Hydrotreating & Co-Processing of Renewable Biofuels
Case Study: Hydrotreated Vegetable Oil (HVO)

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Introduction

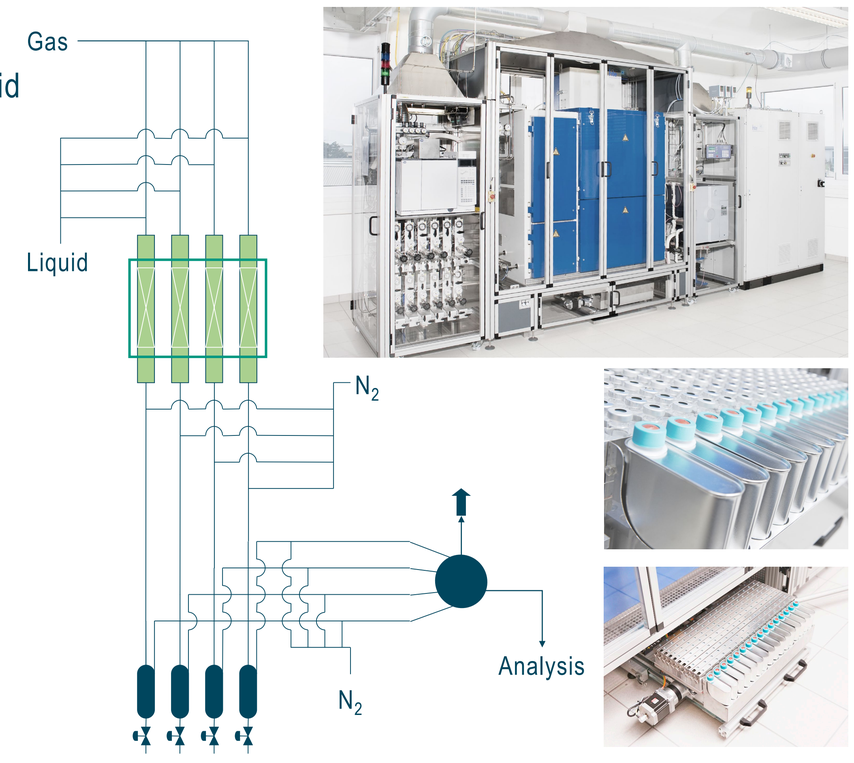
Rapeseed oil as a 1st generation feedstock for biofuel applications offers advantages in terms of its low costs and good flow characteristics. Rapeseed oil contains over 90 % C18-triglycerides and exhibits a high boiling point compared to diesel and VGO, but is still liquid at room temperature due to its unsaturated double bonds. The main goal with this project is to investigate the processing of bio-feedstocks as alternative hydrocarbon sources in high throughput catalytic experimentation. This poster describes the hydrogenation of rapeseed oil over non-sulfided / sulfided hydrodesulfurization (HDS) catalysts to obtain long chain alcohols or alkanes.

Experimental & Results

Multi-fold hydrotreating unit

- 16 reactors in parallel
- Common feed for gas and liquid
- Common active back pressure regulation
- Catalyst volume 1 – 1.5 mL
- Temperature 25 – 450°C
- Pressure 1 – 160 bar(g)
- LHSV 0.5 – 4 hr-1
- GTO 100 – 2000 NL/L
- Particulates 125 – 160 µm
- hteControl™ software for automated process control

Experimental setup

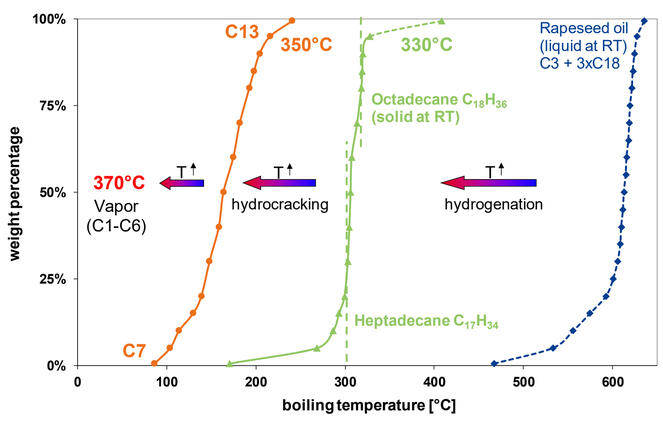


- Automated withdrawal of liquid samples
- 10 sampling rows of 5 mL sample vials + 400 mL waste container
- Heatable up to 120°C
- Sample ID via barcode

Hydrogenation Over Sulfided Catalysts

- Sulfided NiMo/Al2O3 and CoMo/Al2O3 catalysts are active for hydrogenation of C=C, C=O, C-O bonds and hydrocracking
- Catalyst volume: 1.0 ml
- Reaction conditions:
- Temperature 330°C, 350°C and 370°C
- Pressure 50 bar(g)
- LHSV 0.5 hr-1
- GTO 2000 NL/L

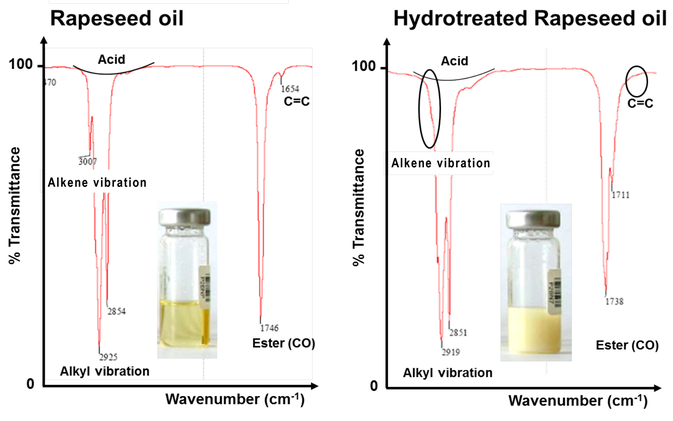
Simulated distillation



Hydrogenation Over Non-sulfided Catalysts

- NiMo/Al2O3 catalyst suitable for hydrogenation of C=C double bonds
- Catalyst volume: 1.0 ml
- Reaction conditions:
- Temperature 200, 225, 250, and 275°C
- Pressure 50 bar(g)
- LHSV 0.375 hr-1 (for 1 ml catalyst)
- GTO 2000 NL/L

Infrared Spectroscopy



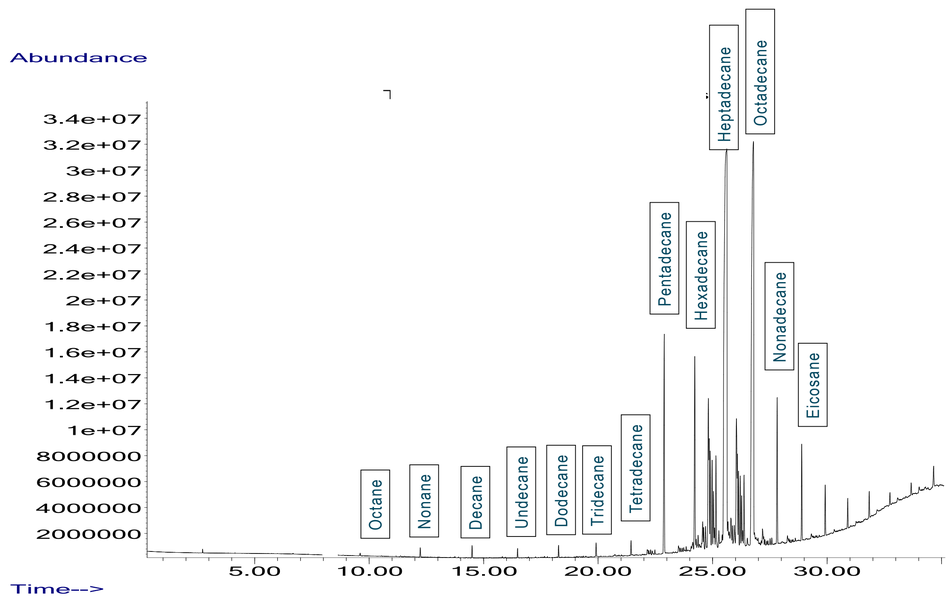
Product distribution

- Different catalysts and reaction conditions result in a wide product distribution
- The processing of acid esters over sulfided catalysts lead to solid n-alkanes in the C17 – C18 range at 330°C

- Octadecane is a hydrogenation product, whereby heptadecane results from a combined hydrogenation and decarboxylation
- No oxygenates were generated

Gas chromatography results

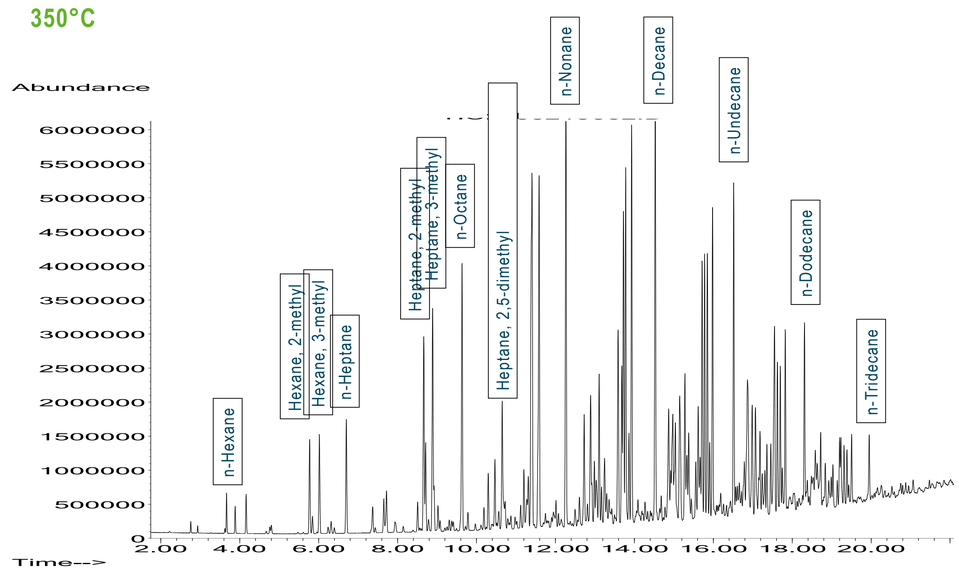
330°C



- By increasing the temperature to 350°C also liquid n-alkanes in the range of C7 – C13 are formed due to additional hydrocracking
- Above 370°C only gaseous products are generated

Gas chromatography results

350°C



Summary and Conclusions

- Parallel testing is applied successful for hydrogenation and hydrocracking of bio-oil (vegetable oil, black liquor, lignin oil, yeast or algae oil)
- hte technologies can handle 1st to 3rd generation bio-oil and its hydroprocessing products
- Bio-feed-oil can result in several different products (liquid, vapor, solid) depending on catalyst and process-conditions

Parallel Catalyst Testing is Applied for Hydrogenation and Hydrocracking Applications Successfully with Several Benefits:

- All catalysts experience the same conditions
- More results in less time of operation
- Small amounts of catalyst required
- Pilot plant data reproduced
- Smaller catalyst volumes require less feed
- Long-term stability and robustness

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