Marine and jet biofuel production via hydrotreating of Triacylglycerides

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The aim of the current research is focused on the upgrading of bio-based triacylglycerides (TAGs) via hydroprocessing to marine and jet bio-fuels. Biogenic residues and wastes were gasified and the syngas was fermented to produce bio-based triacylglycerides (TAGs). Bio-fuels were produced via TAG hydrotreatment. The overall process, combining thermochemical, biological and thermocatalytic parts is based on the gasification of biomass and other biogenic waste in a Dual Fluidized Bed gasifier and the 2-stage fermentation of the produced syngas. Through this process the syngas is converted to acetate (1st stage) and then the acetate is converted to TAGs (2nd stage). The produced TAGs contained medium and long fatty acids were hydrotreated and isomerized after the necessary separation and purification and the end-products are jet- and bunker-like biofuels, respectively.

More specifically, three specific types of biogenic residues were examined, such as agricultural wastes (i.e. pruning from olive trees or wheat straw) and biogenic wastes from ports and/or airports. The current manuscript, will present the step of TAGs upgrading via hydroprocessing targeting jet- and bunker-like biofuels. The hydrotreatment experiments were performed in the small-scale pilot plant TRL 3 of CERTH. This TRL 3 pilot plant is a small industrial system which is operated to generate information about the behaviour of the system for use in design of larger facilities. The current hydrotreating/hydrocracking unit allows testing in a targeted operating window, including reactor temperature (100°-400°C), pressure (40-135 bar) and feed H2-to-oil ratio (100 – 500 nl/l) simulating the industrial operating conditions of the refineries. The pilot plant consists of a stainless-steel continuous flow tubular reactor (15.8 mm I.D. and 704 mm in length) containing six independent heating zones, sustaining the desired temperature profile within the reactor. The temperature of each catalyst bed is monitored and controlled via the six independent thermocouples placed inside a thermo-well. The hydrogen flow-rate is regulated by a mass flow controller whereas the liquid feed system is regulated by a high-pressure liquid piston pump. After the liquid feed is mixed with the high-pressure hydrogen at a regular T-joint, it enters the fixed-bed down-flow reactor, where the desired hydrotreating reactions take place. The product exits the reactor, condenses (at 35°-40°C) and is finally flashed via a high-pressure low-temperature separator, where the gas and liquid phase products separate.

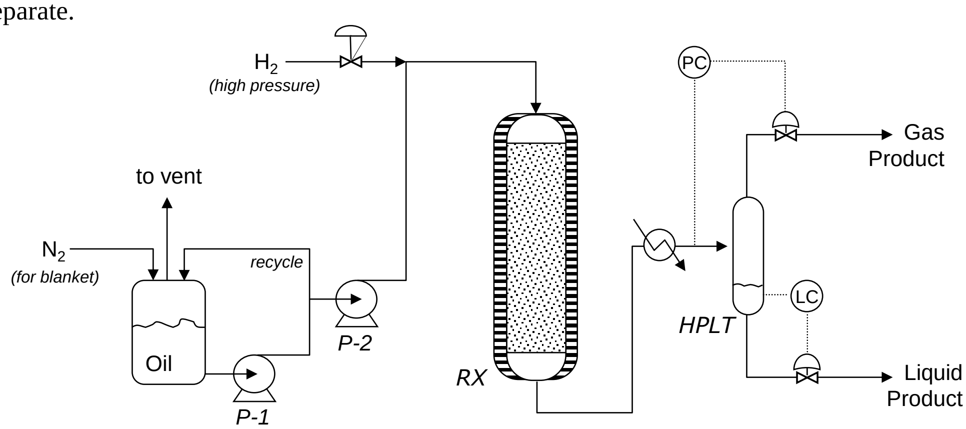

Figure 1 Simplified diagram of the VB01 TRL 3 hydroprocessing pilot plant

The main target was to investigate the effect of the key hydrotreating parameters during the upgrading of TAGs in terms of product quality and catalyst performance. To that aim, three reaction temperatures were tested, two H_2/oil ratio and two reactor pressures. For the aim of the current investigation, a commercial NiMo catalyst was employed that has presented very good results with similar biomass feedstocks in the past. As the catalyst is a commercial one, no more details are available. The examined operating window is presented in the following table 1 via five conditions.

Table 1 Operating parameters examined

Parameters	Units	Condition 1	Condition 2	Condition 3	Condition 4	Condition 5
Pressure	psi	1000	1000	1000	1600	Otpt.
Temperature	°C	300	330	360	Opt.	Opt.
H2/oil ratio	scfb	3000	3000	3000	3000	5000
LHSV	hr^{-1}	1	1	1	1	1

The results have shown that the most influential parameter is the reaction temperature that strongly affects the mass recovery curve of the product. In general, higher reaction temperatures favour hydrocracking reactions leading to lighter hydrocarbons in jet fuel range. On the other hand, lower hydrotreating temperature leads to heavier hydrocarbons in marine fuel range. Thus, the choice of reaction temperature is very important as it affects the final distillation range and thus the marine fuel and jet fuel yields of the product.

Pressure is also influencing the hydrotreating reactions and more specifically, the higher the pressure the lighter the product is. However, the effect of pressure is not as strong as that of temperature. Furthermore, as higher pressures and temperatures favour hydrocracking reactions, this result in higher hydrogen consumption. The hydrogen consumption increased as the heavier hydrocarbons are cracking to lighter ones.

Finally, the higher H2/oi ratio, also leads to lighter products with an increase n hydrogen consumption. Thus, the choice of the optimum operating parameters is very important and depends first of all from the targeted products (marine or jet range biofuels) and also from the optimum hydrogen consumption. In general, high quality jet and bunker biofuels have been produced via hydrotreatment of TAGs

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