Hydrogenolysis of glycerol to ‘Green’ propylene glycol: 
Experimental investigation and Microkinetic study

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Introduction

- Hydrogenolysis of biomass derived glycerol can be an important process for a bio-diesel plant. Glycerol can be converted to value added products like 1,2 propanediol, which can increase the profitability of such a plant.
- Microkinetic modeling is an important tool which can be used to draw mechanistic insights into the reaction.
- In this work, microkinetic modeling will be used to draw mechanistic insights into the reaction mechanism, deactivation of the catalyst and to search for alternative catalysts.

Experimental Investigation

Hydrogenolysis experiments were performed in a High Throughput Kinetic Setup, which in this case is a trickle bed three phase tubular reactor.

Reaction Conditions:
Pressure = 65 - 80 bar
Temperature = 160 – 240 °C

Parameter Estimation

- Parameter estimates from the first non-isothermal regression analysis performed using the experimental data.
- Model regressed is a simplified version of the model described above. To account propylene glycol, glycerol and acetal.

\[
\begin{align*}
H_2 + 2 \theta_1 & \xrightarrow{\text{H}_2, \text{glycerol}} 2 \text{H}_2\theta_1 \\
G + \theta_1 & \xrightarrow{\text{H}_2, \text{glycerol}} \text{G} + \theta_1 \\
\text{GP} + \theta_1 & \xrightarrow{\text{H}_2, \text{glycerol}} \text{A} + \theta_1 \\
2 \theta_1 + \theta_2 & \xrightarrow{\text{H}_2, \text{glycerol}} \theta_1 + 2 \theta_1 \\
\theta_2 + \theta_1 & \xrightarrow{\text{H}_2, \text{glycerol}} \theta_1 + \theta_2
\end{align*}
\]

- Reaction network based on the mechanism proposed by Gandarias, et al., adapted to the products observed during the experimental investigation.
- Current modeling efforts in this presentation has been towards modeling glycerol, acetal and propylene glycol. This is due to limited number of kinetic data that has been obtained thus far.

Reaction Mechanism

Results

Parameter Estimation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>95% Confidence Interval</th>
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<tbody>
<tr>
<td>(n_{\text{H}_2}) ([\text{mol g}^{-1} \text{s}^{-1}])</td>
<td>6.83 (10^2) \pm 4.41 (10^2)</td>
</tr>
<tr>
<td>(n_{\text{G}}) ([\text{mol g}^{-1} \text{s}^{-1}])</td>
<td>6.27 (10^2) \pm 1.90 (10^2)</td>
</tr>
<tr>
<td>(q_{\text{H}_2}) ([\text{mol g}^{-1} \text{s}^{-1}])</td>
<td>2.20 (10^2) \pm 1.03</td>
</tr>
<tr>
<td>(q_{\text{G}}) ([\text{mol g}^{-1} \text{s}^{-1}])</td>
<td>4.01 (10^2) \pm 0.459</td>
</tr>
<tr>
<td>(e_{\text{H}_2}) ([\text{mol g}^{-1} \text{s}^{-1}])</td>
<td>6.1 \pm 1.34</td>
</tr>
<tr>
<td>(e_{\text{G}}) ([\text{mol g}^{-1} \text{s}^{-1}])</td>
<td>0.7 \pm 0.8</td>
</tr>
<tr>
<td>(\Delta h_{\text{H}_2}) ([\text{kJ mol}^{-1}])</td>
<td>20.4 \pm 0.3</td>
</tr>
<tr>
<td>(\Delta h_{\text{G}}) ([\text{kJ mol}^{-1}])</td>
<td>0.4 \pm 0.8</td>
</tr>
</tbody>
</table>

Conclusion

- Initial modeling effort iterates the need for data points at lower space times. This is clearly evident from the lower predictability of the model at lower space times.

Future work

- Expand the kinetic data set in order to precisely estimate all the parameters in the afore mentioned model.
- Test for model adequacy and adapt the model if necessary.
- Perform long term deactivation experiments to investigate the causes of catalyst deactivation and incorporate the same in the model.
- Study the possibility of in-situ regeneration of the catalyst.
- Study alternate catalysts that can be used to replace the currently studied one.

Acknowledgement

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