characteristics we proceeded to recommend the gasifier and gasification medium. Finally, a chemical equilibrium model is introduced to estimate the composition of the gas produced and to study the effect of the temperature and operation pressure in the quality of the gas produced. The gasification process considers a fluidized bed gasifier and the simulated results are compared with experimental data. The results showed that the simulation approach accurately represents the gasification process and allows considering the simulation for some other biomass residues.

Keywords: Palm oil biomass residual; gasification; methanol synthesis; syngas.

1. Introduction

Most of the oil used for the world biodiesel industry comes from plantations such as palm oil, soy, rape, and sunflower. The world palm oil production is close to 30.5x10⁶ ton/year, where Malaysia, Indonesia, Nigeria, Thailand and Colombia are the main producers (Sumathi et al, 2007). In Colombia, more than 160x10³ hectares are used to produce 3.24x10⁶ tons of Fresh Fruit Bunches (FFB) yearly, which represents 709x10³ tons of Empty Fruit Bunches (EFB), 431x10³ tons of fiber, and 210x10³ tons of shells (Fedepalma, 2006). The majority of the residues are used for composting, animal food, and to produce steam and energy (Yusoff, 2006). Colombian biodiesel is produced from palm oil and methanol. The latest could be obtained from palm oil biomass residue gasification (Chew and Bhatia S, 2008). The syngas required to produce biomethanol could be attained from the process shown in Figure 1 (Minteer, 2006). This process includes pre-treatment for the biomass (drying and size reduction), gasification according to the biomass physical characteristics, cleaning of the gas produced, and the final methanol catalytic synthesis.

Palm Oil Residues

African oil palm (Elaeis guineensis) is grown for alimentary purposes. The amount of oil attained from this plant is five to seven times larger than some other oleaginous plants such as: peanut, sunflower, sesame, and soy. The oil is obtained from the pulp as well as from the seed. The biomass residues from the process are EFB (Empty fresh bunches), fiber and shells. The amount of each residue is presented in Table 1 (Arrieta et al, 2007).

Table 1. Biomass residues produced during the processing of palm oil

<table>
<thead>
<tr>
<th>Mat</th>
<th>% ash function of Fresh Fruit Bunches</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min.</td>
</tr>
<tr>
<td>EFB</td>
<td>17.7</td>
</tr>
<tr>
<td>Fiber</td>
<td>11.6</td>
</tr>
<tr>
<td>Shells</td>
<td>5</td>
</tr>
</tbody>
</table>

Figure 1. Process diagram for Methanol production from biomass.

In many cases, the usage of the residues is not very efficient due to the restrictions associated to the equipment and the biomass quality variation to obtain a fuel (Husain and Zaina, 2003), never the less, experimental results showing the products have been carried out (Yan et al., 2005).
The relevant analysis for the biomass gasification process is presented in Tables 2, 3, and 4, where the proximate, chemical composition and ultimate analysis are shown respectively.

Table 2. Palm Oil Biomass Proximate Analysis (dry base) and initial humidity content. (Quaak et al, 1999; U.S Department of Energy, 1988).

<table>
<thead>
<tr>
<th>Material</th>
<th>Energy (kJ/Kg)</th>
<th>Volatile Matter (%</th>
<th>Humidity Initial %</th>
<th>Ash %</th>
<th>Carbon Fixed %</th>
<th>Sulfur Total %</th>
<th>Humidity Residual %</th>
</tr>
</thead>
<tbody>
<tr>
<td>EFB</td>
<td>19599</td>
<td>71.9</td>
<td>6.7</td>
<td>5.3</td>
<td>16.1</td>
<td>0.12</td>
<td>60</td>
</tr>
<tr>
<td>Fiber</td>
<td>18711</td>
<td>70.7</td>
<td>7.4</td>
<td>3.3</td>
<td>18.6</td>
<td>0.15</td>
<td>39</td>
</tr>
<tr>
<td>Shell</td>
<td>20490</td>
<td>71.2</td>
<td>7.4</td>
<td>2.1</td>
<td>19.3</td>
<td>0.08</td>
<td>19</td>
</tr>
</tbody>
</table>

According to Table 2, and taking into consideration the manipulation required to process the different residues obtained from the palm, the biomass can be categorized for energy generation as shells, fiber and EFB.

Table 3. Palm Oil biomass chemical composition. (Chew and Bhatia, 2008 (1); Abdullah and Gerhauser, 2008 (2); Kelly-Yong and Lee, 2007(3)).

<table>
<thead>
<tr>
<th>Component</th>
<th>EFB (2)</th>
<th>EFB (3)</th>
<th>Fiber (1)</th>
<th>Fiber (2)</th>
<th>Log (1)</th>
<th>Shell (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash</td>
<td>-</td>
<td>1.6</td>
<td>4.89</td>
<td>3.5</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Lignin</td>
<td>18.1</td>
<td>22.1</td>
<td>24.89</td>
<td>27.7</td>
<td>20.3</td>
<td>50.7</td>
</tr>
<tr>
<td>Holocellulose</td>
<td>-</td>
<td>-</td>
<td>52.05</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cellulose</td>
<td>59.7</td>
<td>38.3</td>
<td>-</td>
<td>33.9</td>
<td>33.9</td>
<td>20.8</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>22.1</td>
<td>35.3</td>
<td>18.2</td>
<td>26.1</td>
<td>-</td>
<td>22.7</td>
</tr>
<tr>
<td>Xylose</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>16.8</td>
<td>-</td>
</tr>
<tr>
<td>Glucose</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>29.0</td>
<td>-</td>
</tr>
<tr>
<td>Extracts</td>
<td>2.7</td>
<td>6.9</td>
<td>4.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4. Palm Oil Biomass Ultimate Analysis (dry base).

<table>
<thead>
<tr>
<th>Component</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>O</th>
<th>LHV (kJ/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EFB</td>
<td>48.79</td>
<td>7.33</td>
<td>0.00</td>
<td>0.68</td>
<td>36.30</td>
<td>18960</td>
</tr>
<tr>
<td>Fiber</td>
<td>50.27</td>
<td>7.07</td>
<td>0.42</td>
<td>0.63</td>
<td>36.28</td>
<td>20640</td>
</tr>
<tr>
<td>Shell</td>
<td>53.78</td>
<td>7.2</td>
<td>0.00</td>
<td>0.51</td>
<td>36.30</td>
<td>22140</td>
</tr>
</tbody>
</table>

2.2 Gasification Stages

In a gasification process, four main physicochemical processes can occur simultaneously in different regions of the gasifier at certain temperatures (Demirbas, 2002), these are:

- **Drying**: (T > 150 °C),
- **Pyrolysis o devolatilization**: (150 – 700 °C),
- **Oxidation**: (700 – 1500 °C) and
- **Reduction**: (800 – 1100 °C).

During the drying, the humidity is removed from the solid by evaporation. In the pyrolysis, a breakdown takes place because the water vapor, organic liquids and non condensing gases separate from the fixed carbon. In the oxidation, the fuel reacts with the oxygen to release heat, while in the reduction the energy is absorbed by the gas.

2.2.1 Pyrolysis and Devolatilization

This stage begins at a temperature close to 350°C. When the temperature reaches 700°C, the process accelerates and a series of complex chemical and physical reactions take place. The composition of the products generated during the devolatilization is function of the temperature, pressure, and composition of the biomass. The pyrolysis process can be represented by the following general reaction (R.1):

\[
\text{Biomass} + \text{Heat} \rightarrow \text{Gases} + \text{Liquid or Vapors} \quad \text{(R.1)}
\]

The products from this reaction can be grouped as: 1) gases such as H₂, CO, CO₂, H₂O, CH₄, 2) tars from long chain hydrocarbons and inorganic molecules, 3) carbon as a solid residual.

2.2.2 Oxidation

In the direct heating gasifiers, the oxidation reaction provides the heat required in the endothermic reactions. The oxygen supplied to the gasifier reacts with the fuel, resulting in CO2 (R.2) and H2O (R.3).

\[
\text{C} + \text{O}_2 \leftrightarrow \text{CO}_2 + \frac{439.77 \text{kJ}}{\text{mol carbon}} \quad \text{(R.2)}
\]
2.2.3 Gasification

The gasification involves a series of endothermic reactions which are stimulated by the heat released in the previous exothermic reactions. These reactions transform the biomass into a flammable gas. The most important reactions are the following.

**Water – Gas:** this reaction involves the carbon partial oxidation due to the water vapor produced during the drying process, the humidity introduced with the air, the biomass break down or the steam supplied to the gasifier. The water vapor reacts with the carbon according to the following heterogeneous reaction (R.4):

\[
C + H_2O \leftrightarrow H_2 + CO - 131.38 \frac{kJ}{mol \, carbon} \tag{R.4}
\]

**CO₂ Reduction:** the carbon dioxide produced in the gasifier can react with the carbon to produce CO according to the following endothermic reaction (R.5):

\[
CO_2 + C \leftrightarrow 2CO - 172.58 \frac{kJ}{mol \, carbon} \tag{R.5}
\]

**Water Gas Shift Reaction:** the water vapor reduction generated by the carbon monoxide is advantageous due to the production of hydrogen. The exothermic reaction governing this process is the following: (R.6):

\[
CO + H_2O \leftrightarrow CO_2 + H_2 - 41.98 \frac{kJ}{mol \, carbon} \tag{R.6}
\]

This reaction increases the H₂/CO ratio in the gas produced, and it is used in the manufacturing of syngas.

**Methane Reaction:** methane is obtained in the gasifier through the following reaction (R.7):

\[
C + 2H_2 \leftrightarrow CH_4 + 74.90 \frac{kJ}{mol \, carbon} \tag{R.7}
\]

This reaction can be accelerated using catalysts based on Nickel, and working at temperatures around 1100°C and pressure ranging from 6 to 8 bars.

The composition of the gas attained from gasification varies depending on the biomass characteristics, the gasification media, operation pressure, temperature, humidity content and type of gasifier (Kirubakaran et al., 2007; Li and Grace, 2003). Although it is difficult to predict the exact composition of the gas produced, chemical equilibrium conditions can help to understand the behavior and performance of the gasifiers under certain operational conditions.

3. Syngas Potential Uses

Figure 2 briefly shows different paths that can be considered for syngas usage. Table 6 shows the syngas requirements for two specific applications (Chew and Bhatia, 2008; Ciferno and Marano, 2002; Kirubakaran et al., 2007). It is necessary to highlight that this study focuses in the gasification of palm oil residues to obtain a syngas adequate for liquid fuels production, such as methanol.

![Figure 2. Possible paths for syngas usage.](image)

According to the literature and experimental works carried out, the following aspects are considered relevant for methanol production form syngas:

- It is convenient to have a fluidized bed gasifier using oxygen and water vapor as oxidant agents. This avoid the presence of nitrogen in the products and save time and energy in the cleaning process. Furthermore, the use of oxygen allows a gas with a better energy content (10–15MJ/Nm³) (Saxena, 2008)

- Even though the gasification process with air is widely used, it produces a syngas with a low energy content, higher humidity, tar and hydrocarbons. The amount of impurities in the syngas is greater, increasing the cleaning process cost.

- The use of steam may cause corrosion in the gasifier, but it is preferable to use it due to a greater conversion of the carbon present in the biomass. Furthermore, the water vapor addition produces tars which are easily catalytically transformed (Milne and Evans, 1998)

- The operation at high pressure reduces tar and long chain hydrocarbons production

- Generally, a single gasification stage does not produce a gas with the required H₂ content, and it is necessary to introduce "water gas shift reactors" in order to adjust the H₂/CO ratio (Demirbas, 2002).

Table 6 presents the chemical composition and physical conditions required by the syngas in order to attain methanol (Ciferno and Marano, 2002; Demirbas, 2002). It is noticed that the (H₂/CO) molar ratio must be close to 2, the diluted quantities of nitrogen, sulfur and water must be low. Nevertheless, these requirements must not be considered as conclusive and final rules.

<table>
<thead>
<tr>
<th>Syngas Requirements for Methanol Production</th>
<th>Methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂/CO</td>
<td>Close to 2</td>
</tr>
<tr>
<td>CO₂</td>
<td>Low</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>Low</td>
</tr>
<tr>
<td>N₂</td>
<td>Low</td>
</tr>
<tr>
<td>H₂O</td>
<td>Low</td>
</tr>
<tr>
<td>Contaminants</td>
<td>&lt; 1 ppm sulfur, Low particles</td>
</tr>
<tr>
<td>Energy Content</td>
<td>Non important</td>
</tr>
<tr>
<td>Pressure, bar</td>
<td>Approx. 50 (liquid phase) 140 (vapor phase)</td>
</tr>
<tr>
<td>Temperature °C</td>
<td>100-200</td>
</tr>
</tbody>
</table>

4. Results and Discussion

4.1 Syngas Composition Estimation and Effect of some Operational Parameters

The equilibrium composition for the gas attained in the gasifier can be estimated using chemical equilibrium conditions along with the ultimate analysis and parameters such as temperature and pressure. The composition also depends on the oxidant introduced per unit of solid fuel. A chemical equilibrium model is presented in order to estimate the composition of the syngas produced. The sulfur introduced by the biomass is neglected. Let consider the following notation:

\[
H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O + 742.00 \frac{kJ}{mol \, carbon} \tag{R.3}
\]
F: Dry base biomass supplied, kg db
W: Biomass humidity, Kg H2O/Kg db
S: Water vapor per kg of dry biomass, Kg H2O/Kg db
A: Dry air per kg of dry biomass, Kg Air/Kg db
Xi: Mass fraction, Kg i/Kg db
yi: Molar fraction, Kg mol i/Kg mol gas

The molar and equilibrium equations are the following:

Molar balance for Carbon C

\[ F \left( \frac{X_C}{12} \right) = n_O (y^{CO} + y^{CO_2} + y^{CH_4}) \]  

(1)

Molar balance for Hydrogen H2

\[ F \left( \frac{X_H}{2} + \frac{S}{18} + \frac{W}{18} \right) = n_O (y^{H_2} + y^{H_2O} + y^{CH_4}) \]  

(2)

Molar balance for O2

\[ F \left( \frac{X_O}{32} + \frac{W}{2+18} + \frac{S}{2+18} + \frac{AX_O}{32} \right) = n_O (y^{CO_2} + \frac{1}{2} y^{CO} + \frac{1}{2} y^{H_2O}) \]  

(3)

Where \( X_{O2} \) is the mass fraction for the oxygen, O2, in the dry air.

Molar balance for N2

\[ F \left( \frac{X_N}{2+14} + \frac{AX_N}{28} \right) = n_O (y^{N_2}) \]  

(4)

Where \( X_{N2} \) is the mass fraction for the nitrogen, N2, in the dry air

Sum of Molar fractions

\[ y^{CO} + y^{H_2} + y^{CO_2} + y^{CH_4} + y^{H_2O} + y^{N_2} = 1 \]  

(5)

Chemical equilibrium for the reaction

\[ e^{[\theta' + \theta H_2 + \theta CO]} = \frac{x_{CH_4}}{x_{H_2}} \left( \frac{P_0}{P_{gas}} \right) \]  

(6)

\[ e^{[\theta' + \theta H_2O + \theta CO_2]} = \frac{x_{CO_2}x_{H_2}}{x_{H_2O}} \left( \frac{P_{gas}}{P_0} \right) \]  

(7)

\[ e^{[\theta' + \theta CO_2 + \theta CO]} = \frac{x_{CO}x_{CO_2}}{x_{CO_2}} \left( \frac{P_{gas}}{P_0} \right) \]  

(8)

\[ g_c = (g_f)_{i} + (h_f - h_{f,i}) - T(S_f)_{i} + T_{0}(S_{f,0})_{i} \]  

(9)

The solution of this system provides the concentration of each component in the syngas. Table 7 presents the parameters and the equilibrium constants (Basu, 2006) used in the solution of the model. The amount of air introduced per unit of dry biomass was obtained using an Equivalence Ratio (ER) of 0.25. ER is defined as the amount of air introduced divided by the amount of air required for a stoichiometric combustion reaction. The results obtained for the syngas composition are presented in Figure 3 and 4.

4.2 Syngas Composition

The results obtained from the simulation includes the concentration for methane (CH4), carbon monoxide (CO), hydrogen (H2), and hydrogen/carbon monoxide (H2/CO) ratio. These results are compared with the values attained by Yan et al. (2005) for palm oil residues.

![Figure 3. Methane molar fraction.](image)

Figure 3 presents the results obtained for methane from the simulation. It shows that methane production decreases as temperature increases for the different pressures considered. It is also noticed that the maximum to minimum molar fraction difference remains quite constant at 0.07 for the different pressure values considered. The effect of the pressure is very significant, increasing the amount of methane produced as this variable increases. Methane molar fraction at 1 bar ranges from 0.08 to 0.01, while at 30 bars, ranges from 0.32 to 0.26. When methane simulated production for 1 bar is compared, at 600°C and 900°C, Yan et al (2005) present the following values: 0.08 and 0.01, which are the same values attained in this paper.

![Figure 4. Carbon monoxide molar fraction.](image)

The simulation results for carbon monoxide are presented in Figure 4. It is noticed that carbon monoxide production increases as temperature increases for the three
different pressures considered. Furthermore, it is also noticed that the concentration values decrease as pressure increases, never the less, this effect is more noticeable for temperatures below 800°C. For temperatures higher than 800°C, the curve for 1 bar presents a point of inflexion, meaning that it reaches a maximum. For the other two pressures, this value was not reached but the curves trends tend to indicate that. When carbon monoxide results for 1 bar are compared, at 600°C and 900°C, Yan et al (2005) present the following values: 0.07 and 0.32, while the simulated results are 0.12 and 0.34 respectively.

Figure 5 presents hydrogen molar concentration. It is noticed that hydrogen production increases as temperature increases for the three different pressures considered. It is also noticed that the concentration values decrease as pressure increases. When hydrogen results for 1 bar are compared, at 600°C and 900°C, Yan et al. (2005) present the following values: 0.28 and 0.41, while the simulated results are 0.28 and 0.39 respectively.

Figure 6 presents the results obtained for water vapour from the simulation. It shows that water vapour production decreases as temperature increases for the different pressures considered. Furthermore, the concentration also decreases as pressure is increased for the process. When methane simulated production for 1 bar is compared, at 600°C and 900°C; Yan et al. (2005) present the following values: 0.12 and 0.01, while the simulated results are 0.09 and 0.007 respectively.

Figure 6. Water vapour concentration.

An important factor to be considered in the biomass gasification, especially when the syngas is produced to be used for methanol or some other hydrocarbons, is the hydrogen/carbon monoxide ratio. In this case, the ratio decreases as temperature as well as pressure increases. It is important to notice that this ratio remains almost constant for temperature values over 750°C.

\[ CO + H_2O \leftrightarrow CO_2 + H_2 \]

For methane steam reforming.

\[ CH_4 + H_2O \leftrightarrow CO + 3H_2 \]

As temperature increases, the reaction tends toward the products. For low temperatures, the second reaction controls the process, reducing the amount of methane and water, and increasing hydrogen and carbon dioxide. At higher temperatures, the first reaction controls the process, decreasing carbon dioxide and hydrogen, and producing carbon monoxide and water. The hydrogen - carbon monoxide ratio decreases as the temperature increases, due to the combined effect of decreasing hydrogen and increasing carbon monoxide.

4.3 Biomass to Methanol Conversion

Figure 8 shows the process diagram for methanol production from syngas produced at the gasification stage. The most important processes involving changes in the composition of the syngas, such as reforming, water gas shift and methanol synthesis reactors are shown. The process is simulated considering the kinetic at the plug flow reactor and the removal of CO2 by mean of amine component separator. The refined methanol is obtained by a liquid methanol phase separator, and final refinement is done using a distillation column for biomethanol as a final product.
The temperature increases. However, the amount of biomethanol obtained increases significantly as the temperature increases. Never the less, this effect is noticeable when the temperature reaches values over 800°C. For pressure, the results show that a lower pressure the amount of methanol produced is greater than at high pressure.

Figure 8. Biomethanol plant process.

Figure 9 presents the biomass to methanol yield. It is noticed that the amount of biomethanol obtained increases significantly as the temperature increases. Never the less, this affect is noticeable when the temperature reaches values over 800°C. For pressure, the results show that a lower pressure the amount of methanol produced is greater than at high pressure.

Figure 9. Biomass to Methanol yield for different temperatures.

5. Conclusions
The Palm oil biomass processing seems to be a feasible alternative for production of second generation biofuels. Obtaining syngas with the required conditions for catalytic synthesis from residual biomass processed in a fluidized bed with atmospheric air and water vapor presents a possible alternative. This analysis helps to decide which way the variables governing the process are supposed to be moved in order to attain the maximum values required, and how they affect the concentrations of the other gases. Never the less, this analysis needs to be complemented with transport equations considering heat and mass transfer in the reactor.

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