Reforming raw synthesis gas from wood gasification

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Introduction

Synthesis gas (syngas) is a mixture of H₂, CO and CO₂ in varying ratios. The mixture is a raw material in the synthesis of several chemicals, e.g. methanol, dimethyl ether, ammonia, and Fischer-Tropsch liquids. Currently, syngas is mainly produced by gasification of coal, or reforming of natural gas and other petroleum fractions. This study was a part of the GreenSyngas project, funded by European Commission under its 7th Framework Program. The project will develop a novel gas conditioning process to clean the product gas derived from gasification of wood. The goal is to produce a syngas ready for use as a feedstock in the production of vehicle fuels [1]. The use of biomass for energy purposes is in principle CO₂ neutral, and so biomass may play an important part in the effort of reducing greenhouse gas emissions to the atmosphere.

The conditioning of the raw gas is challenging, as it will contain an unacceptable amount of contaminants. Gas cleaning will involve several steps, e.g. removal of alkali metals and particulates, sulphur (COS, H₂S), and ammonia. Higher hydrocarbons, tars, may cause problems due to condensation and plugging of pipes and processing units, and need to be removed. In order for the process to be economically viable, it is necessary to convert and utilise the tars and other unconverted hydrocarbons. The objective of this study is the reforming of the raw syngas from gasification to convert the hydrocarbons to syngas, focusing on reaction kinetics and catalyst stability.

Materials and Methods

Steam reforming experiments are carried out in order to reform a gas mixture resembling the raw product gas from a pilot gasifier. A range of variables are studied. The catalysts reported here were derived from hydroxalite-like materials and loaded with cobalt and nickel in varying ratios [2]. They were characterised by means of XRD, N₂ sorption, H₂ chemisorption, and STEM. The reforming experiments were carried out in a fixed bed micro-reactor. The reactor was a stainless steel tube with inner diameter 1.0 cm. The syngas contained 12% CH₄, 5% C₂H₄, 35% H₂, 23% CO, and 25% CO₂. 2-naphthol was used as a tar model compound. This compound was dissolved in water, and the solution was evaporated in a furnace before it was fed to the reactor. The overall concentration of tar in the reactant mixture was equal to 0.6 g Nm⁻³. This corresponds with the actual concentration of tar in the raw gas from the pilot plant.

The composition of the gas product was determined by a micro-GC. The liquid products were separated from the gas in a condensation tank. The amount of tars in the condensed product, from which the tar conversion was estimated, was found by means of UV-VIS.

Results and Discussion

The results from the catalyst characterisation are summarised in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bulk composition [wt-% Ni-wt-% Co]</th>
<th>BET surface area [m² g⁻¹]</th>
<th>Particle diameter [nm]</th>
<th>Metal surface area [m² g⁻¹]</th>
<th>Dispersion [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>40 - 0</td>
<td>153</td>
<td>7</td>
<td>36.9</td>
<td>13.9</td>
</tr>
<tr>
<td>B</td>
<td>10 - 30</td>
<td>106</td>
<td>15</td>
<td>17.5</td>
<td>6.5</td>
</tr>
<tr>
<td>C</td>
<td>0 - 40</td>
<td>103</td>
<td>15</td>
<td>17.6</td>
<td>6.5</td>
</tr>
</tbody>
</table>

An example of the conversion of methane and ethene as a function of time over catalyst B is shown in Figure 1. The reaction conditions were: 720 °C, atmospheric pressure, S/C ratio 2.5, and the gas flow rate was 50 cm³ s⁻¹ gcat⁻¹.

Figure 1. Conversion of methane (■) and ethene (●) in steam reforming experiments.

The initial results were good with respect to catalysts stability. No deactivation was detected during the first hours of experiments. The rate of conversion is higher for ethane compared to methane, as expected. The increase in activity with time on stream is surprising, but could be linked with incomplete reduction of the catalyst or oxidation by steam. UV-VIS measurements of the collected condensed liquid indicate that most of the model tar component is converted in this experiment.

References

1. http://www.eat.lth.se/greensyngas/