Rice Husk Gasification in a Two-Stage Reactor: Effect of K2CO3 on H2/CO Ratio in Homogeneous and Heterogeneous Tar Cracking

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The objective of this work was to investigate the use of catalyst to enhance H2/CO ratio and syngas production during homogeneous and heterogeneous tar cracking of rice husk biomass. The experiments were performed at atmospheric pressure in indirectly heated two-stage gasification system. The pyrolysis chamber temperature was set at 500°C and that of gasification chamber was varied between 800°C and 900°C for different experimental runs. Homogeneous and heterogeneous gasification was performed at different operating conditions. Results obtained show that catalyst helped in increasing H2/CO ratio and heterogeneous gasification showed better results than homogeneous gasification.

Keywords: Pyrolysis, Gasification, Syngas, Catalysis, H2/CO Ratio

Introduction

The world is undergoing a tremendous shift to clean energy today. Fossil fuels or non-renewable sources of energy are depleting at a rapid rate. There is a rising need to replace these sources not only due to their unavailability but also to avoid anthropogenic or human caused climate change, due to excessive CO2 emissions from these sources. Recently, more renewable energy generating sources has been installed as compared to coal, as countries are taking advantage of cost reductions in producing clean energy and the massive increase in funding for the same. Biomass energy source is renewable and sustainable, used to harvest electricity and other types of energy. Biomass can either be combusted directly to give heat or be converted into different types of biofuels. Biomass char is reported to have a good catalytic activity, effective and low cost catalyst for tar conversion compared with other catalysts such as calcined dolomite, olivine, biomass ash and nickel. The objective of the present work was to investigate the use of catalyst K2CO3 to enhance H2/CO ratio and syngas production during homogeneous and heterogeneous gasification of rice husk.

Experimental setup

Materials

Rice husk obtained from a local rice mill was used as feed stock for the experiments. The particle size of this feed was less than 1000µm, obtained after grinding and sieving. The biomass was dried in an oven at 105°C (378K) for about 6 hours to remove moisture and then stored in air-tight bag for further experimental work. 50 gms of rice husk biomass was used as feed for each run. Experiments were carried out at varying reaction conditions to analyze yield of syngas production without catalyst and with catalyst potassium carbonate (K2CO3).

Apparatus

The experiments were performed at atmospheric pressure in indirectly heated two-stage gasification system. The detailed design of this system is available in our earlier research work. Its major components are a pyrolysis chamber 250mm long, and a gasification chamber 350mm long, the two of which are connected by a throated flange 170mm long. The first stage of the system is the pyrolysis chamber. The rice husk is fed from the top. The top is fitted with a T-piece connecting the inlet of the gas supply to the reactor. The temperature of this chamber is measured using a K-type thermocouple. The second stage of the system is the gasification chamber. This is the tar destruction section leading to the production of syngas. If the reaction taking place is homogeneous, this section can be left empty. In case a catalyst is being used, it can be packed in this chamber. Both the stages are heated using heating coils with PID controllers. A U-tube is provided below the second stage in order to capture
tar. This U-tube is kept immersed in ice bath. The important reactions during gasification were given in earlier work.\textsuperscript{9,10}

**Gas and tar analysis**

The gasification of biomass yields three products: char, tar and gas. Gas chromatograph (GC) was used to detect the composition of constituent gaseous products. Two carrier gases are used for this purpose: Nitrogen to detect hydrogen and helium to detect all other gases.\textsuperscript{11} The tar trap was washed with a solvent (4:1 chloroform: methanol mixture) several times until the trap gives a clear wash colourless liquid from initial brownish liquid due to the presence of tar. The solution was then filtered, first using ordinary filter to reduce the carbon load on the next filtration through whatman filter paper of grade 42, and collected in the sampling flask of rotary evaporator. The rotary evaporator was operated at 60°C, 130 rpm for 15 min. The flask along with the tar was weighed when it cooled down to room temperature and then weight of the flask was removed from the recorded weight in order to obtain weight of tar produced.

**Results and Discussion**

Several experiments have been performed by changing the operating conditions as well as the use of catalyst considering both homogeneous and heterogeneous cracking of tar.

**Homogeneous tar cracking with and without catalyst**

Pyrolysis chamber temperature was set constant at 500°C while gasification chamber temperature was varied from 800°C to 900°C. The flow of inert N\textsubscript{2} gas at one litre per minutes through a mass flow controller was injected from top of reactor to sweep the gaseous volatiles downwards to the tar trap, dipped in ice bath. The flow of air at one litre per minutes was passed through a mass flow controller into the second stage for the gasification reactions to take place. The rice husk was gasified with and without using catalyst K\textsubscript{2}CO\textsubscript{3}. The experiments in the presence of catalyst K\textsubscript{2}CO\textsubscript{3} were carried out by mixing it with the feed biomass in the first stage at 500°C. The amount of catalyst used is 3% by weight of feed. For all the experimental runs, the second chamber was kept empty to study homogeneous gasification. The products of these experiments were collected in standard 10 litres gas sampling bags and were identified and analysed using gas chromatograph (GC). It is observed from Table 1 that at higher temperature of 900°C, better H\textsubscript{2}/CO ratio is obtained as compared to 800°C. It is because higher temperature is more favourable for gasification as well as it leads to the production of more hydrogen gas. It can also be seen that using K\textsubscript{2}CO\textsubscript{3} with rice husk has helped in increasing the amount of H\textsubscript{2} and CO\textsubscript{2} produced and reduced the amount of CO and in turn increasing H\textsubscript{2}/CO ratio. This occurs because the catalyst has the effect on water gas shift reaction. Hence, as shown in Figure 1, high temperature of 900°C in gasification chamber with catalyst K\textsubscript{2}CO\textsubscript{3} yields the highest ratio. Further, the experiments were performed by varying the temperature of second stage as 800°C and 900°C and keeping the first stage temperature as 500°C and passing air in both the stages instead of passing nitrogen for first stage. The results of the experiments carried out by mixing rice husk with catalyst K\textsubscript{2}CO\textsubscript{3} and without catalyst are shown in Table 2. When air is passed in both the stages, the biomass undergoes complete combustion. Hence, the char produced has undergone reactions releasing volatile components and more of CO and CO\textsubscript{2}. As seen from Table 2 and Figure 2, the H\textsubscript{2}/CO ratio is not increasing by using catalyst due to some unknown reactions that might have occurred during gasification due to the presence of K\textsubscript{2}CO\textsubscript{3}. The amount of syngas is found to be maximum for 800°C.

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**Table 1** — Product yield (vol\%) during homogeneous gasification of rice husk in N\textsubscript{2}+air medium.

<table>
<thead>
<tr>
<th>Sr No</th>
<th>T (°C)</th>
<th>Catalyst (K\textsubscript{2}CO\textsubscript{3})</th>
<th>CO</th>
<th>O\textsubscript{2}</th>
<th>CO\textsubscript{2}</th>
<th>H\textsubscript{2}</th>
<th>H\textsubscript{2}/CO ratio</th>
<th>CO+H\textsubscript{2}</th>
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<tr>
<td>1</td>
<td>800</td>
<td>No</td>
<td>50.99</td>
<td>6.49</td>
<td>35.09</td>
<td>7.41</td>
<td>0.1453</td>
<td>58.4</td>
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<td></td>
<td>Yes</td>
<td>38.6</td>
<td>5.43</td>
<td>35.2</td>
<td>20.88</td>
<td>0.541</td>
<td>59.5</td>
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<td>No</td>
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<td>6.79</td>
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<td>22.74</td>
<td>0.6088</td>
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<td>11.32</td>
<td>37.64</td>
<td>24.17</td>
<td>0.899</td>
<td>51.0</td>
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</table>

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![Fig.1 — H\textsubscript{2}/CO ratio at different temperature in homogeneous gasification in N\textsubscript{2}+Air medium (RH-rice husk).](image)
with catalyst since CO formed is maximum, which is opposite to the behavior of catalysis in N₂+ air medium.

**Heterogeneous tar cracking with and without catalyst**

The temperature of the gasification chamber was set at 900°C while that of the pyrolysis chamber was set at 500°C. A flow of N₂ gas through a mass flow controller (rotameter) was also injected from the top of the reactor to sweep the gaseous volatiles downwards to the tar trap, dipped in an ice bath. The flow of air at one litre per minutes was passed through a mass flow controller into the second stage for the gasification reactions to take place. The reaction conditions were altered by changing the temperature of gasification chamber to 800°C while keeping that of the pyrolysis chamber constant at 500°C. The products of these experiments were collected in standard 10 litres gas collecting bags and were identified and analysed using gas GC. In all the experimental runs, the second stage of the reactor was char bed to study heterogeneous gasification. This char is obtained during homogeneous gasification of rice husk in N₂+air medium (in absence of catalyst). For each experimental run fresh bed of char of height 10 cm equivalent of 50 gm of char was used. Table 3 shows the result of the experiments performed with and without catalyst K₂CO₃ in N₂+air medium. As seen from Table 3 and Figure 3, a fixed bed of char in second stage has increased the H₂/CO ratio when compared to homogeneous gasification in N₂+air medium with and without catalyst. This is due to fact that the char also contain some volatile compounds which gets released when treated again at high temperature and it also helps in reducing tar. The char bed tries to extract the volatile compounds from it and make it available for gasification reactions. Also when CO₂ and H₂O are passed through a hot bed of char, the carbon present in this bed is highly reactive towards oxygen and thus successfully strips off the oxygen present in the carbon dioxide and water vapor molecules, thus reducing them. The oxygen is then redistributed in as many single bond sites as possible. Oxygen has a higher affinity to the bond site than to carbon itself. All available diatomic oxygen bond to the available carbon sites until no more oxygen is available. This is when reduction reaches an end. Thus, CO₂ is reduced to two CO molecules and H₂O is reduced to H₂ and CO. The results also shows that volume % of syngas has increased when bed of char is used as compared to homogeneous gasification.

![Fig. 2 — H₂/CO ratio at different temperature in homogeneous gasification in air + air medium (RH-rice husk).](image)

![Fig. 3 — H₂/CO ratio at different temperature in heterogeneous gasification in N₂+Air medium (RH-rice husk).](image)

**Table 2 — Product yield (vol%) during homogeneous gasification of rice husk in air+air medium.**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>T (°C)</th>
<th>Catalyst (K₂CO₃)</th>
<th>CO</th>
<th>O₂</th>
<th>CO₂</th>
<th>H₂</th>
<th>H₂/CO ratio</th>
<th>CO+H₂</th>
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<td>1</td>
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<td>No</td>
<td>31.27</td>
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<td>69.97</td>
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<td>33.68</td>
<td>24.19</td>
<td>0.574</td>
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**Table 3 — Product yield (vol%) during heterogeneous gasification of rice husk in N₂+air medium.**

<table>
<thead>
<tr>
<th>Sr No</th>
<th>T (°C)</th>
<th>Catalyst (K₂CO₃)</th>
<th>CO</th>
<th>O₂</th>
<th>CO₂</th>
<th>H₂</th>
<th>H₂/CO ratio</th>
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<td>Yes</td>
<td>38.3</td>
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<td>17.56</td>
<td>44.14</td>
<td>1.15</td>
<td>82.44</td>
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</table>
Conclusions
The experiments were performed at atmospheric pressure in indirectly heated two-stage gasification system to investigate the use of catalyst K$_2$CO$_3$ to enhance H$_2$/CO ratio and syngas production during homogeneous and heterogeneous gasification of rice husk. The pyrolysis chamber temperature was set at 500°C and that of gasification chamber was varied between 800°C and 900°C for different experimental runs. It was found that the catalyst was successful in increasing H$_2$/CO ratio except for the case of homogeneous gasification by passing air in both pyrolysis and gasification chambers, where some unwanted reactions might have occurred which hindered the function of catalyst. Heterogeneous catalysis showed quite promising results since using a bed of char in second stage helped in increasing the production of hydrogen gas, whereas passing air in pyrolysis chamber aided its production. Further, it can be seen that heterogeneous catalysis produces more volume of syngas compared to homogeneous catalysis for same amount of feed and operating conditions.

References