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## Pyrolysis oil upgrading to transportation fuels by catalytic hydrotreatment

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## Summary

Environmental concerns and possible future shortages have boosted research on alternatives for fossil derived liquid transportation fuels. Biomass is considered a promising alternative due to its abundance and renewability. Various products from different biomass sources have been proposed. Well known examples are biodiesel from plant oils and bioethanol from starch. A potentially very interesting, second generation transportation fuel is pyrolysis oil, obtained by flash pyrolysis of lignocellulosic biomass in yields up to 70 %-wt. In this process, the biomass is heated to temperatures of 400-600 °C in an oxygen free atmosphere for short residence times. As such, the oil is not suitable as a biofuel for internal combustion engines due to its high oxygen content (ca. 40%-wt) and low pH (ca. 2.5) and upgrading is required.

It is not likely to achieve these goals merely by physical separation of the pyrolysis oil into fractions as is common practice for crude oil. Distillation (even under vacuum) leads to undesirable chemical changes and the formation of large amounts of solid materials. Chemical modifications appear to be more attractive. It is expected that the product properties are improved considerably by reducing the oxygen content of bio-oil by deoxygenation. This deoxygenation process should preferably be performed simultaneously with a process to reduce the amounts of high molecular weight components in the pyrolysis oil (i.e. cracking). An attractive option is catalytic hydrotreatment (HDO) at high hydrogen pressure (100-200 bar) and high temperatures (250-400 °C) to remove oxygen in the form of water by means of a catalyst (eq. 1).



HDO of fast pyrolysis has been studied in the past and commonly typical hydrodesulphurisation (HDS) catalysts for fossil feeds like sulphided NiMo/Al<sub>2</sub>O<sub>3</sub> and CoMo/Al<sub>2</sub>O<sub>3</sub> were employed. Various reactor concepts have been explored and a reactor configuration with two separate reactors operated at different temperatures seems preferred. In the first stage, the pyrolysis oil is hydrotreated below 280 °C to convert the most reactive compounds as to avoid excessive coking. Subsequently, the actual deoxygenation reactions occur at higher temperatures (350-450 °C).

This thesis deals with the conversion of pyrolysis oil into a transportation fuel by means of catalytic hydrotreatment. A general introduction to the subject will be provided in **Chapter 1**.

The first step in the research was the identification of suitable (improved) catalysts for the hydrotreatment of fast pyrolysis oil. A variety of heterogeneous catalysts have been tested, ranging from noble metal catalysts like Ru/C, Ru/TiO<sub>2</sub>, Ru/Al<sub>2</sub>O<sub>3</sub>, Pt/C and Pd/C to typical hydrotreatment catalysts like sulphided NiMo/Al<sub>2</sub>O<sub>3</sub> and CoMo/Al<sub>2</sub>O<sub>3</sub> (**Chapter 2**). The reactions were carried out at two operating conditions, for mild (250 °C, 100 bar) and deep hydrotreatment (350 °C, 200 bar) in a batch set-up. Under these conditions, the Ru/C catalyst is superior to classical hydrotreating catalysts with respect to oil yield (up to 60 %-wt.) and deoxygenation level (up to 90 %). The upgraded products were less acidic and contained less water than the original pyrolysis oil. The energy content was about 40 MJ/kg, which is about twice the value of pyrolysis oil. Analyses of the products by NMR and 2D-GC showed that the upgraded pyrolysis oil contained less organic acids, aldehydes, ketones and ethers than the feed whereas the amounts of phenolics and alkanes were considerably higher.

Further experimental studies to determine the effect of the reaction time on the oil yield and elemental compositions of the product phases were performed using the Ru/C catalysts (**Chapter 3**). The reactions were carried out at 350 °C and 200 bar pressure in a batch reactor set-up. Highest oil yields (65 %-wt.) were obtained after 4 h using a 5 %-wt. catalyst intake on fast pyrolysis oil. Longer reaction times lead to a reduction of the oil yield due to the formation of gas phase components (methane, ethane, propane, CO/CO<sub>2</sub>). A separation scheme involving various solvent-solvent extractions was applied to gain insights in the molecular processes taking place during catalytic hydrotreatment. It appears that the carbohydrate fraction of fast pyrolysis oil is very reactive. The observations are rationalized by a set of reaction pathways for the various product phases. **Chapter 4** presents an experimental study to gain insights in catalyst stability when using Ru/C catalysts for the hydrotreatment of fast pyrolysis oil (350 °C and 200 bar) in a batch set-up. A considerable reduction in the liquid yield, increased solids formation, a reduction in the H/C ratio of the liquid product and a lowering of the extent of methane in the gas phase was observed after a number of catalyst recycles. Characterization of the

catalyst before and after reaction using TEM, chemo- and physisorption showed significant coke deposition on the catalyst and a decrease in metal dispersion and pore volume. The application of in house prepared Ru/C catalysts for both the hydrotreatment of fast pyrolysis oil and phenol using different Ru-precursors ( $\text{RuCl}_3$ ,  $\text{Ru}(\text{NO}_3)(\text{NO})_3$  and  $\text{Ru}(\text{acac})_3$ ) resulted in distinct differences in product yield and elemental composition of the liquid phase. The catalyst prepared using  $\text{RuCl}_3$  as the precursor at a ruthenium loading of 5 %-wt. showed the highest activity for the hydrogenation of pyrolysis oil and gave the lowest decrease in BET area and dispersion.

To gain insights in the molecular processes and to explain experimental trends for the HDO of the fast pyrolysis oils, model component experiments have been conducted with carbohydrates (**Chapter 5**). The catalytic hydrotreatment of representative model components for the carbohydrate fraction (D-glucose and D-cellobiose) present in concentrations of 20 to 40 % in fast pyrolysis oils was explored in detail. The hydrotreatment was conducted at a temperature of 250 °C and 100 bar using Ru and Pd on carbon catalysts in water. Two parallel reaction pathways were observed, a thermal, non-catalysed, pathway leading to insoluble humins (char) and a hydrogenation pathway leading to smaller polyols and gaseous hydrocarbons like methane and ethane.

Kilogram quantities of an HDO oil were produced and tested in a diesel engine (**Chapter 6**). Two different hydroprocessed fast pyrolysis oil samples were prepared using Ru/C as the catalysts, viz. a mild HDO product obtained at 320-340 °C and 200-250 bar pressure and a typical deep HDO product (340 °C and 200 bar). The products were successfully tested as a diesel substitute in a small high-speed stationary 5 kW diesel engine. Undiluted hydroprocessed oils (mild HDO or 2<sup>nd</sup> stage oils) were used at optimized conditions for a few hours of operation without problems. The exhaust emissions showed a higher CO but a lower  $\text{NO}_x$  content when compared to diesel, but this is subject to further optimization. After a test of 1.5 h, the injectors were visually analyzed by Scanning Electrode Microscopy. Coke deposit and corrosion and/or erosion of the injectors were absent for runs performed at optimised conditions.

