

Producing Diesel Fuel by Co-Hydrogenation of Vegetable Oil with Gas Oil

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During the investigation our goal was the production of partially bio derived fuels in the gas oil boiling point range. In the last few years, to eliminate the unfavourable properties of biodiesels (FAME) intensive research has begun to convert the triglycerides (e.g. vegetable oils, fats, etc.) to products with other chemical structure. One of the examined different thermal and catalytic possibilities can be the positive solution the quality improvement of vegetable oils and gas oils together (co-processing). The aim of our experimental work was to produce product mixtures with high yield, and with maximum 10 mg/kg sulphur content from mixtures of high-sulphur gas oil (about 1.0%) and vegetable oil raw materials. In the co-hydrogenation experiments we applied mixtures of gas oil with different vegetable oil content (0 %, 5 %, 15 %, 25 %, 100 %). NiMo/Al₂O₃ catalyst with targeted composition was used as a catalyst. In case of all feedstocks the same process parameter combinations were used (T=300-380 °C, P=60-80 bar, LHSV=1.0 h⁻¹, H₂/HC=600 Nm³/m³), which were selected on basis of the results of our pre-experiments. We investigated the effect of the process parameters and the vegetable oil content of the feedstocks on the yield, the physical-, chemical- and application properties of the main product.

On the basis of the results we obtained that both the vegetable oil conversion reactions (saturation of olefinic double bonds, deoxygenation) and gas oil quality improvement reactions (heteroatom-, mainly sulphur removal, aromatic content reduction) took place. Under the favourable operational conditions (360-380 °C, P=80 bar, LHSV=1.0 h⁻¹, H₂/HC=600 Nm³/m³ and 15% vegetable oil content of feed) the main properties of the high-yield products except for the CFPP value satisfied the requirements of standard EN 590:2009. The amount of vegetable oil higher than 15% reduced the desulphurisation efficiency, whereas the removal of heteroatoms took place on the same active centres of the catalyst, so the deoxygenation reactions forced back the desulphurisation reactions because of the intake of large quantities of oxygen with the triglyceride molecule.

Based on the results we concluded that an existing hydrogenation plant may be suitable for the co-processing of vegetable oil and gas oil mixtures. In a single step the quality improvement of gas oil (sulphur, nitrogen, aromatic content reduction) and the vegetable oil conversion to n- and i-paraffins can be achieved. The products - depending on the vegetable oil content of the feedstocks – have an increased n- and i-paraffin content, so their cetane numbers must be high, too.

1. Introduction

The aspiration for the use of the bio derived fuels in the recent decades has come into view in the whole world. The principal impulsions of the aspiration are the increasing need for the mobility, the depletion of oil stocks, the dependence of crude oil and import energy sources and the need to reduce the environmental pollution. The energy demand of passenger and freight transport is covered mostly from fossil fuels today. To partially redeem these (cover the increase of the usage), furthermore to improve their quality the favourable solution would be the usage of biofuels from biomass as a renewable energy source. Currently, the research and the continuously growing application of the second-generation biofuels produced from renewable sources can certainly contribute to these demands. The consumption of fuels is characterized by the dieselization, so our goal was the production of a partially bio derived fuel in the gas oil boiling point range.

The currently utilised first-generation biodiesels (fatty acid methyl esters) and their production technologies have a lot of unfavourable properties (e.g. poor heat and oxidation, and thus poor storage stability caused by high unsaturated content, corrosion problems caused by high water content, sensitivity to hydrolysis, unfavourable cold properties, less energy content, etc.). To eliminate these unfavourable properties the researchers of the world proposed a number of different processes to produce biofuels from triglyceride-containing materials (Hancsók et al. 2007ab). One of the examined different thermal and catalytic possibilities may be the positive solution the co-hydrogenation of vegetable oils and gas oils together (Krár et al. 2010; Huber et al. 2007; Melis et al. 2009). However, some research results suggest that with the conversation of gas oil with high sulphur content (0.6-1.2%) and vegetable oil mixtures the catalytic alteration cannot reduce the sulphur content of the products to or under 10 mg/kg, which is expected in the EU (Mikulec et al. 2010; Bezergianni et al., 2009). Therefore, there is a need to develop catalysts and find proper process conditions to produce diesel fuel which fulfils the requirements of the standard (EN 590:2009).

2. Experimental

2.1 Experiment setup

The aim of our experimental work was to select a catalyst which is suitable under appropriate process conditions to produce product mixtures with high yield, and with maximum 10 mg/kg sulphur content from mixtures of high-sulphur (1.0%) heavy gas oil from Russian crude oil and Hungarian vegetable oil (sunflower oil) as raw materials. In the co-hydrogenation experiments we applied mixtures of raw materials with different vegetable oil content (0%, 5%, 15%, 25%, 100%) (Table 1). To the pure vegetable oil feedstocks 1000 mg/kg sulphur was added in the form of dimethyl disulfide to preserve (maintain) the catalytic activity of the sulfide state catalyst. NiMo/Al₂O₃ catalyst with targeted composition was used as a catalyst, which was selected on the basis of the results of the pre-experiments with a number of catalyst compositions, which were carried out by our research group. In case of all feedstocks the same process parameter combinations were used (T=300-380 °C, P=60-80 bar, LHSV=1.0 h⁻¹, H₂/HC=600 Nm³/m³). We investigated the effect of the process parameters and the vegetable oil content of the feedstocks on the yield, the physical-,

chemical- and application properties of the main product in continuous mode in laboratory pilot equipment and on steady-activity catalysts. The properties of the feedstocks and the products were specified according to the specifications of the EN 590:2009 “Automotive fuels – Diesel” standard.

Table 1: Properties of feedstocks.

Properties	Gas oil (GO) F1	95% GO +5% SO F2	85% GO +15% SO F3	75% GO +25% SO F4	Sunflower oil (SO) F5
Density (15.6°C), g/cm ³	0.8513	0.8553	0.8615	0.8695	0.9226
Viscosity (40°C), mm ² /s	5.36	6.68	9.18	11.81	31.11
Acid numb., mg KOH/g	0.03	0.03	0.04	0.04	0.08
Iodine numb., g I ₂ /100 g	0.5	4	17	36	122
Aromatic content, %	37.60	35.79	31.91	28.23	0.00
CFPP, °C	2	3	4	7	20
Sulphur content, mg/kg	10370	9860	8815	7770	1000
Nitrogen content, mg/kg	228	216	194	172	7
Oxygen content, %	16 mg/kg	0.57	1.72	2.87	11.50
Flash point, °C	79	80	80	81	>300
Distillation characteristics (EN ISO 3405:2000)					
IBP	213	212	214	213	*
10 v/v%	279	285	288	292	*
50 v/v%	324	329	335	340	*
90 v/v%	355	363	*	*	*
FBP	368	*	*	*	*
Cetane number	49	48	47	45	36

* can not be measured because of the thermal decomposition of sunflower oil
CFPP: Cold Filter Plugging Point

2.2 Results and discussions

The product mixtures obtained during the heterogenous catalytic conversion of the different feedstocks were separated to gas phase, aqueous phase and organic phase. The gas phase separated in the separator of the experimental equipment contained carbon-monoxide and carbon-dioxide forming in the deoxygenation reactions (hydrodeoxygenation, decarbonylation, decarboxylation), propane forming from the triglyceride molecule, hydrogen-sulphide and ammonia forming in the heteroatom removing reactions from the gas oil part of the feedstock, and in addition it contained light hydrocarbon by-products (C₁-C₄) forming in the cracking reactions (as a valuable by-product). The aqueous phase contained water (forming in the reduction of triglycerides), hydrocarbons and different oxygen containing compounds. After the splitting of the aqueous phase, we separated the main product fraction (gas oil boiling point range fraction – mainly C₁₁-C₂₂ hydrocarbons till boiling point of 360 °C) and the residue from the organic phase via vacuum distillation. Components below the boiling point of 180 °C (gasoline) were absent in the product. The incidentally obtained residual fraction contained the not converted triglycerides, the formed or rather not converted di-

and monoglycerides, and hydrocarbons with higher carbon numbers originating from the feedstock or being intermediates, and also carboxylic acids and esters.

The yield of the gas phase product increased with the increasing temperature and pressure in case of all the feedstocks. In this paper we introduce the yields and the properties of the products obtained at the most preferential pressure (80 bar) as a function of the temperature. At higher temperatures the triglycerides were increasingly converted, and the undesired (productive of non gas oil products) hydrocracking reactions came to the front, too. The yield of the aqueous part of the fluid phase product mixture changed as a maximum curve, because at low temperatures the conversion of the triglycerides is not complete yet, and at high temperatures (360-380 °C) where the conversion is almost complete, the rate of water forming reactions decreases. The yield of the organic liquid phase decreased with the increasing temperature because of the high yield (up to about 20 %) of the by-products (CO, CO₂, H₂O, C₃H₈) with the increasing temperature and on the other hand because of the hydrocracking of the hydrocarbon chains (Figure 1). In case of pure gas oil feedstock, the yield of the organic liquid product mixture was above 92 % in all cases, and with pure vegetable oil it was about 82-90 % in every case. The liquid organic product mixture was separated into two fractions: gas oil boiling point range main fraction and residual fraction. The decreasing of the residual fraction demonstrates the increase of the conversion with the increasing temperature (Figure 2). In case of pour vegetable oil, the yield of the residual fraction was approximately 10 % at 300 °C, and with the increasing temperature, at 360 °C it decreased to 0 % while in case of mixture feedstocks the conversion of the triglycerides was already complete at 340 °C.

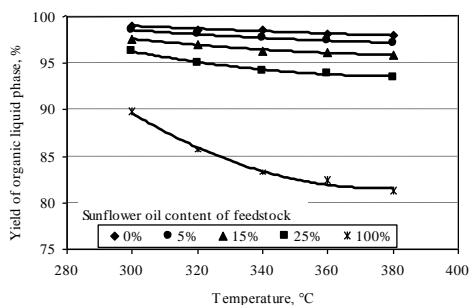


Figure 1: Yield of organic liquid phase.

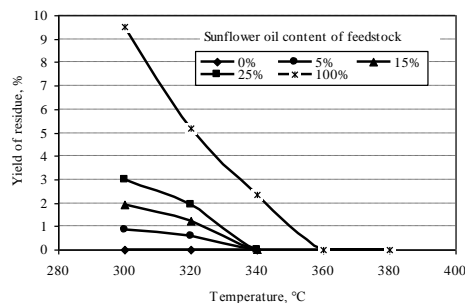


Figure 2: Yield of residue.

As a matter of course, the yield of the main product in case of pure gas oil feedstock was the same as the yield of the organic product mixture, and it decreased with the increasing temperature of the catalytic conversion. In case of vegetable oil feedstock this yield increased with increasing temperature, because of the triglyceride conversion. In case of mixture feedstocks, the yield of the main product was between the two mentioned rates of the yield in function of the temperature (Figure 3).

The sulphur content of the main products decreased by increasing the temperature (Figure 4). At 300 °C – with the reduction in the sulphur content of the feedstocks because of the dilution effect of the vegetable oil – in case of mixture feedstocks the product from 25 % sunflower oil containing feedstock had the lowest sulphur content. At 360-380 °C the products from F2 and F3 feedstocks had almost the same sulphur

content as the products from F1 feedstock. The products from F4 feedstock had higher sulphur content because the high oxygen content of the triglycerides inhibited the desulphurization reactions, and on the side of feedstocks, the dilution effect of the vegetable oil could not offset the decreased desulphurization efficiency. At 380 °C from the F1, F2, F3 feedstocks, less than 10 mg/kg sulphur containing products were made.

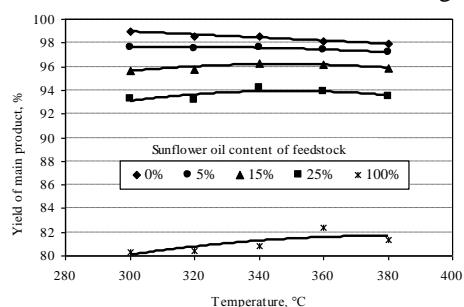


Figure 3: Yield of main product.

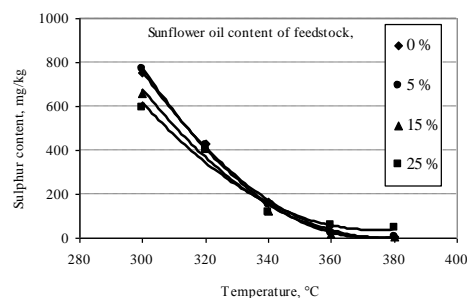


Figure 4: Sulphur content of main product.

The aromatic content of the main product changed as a minimum curve in function of the temperature, its favourable range was 340-360 °C (Figure 5). By increasing the vegetable oil content of the feedstocks the aromatic content of the products decreased, partly because of the aromatic hydrogenation reactions, and partly because the feedstocks had inherently less aromatic content due to the dilution effect. This turn was caused by the mixing of sunflower oil. The lowest aromatic content achieved was 18 %. The cold filter plugging point of the products increased by increasing the vegetable content of the feedstocks because of the produced large quantities of n-paraffins (Figure 6). However, at 360-380 °C from the F4 feedstock products were made which had almost the same CFPP value as the products produced from pure gas oil.

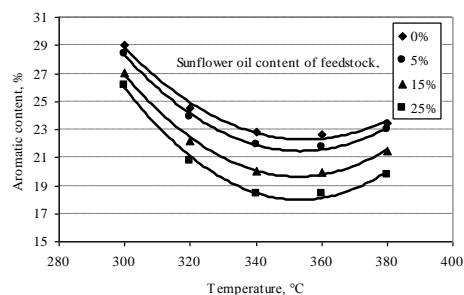


Figure 5: Aromatic content of main product.

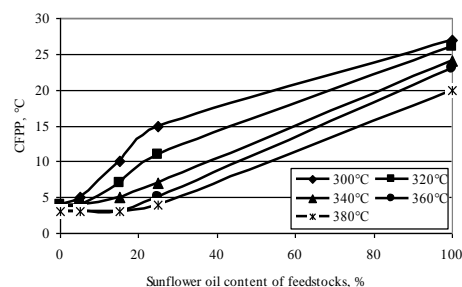


Figure 6: CFPP of main product.

3. Conclusions

On the basis of the results gained from the catalytic co-hydrogenation of the gas oil containing sunflower oil in different percentage on targeted composition NiMo/Al₂O₃ catalyst we obtained that both the vegetable oil conversion reactions (olefinic double saturation, deoxygenation) and the gas oil quality improvement reactions (heteroatom removal, aromatic content reduction) took place. Under the favourable operational

conditions (360-380 °C, P=80 bar, LHSV=1.0 h⁻¹, H₂/HC=600 Nm³/m³ and 15% vegetable oil content of feed) the main properties (total aromatic content: 20%, sulphur content: <10 mg/kg) of the high-yield products except for the CFPP value (3 °C) satisfied the requirements of standard EN 590:2009 for diesel fuels. The amount of vegetable oil higher than 15% reduced the desulphurisation efficiency, whereas the removal of heteroatoms took place on the same active centers of the catalyst. So the deoxygenation reactions forced back the desulphurisation reactions because of the intake of large quantities of oxygen with the triglyceride molecule of the vegetable oil.

Based on the results we concluded that an existing hydrogenation plant (with a suitable pressure reactor) with a slight alteration may be suitable for the co-processing of vegetable oil and gas oil mixtures. In a single step the quality improvement of gas oil (sulphur, nitrogen, aromatic content reduction) and the vegetable oil conversion to n- and i-paraffins can be achieved. The products - depending on the vegetable oil content of the feedstock - have augmented n- and i-paraffin content. The products with high cetane number (50-80 units depending on the n- and i-paraffin content of the products) have unfavourable cold properties (CFPP: about 0-15 °C) so the isomerisation and/or the additivition is necessary. With this process gas oils which cannot be converted to products with adequate cetane number can be processed because the paraffins produced from the triglycerides caused a significant increase in the cetane number.

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