CHAPTER 3

EXPERIMENTAL SETUP AND METHODOLOGY

3.1 FLUIDIZED BED GASIFIER TEST SETUP

A laboratory scale bubbling fluidized bed gasifier system was designed, fabricated and installed at Energy Lab, Institute for Energy Studies, Anna University, Chennai, India for an experimental investigation. The schematic diagram of an experimental set up is shown in Figure 3.1. A photographic view of the experimental setup is shown in Figure 3.2. The main elements of the installation are: the fluidized bed gasifier, a steam generator, cleaning and sampling system, temperature control system, and the measurement equipment consists of a Siemens make gas chromatograph for gas quality measurement as well as thermocouples and manometer for temperature and pressure control inside the reactor.

A fluidized bed system with screw feeder, microprocessor based automatic control unit was fabricated in this work for analyzing the fuel gas behavior and distribution of product yields of different agricultural residues (coconut shell, groundnut shell, rice husk) and sawdust samples. The system consisted of an external electric heater inside the reactor, cyclone, blower, water scrubber, burners and dry filter, Chromel - Alumel thermocouples, and microprocessor based automatic control unit with temperature indicators, PID (Proportional–Integral–Derivative) controller, heating rate and temperature setting unit. The gasifier unit detail describe in Table 3.1.
1 – control panel; 2 – air blower; 3 – Variable displacement drive motor; 4 – biomass hopper; 5 – steam generator; 6 – Thermo couple; 7 – free board; 8 – Suction blower; 9 – flare; 10 – cyclone; 11 – blower motor; 12 – water scrubber; 13 – water inlet; 14 – to gas analyser; 15 – burner; 16 – dry filter; 17 – fluidized bed gasifier

**Figure 3.1** Experimental fluidized bed gasification system
Table 3.1 Main design and operating features of the bubbling fluidized bed gasifier

<table>
<thead>
<tr>
<th>Type of gasifier</th>
<th>Bubbling fluidized bed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geometrical parameters</td>
<td>ID: 108 mm; total height : 1400 mm</td>
</tr>
<tr>
<td>Heating Type</td>
<td>External electric heating</td>
</tr>
<tr>
<td>Cooling medium</td>
<td>Water</td>
</tr>
<tr>
<td>Feedstock capacity</td>
<td>5-20 kg / h (depending on the type of fuel)</td>
</tr>
<tr>
<td>Feeding equipment</td>
<td>Screw feeder</td>
</tr>
<tr>
<td>Gasifying agents</td>
<td>Air, Steam</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>650 - 950 ºC</td>
</tr>
<tr>
<td>Heating rate</td>
<td>1-60ºC/min</td>
</tr>
<tr>
<td>Feed stock</td>
<td>Coconut shell, groundnut shell, rice husk,</td>
</tr>
<tr>
<td></td>
<td>and saw dust</td>
</tr>
<tr>
<td>Main process variables</td>
<td>Reactor temperature, steam to Biomass ratio</td>
</tr>
<tr>
<td>Fuel gas treatments</td>
<td>Cyclone, Water scrubber, Dry filter</td>
</tr>
</tbody>
</table>

The details of various components, fabrication details, preparation of samples and its properties, experimental procedures are discussed in this chapter. The heating coils were wired at the centre of the furnace and it was insulated with ceramic fiber blankets to prevent the heat loss from the heating coil to atmosphere. The ceramic fiber layer was covered with mild steel sheets as an outer cover. 310 grade stainless steel pipes were used as reactor for heating the samples.

The details of components of the bubbling fluidized bed gasifier have been developed are explained here.
**Figure 3.2** A pictorial view of the experimental setup

**Gasifier:** The bubbling fluidized bed vessel used for the gasification experiments is made of stainless steel. The gasifier is a 0.108 m inside diameter with a length of 1.4 m. The producer gas outlet pipe comes out from the top of the gasifier. The gasifier is fitted with a multiple hole distributor plate of 105 mm diameter was used for air distribution. Figure 3.3 shows the distributor used for this experimental work. The stainless steel gasifier vessel is placed inside an electric furnace such that its surface could get maximum exposure to heating coils for better heat transfer. The gasifier temperature was controlled using a thermocouple with a control panel system. The temperature measurement was carried out with Chromel-Alumel
thermocouples. The control of gasifier temperature is very important to avoid problems resulting from the agglomeration of the ash and bed materials, and subsequent blockage of flow through the system. The ash from the reactor was disposed off periodically through a lock hopper arrangement.

![Photographic view of the distributor plate](image)

**Figure 3.3** A Photographic view of the distributor plate

**Biomass feeding system:** The biomass feeding system consists of two screw feeders with a hopper, the upper feeder is connected to a variable speed drive system that controls the fuel feed rate and supplies the same to the lower screw feeder. The feed was calibrated with rpm of the drive motor. This lower feeder, attached to the gasifier through a feeding port at the height of 0.125 m above the distributor plate, was maintain at a high speed to avoid pyrolysis of biomass inside the screw feeder. This high speed screw feeder pushes the biomass materials instantaneously into the bottom dense region of the fluidized bed. A lock hopper arrangement is located on top of the upper feeder which was filled from the storage of fuel after certain intervals of time during experiment. The mass flow rate of biomass fuels was maintained at the desired operating conditions.

**Steam generator:** The saturated steam was obtained from a small electrically heated boiler and the steam from the boiler was feed to the gasifier above the distributor plate and the quantity of steam was maintained
to keep the gasifier bed in fluidized conditions. The pictorial view of the steam generator is shown in Figure 3.4.

Figure 3.4  Pictorial view of the steam generator

**Gas cleaning and cooling system:** The product gas from the gasifier was made dust-free and cleaned by passing it through a gas cleaning and cooling system before it was being put into gas chromatograph for gas analysis. The hot fuel gas from the fluidized bed gasifier was made to pass through a cyclone to remove the larger particles. After passing through the cyclone, the gas still contained dust particles and tar and hence, it is further cooled and cleaned by passing it through a water scrubber and dry filter.

**Gas flow measurement system:** An orifice plate was positioned on the duct between dry filter and suction blower to measure the gas production rate of the fluidized bed gasifier. The pressure drop across this plate was measured using a differential pressure manometer and this pressure drop was then used to estimate the flow rate of the gases through the orifice plate.
3.2 PROCESS INSTRUMENTATION AND CONTROL

The dry and clean product gas was then analyzed in a Siemens make Online Gas Analyzers viz. Oxymat 61 (Estimates O₂ using paramagnetic principle), Ultramat 23 (Estimates CO, CO₂, and CH₄ using Non Dispersive Infrared multilayer technology) and Calomat 61 (Estimates H₂ using thermal conductivity principle). Figure 3.5 shows the pictorial view of the gas analyzer facilities available in Energy lab, Institute for Energy lab, Anna University, Chennai, India.

![Figure 3.5 Pictorial view of the on line gas analyzer](image)

3.3 BIOMASS SAMPLE PREPARATION

The moisture content in all the samples was initially removed by exposing to natural sun light for a period of 2 weeks. Then all the samples were crushed in the mills, followed by separating into different particle size ranges. The standard sieve (IS designation 460-1962) separator was used to separate the crushed samples into different particle size ranges. The overall sample preparation process is describe as shown in Figure 3.6.
Figure 3.6 The overall sample preparation process

Figure 3.6 shows that the photographic view of the sieve analyzer for separating the biomass samples into different particle size ranges.

Figure 3.7 Photographic views of the sieve analyzer for separating the biomass samples into different particle size ranges.
3.4 SAMPLE TESTING

Compositions of the biomass samples are very essential for this study because it influences the gasification process. Chemical composition and structure of agricultural residues differ from crop to crop and is affected by season, soil type and irrigation conditions. The components and elements present with all the samples and higher heating values of the samples were analyzed in the SGS India Pvt. limited laboratory, Chennai. The samples were tested after crushing and natural drying process for the removal of moisture present in the sample. Figure 3.8 shows the pictorial view of weighing machine used for the experimental work. The carbon, hydrogen, oxygen and nitrogen percentage were found by elemental analysis, volatile matter, fixed carbon and moisture content were found from the component analysis. The protocols used for analyzing the different composition of the samples are given in Table 3.2.

Figure 3.8 Photographic view of the Weighing Machine
Table 3.2  Standards used for analysis

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Protocol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content (%)</td>
<td>ASTM D 3173:2003</td>
</tr>
<tr>
<td>Components</td>
<td></td>
</tr>
<tr>
<td>Volatiles</td>
<td>ASTM D 5142-02 a</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>ASTM D 3172-89</td>
</tr>
<tr>
<td>Ash</td>
<td>ASTM D 3174:2004</td>
</tr>
<tr>
<td>Elemental Analysis</td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>ASTM 5375 2002</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>ASTM 5375 2002</td>
</tr>
<tr>
<td>Oxygen</td>
<td>By difference</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>ASTM 5375 2002</td>
</tr>
<tr>
<td>Sulphur</td>
<td>IS: 4668:1985</td>
</tr>
<tr>
<td>Higher Calorific value (kJ/kg)</td>
<td>ASTM D 5865:2007</td>
</tr>
</tbody>
</table>

3.5  BIOMASS FUELS

The biomass used in the experiments were the rice husk, coconut shell, groundnut shell and saw dust and silica sand as bed materials. No additional catalyst or limestone was used in the gasifier. Photographic views of the selected biomass fuels is described in Figure 3.9.

3.5.1  Rice Husk as a Fuel

Rice husk is abundantly available as an agricultural residue in Tamil nadu, India. Thus, rice husk was selected as the representative biomass for the present investigation. It is estimated from Table 3.3 that the ultimate analysis of rice husk, on basis of dry and ash free condition, yields a typical mass composition of 50.45 % carbon, 41.46 % oxygen and 6.58 % hydrogen with the balance part comprised traces of nitrogen and sulphur. Considering the major elements, the fuel may be represented on a molar basis as CH$_{1.55}$O$_{0.63}$. The theoretical air fuel ratio ($A/F_{th}$) required for the rice husk
was estimated as 6.26. The proximate and ultimate analyses of rice husk have been presented in the Table 3.3.

(a) Rice husk  
(b) Groundnut shell  
(c) Coconut shell (Pulverized)  
(d) Saw dust

Figure 3.9 Photographic views of the selected biomass fuels

Table 3.3 Proximate and Ultimate Analysis of Rice Husk

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Parameters</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content : (Wt. % wet basis)</td>
<td>9.45</td>
<td></td>
</tr>
<tr>
<td><strong>Proximate analysis</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volatile matter</td>
<td>70.6</td>
<td></td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>2.97</td>
<td></td>
</tr>
<tr>
<td>Ash</td>
<td>17.09</td>
<td></td>
</tr>
<tr>
<td><strong>Ultimate analysis</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon (C)</td>
<td>50.45</td>
<td></td>
</tr>
<tr>
<td>Hydrogen (H)</td>
<td>6.58</td>
<td></td>
</tr>
<tr>
<td>Oxygen (O)</td>
<td>41.46</td>
<td></td>
</tr>
<tr>
<td>Nitrogen (N)</td>
<td>1.49</td>
<td></td>
</tr>
<tr>
<td>Sulphur (S)</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>Higher Calorific value (kJ/kg)</td>
<td>19,807</td>
<td></td>
</tr>
</tbody>
</table>
3.5.2 **Groundnut Shell as a Fuel**

The second biomass used in this study was groundnut shell which was procured locally in Thiruvallur near Chennai, Tamilnadu, India. Groundnut shell sample was dried naturally in air and milled. The components and elements present with the samples and properties are illustrated in the Table 3.4. The HHV and moisture content (wet basis) of the sample are 16.91 MJ/kg and 11.12 % respectively. India is the second largest producer of groundnuts after China. Groundnut is the largest oilseed in India in terms of production.

It accounted for 35.99 % of the oilseeds production of the country during 2007-08. In India, Gujarat is the largest producer contributing 25 % of the total production followed by Tamil Nadu (22.48 %), Andhra Pradesh (18.81 %), Karnataka (12.64 %) and Maharashtra (10.09 %) during 2006-07. Every part of groundnut shell is commercially useful. Groundnut is also called as the ‘king’ of oilseeds. It is one of the most important food and cash crops of our country. Groundnut shell has great potential for commercial use. It is used as a fuel, filler in cattle feed, hard particleboard, cork substitute, activated carbon, etc. As a biomass fuel, groundnut shell is a form of energy source to replace the requirement of fossil fuels in the future, as it is abundant, clean, and carbon dioxide neutral. In worldwide level, about two-fifths of the existing biomass energy potential is used. In most areas of the world the current biomass use is clearly below the available potential (van der Drift et al 2001; Matti Parikka 2004). The groundnut oil is primarily needed as a cooking agent but it also has some industrial uses like in paint, varnish, lubricating oil, soap, furniture polish etc. The only waste product from the ground nut is its shell, which contain considerable amount of energy.
Table 3.4  Proximate and ultimate analysis of Groundnut shell

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Parameters</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content</td>
<td>(Wt. % wet basis)</td>
<td>11.12</td>
</tr>
<tr>
<td><strong>Proximate analysis</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volatile matter</td>
<td></td>
<td>65.13</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td></td>
<td>20.86</td>
</tr>
<tr>
<td>Ash</td>
<td></td>
<td>2.89</td>
</tr>
<tr>
<td><strong>Ultimate analysis</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon (C)</td>
<td></td>
<td>52.96</td>
</tr>
<tr>
<td>Hydrogen (H)</td>
<td></td>
<td>6.24</td>
</tr>
<tr>
<td>Oxygen (O)</td>
<td></td>
<td>40.20</td>
</tr>
<tr>
<td>Nitrogen (N)</td>
<td></td>
<td>0.59</td>
</tr>
<tr>
<td>Sulphur (S)</td>
<td></td>
<td>0.22</td>
</tr>
<tr>
<td>Higher Calorific value (kJ/kg)</td>
<td></td>
<td>16,910</td>
</tr>
</tbody>
</table>

The ultimate analysis of groundnut shell, on basis of dry and ash free condition, yields a typical mass composition of 52.96 % carbon, 40.20 % oxygen and 6.24 % hydrogen with the balance part comprised of traces of nitrogen and sulphur. Considering the major elements, the fuel may be represented on a molar basis as CH_{1.40}O_{0.57}. The (A/F)_th required for the groundnut shell was estimated as 6.83.

3.5.3  Coconut Shell as a Fuel

Coconut shell was selected as a third biomass fuel for the present investigation. Traditional areas of coconut cultivation in India are the states of Kerala, Tamil Nadu, Karnataka, Goa, Andhra Pradesh, Orissa, West Bengal, Pondicherry, Maharashtra and the islands of Lakshadweep and Andaman and Nicobar. Four southern states put together account for almost 92% of the total production in the country are Kerala (45.22%), Tamil Nadu (26.56%), Karnataka (10.85%), and Andhra Pradesh (8.93%).
Other states like Goa, Maharashtra, Orissa, West Bengal, and those in the northeast like Tripura and Assam account for the remaining 8.44%. Kerala, which has the largest number of coconut trees, is famous for its coconut-based products like coconut water, copra, coconut oil, coconut cake (also called coconut meal, copra cake, or copra meal), coconut toddy, coconut shell-based products, coconut wood-based products, coconut leaves, and coir pith. In these days of energy shortage, the worth of the coconut as energy source deserves consideration. It is estimated from Table 3.5 that the ultimate analysis of Coconut shell, on basis of dry and ash free condition, yields a typical mass composition of 53.73 % carbon, 38.45 % oxygen and 6.15 % hydrogen with the balance part comprised of traces of nitrogen and sulphur. Considering the major elements, the fuel may be represented on a molar basis as \( \text{CH}_1.36\text{O}_{0.54} \). The (\( A /F \)) required for the coconut shell was estimated as 6.60.

### Table 3.5 Proximate and ultimate analysis of Coconut shell

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Parameters</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content (Wt. % wet basis)</td>
<td>6.98</td>
<td></td>
</tr>
<tr>
<td><strong>Proximate analysis</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volatile matter</td>
<td>72.93</td>
<td></td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>19.48</td>
<td></td>
</tr>
<tr>
<td>Ash</td>
<td>0.61</td>
<td></td>
</tr>
<tr>
<td><strong>Ultimate analysis</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon (C)</td>
<td>53.73</td>
<td></td>
</tr>
<tr>
<td>Hydrogen (H)</td>
<td>6.15</td>
<td></td>
</tr>
<tr>
<td>Oxygen (O)</td>
<td>38.45</td>
<td></td>
</tr>
<tr>
<td>Nitrogen (N)</td>
<td>0.86</td>
<td></td>
</tr>
<tr>
<td>Sulphur (S)</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>Higher Calorific value (kJ/kg)</td>
<td>20,888</td>
<td></td>
</tr>
</tbody>
</table>
3.5.4 Saw dust as a Fuel

Saw dust was selected as a fourth biomass fuel for the present investigation. The sawdust was collected from the sawmill located in Ambattur, Chennai, in which it was generated during sizing of different wood related products. It is estimated from Table 3.6 that the ultimate analysis of saw dust, on basis of dry and ash free condition, yields a typical mass composition of 54.04% carbon, 38.10% oxygen and 6.36% hydrogen with the balance part comprised of traces of nitrogen and sulphur. Considering the major elements, the fuel may be represented on a molar basis as CH$_{1.41}$O$_{0.53}$. The (A/F)$_{th}$ required for saw dust was estimated as 6.74.

Table 3.6 Proximate and ultimate analysis of Sawdust

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Parameters</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content</td>
<td>(Wt. % wet basis)</td>
<td>7.83</td>
</tr>
<tr>
<td>Proximate analysis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volatile matter</td>
<td></td>
<td>75.84</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td></td>
<td>16.39</td>
</tr>
<tr>
<td>Ash</td>
<td></td>
<td>0.77</td>
</tr>
<tr>
<td>Ultimate analysis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon (C)</td>
<td></td>
<td>54.04</td>
</tr>
<tr>
<td>Hydrogen (H)</td>
<td></td>
<td>6.36</td>
</tr>
<tr>
<td>Oxygen (O)</td>
<td></td>
<td>38.10</td>
</tr>
<tr>
<td>Nitrogen (N)</td>
<td></td>
<td>0.52</td>
</tr>
<tr>
<td>Sulphur (S)</td>
<td></td>
<td>0.21</td>
</tr>
<tr>
<td>Higher Calorific value (kJ/kg)</td>
<td></td>
<td>20,728</td>
</tr>
</tbody>
</table>

Tests of above biomass fuels characteristics shows that all the samples having more amounts of carbon and oxygen (the carbon content varies between 50% and 54% and the oxygen content varies between 38% and 45.21%). As compared to Carbon and Oxygen, the Hydrogen content is low
and the values are between 6% and 7%. The Sulfur content in all the samples is very low with less than 0.25%. Which indicate that the usage of biomass will not create any environmental related problems. The fixed carbon, ash and moisture content vary with individual samples. The coconut shell, corncob and sawdust having more fixed carbon and very low ash content, the groundnut shell also contains more fixed carbon but the ash content is more compared with both coconut shell and saw dust. The analysis show that rice husk have very high amount of ash as compared with all other samples in this study. Composition varies with all the samples and this will be useful for studying the influence of different composition on gas yields.

3.6 BED MATERIAL

Silica sand particles, which are group B particles as per Geldart’s classification, were used as bed materials. The sand is solid inert material and the high heat retention capacity makes it suitable for use in fluidized bed system. The sand particles in a mixture ensure proper fluidization and maintain the uniform temperature through out the gasification zone. In the present study, there are six sieves were selected with aperture sizes of 1000, 850, 710, 600, 500 and 355 µm as per the specifications of IS: 460 (Part-I)-1985 to get the suitable size of sand. The sieves were arranged in descending order of their dimensions with a pan at the end. Then the set of sieves is installed in the sieve shaker machine and sand is poured on top of the first sieve. Table 3.7 shows the sieve analysis of sand particles.

The machine is first operated for 10 minutes and the sand passing through 1000 µm and retained at 850 µm is collected. The average aperture size 925 µm is considered as the mean diameter of the sand particles.
Table 3.7 Sieve analysis of Sand particles

<table>
<thead>
<tr>
<th>Sieve aperture size (µm)</th>
<th>Mass particles retained in sieve (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>None</td>
</tr>
<tr>
<td>850</td>
<td>22.6</td>
</tr>
<tr>
<td>710</td>
<td>36.4</td>
</tr>
<tr>
<td>600</td>
<td>105</td>
</tr>
<tr>
<td>500</td>
<td>125</td>
</tr>
<tr>
<td>355</td>
<td>122</td>
</tr>
<tr>
<td>300</td>
<td>85</td>
</tr>
<tr>
<td>Total mass of samples (g)</td>
<td>496</td>
</tr>
</tbody>
</table>

Similarly the mean particle size is 655 µm for the sand passing through 710 µm and retained at 600 µm and the mean particle diameter is 400 µm for the sand passing through 500 µm and retained at 355 µm. From the hydrodynamic analysis, 334 µm is found to be suitable for better fuel particle mixing characteristics.

Table 3.8 Mass fraction of Sand particles of given sizes

<table>
<thead>
<tr>
<th>Aperture size range (µm)</th>
<th>d_i (µm)</th>
<th>x_i</th>
<th>x_i / d_i</th>
</tr>
</thead>
<tbody>
<tr>
<td>850-1000</td>
<td>925</td>
<td>0.243</td>
<td>26.30 x 10^{-5}</td>
</tr>
<tr>
<td>710-850</td>
<td>780</td>
<td>0.663</td>
<td>85.0 x 10^{-5}</td>
</tr>
<tr>
<td>600-710</td>
<td>655</td>
<td>0.132</td>
<td>20.10 x 10^{-5}</td>
</tr>
<tr>
<td>500-600</td>
<td>550</td>
<td>0.687</td>
<td>125.0 x 10^{-5}</td>
</tr>
<tr>
<td>355-500</td>
<td>428</td>
<td>0.184</td>
<td>43.0 x 10^{-5}</td>
</tr>
</tbody>
</table>

$$\sum \frac{x_i}{d_i} = 299.4 \times 10^{-5} \text{ µm}^{-1}$$
Figure 3.10 shows a plot of $x_i$ versus $d_i$ from the Table 3.7.

The mean particle size of sand $d_m = \left( \frac{\sum(x_i/d_i)}{\sum x_i} \right)^{-1}$

Where $d_i =$ arithmetic mean of two adjacent sieve aperture sizes.

$$\frac{1}{d_m} = \sum \frac{x_i}{d_i} = 299.4 \times 10^{-5}$$

$$d_m = \frac{1}{299.4 \times 10^{-5}}$$

The mean particle size ($d_m$) = 334 µm

Figure 3.10 Cumulative particle size distribution of used silica sand samples

3.7 OPERATING METHODOLOGY

Experiments were conducted in a fluidized bed gasifier with the selected agricultural residues ((a) rice husk (b) coconut shell (c) groundnut shell and (d) saw dust with the variations of the following parameters.
- Bed temperature ranges from 650 to 900°C
- Steam to Biomass ratio ranges from 0 to 1.0
- Physical and chemical properties of samples in terms of particle density, ash, oxygen and carbon content in the sample.

The experimental schedule has been designed in order to analyze the individual effects of the main parameters governing the producer gas quality (composition, production) and the gasification performance (gas yield, energy content of the fuel gas), such as: a) varying the bed temperature in the range from 650 °C to 900 °C; b) varying the steam to biomass ratio in the range from 0 to 1. At the start of each experimental run, the agricultural residue (Coconut Shell, Groundnut Shell, Rice husk and Sawdust) was added to the hopper. In order to study the fluidization behaviour of the selected material, it is loaded in to the bed and then fluidized vigorously to break down any packing or interlocking of the particles. The air flow rate is gradually decreased in steps and the pressure drop across the bed is recorded for each air flow rate. In order to study the fluidization behaviour of the selected biomass fuels, each fuel is first loaded in the bed. The air supply is increased gradually to bring the bed of particles into fluization regime. Then the velocity is gradually decreased, while recording the pressure drop across the bed. In compare with other fuels, for rice husk high superficial velocities are required to fluidize the rice husk particles because of their inter-particle friction due to their rough abrasive surfaces. The minimum fluidized bed velocity is found to be about 50 cm / s from its pressure drop curve.

To start the experiment test, the furnace heater was set at the selected operating temperature. At the beginning of the experiment, the reactor was charged with 3 kg of silica sand of mean diameter 0.334 mm as a bed material, which helped in stable fluidization and better heat transfer.
After the bed temperature reached the desired level and became remained steady, the samples were fed to the fluidized bed reactor and the flow rate of biomass was controlled by a variable speed motor drive. The supply of air was gradually reduced and the super heated steam at 200 ºC was introduced at the side of the reactor. The bed was operated in fluidized condition with air as fluidizing medium and steam as gasifying medium and the test began. Five samples were taken at an interval of 3 minutes after the test ran in a stable state. Normally each experiment was repeated two times and the results were good agreement. The gas stream was passes through a water scrubber followed by a dry filter. Grab samples of cool, clean and dry gas were collected and analyzed in on line gas analyzer for the permanent gases H₂, CO, CO₂ and CH₄.

Experiments performed in the fluidized bed gasifier were carried out in two groups for all the samples. In the first, to determine the effect of the temperature (650 to 900 ºC) on the gas composition, gas yield, LHV, carbon conversion efficiency at a constant fuel feed rate and equivalence ratio. The second group of experiments was performed in order to determine the effect of steam to biomass ratio (0 to 1.0) on the gas composition, gas yield, LHV, carbon conversion efficiency. The biomass flow rate for the selected fuels rice husk, coconut shell, groundnut shell and sawdust were varied from 1.5 to 6 kg/h, 4 to 18 kg/hr, 8 to 35 kg/h and 5 to 25 kg/h respectively.

Equilibrium modeling was carried out to predict the producer gas composition under varying performance influencing parameters, viz., temperature, steam to biomass ratio. The results were compared with the experimental output. Thermodynamic equilibrium composition prediction is the important step in modeling the gasification process. Here the biomass is represented as CHₓOᵧ. The biomass is reacted with steam and air to give
product gases viz. CO, CO₂, H₂ and CH₄. The model assumes that the principle reactions are at thermodynamic equilibrium. The model equations containing three atom balances (C, O, and H) and three equilibrium relations are solved for gas compositions.

3.8 DATA REDUCTION

The main performance characteristics evaluated from the measured data were equivalence ratio, carbon conversion efficiency, heating value (Lv et al. 2004).

i) Equivalence ratio:

\[
\text{E.R.} = \frac{\text{Weight of oxygen (air)} / \text{weight of dry biomass}}{\text{Stoichiometric oxygen (air) weight of dry biomass}}
\]  

(3.1)

ii) Hot gas efficiency:

\[
\eta_{\text{hot gas efficiency}} = \frac{\text{Fuel gas flow rate (m}^3/\text{h}) \times \text{HHV of gas (kJ/m}^3) \times 100}{\text{Fuel consumption (kg/h) \times HHV of fuel (kJ/kg)}}
\]  

(3.2)

iii) Cold gas efficiency:

\[
\eta_{\text{cold gas efficiency}} = \frac{\text{LHV of gas (kJ/m}^3) \times \text{Fuel gas production (m}^3/\text{kg}) \times 100}{\text{LHV of the biomass fed in the system (kJ/kg)}}
\]  

(3.3)

iv) Carbon conversion efficiency:

\[
\eta_{\text{Carbon conversion}} = \frac{\text{G}_y(\text{CO}\% + \text{CH}_4\% + \text{CO}_2\%) \times 12}{22.4 \times \text{C}\%} \times 100
\]  

(3.4)

where C% is the mass percentage of carbon in the feed obtained from the ultimate analysis of the biomass.

v) Gas Yield:

\[
G_y = \frac{\text{Product gas (Nm}^3)}{\text{Dry biomass (kg)}}
\]  

(3.5)
vi) Dry product gas low heating value, LHV (kJ/ Nm$^3$)

$$LHV = (30.0 \times CO + 25.7 \times H_2 + 85.4 \times CH_4 + 151.3 \times C_n H_m) + 4.2 \text{ kJ / Nm}^3$$  \hspace{1cm} (3.6)

where CO, H$_2$, etc. are the gas concentrations of the product gas.

vii) The HHV of the dry gas was determined from the following equation (Xiao et al 2006):

$$HHV = (H_2\% \times 30.52 + CO\% \times 30.18 + CH_4\% \times 95)$$

$$\times 4.1868 \text{ (MJ/Nm}^3\text{)}$$  \hspace{1cm} (3.7)

where H$_2$, CO and CH$_4$ are the volumetric percentage in the fuel gas.

3.9 MODELING

To model the gasification process in detail, knowledge of chemical reaction kinetics is required which is not available in open literature. Thermodynamic equilibrium composition prediction is the important step in modeling the gasification process. Here the biomass is represented as CH$_x$O$_y$. The biomass is reacted with steam and air to give product gases viz. CO, CO$_2$, H$_2$ and CH$_4$. The model assumes that the principle reactions are at thermodynamic equilibrium. The model equations containing four atom balances (C, O, H and N) and three equilibrium relations are solved for gas compositions. The four types of biomasses are used for prediction of equilibrium gas compositions. The process of biomass gasification involves three steps, which are: the initial devolatiliation or pyrolysis step which produces volatile matter and a char residue, followed by secondary reactions involving the volatile products and finally, the gasification reactions of the remaining carbonaceous residue with steam and carbon dioxide. The biomass
devolatilization occurs instantaneously after its introduction to the reactor resulting in volatiles and char.

Different types of models have been developed by Vamvuka et al (1995), Ruggiero and manfrida (1999) for gasification systems - kinetic, equilibrium and others. Unlike kinetic models that predict the progress and product composition at different positions along a reactor, an equilibrium model predicts the maximum achievable yield of a desired product from a reacting system. It also provides a useful design aid in evaluating the limiting possible behaviour of a complex reacting system which is difficult to reproduce experimentally or in commercial operation.

At chemical equilibrium, a reacting system is at its most stable composition, a condition achieved when the entropy of the system is maximized, while its Gibbs free energy is minimized.

Smith and Missen (1982) described two approaches for equilibrium modeling: stoichiometric and non-stoichiometric. The stoichiometric approach requires a clearly defined reaction mechanism incorporating all chemical reactions and species involved. In a non-stoichiometric formulation, on the other hand, no particular reaction mechanism or species are involved in the numerical solution. The only input needed to specify the feed is its elemental composition, which can be readily obtained from ultimate analysis data. This method is particularly suitable for problems with unclear reaction mechanisms as well as feed streams like biomass, whose precise chemical compositions are unknown. In the equilibrium model, the reactor is implicitly considered to be zero-dimensional, i.e. neither spatial distribution nor change of parameters with time is considered because all forward and reverse reactions have reached chemical equilibrium. The molar inflow for any individual element involved in the chemical reactions can then be written as the sum of moles of that element in the various feed streams.
3.9.1 Assumptions

In view of this, a thermodynamic equilibrium model was used to predict the gas composition. The basic assumptions of the present model are:

- Biomass is represented by the general formula CH$_x$O$_y$.
- The ideal gas laws are valid.
- All reactions are at thermodynamic equilibrium.
- The gasification products contain CO$_2$, CO, H$_2$, CH$_4$, N$_2$, H$_2$O.
- Nitrogen present in both fuel and air is inert.
- The pressure is atmospheric and constant in the char bed.
- Ash is inert and is not involved in any reactions, either as a chemical species or as a catalyst.
- No gas is accumulated in the char bed.
- There is no tar in the gasification zone.

To develop the model, the chemical formula of rice husk as a biomass feedstock is defined as CH$_{1.56}$O$_{0.62}$. The global air-steam gasification reaction can be written as follows (Koroneos and Lykidou 2011)

\[
\text{CH}_x\text{O}_y + w \text{H}_2\text{O} + m (\text{O}_2 + 3.76\text{N}_2) = x_1\text{H}_2 + x_2\text{CO} + x_3\text{CO}_2 \\
+ x_4\text{H}_2\text{O} + x_5\text{CH}_4 + 3.76m\text{N}_2 \quad (3.8)
\]

where, $x$ and $y$ are the number of atoms of hydrogen and oxygen per number of carbon in the biomass. The moisture content of the biomass is neglected and the product quality depends on the $x$ and $y$.
The above reaction represents an overall reaction but a number of competing intermediate reactions take place during the process. These are,

1) Oxidation :
\[ C + O_2 \rightarrow CO_2 \quad \Delta H^0_r = -393.8 \text{ kJ / mol} \] (3.9)

2) Steam gasification :
\[ C + H_2O \rightarrow CO + H_2 \quad \Delta H^0_r = +131.3 \text{ kJ / mol} \] (3.10)

3) Boudouard reaction :
\[ C + CO_2 \rightarrow 2 CO \quad \Delta H^0_r = +172.6 \text{ kJ / mol} \] (3.11)

4) Methanation reaction :
\[ C + 2H_2 = CH_4 \quad \Delta H^0_r = -74.9 \text{ kJ / mol} \] (3.12)

5) Water gas-shift reaction :
\[ CO + H_2O = CO_2 + H_2 \quad \Delta H^0_r = -41.2 \text{ kJ / mol} \] (3.13)

According to Von Fredersdorff and Elliot (1963), the three reactions namely, Boudouard (equation 3.11), steam gasification (equation 3.10) and methanation (equation 3.12) are in equilibrium and the water gas shift reaction (equation 3.13) is a combination of the Boudouard and steam gasification reactions. Hence, the water gas shift and methanation reaction could be considered to be in equilibrium. Oxidation reaction (equation 3.9) is typically assumed to be very fast and goes to completion.

To find the five unknown species i.e. \( x_1, x_2, x_3, x_4 \) and \( x_5 \) of the fuel gas, five equations are required. Those equations are generated using mass balance and equilibrium constant relationships.
3.9.2 Mass balance

Considering the global air-steam gasification reaction in equation (3.8), the first three equations were formulated by balancing each chemical element as shown in equation (3.14) to equation (3.16) (Ramirez et al 2007).

Taking atom balances on carbon, oxygen, hydrogen and nitrogen, we obtain,

\[
\begin{align*}
\text{Carbon} & : 1 = x_2 + x_3 + x_5 & (3.14) \\
\text{Oxygen} & : y + w + 2 m = x_2 + 2 x_3 + x_4 & (3.15) \\
\text{Hydrogen} & : x + 2 w = 2 x_1 + 2 x_4 + 4 x_5 & (3.16)
\end{align*}
\]

3.10 THERMODYNAMIC EQUILIBRIUM

Equilibrium is explained either by minimization of Gibb’s free energy or using an equilibrium constant. To minimize the Gibb’s free energy, constrained optimization methods are generally employed. Thus, to avoid complicated mathematical theories associated with this Gibb’s free energy approach, the present model in this study is based on the equilibrium constant method, although it has been developed based on thermodynamic equilibrium.

From the Zainal et al (2001), the equilibrium constant $K$ is a function of temperature and can be written as,

\[
\ln K_e = -\frac{\Delta G^0}{RT} \quad (3.17)
\]

where, $\Delta G^0$ is the Gibb’s free energy (kJ/mol), $T$ is the temperature in K and $R$ is the universal gas constant in consistent units.
Equation (3.17) can be rewritten as,

\[- RT \ln K_e = \Delta G^0 \]  \hspace{1cm} (3.18)

\[ \frac{d \ln K}{dT} = \frac{DH^0}{RT^2} \]  \hspace{1cm} (3.19)

Integrating equation (3.19), the heat of formation can be calculated as follows,

\[ \ln K = \vartheta \frac{DH^0}{RT^2} dT + I \]  \hspace{1cm} (3.20)

The $\Delta H^0$ can also be calculated as per the following equations as suggested by Robert and Don (1984)

\[ \frac{DH^0}{R} = \frac{J}{R} + \frac{DA.T}{2} + \frac{DB.T^2}{6} + \frac{DCT^3}{3} - \frac{DD}{T} \]  \hspace{1cm} (3.21)

Substituting equation (3.21) into equation (3.20), one gets

\[ \ln K = \frac{J}{R} + \frac{DA}{R} \ln T + \frac{DB.T}{2} + \frac{DCT^2}{6} + \frac{DD}{2T^2} + I \]  \hspace{1cm} (3.22)

The dependence of $\Delta G^0$ on temperature can be analyzed as per the following equation,

\[ DG^0 = J - \frac{R.T}{\xi} \hat{D.A.} \ln T + \frac{DB.T}{2} + \frac{DCT^2}{6} + \frac{DT}{2T^2} + \frac{\dot{u}}{\dot{u}} \]  \hspace{1cm} (3.23)

Both J and I are respectively calculated from equation (3.21) and equation (3.23) corresponding to temperature 298 K.
The equilibrium constants for the chemical reactions corresponding to equation (3.22) and (3.23) are assumed to be \(K_1\) and \(K_2\) respectively. In the analyses, suffixes 1 and 2 have been used for I, J and other constants associated with the calculations of \(K_1\) and \(K_2\) using equation (3.22) and (3.23).

The equilibrium relations for the three reactions (other than oxidation) are,

1) Methanation reaction

\[
K_1 = \frac{x_5}{(x_1)^2} \tag{3.24}
\]

The equilibrium constant, \(K_1\) is solved using the following steps which are expressed as follows:

For the reaction in equation (3.23), the following relation may be written.

\[
\Delta = CH_4 - C - 2H_2 \tag{3.25}
\]

The equations to determine the values of \(\Delta A\), \(\Delta B\), \(\Delta C\), \(\Delta D\) can be written as per Robert and Don (1984), one gets

\[
DA_1 = A_{CH_4} - A_C - 2A_{H_2} \tag{3.26}
\]

\[
DB_1 = B_{CH_4} - B_C - 2B_{H_2} \tag{3.27}
\]

\[
DC_1 = C_{CH_4} - C_C - 2C_{H_2} \tag{3.28}
\]

\[
DD_1 = D_{CH_4} - D_C - 2D_{H_2} \tag{3.29}
\]
Using the data of heat capacity constants A, B, C and D from Table 3.9 adapted from Robert and Don (1984).

\[ \Delta A_1 = 1.702 - 1.771 - 2(3.249) = -6.567 \quad (3.30) \]

\[ \Delta B_1 = (9.081 - 0.771 - 2(0.422)) \times 10^{-3} = 7.466 \times 10^{-3} \quad (3.31) \]

\[ \Delta C_1 = (-2.164 - 0 - 2(0)) \times 10^6 = -2.164 \times 10^6 \quad (3.32) \]

\[ \Delta D_1 = (0 - (-0.867) - 2(0.0833)) \times 10^5 = 0.701 \times 10^5 \quad (3.33) \]

**Table 3.9 Heat capacity constants A, B, C and D**

<table>
<thead>
<tr>
<th>Chemical Species</th>
<th>(T_{\text{max}}, \text{K})</th>
<th>A</th>
<th>(10^{-3} \text{B})</th>
<th>(10^6 \text{C})</th>
<th>(10^5 \text{D})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>1500</td>
<td>1.702</td>
<td>9.081</td>
<td>-2.164</td>
<td>-</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>3000</td>
<td>3.249</td>
<td>0.422</td>
<td>-</td>
<td>0.083</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>2500</td>
<td>3.376</td>
<td>0.557</td>
<td>-</td>
<td>-0.031</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>2000</td>
<td>5.457</td>
<td>1.047</td>
<td>-</td>
<td>-1.157</td>
</tr>
<tr>
<td>Water</td>
<td>2000</td>
<td>3.470</td>
<td>1.450</td>
<td>-</td>
<td>0.121</td>
</tr>
<tr>
<td>Carbon</td>
<td>2000</td>
<td>1.771</td>
<td>0.771</td>
<td>-</td>
<td>0.867</td>
</tr>
</tbody>
</table>

Source: Robert and Don (1984)

The values of the heat of formation and the Gibbs function of formation for various gas compositions are available in Table 3.10 (Stull and Prophet (1971)) and Table 3.11 (Stull and Prophet (1971)) respectively.

Calculation of constants \(J_1\) and \(I_1\) in equation (3.21) and (3.23) at 298.15 K requires the values for \((\Delta H^0_{298})_1\) and \((\Delta G^0_{298})_1\).

\[
(\Delta H^0_{298})_1 = (\Delta H^0_{298})_{\text{CH}_4} - (\Delta H^0_{298})_{\text{C}} - (\Delta H^0_{298})_{\text{H}_2}
\]
\[
(DH_{298}^0)_1 = -74520 - 0 = -74520
\]

\[
(DG_{298}^0)_1 = (DG_{298}^0)_{CH_4} - (DG_{298}^0)_C - (DG_{298}^0)_{H_2} 
= -50460 - 0 = -50460
\]  \hspace{1cm} (3.35)

**Table 3.10 Heat of formation at 298.15 K in kJ/kmol**

<table>
<thead>
<tr>
<th>Chemical Species</th>
<th>Phase</th>
<th>( \Delta H_{298}^o )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>g</td>
<td>-241818</td>
</tr>
<tr>
<td>Water</td>
<td>l</td>
<td>-285830</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>g</td>
<td>-393509</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>g</td>
<td>-110525</td>
</tr>
<tr>
<td>Methane</td>
<td>g</td>
<td>-74520</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>g</td>
<td>0</td>
</tr>
<tr>
<td>Oxygen</td>
<td>g</td>
<td>0</td>
</tr>
</tbody>
</table>

Source: Stull and Prophet (1971)

**Table 3.11 Gibb’s function of formation at 298.15 K in kJ / kmol**

<table>
<thead>
<tr>
<th>Chemical Species</th>
<th>Phase</th>
<th>( \Delta G_{298}^o )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>g</td>
<td>-228572</td>
</tr>
<tr>
<td>Water</td>
<td>l</td>
<td>-237129</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>g</td>
<td>-394359</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>g</td>
<td>-137169</td>
</tr>
<tr>
<td>Methane</td>
<td>g</td>
<td>-50460</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>g</td>
<td>0</td>
</tr>
<tr>
<td>Oxygen</td>
<td>g</td>
<td>0</td>
</tr>
</tbody>
</table>

Source: Stull and Prophet (1971).
Substituting the known values into equation (3.21) for $T = 298.15$ K gives,

$$\frac{-74520}{8.314} = \frac{J_1}{8.314} + (-6.657)298.15 + \frac{7.466 \times 10^{-3}}{2} 298.15^2$$

$$+ \frac{(-2.164 \times 10^{-6})}{3} 298.15^3 - \frac{0.701 \times 10^5}{298.15}$$

$$\rightarrow J_1 = -58886.8$$

Substituting the known values into equation (3.23) for $T = 298.15$ K, it gives,

$$-50460 = -58886.8 - 8.314(298.15) [-6.567 \ln 298.15$$

$$+ \frac{7.466 \times 10^{-3}}{2} 298.15 + \frac{(2.164 \times 10^{-6})}{3} 298.15^2$$

$$+ \frac{0.701 \times 10^5}{(2 \times 298.15)^3} + I_1$$

$$\rightarrow I_1 = 32.534$$

Therefore the general equation for $K_1$ in equation (3.22) is

$$\ln K_1 = \frac{7082.848}{T} + (-6.567) \ln(T) + \frac{7.466 \times 10^{-3}}{2} T$$

$$+ \frac{(-2.164 \times 10^{-6})}{6} T^2 + \frac{0.701 \times 10^5}{2(T)^3} + 32.534$$

The equilibrium constant $K_1$ for any temperature $T$ can be obtained by substituting the temperature into equation (3.38).
The equilibrium constant $K_2$ for Water gas shift reaction in equation (3.13) may be expressed as,

$$K_2 = \frac{x_3}{x_2} \frac{x_1}{x_4}$$  \hspace{1cm} (3.39)

The equilibrium constant $(K_2)$ is solved using the following steps which are expressed as follows,

For the reaction in equation (3.13), the following relation can be written as,

$$\Lambda = \text{CO}_2 + \text{H}_2 - \text{CO} - \text{H}_2\text{O}$$ \hspace{1cm} (3.40)

The equations to determine the values of $\Delta A_2$, $\Delta B_2$, $\Delta C_2$ and $\Delta D_2$ can be written as Robert and Don (1984), ones gets,

$$DA_2 = A_{\text{CO}_2} + A_{\text{H}_2} - A_{\text{CO}} - A_{\text{H}_2\text{O}}$$ \hspace{1cm} (3.41)

$$DB_2 = B_{\text{CO}_2} + B_{\text{H}_2} - B_{\text{CO}} - B_{\text{H}_2\text{O}}$$ \hspace{1cm} (3.42)

$$DC_2 = C_{\text{CO}_2} + C_{\text{H}_2} - C_{\text{CO}} - C_{\text{H}_2\text{O}}$$ \hspace{1cm} (3.43)

$$DD_2 = D_{\text{CO}_2} + D_{\text{H}_2} - D_{\text{CO}} - D_{\text{H}_2\text{O}}$$ \hspace{1cm} (3.44)

Using the data of heat capacity constants $A$, $B$, $C$ and $D$ from Table 3.9, Robert and Don (1984),

$$\Delta A_2 = 5.457 + 3.249 - 3.376 - 3.470 = 1.86$$ \hspace{1cm} (3.45)

$$\Delta B_2 = (1.047 + 0.422 - 0.557 - 1.45) \times 10^{-3} = -0.538 \times 10^{-3}$$ \hspace{1cm} (3.46)

$$\Delta C_2 = (0 + 0 - 0 - 0) = 0$$ \hspace{1cm} (3.47)
\[
\Delta D_2 = (-1.157 + 0.083 - (-0.031) - 0.121) \times 10^5 \\
= -1.164 \times 10^5
\]  

(3.48)

Calculation of constants \(J_2\) and \(I_2\) in equation (3.20) and (3.22) at 298.15 K requires the values for \((\Delta H_{298}^0)_2\) and \((\Delta G_{298}^0)_2\). This data of the heat of formation and the Gibb’s function of formation of various species are available from Table 3.8 and Table 3.9 respectively.

\[
(\Delta H_{298}^0)_2 = (\Delta H_{298}^0)_{CO_2} + (\Delta H_{298}^0)_{H_2} - (\Delta H_{298}^0)_{CO} - (\Delta H_{298}^0)_{H_2O} \quad (3.49)
\]

\[
(\Delta H_{298}^0)_2 = -393509 + 0 - (-110525) - (-231818) = -41166
\]

and

\[
(\Delta G_{298}^0)_2 = (\Delta G_{298}^0)_{CO_2} + (\Delta G_{298}^0)_{H_2} - (\Delta G_{298}^0)_{CO} - (\Delta G_{298}^0)_{H_2O} \quad (3.50)
\]

\[
(\Delta G_{298}^0)_2 = -394359 + 0 - (-137169) - (-228572) = -28618
\]

Substituting the known values into equation (3.21) for \(T = 298.15\) K, it gives

\[
\frac{-41166}{8.314} = \frac{J_2}{8.314} + (1.86)298.15 + \frac{(-0.538 \times 10^3)}{2}298.15^2 + 0 - \frac{1.164 \times 10^5}{298.15}
\]

(3.51)

\[
\rightarrow J_2 = -48823.2
\]

Substituting the known values into equation (3.22) for \(T = 298.15\) K

\[
-28618 = -48823.2 - 8.314(298.15)[1.86 \ln 298.15
\]

\[
+ \frac{0.538 \times 10^3}{2}298.15 + 0 - \frac{1.164 \times 10^5}{2(298.15)^2} + I_2]
\]

(3.52)
\[ \rightarrow I_2 = -18.0156. \]

Therefore the general equation for \( K_2 \) using equation (3.23) is,

\[
\ln K_2 = \frac{5872.4}{T} + 1.86 \ln(T) - \frac{0.538 \times 10^3}{2} T + \frac{(-1.164 \times 10^5)}{2(T)^2} - 18.0156
\]

(3.53)

The equilibrium constant \( K_2 \) for any temperature \( T \) can be obtained by substituting temperature \( T \) into equation (3.53).

The molar concentration of individual species for global reaction of equation (1) could be predicted by using \( K_1 \) and \( K_2 \).

By solving equations (3.14), (3.15), (3.16), (3.24) and (3.39) the following Correlations are obtained which include the molar concentrations \( x_1, x_2 \) and \( x_3 \), and also the equilibrium constants \( K_1 \) and \( K_2 \)

\[
K_1 x_1^2 + x_2 + x_3 - 1 = 0 \quad (3.54)
\]

\[
K_2 x_1 x_2 - \{ w + m - (2-x) \} K_2 x_2 - 2K_2 x_2^2 + x_1 x_3 - 2K_2 x_2 x_3 = 0 \quad (3.55)
\]

\[
x_1 - 3x_2 - 4x_3 + (2 + y - x) = 0 \quad (3.56)
\]

The molar concentrations \( x_1, x_2 \) and \( x_3 \) are predicted by solving the equations (3.14 - 3.16), (3.24) to (3.39). The molar concentration \( x_4 \) and \( x_5 \) are then calculated with known values of \( x_1, x_2 \) and \( x_3 \) using the following equations.

\[
x_4 = w + m + x/2 - x_1 - 2(1 - x_2 - x_3) \quad (3.57)
\]

\[
x_5 = 1 - x_2 - x_3 \quad (3.58)
\]
where, x and y are the number of atoms of hydrogen and oxygen per number of carbon in the biomass. The moisture content of the biomass is neglected and the product quality depends on the x and y.

### 3.11 ENERGY BALANCE

Energy balance equation of reactants and products of global steam gasification reaction in equation (3.8) is shown in the following.

\[
(H^o_{f,m} + w \cdot H_{H_2O}) + m \cdot H_{H_2O(g)} + Q_{in} = x_1 \left( H^o_{f,n_2} + \Delta T \cdot Cp_{H_2} \right) + x_2 \left( H^o_{f,CO} + \Delta T \cdot Cp_{CO} \right) + x_3 \left( H^o_{f,CO_2} + \Delta T \cdot Cp_{CO_2} \right) + x_4 \left( H^o_{f,n_2(vap)} + \Delta T \cdot Cp_{H_2O} \right) + x_5 \left( H^o_{f,CH_4} + \Delta T \cdot Cp_{CH_4} \right)
\]  
(3.59)

The heat balance equation (3.59) contains a term \( Q_{in} \) which stands for the external heat addition required for endothermic reactions to occur.

\[
\left\{ H^o_{f,m} + w \cdot (H^o_{H_2O(l)} + H_{vap}) \right\} + m \cdot \left\{ H_{H_2O(g)} + \Delta T \cdot f_{H_2O(g)} \right\} + Q_{in} = x_1 \left( H^o_{f,n_2} + \Delta T \cdot Cp_{H_2} \right) + x_2 \left( H^o_{f,CO} + \Delta T \cdot Cp_{CO} \right) + x_3 \left( H^o_{f,CO_2} + \Delta T \cdot Cp_{CO_2} \right) + x_4 \left( H^o_{f,n_2(vap)} + \Delta T \cdot Cp_{H_2O} \right) + x_5 \left( H^o_{f,CH_4} + \Delta T \cdot Cp_{CH_4} \right)
\]
(3.60)

Since \( H^o_{f,n_2} = 0 \) then the above equation may be written as,

\[
\Rightarrow \left\{ H^o_{f,m} + w \cdot (H^o_{H_2O(l)} + H_{vap}) \right\} + m \cdot \left\{ H^o_{H_2O(g)} + \Delta T \cdot f_{H_2O(g)} \right\} + Q_{in} = x_1 \left( \Delta T \cdot Cp_{H_2} \right) + x_2 \left( H^o_{f,CO} + \Delta T \cdot Cp_{CO} \right) + x_3 \left( H^o_{f,CO_2} + \Delta T \cdot Cp_{CO_2} \right) + x_4 \left( H^o_{f,n_2(vap)} + \Delta T \cdot Cp_{H_2O} \right) + x_5 \left( H^o_{f,CH_4} + \Delta T \cdot Cp_{CH_4} \right)
\]
(3.61)

\[
\Rightarrow H^o_{f,m} + w \cdot dH_{H_2O} + m \cdot dH_{H_2O(g)} + Q_{in} = x_1 \cdot dH_{H_2} + x_2 \cdot dH_{CO} + x_3 \cdot dH_{CO_2} + x_4 \cdot dH_{H_2O(g)} + x_5 \cdot dH_{CH_4}
\]
(3.62)

\[
\Rightarrow H^o_{f,m} + w \cdot dH_{H_2O} + m \cdot dH_{H_2O(g)} + Q_{in}
\]
Now the expression of $Q_m$ may be stated as follows,

$$Q_m = a_1 x_1 + a_2 x_2 + a_3 x_3 + a_4 w + a_5 m + a_6$$

(3.66)

where,

$$a_1 = \left\{ \begin{array}{c} \left\{ dH_{H_2} - dH_{H_2O(g)} \right\} \end{array} \right.$$ 

$$a_2 = \left\{ \begin{array}{c} \left\{ dH_{CO} + 2dH_{H_2O} - dH_{CH_4} \right\} \end{array} \right.$$ 

$$a_3 = \left\{ \begin{array}{c} \left\{ dH_{CO_2} + 2dH_{H_2O} - dH_{CH_4} \right\} \end{array} \right.$$ 

$$a_4 = \left\{ \begin{array}{c} \left\{ dH_{H_2O(g)} - dH_{H_2O(RH)} \right\} \end{array} \right.$$ 

$$a_5 = \left\{ \begin{array}{c} \left\{ dH_{H_2O(g)} - dH_{H_2O(FS)} \right\} \end{array} \right.$$ 

$$a_6 = \left\{ \begin{array}{c} \left\{ dH_{CH_4} - H^o_{f_{sm}} - (2-x) dH_{H_2O(g)} \right\} \end{array} \right.$$ 

(3.67)
\[ dH_{H_2} = H^\circ_{f\ H_2} + \Delta T \cdot Cp_{H_2} \]

\[ \Rightarrow dH_{H_2} = \Delta T \left[ A_{H_2} + B_{H_2} \cdot T_m + \frac{C_{H_2}}{3} \left( 4 \cdot T^2_m - T_1 T_2 \right) + \frac{D_{H_2}}{T_1 T_2} \right] \quad (3.68) \]

\[ dH_{CO} = H^\circ_{f\ CO} + \Delta T \cdot Cp_{CO} \]

\[ \Rightarrow dH_{CO} = H^\circ_{f\ CO} + \Delta T \left[ A_{CO} + B_{CO} \cdot T_m + \frac{C_{CO}}{3} \left( 4 \cdot T^2_m - T_1 T_2 \right) + \frac{D_{CO}}{T_1 T_2} \right] \quad (3.69) \]

\[ dH_{CO_2} = H^\circ_{f\ CO_2} + \Delta T \cdot Cp_{CO_2} \]

\[ \Rightarrow dH_{CO_2} = H^\circ_{f\ CO_2} + \Delta T \left[ A_{CO_2} + B_{CO_2} \cdot T_m + \frac{C_{CO_2}}{3} \left( 4 \cdot T^2_m - T_1 T_2 \right) + \frac{D_{CO_2}}{T_1 T_2} \right] \quad (3.70) \]

\[ dH_{CH_4} = H^\circ_{f\ CH_4} + \Delta T \cdot Cp_{CH_4} \]

\[ \Rightarrow dH_{CH_4} = H^\circ_{f\ CH_4} + \Delta T \left[ A_{CH_4} + B_{CH_4} \cdot T_m + \frac{C_{CH_4}}{3} \left( 4 \cdot T^2_m - T_1 T_2 \right) + \frac{D_{CH_4}}{T_1 T_2} \right] \quad (3.71) \]

\[ dH_{H_2O(\text{air})} = H^\circ_{f\ H_2O(\text{air})} + H_{\text{vap}} \quad (3.72) \]

\[ dH_{H_2O(FS)} = H^\circ_{f\ H_2O(FS)} + \Delta T_{FS} \cdot Cp_{H_2O(FS)} \]

\[ \Rightarrow dH_{H_2O(FS)} = H^\circ_{f\ H_2O(FS)} + \Delta T_{FS} \left[ A_{H_2O(FS)} + B_{H_2O(FS)} \cdot T_m(FS) + \frac{C_{H_2O(FS)}}{3} \left( 4 \cdot T^2_m(FS) - T_1 T_{FS} \right) + \frac{D_{H_2O(FS)}}{T_1 T_{FS}} \right] \quad (3.73) \]

\[ dH_{H_2O(\text{g})} = H^\circ_{f\ H_2O(\text{g})} + \Delta T_{FS} \cdot Cp_{H_2O(\text{g})} \]
\begin{equation}
\begin{aligned}
\frac{dH_{H_2O(g)}}{dT} &= H^\circ_{H_2O(g)} + \frac{\Delta T}{3} \left[ \frac{A_{H_2O(g)}}{R} + B_{H_2O(g)} T + \frac{D_{H_2O(g)}}{T_2} \right] \\
\end{aligned}
\tag{3.74}
\end{equation}

The heating value of biomass material, \( H^\circ_{RH} \) is determined experimentally. However, theoretically, the heat of formation equation of rice husk biomass from solid carbon, hydrogen and oxygen can be given by the following equation, although this equation does not occur in reality.

\begin{equation}
C_{(s)} + \frac{x}{2} H_2(g) + \frac{y}{2} O_2(g) = C H_x O_y 
\tag{3.75}
\end{equation}

On the basis of above assumption, the heat of formation of rice husk having molecular formula CH\(_{1.55}\) O \(_{0.63}\) can be obtained from the following equations.

\begin{equation}
C + O_2 = CO_2, \quad \Delta H_c = -393509 \tag{3.76}
\end{equation}

\begin{equation}
0.465 H_2 + 0.2325 O_2 = 0.465 H_2O, \quad \Delta H_c = -241818 \tag{3.77}
\end{equation}

\begin{equation}
CO_2 + 0.465 H_2O = C H_{0.93} O_{0.71} + 0.8775 O_2, \quad \Delta H_c = -393509 \tag{3.78}
\end{equation}

\begin{equation}
C + 0.465 H_2 + 0.355 O_2 = C H_{0.93} O_{0.71}, \quad H^\circ_{RH} = -124665 \tag{3.79}
\end{equation}

The heat of formation of rice husk is estimated to be \(-124665\) kJ / kmol.

The heat of formation for any biomass material can be determined if the ultimate analysis and the heating value are known. The heating value can be experimentally determined by a bomb calorimeter and according to
Reed (1985), the heat of formation in MJ/kg of any biomass material can be calculated with reasonably good accuracy from the following equation

\[ \Delta H_c = 0.2326(146.58 \, C + 56.878 \, H - 51.53 \, O - 6.58 \, A + 29.45) \]  

(3.80)

where C, H, O and A are the mass fractions of carbon, hydrogen, oxygen and ash respectively in the dry biomass which are obtained from the ultimate analyses for various biomass fuels. The dependence of specific heat on temperature is given by various empirical equations and most simplified version is adapted from Robert and Don (1984) is,

\[ C_{p,am} = R \left[ A + B T_{am} + C(4T_{am}^2 - T_1 T_2) / 3 + D / (T_1 T_2) \right] \]  

(3.81)

By solving the heat balance equation, the amount of heat required, \( Q_{in} \), for endothermic reactions have been predicted. The flow chart of the modeling process is shown in Figure 3.11.

---

**Figure 3.11 Flow chart for modeling of air-steam gasification process**