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## Master Thesis

A study on reaction pathways and mass transfer effects for the catalytic hydrotreatment of pyrolysis oil using a Ruthenium on carbon catalyst

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## Abstract

Renewable energy is becoming ever more interesting as an alternative for fossil fuels. Fast pyrolysis of biomass produces a liquid energy carrier known as fast pyrolysis oil. However, fast pyrolysis oils as such have a limited number of applications due to some unfavorable properties like high acidity, low energy density and the presence of oxygen in the form of a variety of chemical functionalities. Upgrading is required to extent the application range.

Here we report a study on the hydrotreatment of pyrolysis oil in a batch reactor set-up using a Ru/C catalyst (200 bar, 80 – 350° and 5 %-wt catalyst of feed) with an emphasis on reaction pathways and the possible effects of mass transfer. Catalytic hydrotreatment experiments at low temperature (<250 °C) indicate that (re-)polymerization is dominant over the hydrogenation/stabilization reactions and higher molecular weight compounds are produced. Most of the high molecular weight compounds are converted at elevated temperature (>250 °C) by hydrodeoxygenation to water-insoluble non-polar medium molecular weight compounds and subsequently to low molecular weight water-insoluble non-polar fragments at the higher temperature (250-350 °C) and prolonged reactions times (hours) by hydrocracking reactions. These findings are supported by experiments where the heating rate from room temperature to reaction temperature was varied systematically.

Mass transfer effects were probed by performing reactions at various stirring rates while keeping all other process variables constant (200 bar, 5%-wt Ru on Ru/C catalyst and 5 %-wt catalyst of feed). The stirring rate seems to have limited effects on product properties and hydrogen uptake, though additional experiments are required to draw definite conclusions.

Inter- and intra- particle mass transfer were investigated by performing reactions at various particle sizes and catalyst intakes while keeping the other process variables constant (200 bar, 1400 RPM and 5%-wt Ru on Ru/C catalyst). Experiments with lower average catalyst particle sizes gave improved product properties (decreasing carbon residue and molecular weight and increasing elemental H/C ratio) and an increase in hydrogen uptake. BET data indicate the occurrence of partly or totally blocked catalyst pores probably caused by polymerization reactions.

When performing experiments with a variable Ru intake, the hydrogen uptake per gram ruthenium is a function of the catalyst intake, with higher intakes leading to lower hydrogen uptakes per g of Ru. This may be explained by gas-liquid mass transfer effects or depletion of the more easily hydrogenated organic compounds at higher hydrogen uptakes. The first explanation is the less likely because the hydrogenation reactions take place at a time scale of hours, whereas gas-liquid mass transfer is expected to occur on a minute timescale.

The effect of the catalyst source was probed by comparing the experimental data for Ru/C catalysts from different catalyst producers (Aldrich, Evonik and KaiDa). The results indicate best catalyst performance for the Aldrich catalyst. The differences in catalyst performance may be due to differences in dispersion of the Ru clusters on the carbon support and/or the use of different catalyst precursors. The former explanation is certainly valid, as shown by HRTEM (Figure 37) pictures.