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Cracking of Sugars for Production of Chemicals

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Introduction

Biomass represents the most readily available source of renewable carbon and is a promising feedstock for sustainable production of chemicals and fuels. While other renewable resources such as solar, water and wind can be used to produce heat and power, biomass can potentially be used for production of chemicals as well as renewable liquid, solid and gaseous fuels. It has previously been shown that fast pyrolysis can be used to convert glucose to glycolaldehyde in high yields (>50 wt%) along with other chemicals by spraying an aqueous solution of glucose into a fluidized bed operated at 500 – 600 °C [1]. This method of sugar conversion is called “sugar cracking”. The product distribution for the sugar cracking process utilizing an aqueous glucose feed is considerably different from fast pyrolysis of crystalline glucose in micropyrolyzers, which only yields 6-7 wt% glycolaldehyde [2,3]. Glycolaldehyde can be hydrogenated in a second step to produce monoethylene glycol (MEG) [4], which is a large commodity chemical with an annual production capacity of 34.8 million tons (2016). MEG is primarily used in the synthesis of polyester fibres and PET bottles (>80%), while other uses include antifreeze [5]. In this work, a kinetic model for sugar cracking is presented along with experiments investigating the effects of operating conditions with the aim to validate the kinetic model.

Materials and Methods

A simple laboratory bubbling fluidized bed reactor was used for the sugar cracking process. The bubbling fluid bed reactor was loaded with particles and was fluidized with nitrogen. The aqueous glucose solution was sprayed into the hot reactor operated at ~500 °C and 1 atm using a spray atomizer. The feed is rapidly heated and the glucose molecules are cracked to produce smaller fragments. The product vapors were carried out of the reactor to a condenser, where the liquid product was condensed and collected after passing through a filter. The condensed liquid product was analyzed using HPLC to quantify the yield of oxygenates. A kinetic model has been set up in an effort to predict the product yields from the sugar cracking process. Seshadri & Westmoreland [6] calculated kinetic parameters for a number of unimolecular and water-catalyzed reactions related to glucose pyrolysis using gas-phase quantum-chemistry and statistical-mechanics calculations. Based on these calculations, a reaction network has been set up assuming instantaneous evaporation of the aqueous glucose droplet and heating to reactor temperature.

Results and Discussion

Simulations using the kinetic model was made under the assumption of plug flow for the experimental conditions for the sugar process. Table 1 shows a comparison between experimental and model product yields. The predicted yields of glycolaldehyde and formaldehyde are in good agreement with the experimentally observed yields. However, the model does not predict the yields of the C3-products well. The model predicts 18 wt% yield of 1,3-dihydroxyacetone, whereas this product is not observed experimentally. Instead, pyruvaldehyde and acetol are the experimentally observed C3-oxygenates. The total yield of C3 products are however well predicted by the model. It should be noted that the model is limited in the number decomposition products, and further decomposition of glycolaldehyde and of other oxygenate products are not included.

<table>
<thead>
<tr>
<th></th>
<th>Exp</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyruvaldehyde</td>
<td>13%</td>
<td>N/A</td>
</tr>
<tr>
<td>Acetol</td>
<td>3%</td>
<td>N/A</td>
</tr>
<tr>
<td>1,3-dihydroxyacetone</td>
<td>0%</td>
<td>18%</td>
</tr>
<tr>
<td>Glycolaldehyde</td>
<td>66%</td>
<td>75%</td>
</tr>
<tr>
<td>Glyoxal</td>
<td>3%</td>
<td>N/A</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>1%</td>
<td>N/A</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>8%</td>
<td>7%</td>
</tr>
<tr>
<td>Sum</td>
<td>94%</td>
<td>100%</td>
</tr>
</tbody>
</table>

Significance

The sugar cracking process is a method for selectively producing glycolaldehyde from renewable feedstocks. Glycolaldehyde can be hydrogenated to MEG, which allows for production of products such as polyester fibres and PET bottles. Obtaining a deeper understanding of the sugar cracking process through further experimental and modeling work is relevant for up-scaling the process, which is already ongoing.

References