Modeling syngas composition in an integrated system of biomass gasification, electrolysis and methanation

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Abstract

Composition of biogenous syngas can be improved by integration of electrolysis powered by irregular energy sources, and methanation. A mathematical model has been developed that helps analyzing the mixing and methanation processes of syngas with excess hydrogen. The paper presents the algorithm of the developed model. Results show that the reactions are highly dependent on the catalyst weight introduced in the methanation reactor, and the stoichiometric ratio of hydrogen and carbon monoxide.

Keywords: Gasification; Hydrogen; Methanation; Reaction rate; Sabatier reaction; Syngas

1. Introduction

Gasification has a high potential for generating energy from biomass [1]. Biomass gasification allows using local renewable resources, thus minimizing the environmental impact through avoided greenhouse gas emissions from energy generation [1] and fuel transporting [2]. Commercialization of biomass gasification technologies is still not implemented on a full scale [2], though developments are existent worldwide [1].

The generated biogenous syngas is mostly used in boilers. A more progressive technology for syngas use is for power production in internal combustion engines, gas turbines or fuel cells, as well as for production of synthetic fuel. For such a complicated end-user technology, high-purity syngas with increased heat value is required.

The content and composition of syngas depend on the type of gasification reactor, the retention time and the temperature in the reactor [3]. Table 1 shows the wide variation of syngas composition.

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Table 1. Variation of volumetric composition of biogenous syngas generated in air blown gasifiers, %

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>CO</td>
<td>15-25</td>
<td>10-22</td>
<td>15-20</td>
<td>8.4</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>12-25</td>
<td>11-12</td>
<td>8-10</td>
<td>10.6</td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>6-20</td>
<td>15-21</td>
<td>10-14</td>
<td>22.6</td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>1-5</td>
<td>1-5</td>
<td>2-3</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>Rest</td>
<td>Rest</td>
<td>Rest</td>
<td>13.7</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>2-6</td>
<td>d.m.</td>
<td>d.m.</td>
<td>40.21</td>
<td></td>
</tr>
<tr>
<td>CₙHₘ</td>
<td>n.s.</td>
<td>0.5-2</td>
<td>n.s.</td>
<td>0.59</td>
<td></td>
</tr>
<tr>
<td>Type of gasifier</td>
<td>n.s.</td>
<td>Fixed bed concurrent</td>
<td>Fixed bed contcurrent</td>
<td>Fluidized bed allothermal</td>
<td></td>
</tr>
</tbody>
</table>

n.s. – not specified

d.m. – dry mass

It can be seen from the Table 1, that depending on the gasification technology used, content of H₂ can vary in a wide range. Also, content of CO and CO₂ vary widely, whereas content of CH₄ generally remains low – up to 5%. Though, the CO and CO₂ content can be reduced and the CH₄ content – increased by using physical-chemical process, where CO and CO₂ react with H₂ in the presence of a catalyst. This process is generally known as methanation and Sabatier reactions. Both reactions are exothermic, and such metals as Ni, Ru, Rh, Pt, Fe, Cu and Co supported on various solids as Al₂O₃, SiO₂, ZrO₂, MgO, CeO₂ or TiO₂ are necessary to catalyze them [6].

The main industrial application of methanation and Sabatier reactions has been the removal of traces of CO from H₂-rich feed gases in ammonia plants [7]. Yet, in recent years, study and industrial application of methanation is gaining popularity as a method for treating syngas. Syngas consists of a gas mixture, but is H₂-deficient to achieve complete conversion of the CO and CO₂ into CH₄ [8]. A methanation unit can be integrated into gasification plants for increase of CH₄ content in syngas by adding H₂ to it. H₂ can be obtained from industries with excess H₂ production or by water electrolysis [9]. In order to achieve the reduction of greenhouse gas emissions, power for hydrogen production must be generated by renewable energy sources, primarily biomass, solar, and wind [10].

The aim of this paper is to present a mathematical model developed for forecasting the composition of a gas mixture after syngas has reacted with H₂ in a methanation reactor in an integrated renewable energy system.

2. Methodology

2.1. The modeled system

The modeled system considers a syngas produced from biomass. It is assumed that the required amount of H₂ is produced in an electrolysis process and is added to the syngas in a gas mixing chamber. In addition, it is assumed that the electricity necessary for the electrolysis process is generated with irregular renewable energy sources – wind and solar (see Fig. 1).
After the syngas has been mixed with H₂ the gas mixture enters a methanation reactor. There, according to Xu and Froment (1989) [11], 11 probable reactions take place. It is believed that among them three play a substantial role, i.e. methanation reaction (R1), water-gas shift reaction (R2) and Sabatier reaction (R3).

\[
\begin{align*}
\text{CO} + 3\text{H}_2 & \leftrightarrow \text{CH}_4 + \text{H}_2\text{O} & \Delta H_R &= -206.28 \text{ kJ/mol} \quad \text{(R1)} \\
\text{CO} + \text{H}_2\text{O} & \leftrightarrow \text{CO}_2 + \text{H}_2 & \Delta H_R &= 41.15 \text{ kJ/mol} \quad \text{(R2)} \\
\text{CO}_2 + 4\text{H}_2 & \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O} & \Delta H_R &= -165.12 \text{ kJ/mol} \quad \text{(R3)}
\end{align*}
\]

Reactions R1 and R3 are exothermic, and temperature in the reactor increases. Thereof, a gas cooling system is required prior to gas storage and use.

2.2. Mathematical model

A mathematical model is developed that helps analyzing the syngas conversion process via methanation and Sabatier reactions. The model is developed for the gas mixing and methanation processes (see the highlighted part in Fig. 1). The model is based on reaction rate and mass balance equations. Algorithm of the model is shown in Figure 2.

The syngas with its specific composition is entered in the model, where system and process parameters are set and defined depending on the selected process’ temperature. For stoichiometric conditions amount of additional H₂ necessary for CO and CO₂ conversion is estimated depending on the existing H₂ content in syngas:

\[
m_{\text{H}_2} = M_{\text{H}_2} \left( n_{\text{CO}} \cdot s_{\text{CO}} + n_{\text{CO}_2} \cdot s_{\text{CO}_2} \right) - m'_{\text{H}_2},
\]

where \(m_{\text{H}_2}\) – mass of additional \(\text{H}_2\) required for CO and \(\text{CO}_2\) conversion (kg), \(M_{\text{H}_2}\) – molar weight of \(\text{H}_2\) (kg/kmol), \(n_{\text{CO}}\) – number of CO moles in syngas (kmol), \(s_{\text{CO}}\) – stoichiometric ratio of \(\text{H}_2\) and CO in the methanation reaction, \(n_{\text{CO}_2}\) – number of \(\text{CO}_2\) moles in syngas (kmol), \(s_{\text{CO}_2}\) – stoichiometric ratio of \(\text{H}_2\) and \(\text{CO}_2\) in the Sabatier reaction, \(m'_{\text{H}_2}\) – mass of \(\text{H}_2\) in syngas (kg).
The gas mixture enters the reaction calculation block that estimates the conversion of CO, CO₂ and H₂ based on rates of the reactions R1, R2 and R3 reported by Xu and Froment (1989) [11]. The conversion rates of gas components are estimated by using Eq. (2).

\[ X_i = \frac{F_{i}^o - F_i}{F_{i}^o} \times 100 \]  
\[ \text{where } X_i \text{ – conversion rate of gas component } i \text{ (%), } F_{i}^o \text{ – number of moles of gas component } i \text{ before methanation reactor (kmol), } F_i \text{ – number of moles of gas component } i \text{ after methanation reactor (kmol).} \]

Composition of the gas mixture after the methanation reaction is estimated according to Eqs. 3 – 8.

\[ F_{CO} = F_{CO}^o - w(r_1 - r_2) \]  
\[ F_{CO_2} = F_{CO_2}^o - w(r_2 + r_3) \]  
\[ F_{H_2} = F_{H_2}^o - w(3r_1 + r_2 + 4r_3) \]  
\[ F_{CH_4} = F_{CH_4}^o + w(r_1 + r_3) \]  
\[ F_{H_2O} = F_{H_2O}^o + w(r_1 + r_2 + 3r_3) \]  
\[ F_j = F_j^o \]

where \( w \) – catalyst weight in the methanation reactor (kg), \( r_k \) – rate of reaction (kmol/kg\textsubscript{catalyst}), where \( k \) – reactions R1, R2 and R3, \( j \) – inert gas components as N\(_2\) and C\(_{o}\)H\(_{m}\).

The model is constructed for stoichiometric conditions, i.e. so that the H\(_2\):CO and H\(_2\):CO\(_2\) ratios \( s_{CO} \) and \( s_{CO_2} \) are 3 and 4, respectively. However, in real systems, the stiochiometric ratio is rarely achieved.
Therefore, in the model for experimental purposes, the ratios can be changed by changing the amount of excess H₂ in the gas mixture:

\[ s_{CO}^* = s_{CO} \cdot \alpha \]  \hspace{1cm} (9) \\
\[ s_{CO_2}^* = s_{CO_2} \cdot \beta \]  \hspace{1cm} (10)

where \( s_{k}^* - H_2 \) and COₓ ratio, \( \alpha \) – coefficient of excess H₂ in reaction with CO, \( \beta \) – coefficient of excess H₂ in reaction with CO₂. \( \alpha = 1 \), when \( s_{\text{real}} = s_{\text{stoich}} \); \( \alpha < 1 \), when \( s_{\text{real}} < s_{\text{stoich}} \); \( \alpha > 1 \), when \( s_{\text{real}} > s_{\text{stoich}} \). The same applies for \( \beta \).

In addition, variations in catalyst weight and inlet and outlet temperatures of reactor can be simulated with the model. All the decision blocks are shown in the model algorithm (see Fig.2).

3. Results

In the simulation experiment, syngas with the composition reported by Kienberger et.al., 2013 [5] was used (see Table 1). The volume of syngas generated in the gasifier was assumed to be \( V_s = 1000 \text{ m}^3 \). Coefficient of excess H₂, \( \alpha \), was changed from 0.25 to 4, whereas, \( \beta \) remained equal to 1. In the methanation reactor, the inlet and outlet temperatures of the gas mixture were \( T_{m1} = 573K \) and \( T_{m2} = 773K \), respectively. The simulation was conducted for catalyst weights \( w_1 = 1000 \text{ kg} \) and \( w_2 = 1500 \text{ kg} \) with an assumption that the catalyst is 100% active. The simulation results are shown in Fig. 3.

![Fig. 3. Simulation results with (a) catalyst weight \( w_1 \); (b) catalyst weight \( w_2 \)](image)

The results clearly show that the reactions highly depend on the catalyst weight \( w \). When \( w \) is larger, higher conversion rates are achieved. Moreover, in case of \( w_2 \), complete conversion of CO₂ is achieved. When \( \alpha \) is increased and \( s_{CO} \) becomes larger than 3, the content of CO increases substantially. This is explained by the processes happening in the reaction R2, where CO₂ and H₂ is converted to CO. Generally, conversion rates of CO, CO₂ and H₂ are driven by the reaction rates. As \( r_1 >> r_3 \), higher CO conversion rate is achieved.

4. Conclusions

A mathematical model has been developed for a renewable energy system, where quality of syngas is increased by methanation reaction. Basing on reaction rate and mass balance equations, the model helps
predicting the composition of gas at the methanation reactor’s outlet. Simulation results show that for higher conversion rates of CO and CO₂, the stoichiometric ratio $s_{CO}$ should be held equal to or lower than 3. In addition, amount of catalyst in the reactor should be increased for higher reaction rates.

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References


Biography

Elina Dace is a researcher and assistant professor in the Riga Technical University (Latvia). Her research interests are related to waste management systems and technologies and alternative energy sources. E. Dace is a co-author of 30 scientific publications and 3 books.