High Temperature Steam and Air Gasification of Non-woody Biomass Wastes

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Abstract: Gasification of non–woody biomass wastes has been conducted experimentally to examine the effect of gasification agent temperature and waste composition on the product gas composition with special focus on the amounts of hydrogen produced. The temperature and chemical composition of gasification agent was controlled using a premixed burner and water injection into the high temperature zone of the flame. Increase in gasifying agent temperature enhanced the volume and heating value of the syngas using pure steam or air/steam as the gasifying agent. Pure steam gasification produced more H₂, CO and CH₄ as compared to air/steam case, in particular at low gasification temperatures. The gasification characteristic of all the biomass wastes examined was similar and depends on the biomass fuel composition. Gasification at higher temperatures resulted in more hydrogen yield in the product stream. The quality of steam used had an important effect on the syngas composition. Much higher yields of hydrogen can be achieved using ultra high temperature steam with negligible amounts of tars and hydrocarbons in the syngas.

Keywords: Non-woody Biomass, Steam Assisted Gasification, Air/Steam Gasification
Introduction

Interest in the use of biomass as sustained fuel continues to grow in many countries around the world. The reason stems from both environmental concerns and sustainable energy availability and recovery. According to international policies of CO$_2$ reduction, the positive environmental issue of biomass utilization is the zero net production of greenhouse gases. In contrast to fossil fuels biomass does not bring any new carbon into the environment so the total carbon balance is equilibrated.

The gasification process requires some gasifying agent that provides oxygen for the formation of CO from solid carbon in the fuel. The gasifying agents can be air, oxygen, steam or CO$_2$. The CO$_2$ is produced during pyrolysis and early oxidation processes and is generally not externally added. The most common agent is air because of its extensive availability at no cost. Air, though cheap, is not a perfect agent because of its nitrogen content. The product gas from air gasification produces a low heating value gas (4-7 MJ/Nm$^3$). Oxygen gasification produces a higher heating value (10-18 MJ/N m$^3$) but has a drawback of relatively high cost associated with oxygen [1]. Steam is another alternative. It also generates a medium calorific value gas (10-14 MJ/N m$^3$). The key advantage is that it increases the hydrogen content of the product gas. The presence of steam is important in case of further catalytic upgrading of the product gas. Steam gasification is however a highly endothermic reaction and requires a temperature in excess of 800°C to take place [2] if no catalyst is used [3,4]. The heat required for the reaction has to be transferred either by partial combustion of fuel in the same reactor (mixing of H$_2$O with oxygen/air [5] or by indirect heating [6, 7].

Gasification produces hydrogen, carbon monoxide, methane, light hydrocarbons and several other undesired compounds, such as, organic aerosols, tars, that may include sodium, potassium and chlorine compounds, ammonia, and hydrocyanic acid. Particularly cumbersome is tar and its significant yield, varying from 1 to 180 g/Nm$^3$, depending on the reactor type, feed gas, fuel type [8]. The development of High Temperature Air Combustion (HiTAC) technology led to first applications of highly preheated gasifying agent in laboratory scale which now appears very promising for practical implementation as ultra High Temperature Air/Steam Gasification (HiTAG) technology [9]. Results from gasification experiments with preheated gasifying agent showed the capability of tar reduction and increase in HHV of the synthesis gas at higher gasification temperatures. The preheated gasifying agent delivers enthalpy that is a substitute to energy released by oxidation or partial oxidation of the feedstock in normal gasification systems, thus more chemical energy contained in the feedstock can be turned into heating value of the yield. In this case, the enthalpy of the feed gas drives the endothermic reactions (water gas and Boudouard reactions) that are the main source of hydrogen and carbon monoxide production in the product stream. This also increases the efficiency of the process. Preheated gasifying agent must be at high enough temperatures that would satisfy the demand for endothermic water gas reaction. Because of the limitations in heat exchangers production, such process has not been economically justified before, and thus not developed. Gasification process usually takes place at high temperatures from 800 to 1800°C. However, with the recent developments in high temperature air combustion and gasification technology [9, 10, 11] it is now possible to have air preheats much in excess of 1100°C.

Temperature, gasification agent and biomass waste composition affects the quality of product gas composition and tars produced during gasification. The objective of this study is to examine the effects of gasification agent temperature and composition on the product syngas composition with special focus on the amounts of hydrogen produced using various biomass wastes.

Methodology

The experimental fixed bed reactor gasification facility utilizes High Temperature Air/Steam Gasification (HiTAG) technology [9]. The facility provides highly preheated gasifying agent to the reactor at any desired temperature. To increase the amount of steam in the reactor, additional water is added to the flame using a syringe pump. The total steam flow rate in the gasifying agent comprises of
steam from the combustion of hydrocarbon fuel and the amount of injected (evaporated) water. The product syngas composition was measured using a micro gas chromatograph.

Gasification section consisted of gasification fuel sample placed in a quartz tube that this tube was placed in an electrically heated tube furnace. The fuel samples were placed in a stainless steel cylindrical cage so that the high temperature gases can flow pass when placed in the quartz tube. The heating coils in the furnace heats up the quartz tube to maintain a desired temperature in the gasification section. The temperature of the furnace is controlled by an additional control unit. During the gasification process, gas temperatures were measured at the inlet and outlet and inside the furnace, and also in front and just behind the biomass fuel sample. Micro-GC allowed setting of all the functions and parameters using the software. A schematic diagram of the high temperature gasification (HiTAG) facility is showed in Fig. 1.

![A schematic diagram of the high air temperature gasification (HiTAG) facility](image)

**Fig.1** A schematic diagram of the high air temperature gasification (HiTAG) facility

Rice husk, rice straw and corn cob were examined here and the results compared with cellulose that represents a baseline case. For each sample moisture content was determined gravimetrically by oven drying method. Lower heating value (LHV) at a constant volume was measured using adiabatic oxygen bomb calorimeter. Proximate and ultimate analyses were determined by a chemical analysis laboratory using standard analytical method. The proximate and ultimate fuel analysis of the samples is shown in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Moisture (%)</th>
<th>Proximate analysis (%dry)</th>
<th>Ultimate analysis (%dry)</th>
<th>LHV MJ/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice Husk</td>
<td>8.20</td>
<td>64.19</td>
<td>14.18</td>
<td>42.54</td>
</tr>
<tr>
<td>Rice Straw</td>
<td>10</td>
<td>67.45</td>
<td>21.00</td>
<td>11.55</td>
</tr>
<tr>
<td>Corn Cob</td>
<td>8.24</td>
<td>87.9</td>
<td>5.3</td>
<td>6.79</td>
</tr>
<tr>
<td>Cellulose</td>
<td>8</td>
<td>84</td>
<td>15.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

**Table 1** Proximate and ultimate analysis of the samples

**Experimental Procedure**

The desired composition and temperature of the gasification agent was directed to the gasification reactor. The combustion of propane in O2 or air provided the gasifying agent consisting of mostly steam, CO2, O2 (and N2) at the desired temperatures. Four gasification agent temperatures (540°C, 780, 930 and 1000°C) have been examined here. Higher heating value (HHV) of syngas produced can be calculated from $\text{HHV} = \sum_{i=1} z_i \cdot \text{HHV}_i$; where, $z_i$=mass fraction of specie $i$, and $\text{HHV}_i$ = HHV of specie $i$. 
Results and Discussion

Air/Steam gasification

The composition of gasification products is directly related to gasifying agent properties of temperature and chemical composition (oxygen, steam and other gases). The gasification characteristic of biomass fuels examined can be observed from graphical record of gasifying agent temperature and species concentration. The concentration of desired species, such as hydrogen and carbon monoxide, is significantly increased with increase in gasifying agent temperature. Fig. 2 shows the effect of gasifying agent temperature on the concentration of H₂ and CO from several different biomass wastes using air/steam mixture as the gasifying agent. The results show strong effect of gasifying agent temperature on the amounts (concentration) of gasification products produced. For all biomass examined, H₂ and CO concentration diminishes at low temperature (540°C) gasification. Significant increase in gasification product yield for both H₂ and CO is observed with temperature increase from 540°C to 1000°C for all the gasification wastes. The small differences with steady increase in temperature could be due to some experimental uncertainty in complex waste-gasifying agent interactions. None the less these results show good agreement with the equilibrium calculations for cellulose presented by the authors [12]. The equilibrium calculation of cellulose shows that concentration of species, such as hydrogen and carbon monoxide increases significantly with increase in gasification temperature up to a certain temperature. Experimentally there appears to be a limiting temperature of about 1200 K after which H₂ concentration does not change considerably. However, the CO continues to increase with increase in gasifying agent temperature. This is attributed to the different energies required for the dissociation of these two species. The experimental trend of gasification products at higher gasification temperature (> 930OC) for rice husk, rice straw and corn cob showed increased production of both H₂ and CO, thus showing good agreement with the equilibrium calculations.

From the experimental results conducted here in this study, the results showed that the overall gasification characteristics of the biomass wastes is similar and depends on fundamental composition of the fuel. However, the specific characteristics of each biomass have some differences. From the experimental results it can be seen that cellulose has a limiting temperature (near to 930°C) beyond which the H₂ production decreases. This is attributed to the increased dissociation of H₂ with increase in temperatures so that the H atom produced is attracted by O atom to form OH radicals in the post reaction zone. This point requires further examination.

Gasification products produced from all three biomass wastes examined showed the same trend for the range of temperatures examined. The yield of H₂ and CO in the gasification products from corn cob is highest, followed by rice husk (low) and rice straw (lowest). These results show good general agreement with the amount of fixed carbon in biomass waste, see Table 1. Corn cob has the lowest amount of fixed carbon (5.3 %) while the rice husk and rice straw has 21.46 % and 21%, respectively.

![Fig. 2 Concentration of H₂ and CO at various gasification temperatures with air/steam mixture as the gasifying agent](image-url)
The increase in percent H\textsubscript{2} concentration per unit degree increase in gasification temperature is now compared by using the lowest gasification agent temperature as the datum. The effect of gasification temperature for each step increase in temperature level is shown in Table 2. The gasifying agent temperature in this study is grouped into four categories based on the magnitude of temperature examined: low temperature (540 oC), medium temperature (780 oC), high temperature (930 oC) and very high temperature (1000 oC). The results show that H\textsubscript{2} concentration continuously increases for all the biomass waste examined, including cellulose, when gasified at medium and high temperatures. In contrast very high gasifying agent temperature does not show significant differences in the amounts of H\textsubscript{2} produced for all the biomass examined. Thus H\textsubscript{2} production per unit degree for each level of temperature examined can be considered as a good indicator to determine the optimum temperature.

**Table 2** Increase in percentage of H\textsubscript{2} concentration per unit degree temperature increase in gasification temperature

<table>
<thead>
<tr>
<th>Gasifying agent temperature (°C)</th>
<th>Increment of H\textsubscript{2} concentration (%mol/C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low temperature (540°C)</td>
<td>Rice husk: 9.46</td>
</tr>
<tr>
<td>Medium temperature (780°C)</td>
<td>Rice husk: 10</td>
</tr>
<tr>
<td>High temperature (930°C)</td>
<td>Rice husk: 9.75</td>
</tr>
<tr>
<td>Very high temperature (1000°C)</td>
<td>Rice husk: 10</td>
</tr>
</tbody>
</table>

**Pure steam gasification**

Pure steam was also used as a gasifying agent for the gasification of biomass waste at various gasification temperatures. The results are compared with the air/steam gasification case. Figure 3 shows the effect of gasification agent temperature on H\textsubscript{2} production. The results show continuous increase of H\textsubscript{2} production with increase in temperature from 540-930°C. The production for H\textsubscript{2} from cellulose, rice husk and rice straw show a limiting temperature when using gasification temperature of 1000°C. Corn cob shows some distinction from the biomass waste examined. The results show the same trend as those obtained using air/steam gasification [12]. This provides some confirmation that the gasification characteristics of biomass wastes are similar and depends on the fundamental composition of the waste and gasification temperature. There appears to be some limiting temperature for the biomass wastes examined. Over the gasification temperature range examined, the limiting temperature for cellulose, rice husk and rice straw appear to be in the vicinity of 930 °C. However, for corn cob, the limiting temperature is slightly higher than cellulose and rice husk. This can be supported from the amount of H\textsubscript{2} produced from corn cob (highest value) as compared to that from rice husk and rice straw.

![Fig.3 Concentration of H2 and CO With temperature for steam as gasifying agent](image-url)
Fig. 4 shows a comparison of H₂ concentration from cellulose, rice husk, rice straw and corn cob using pure steam and air/steam as the gasifying agent. The results show that for all biomass examined, including cellulose, pure steam produces higher H₂ concentration in the gasified product stream as compared to the air/steam for each respective waste gasifying temperature. Gasification at low temperature with pure steam clearly shows significant increase in H₂ concentration as compared to the air/steam case. Increase in gasifying agent temperature resulted in increased H₂ concentration for the operating temperature range of 540-930°C. The gasification products decrease when using gasification temperature of 1000°C or more for cellulose, rice husk and rice straw.

**Fig. 4** Concentration of H₂ using pure steam and air/steam as gasifying agent

CO concentration in the gasified product stream using pure steam and air/steam mixture is shown in Fig. 5.
A comparison of CH$_4$ concentration for the biomass wastes examined using pure steam and air/steam is shown in Fig. 6. The different gases concentration in the product stream was used to estimate the heating value of the product gas stream. The results showed that high temperature gasification assists in enhancing the heating value of the product gas stream. This could provide potential for selectively controlling the process to obtain the desired product gas composition for various applications.
HHV of gasification products

Higher heating value of gasification product produced from biomass waste tested at various gasifying agent temperature for pure steam and air/steam were calculated and compared. HHV of HHV from biomass waste tested for using pure steam and air/steam presented in Fig 7. The results showed that increasing gasification agent temperature resulted in increasing of heating value of gasification products for all biomass wastes tested including cellulose. Pure steam used enhanced more amount of gasification products in case of using low temperature gasification agent. From the condition tested amount of steam in gasifying agent is the same.

Fig.7 HHV of gasification product with pure steam and air/steam

Conclusions

Gasification of biomass wastes has been conducted experimentally to examine the effect of gasification agent temperature and composition on the product gas composition with special emphasis on the amounts of hydrogen produced. The quality of gasification agent was controlled for temperature and composition using a premixed burner and water injection into the high temperature zone of the flame. Pure steam and air/steam gasification agent at low to very high temperatures have been used to examine the gasification of rice husk, rice straw, and corn cob. The results are compared for the baseline case of cellulose. The results showed strong impact of gasification agent temperature and composition on the amounts of hydrogen produced. It is observed that the concentration and heating value of gasification products strongly depends on the gasifying agent temperature. For all the biomass examined the concentration of $H_2$ and CO diminished at low gasification temperatures ($540^\circ C$). Significant increase in gasification products was found at higher temperatures ($540$ to $930^\circ C$). Pure steam produced higher concentration of gasification products ($H_2$ and CO) as compared to air/steam mixture at any given gasification temperature for all the wastes examined. The heating value of gasification products was higher with pure steam than air/steam at low gasification temperatures.

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References


