Hydrogen Assisted Lignin Depolymerization with Pulp Mill Catalysts

The wooden material lignin could be transformed into biofuel. As part of the development of such a process, large lignin molecules were cleaved into smaller fragments. Since lignin is resistant to degradation, hydrogen gas and catalysts were used to aid the cleavage.

Lignin is a by-product in the pulp and paper industry since it is not wanted in the paper. When lignin has been separated from cellulose in the wood, it is called black liquor. The process idea is to convert black liquor to a lignin-rich oil that can enter an existing petroleum refinery. In this way, part of the fuel produced at the refinery would be renewable and emissions of fossil CO_2 could be reduced. The process idea is based on three steps, filtration, hydrothermal treatment and catalysis and purification. The back liquor can be filtered through a membrane so that the concentration of lignin is increased and valuable chemicals are separated from the lignin and can be returned to the pulp and paper mill. The lignin can then be treated with heat, catalysts and hydrogen gas to reduce its molecular size. Water and salts needs to be removed before the lignin-rich oil can enter a petroleum refinery as a renewable feedstock. This work has been focused on the hydrothermal treatment and catalysis part of the process.

Two model compounds and two pulp mill catalysts were tested in combination with high-pressure hydrogen gas, 190 bar at 220 °C. Blank experiments without catalyst were also performed, with and without hydrogen gas.

In order to achieve the same qualities as petroleum products, it was desired to reduce the amount of oxygen present in the lignin. Since the oxygen content cannot be measured directly, the sulfur content was used as an indicator. The sulfur and oxygen incorporated in the lignin molecules are affected in the same way during reactions with lignin. It was shown that the hydrogen gas reduced the content of sulfur in the lignin after treatment. The best catalyst in combination with hydrogen gas reduced the sulfur content to 1/3 of the original content. It is likely that the oxygen content was reduced by the same factor.

It was found the blank experiment without any catalyst or hydrogen gas reduced the size of the largest molecules. In the starting material, there were molecules in the size range up to 100 kDa, whereas, there were no molecules larger than 11 kDa after the blank experiment. Most of the molecules seemed to be in the range 2-3 kDa. The catalysts tested showed the same result as the blank experiment when the reaction was in progress for 15 minutes. This means that none of the catalysts had any effect. Neither did the combination with hydrogen gas show any effect for the 15-minute experiments. However, for one of the model substance catalysts, the reaction time was increased to 20 hours. The results were smaller molecules than the 15-minute experiments. There were no molecules larger than 10 kDa and most of the molecules seemed to be around 1 kDa. More blank experiments with long reaction time needs to be performed in order to investigate the effect of the catalyst.