Thermodynamics Equilibrium Analysis of Gasification Lecture G-L8-2

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Introduction

- Gasification is a process in which a carbon containing feedstock is thermo-chemically converted into syngas comprising hydrogen (H2) and carbon monoxide (CO).
- Gasification adds value to low or negative value feedstocks by converting them into valuable fuel and/or chemical. Typical feedstock used in the gasification process are coal, biomass and industrial/municipal/agricultural as well as hazardous waste.
- The production of syngas using gasification is a complex process that depends on several factors including the composition of feedstock, the gasifier conditions, temperature and pressure, and the type and amount of oxidizer and moderator (CO2 or Steam).
- The process of gasification utilizes the partial combustion of feedstock by carefully controlling the amount of oxidizer. The amount of oxidizer also controls the temperature of the gasification process, which is the most important parameter of gasifier.
• Gasification process is a series of exothermic and endothermic process. Therefore a substantial amount of thermal energy is required to sustain the process which provided by either an external source of heat or by partial combustion of feedstock.

• During the partial combustion a considerable amount (~25%) of feedstock is burned by the gasification process providing energy to moisture release, devolatilization, the endothermic Boudouard and gas shift reactions as well as the unrecovered sensible heat of the product gas species and the ash.
• This amount is mainly dependant upon the composition and the heating value of the feedstock. The gasification process mainly consists of initial preheating of the feedstock that leads to drying.

• Further increase in temperature causes pyrolysis during which light hydrocarbon (volatiles) start evolving from the feedstock. Finally, the char present in the feedstock either gasified or combusted leaving behind ash. Depending upon the process parameter gasification results mainly in formation of CO, H2, CH4 and CO2.
• The efficiency of gasification process is the major concern that decides the feasibility for the designed system. The efficiency is measured in terms of product syngas heating value to the heating value of feedstock.

• This type of efficiency is termed as cold gasification efficiency (CGE) as it ignores the resulted gas and ash sensible heat and it is widely used to evaluate the effectiveness of gasification process.
• The only major clean element present in the product gas is H2, because H2 combust to produce water. On other hand both CO and CH4 are inclined to produce CO2 during the combustion and thus producing environmental problems.

• The methane gas can be converted into H2 and CO at high temperature but the problem still remain with CO as it combust to give CO2. Therefore, the shift reaction is widely used to convert CO into H2.
• The remaining CO2 is typically separated from the system prior to utilization of the gasification product into power generation, i.e. Brayton Gas turbine cycle or fuel cell.

• In this way the clean fuel is produce in term of H2 gas. So, the extent of H2 from the gasification system is depending upon both the direct H2 gas production from feedstock and indirect production via CO shift reaction. In this way CO also contribute in the formation of clean fuel and add the value in CGE.
• Thermodynamic equilibrium modeling approach is widely used to evaluate the performance of gasification system in terms product gas composition and efficiency.

• Entrained flow gasifiers are the most amenable for equilibrium modeling than the fixed/moving and the bobbling bed gasifiers due to the higher conversion temperature (~1300oK), smaller particle size (10µm-0.1mm), higher mixing and heating rate environments (~3000-10,000K/s) and the fastest conversion rate.
Assumptions

• Samples are taken as dry and ash free.
• Steady state flow is considered inside the gasifier.
• Potential and kinetic energies are neglected.
• Only the major species are considered in the product gases, i.e CO, CO2, H2, CH4 and N2.
• The contribution of ash in energy equation is neglected.
• Ideal gas behavior is considered for all gas phase.
• The gasifier is considered to operate isothermally.
• No heat losses are considered from the gasifier, i.e adiabatic condition.
• Infinite residence time is considered, so that the reaction have ample amount of time to take place.
• At each gasification step, all product gases are considered at same temperature.
Feedstock Characterization

- The baseline calculations are performed using four different feedstocks. The feedstocks are selected to represent the different regions of Van Krevelen diagram.
Table 1: Ultimate analysis of feedstock based on dry ash free (DAF) basis

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>C %Wt</th>
<th>H %Wt</th>
<th>O %Wt</th>
<th>N %Wt</th>
<th>S %Wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>RTC coal</td>
<td>82.17</td>
<td>5.60</td>
<td>8.60</td>
<td>2.50</td>
<td>1.13</td>
</tr>
<tr>
<td>Pine needles</td>
<td>48.58</td>
<td>6.30</td>
<td>43.64</td>
<td>1.48</td>
<td>0.00</td>
</tr>
<tr>
<td>Ply-wood</td>
<td>49.59</td>
<td>6.28</td>
<td>43.74</td>
<td>0.39</td>
<td>0.00</td>
</tr>
<tr>
<td>Lignite[17]</td>
<td>66.03</td>
<td>4.65</td>
<td>25.64</td>
<td>2.07</td>
<td>1.62</td>
</tr>
</tbody>
</table>
### Table 2: Empirical formula and heating value (HHV) of feedstock

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Empirical formula</th>
<th>HHV KJ/Kmole</th>
<th>HHV MJ/Kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>RTC coal</td>
<td>$CH_{0.7946}O_{0.0670}N_{0.0260}$</td>
<td>502928</td>
<td>34.38</td>
</tr>
<tr>
<td>Pine needles</td>
<td>$CH_{1.5550}O_{0.6736}N_{0.0261}$</td>
<td>489784</td>
<td>19.83</td>
</tr>
<tr>
<td>Ply-wood</td>
<td>$CH_{1.5196}O_{0.6615}N_{0.0067}$</td>
<td>487566</td>
<td>20.14</td>
</tr>
<tr>
<td>Lignite</td>
<td>$CH_{0.8450}O_{0.2912}N_{0.0268}$</td>
<td>469939</td>
<td>26.28</td>
</tr>
</tbody>
</table>
Gasification Model

\[ CH_xO_yN_z + m(O_2 + 3.76N_2) \rightarrow x_1H_2 + x_2CO + x_3CO_2 + x_4H_2O + x_5CH_4 + x_6C + (z/2 + 3.76m)N_2 \]
• where \(x, y\) and \(z\) are number of atoms of hydrogen, oxygen and nitrogen based on a single atom of carbon.
• The right hand side of Equation contains a single kmole of feedstock and known kmole of air \((m)\).
• The left hand side of the Equation composed of six unknowns, where, \(x_1, x_2, x_3, x_4, x_5\) and \(x_6\) are the kmole of each corresponding species. Nitrogen \((N_2)\) is not taken as an unknown because it is just a sum from the feedstock and oxidizer. Also, \(N_2\) is taken as un-reacted specie, so it goes in the reaction and comes out un-reacted.
• The one thing worth to mention at this point, that all the quantities \(x, y, z, x_1, x_2, x_3, x_4, x_5\) and \(x_6\) are based on single atom of carbon present in feedstock.
Species mass balance

• To calculate the value of six unknown, six equations are required. Three equations can be derived by the conservation of elemental mass present in the reactants and products. Followings are the mass balance of each element:
carbon balance
\[ x_2 + x_3 + x_5 + x_6 - 1 = 0 \] (3)

hydrogen balance
\[ 2x_1 + 2x_4 + 4x_5 - x = 0 \] (4)

oxygen balance
\[ x_2 + 2x_3 + x_4 - y - 2m = 0 \] (5)
Equilibrium constant formulation

• Now three more equations are required that solved together with equation (3), (4) and (5) to calculate the equilibrium composition of product syngas. These equations are derived using the knowledge of equilibrium constants of elementary reactions. We take the elementary reactions as the intermediate reactions that leads to complete gasification. Solid carbon elementary reactions involving carbon (C), CO, CO2, H2, water (H2O) and CH4 are necessary to describe the overall gasification process. The reactions are as follows,
boudouard reaction

\[ C + CO_2 \rightarrow 2CO \] \hspace{1cm} (6)

CO shift reaction

\[ CO + H_2O \rightarrow CO_2 + H_2 \] \hspace{1cm} (7)

methanation reaction

\[ C + 2H_2 \rightarrow CH_4 \] \hspace{1cm} (8)
Equilibrium constant for boudouard reaction

\[ K_1 = \frac{x_2^2}{x_3 x_{total}} \]  \hspace{1cm} (9)

Equilibrium constant for CO shift reaction

\[ K_2 = \frac{x_3 x_1}{x_2 x_4} \]  \hspace{1cm} (10)

Equilibrium constant for methanation reaction

\[ K_3 = \frac{x_5 x_{total}}{x_1^2} \]  \hspace{1cm} (11)

where \( x_{total} \) is the total number of moles present in the product of Equation (2). That brings a new equation in the system and it is the total sum of moles of product species as follows,
\[ x_{total} = x_1 + x_2 + x_3 + x_4 + x_5 + \left( \frac{Z}{2} + 3.76m \right) \quad (12) \]

The value of equilibrium constant is found out at constant temperature and pressure using the standard state Gibbs function of change (\( \Delta G^o_T \)) [21].

\[ K_i = e^{-\frac{\Delta G^o_T}{RT}} , i = 1,2,3 \quad (13) \]