

## Hydrotreating of Renewable Feedstocks – Process Design based on Understanding of Reaction Routes

Rasmus G. Egeberg\*, Bjørn Donniss, Peder Blom and Kim G. Knudsen  
Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Kgs Lyngby, Denmark  
\*rce@topsoe.dk (corresponding author)

### Introduction

The conversion of renewable bio-feedstocks into transportation fuels in order to reduce our dependence on fossil fuels has led to a number of new processes and fuel formulations. For diesel cars, most of the biodiesel presently available is fatty acid methyl esters (FAME) prepared by transesterification of vegetable oils or tallow. However, FAME is not a stable fuel and has poor cold flow properties [1]. Another route to a renewable diesel fuel is to hydrotreat either a pure renewable feed or a mixture hereof with fossil diesel. The conversion of pure vegetable oils was demonstrated already in the 1980's [2, 3] and these reactions may take place over traditional sulfidic hydrotreating catalysts [3]. In the *co-processing* scheme, triglycerides are converted to alkanes at the same time as the fossil part of the feed is hydrosulfurized.

The hydrotreating process offers a number of advantages both in form of feed flexibility, product characteristics, and compatibility with existing fuel infrastructure. However, the process also consumes large amounts of hydrogen, cause higher exotherm and yield by-products (e.g. CO, CO<sub>2</sub>, H<sub>2</sub>O) that may require a revamp of the hydrotreater and the use of specialized catalyst systems.

In order to investigate the routes by which triglycerides react with hydrogen to form alkanes a series of micro reactor and pilot plant tests were performed [4].

### Materials and Methods

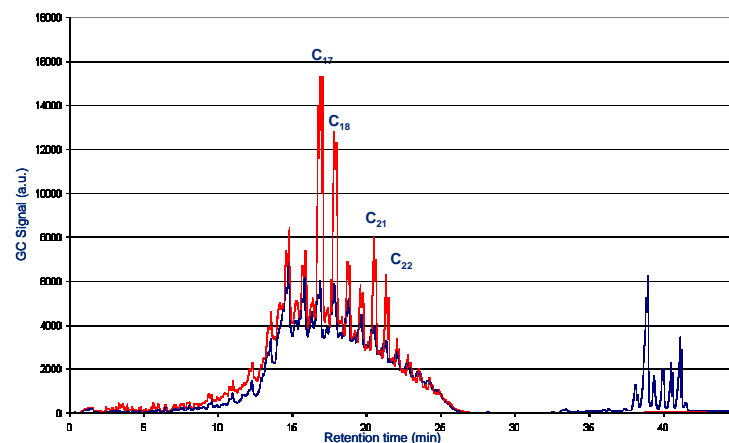
Model compound tests of methyl laurate and a number of alcohols, ketones and aldehydes were performed in a once-through microscale reactor using Haldor Topsøe TK-565 and TK-559 BRIM™ catalysts. Products were analyzed by on-line GC and GC-MS for specifications of specific compounds. Real-feed tests with blends of rapeseed oil and Kuwait light gas oil (LGO) were conducted in a once-through, trickle bed reactor using Haldor Topsøe TK-575 BRIM™. Pilot plant studies of blends comprising tall oil derived material were also conducted. The experimental details are given in [4].

### Results and Discussion

Hydrogenation of triglycerides can follow a decarboxylation and/or a hydrodeoxygenation (HDO) route. The relative importance of these two reaction mechanisms may be judged from the yield of gases or from the simulated distillation GC chromatograms (Figure 1) since the decarboxylation route give alkanes with 1 carbon atom less than the HDO route. The amount of rapeseed oil in the feed could be correlated with the product properties such as density, cetane index and cloud point. Also, the effect of processing rapeseed oil on HDS activity was quantified.

The real feed tests also showed that relatively large amounts of water, propane, carbon dioxide, carbon monoxide and methane were formed. Experiments clearly showed that the water-gas-shift and methanization reactions in the hydrotreater need to be considered in order to model the results.

The model compound studies shed light on the intermediates and gave a clear indication that the HDO reaction route is not a simple hydrogenation of the connecting oxygens followed by stepwise catalytic hydrogenation to alkanes. Rather, the HDO route appears to proceed via an adsorbed enol intermediate.



**Figure 1.** Simulated distillation chromatogram of feed (blue) and liquid product (red) from co-processing a blend of LGO and rapeseed oil in a hydrotreating reactor.

### Significance

As the reaction route is intimately linked with yields, hydrogen consumption and product properties, the findings have profound influence on the design of process and catalysts for hydrotreating renewable material. As hydrogen consumption and reaction exotherm is considerably larger than in conventional hydrotreaters, catalyst and operating conditions must be designed to ensure a long cycle length. This is exemplified by the design of a revamped industrial unit for co-processing tall oil derived material into EN 590 ultra-low sulfur diesel.

### References

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