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Stoichiometric Equilibrium Model based Assessment of Hydrogen Generation through Biomass Gasification

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Abstract

Hydrogen produced from renewable energy sources is clean and sustainable. Biomass gasification has a significant role in the context of hydrogen generation from biomass. Assessment of the performance of biomass gasification process regarding the product gas yield and composition can be performed using mathematical models. Among the different mathematical models, thermodynamic equilibrium models are simple and useful tools for the first estimate and preliminary comparison and assessment of gasification process. A stoichiometric thermodynamic equilibrium model is developed here, and its performance is validated for steam gasification and air-steam gasification. The model is then used to assess the feasibility of different biomass feedstock for gasification based on hydrogen yield and lower heating value.

Keywords: Biomass; Stoichiometric thermodynamic equilibrium model; Steam gasification; Air-steam gasification.

1. Introduction

Sustainable energy generation has to become the key focus of the current world energy scenario relying on clean and renewable energy resources. Hydrogen produced from carbon neutral biomass is significant in this perspective. Biomass gasification is a thermochemical process by which hydrogen is extracted from biomass. In gasification biomass is partially oxidised at a temperature around 800 °C to produce a gaseous mixture widely known as producer gas. It consists mainly of hydrogen, carbon monoxide, carbon dioxide and methane along with char and tar. The quality and composition of the product gas generated in gasification in a gasifier is influenced by the nature of biomass, gasification media and key operating parameters like reactor temperature (T), equivalence ratio (ER), and steam to biomass ratio (SBR). It is possible to evaluate the performance of gasification regarding product gas
yield and composition and make predictions concerning the quantity and quality of product gas by using mathematical models [1].

Researchers have formulated different models like thermodynamic equilibrium [2, 3], kinetic [4, 5] computational fluid dynamics [6, 7] and artificial neural network [8, 9] to analyse gasification [10]. Arnqvist et al. [11], Ahmed et al. [12] and Baruah et al. [1] present a detailed review of different gasification models. The review of the gasification models reveals that the thermodynamic equilibrium model (TEM) is a simple and useful tool for the first estimate and preliminary comparison and judgement of gasification process. According to Li et al. [13], TEM is valuable as it can predict the thermodynamic limits. TEM though independent of gasifier design conveniently studies the influence of fuel and process parameters and makes a reasonable prediction of the maximum achievable yield of a particular product useful for a designer.

2. Model Development

The concept of thermodynamic equilibrium model is based on the second law of thermodynamics as applied to chemical reacting systems [14]. Accordingly all spontaneous processes occurring in a chemical system proceed in the direction so as to increase overall entropy. When system composition reaches the situation where overall entropy is maximum equilibrium state is attained. The analysis is then carried out through different approaches to determine the equilibrium composition. A stoichiometric thermodynamic equilibrium model (STEM) based on specific chemical reactions are used here for the estimation of product gas composition. Thermodynamic equilibrium models do not require any knowledge of the mechanisms of transformation. Moreover, they are independent of the reactor and not limited to a specified range of operating conditions. A STEM is formulated to assess the hydrogen yield from different locally available biomasses at specified operating conditions to select the most appropriate one.

Biomass gasification being a complex process the formulation of the mathematical model requires certain assumptions as follows:
1. The biomass is modelled considering the carbon, hydrogen and oxygen atoms only.
2. The gasifier is a steady state system with uniform pressure and temperature.
3. At equilibrium the reaction system achieves the most stable composition.
4. Gases H₂, CO, CO₂, CH₄, H₂O and N₂ considered in the reaction system behaves ideally.
5. Gasification reaction rate is fast enough and residence time is long enough for the equilibrium state.
6. No tar is supposed to leave the reaction system at the end of the process.
7. The fraction of char that bypasses the reaction zone remains unreacted.

2.1. Problem formulation and description

Let M kg of dry ash free biomass produce 1 Nm³ of product gas in a biomass gasification system maintained at 1 atm. The elemental composition of biomass based on ultimate analysis is expressed in weight percentages of carbon (C), hydrogen (H), and oxygen (O). As biomass contains only negligible amount of nitrogen and sulphur they are not considered. M₀ and Aₘ respectively denote the moisture and ash percentage of the biomass based on proximate analysis. Let Vₜ, Vₐ, V₉, V₂, V₈, and V₆ represent the volume fractions of hydrogen (H₂), carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), water vapour (H₂O) and nitrogen (N₂), respectively present in 1 Nm³ product gas. Aₗ represents the mass of air in kg/kg of biomass while Oₙ and Nₙ are mass fractions of oxygen and nitrogen respectively in the air supplied. S indicates the mass of super-heated steam provided/kg of dry ash free biomass while W denotes the mass of moisture content of biomass feedstock/kg of dry ash free biomass.

Global gasification reaction equation is modified as follows as per the assumptions made.

\[
M \left( \frac{C}{12} \frac{H}{2} \frac{O}{32} \right) + \frac{(S + W)}{18} + M \left( \frac{AR \cdot O_A}{32} + \frac{AR \cdot N_A}{28} \right) \rightarrow \frac{(V_{H_2} + V_{CO} + V_{CO_2} + V_{CH_4} + V_{H_2O} + V_{N_2})}{22.4} \tag{1}
\]

The carbon conversion efficiency (B) of gasification process will be less than 100% as a small fraction of char bypasses the reaction zone. Experimental investigations [15, 16] on carbon conversion efficiency reveal that it varies from 85 to 95% depending on the type of gasification process. Baruah et al. [1] observed that the carbon conversion
efficiency increases with increase in reactor temperature up to a certain reactor temperature and then remained constant. A char conversion model is formulated with these inputs after repeated trials. Modified global gasification reaction equation contains seven unknowns which include the volume fractions of the constituent gases, \( V_{CH_4}, V_{CO}, V_{CO_2}, V_{H_2O}, V_{N_2} \), and the mass of dry ash free biomass \((M)\) to produce 1 Nm\(^3\) product gas. Four linear equations can be formed based on carbon, hydrogen, oxygen, and nitrogen molar mass balance between inflow and outflow streams. A fifth linear equation can be formed based on the stated assumption that the volume fractions of all constituents of the product gas add up to 1. The remaining two equations can be formed by assuming that all the reactions occurring in the gasification zone are in thermodynamic equilibrium.

Carbon balancing:
\[
V_{CO} + V_{CO_2} + V_{CH_4} = 22.4 * \frac{C}{100} * M
\]  
\[ (2) \]

Hydrogen balancing:
\[
V_{H_2} + 2 * V_{CH_4} + V_{H_2O} = 22.4 * \left( \frac{S}{18} + \frac{H}{200} + \frac{W}{18} \right) * M
\]  
\[ (3) \]

Oxygen balancing:
\[
0.5 * V_{CO} + 0.5 * V_{CO_2} + 0.5 * V_{H_2O} = (0.623 * (S + W) + 0.701 * (\frac{O}{100}) + (AR * ER * 0.23)) * M
\]  
\[ (4) \]

Nitrogen balancing:
\[
V_{N_2} = (0.8 * (\frac{N}{100}) + 0.8 * AR * ER * 0.75) * M
\]  
\[ (5) \]

As the product of gasification is assumed to be 1 Nm\(^3\), the volume fractions of all the constituents add up to 1.

\[
V_{H_2} + V_{CO} + V_{CO_2} + V_{CH_4} + V_{H_2O} + V_{N_2} = 1
\]  
\[ (6) \]

Considering the prominent reactions occurring in the gasification zone:

Boudouard reaction:
\[
C + CO \leftrightarrow 2CO
\]  
\[ (7) \]

Water gas reaction:
\[
C + H_2O \leftrightarrow CO + H_2
\]  
\[ (8) \]

Water gas shift reaction:
\[
CO + H_2O \leftrightarrow CO_2 + H_2
\]  
\[ (9) \]

Methane reaction:
\[
C + 2H_2 \leftrightarrow CH_4
\]  
\[ (10) \]

Combinations of equations (7) and (8) will give the water gas shift reaction equation (9). Hence equations (9) and (10) are only considered to formulate the equations for equilibrium constants.

The equilibrium constant \( K_1 \) of water gas shift reaction (9) is given by,

\[
K_1 = \frac{P_{CO_2} * P_{H_2}}{P_{CO} * P_{H_2O}} = \frac{V_{CO_2} * V_{H_2}}{V_{CO} * V_{H_2O}}
\]  
\[ (11) \]

\[
V_{CO} * V_{H_2O} * K_1 = V_{CO_2} * V_{H_2}
\]  
\[ (12) \]

The equilibrium constant \( K_2 \) of methane reaction (10) is given by,
Equilibrium constants $K_1$ and $K_2$ can be expressed as functions of temperature [3] considering product gas as ideal.

$$K_2 = \frac{P_{CH_4}}{(P_{H_2})^2} = \frac{V_{CH_4}}{(V_{H_2})^2}$$
(13)

$$ (V_{H_2})^2 * K_2 = V_{CH_4}$$
(14)

Thus to determine seven unknowns there are five linear equations (2, 4, 6, 8 and 10) and two non-linear equations (12 and 14). Volume fractions of the product gas constituents and the mass of dry ash free biomass consumed can be obtained by simultaneously solving these equations using Newton – Raphson method in MATLAB platform which uses the results of ultimate and proximate analysis of biomass as input data. Once the volume fractions are determined the lower heating value of the product gas can also be calculated from the gas composition and is expressed in volume basis [17] as shown in equation (17).

$$LHV = 10.79*V_{H_2} + 12.26*V_{CO} + 35.81*V_{CH_4}$$
(17)

### 2.2 Model validation and performance assessment

Stoichiometric equilibrium model though simple, deviations from the experimental results are likely to occur due to the various assumptions considered during the formulation of the model. In reality, the reaction system might not have reached equilibrium. To account these factors, modifications are made in the estimated values of equilibrium constants. These changes will augment the predictions. The accuracy of the model is checked by comparing predicted gas composition from the proposed model with experimental results. The error in prediction is estimated with statistical parameter of root mean square (RMS) value [2, 18, 19, 20] shown in equation (18).

$$RMS = \sqrt{\frac{\sum (X_e - X_p)^2}{N}}$$
(18)

$X_e$, $X_p$ and $N$ are experimental data, predicted value, and number of observations, respectively.

Assessment of STEM is carried out by comparing the experimental results (EXP) based on the investigations by Loha et al. [18] for steam gasification and Turn et al. [21] for air-steam gasification respectively, with the predictions made by STEM. The chemical characteristics of rice husk and saw dust used in the experiments are presented in Table 1.

<table>
<thead>
<tr>
<th>Table 1. Chemical characteristics of biomass</th>
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<tr>
<td><strong>Ultimate Analysis (% Wt.)</strong></td>
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<tr>
<td>Biomass</td>
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<tr>
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<tr>
<td>Rice Husk</td>
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<td>Sawdust</td>
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<td>Sawdust</td>
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</table>

Loha et al. [18] performed steam gasification in a fluidised bed gasifier using rice husk as the biomass at an average bed temperature of 1023 K with different steam to biomass ratio (SBR). A comparison between the gas
yields as volume percentages for EXP and STEM for different SBR is represented using a cluster bar chart in Fig. 1. Comparison of hydrogen yield for different cases is separately shown in Fig. 2. It is observed that the error in prediction (RMSE) for different cases is less than 3.7 which is within the reasonable limits.

Fig. 1. Comparison of gas yield between the experimental results (EXP) and STEM for different SBR at 1023 K

Fig. 2. Comparison of hydrogen yield between the experimental results (EXP) and STEM for different SBR at 1023 K

Fig. 3. Comparison of gas yield between the experimental results (EXP) and STEM for different temperature at SBR=1.4 and ER =0.18
Assessment of STEM is further carried out by comparing the experimental results (EXP) from the investigations by Turn et al. [21] on biomass air-steam gasification with the predictions made by STEM. Gasification is performed in a fluidised bed gasifier using sawdust as the biomass at different bed temperature while keeping steam to biomass ratio (SBR) and equivalence ratio (ER) as 1.4 and 0.18 respectively throughout. A comparison between the gas yields at various temperatures in volume percentages is represented in Fig. 3 and hydrogen yield for different cases in Fig. 4. It is observed that the error in prediction (RMSE) for different cases is less than 3.5 except in the first instance (RMSE above 5). The predictions made by STEM are within the reasonable limits.

![Fig. 4. Comparison of hydrogen yield between the experimental results (EXP) and STEM for different temperature at SBR=1.4 and ER =0.18](image)

### 3. Assessment of feedstock’s feasibility with STEM

Hydrogen yield and heating value of product gas generated in gasification depend on the biomass feedstock. The feasibility of different biomass feedstock for gasification can be assessed using STEM based on hydrogen yield and lower heating value (LHV). Appropriate biomass for gasification can be selected from the locally available lot. Chemical characteristics of seven different biomasses along with their predicted hydrogen yields and heating values are presented in Table 2. The predictions are made at standard operating conditions of average bed temperature of 1073 K and SBR = 1 for steam gasification and for air-steam gasification, at ER=0.22.

**Table 2. Chemical characteristics of locally available biomass and their predicted hydrogen yields and lower heating value**

<table>
<thead>
<tr>
<th>Feed Stock</th>
<th>Composition (%)</th>
<th>Steam Gasification</th>
<th>Air-steam Gasification</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
<td>O</td>
</tr>
<tr>
<td>Coffee Husk (BM1)</td>
<td>42.1</td>
<td>6.33</td>
<td>49</td>
</tr>
<tr>
<td>Saw dust (BM2)</td>
<td>46.5</td>
<td>5.82</td>
<td>47.5</td>
</tr>
<tr>
<td>Rubber Seed Shell (BM3)</td>
<td>47.15</td>
<td>8.34</td>
<td>42.3</td>
</tr>
<tr>
<td>Coconut shell (BM4)</td>
<td>45.6</td>
<td>5.61</td>
<td>48.2</td>
</tr>
<tr>
<td>Coir pith (BM5)</td>
<td>44.1</td>
<td>4.09</td>
<td>51.2</td>
</tr>
<tr>
<td>SCF (BM6)</td>
<td>36.6</td>
<td>4.56</td>
<td>57.4</td>
</tr>
<tr>
<td>Rice Husk (BM7)</td>
<td>34.35</td>
<td>5.22</td>
<td>57.7</td>
</tr>
</tbody>
</table>


4. Results and discussion

Figure 5 (a) illustrates the predictions on hydrogen yield from steam gasification and air-steam gasification for various biomasses. Steam gasification will generate more hydrogen because of the water gas shift reaction occurring in the presence of large quantities of super-heated steam [10]. However, the hydrogen generated depends upon the H/C and O/C ratios. Biomass with higher H/C ratio and lower O/C will have higher hydrogen yield [10]. Predictions on the hydrogen yield from rubber seed shell (BM3) and rice husk (BM7) reveal that the former (having higher H/C ratio and lower O/C) will generate more hydrogen than rice husk (with lower H/C ratio and higher O/C ratio). Among the different biomasses, rubber seed shell (BM3) with higher H/C ratio will yield maximum hydrogen (85.4 g). Other biomasses like sawdust (BM2), coconut shell (BM 4), and coffee husk (BM1) have the potential of appropriate biomass for gasification. They can be recommended for high end use applications. However, coir pith (BM5), rice husk (BM7) and shredded coconut frond (SCF) (BM6) have low hydrogen yield because of higher O/C ratio. Being locally available in plenty they can be used for lower end use applications. Air-steam gasification considered for hydrogen generation makes use of the exothermic heat generation within the process to sustain the gasification reactions which are generally endothermic. This action will reduce the external heat requirement necessary to maintain the gasification. The quantification of reduction in heat input and other economic concerns are not the subject of interest in this work.

The predictions of heating value for different biomasses undergoing steam gasification and air-steam gasification are presented in Fig. 5(b). Biomasses are characterised by high O/C ratio. It is observed from Fig. 5(b) that biomasses with higher hydrogen yields have higher heating value. Rubber seed shell (BM3) having higher hydrogen yield will have more heating value. It is predicted that steam gasification will generate producer gas having heating value more than 10 MJ/Nm³ compared to air-steam gasification that produces product gas with heating value more than 5 MJ/Nm³. Among the different biomasses, Rubber seed shell generates product gas with heating value 11.66 MJ/Nm³ (steam gasification) and 6.34 MJ/Nm³ (air-steam gasification). SCF with more O/C ratio will generate product gas with lower heating value.

5. Conclusion

Appropriate selection of biomass is necessary to maximize the yield of the product gas in the gasification process. Thermodynamic equilibrium models are simple mathematical tools to do a preliminary feasibility study in the gasification process. The STEM model formulated for this purpose is tested, and its performance is validated using the statistical parameter RMSE. This model is used to predict the hydrogen yield and heating value of the locally available biomasses. It is observed that the feedstock with maximum H/C ratio and minimum O/C ratio have the potential to generate hydrogen having yields above 85 g/kg of dry ash free biomass and heating value above
11 MJ/Nm³ for steam gasification. However for air-steam gasification, yield and heating value are reduced by about 50% with the advantage of lower heat input for the gasification process.

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References