Fuel Purpose Hydrotreating of Free Fatty Acid By-products and Heavy Straight Run Gas Oil

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The European Union (EU) has set a target in the 2009/28/EC directive, which aims that the share of biofuels in transportation has to be at least 10 energy % in 2020. However, only half of this target can be met by first generation biofuels (produced from sugars, oil crops, etc.). For this reason, the EU supports and encourages the development and application of advanced biofuels (0.5 energy % indicative target in 2015/1513/EC directive). So, the research and development of newer generation biofuels for Diesel engines are important, due to the high level gas oil consumption of the EU. Nowadays, the most widely used biocomponent of gas oils is biodiesel, which consists of a mixture of various fatty acid methyl esters (FAME) and has many disadvantages. The actual diesel fuel product standard of EU (EN 590:2013) limits the blending rate of biodiesel to 7.0 V/V % and the preEN 16734 limits biodiesel to 10.0 V/V% maximum. .
Biodiesel could be replaced by bio gas oil, which is produced by catalytic hydrogenation of triglycerides and/or fatty acids from different origins (e.g. wastes, animal fats). Bio gas oil is a mixture of n- and iso-paraffins in gas oil boiling range and they are the most favourable energy source for running Diesel engines. The second generation bio gas oil is an excellent gas oil blending component and it is preferred by the car manufacturers, too. Consequently, the aim of our research work was to produce advanced biofuel, a gas oil blending component with bio gas oil content from waste feedstock.
During our experiments we investigated the fuel purpose hydrogenation of waste free fatty acid by-products of vegetable oil processing (0 %, 3 %, 5 %, 10 %, 20 %) and heavy straight run gas oil mixtures on a commercial $NiMo/Al_2O_3$ catalyst. The effects of feed compositions and process parameters (temperature, pressure, liquid hourly space velocity (LHSV), hydrogen/feedstock ratio) on the quality and quantity of the main product were investigated. The applied process parameters were the following: P = 40 - 50 - 60 bar, T = 300 - 375 °C, LSHV = 1.0 - 2.0 h^{-1}, hydrogen/feedstock ratio = 400 Nm^3/m^3.

1. Introduction

The main factors of the world's energy need are the increasing number of population and the development of the economy. The energy demand is continuously growing (BP, 2015), but the stocks of the most important energy source (crude oil) are limited. The research and development of alternative fuels are necessary to contribute to the sustainable development and mobility (Zöldy, 2011).

Nowadays, in the European Union and most of the world, the most widely used biocomponent of gas oils is biodiesel, which has many disadvantages (bad thermal and oxidation stability, high CFPP, lower energy content, etc.) (Knothe, 2010). Due to these disadvantages, the EU diesel fuel standard (EN 590:2013) limits the blending rate of biodiesel to 7.0 V/V %. On the other hand the OEMs banned FAME from their highest quality WWFC 5th category diesel fuel [WWFC 5th edition].

Biodiesel is mainly produced from different vegetable oils, which negatively affect the cultivation of food and feed crops (Anuar and Abdullah, 2016). Thus, the EU encourages and supports the research and development of advanced biofuels, which feedstocks are not influencing that (e.g. wastes, algae etc.). As a result of this the 2015/1513/EC directive sets an indicative target for advanced biofuels as 0.5 energy %.

Furthermore, the EU will count these waste based alternative fuels double to the 10 % target for renewable energy in transport (EU, 2015).

1.1 Bio gas oil

The production and use of bio gas oils could be an answer to the increasing quality and quantity needs of diesel fuels. Bio gas oil is a mixture of n- and iso-paraffins in gas oil boiling range produced by special hydrocracking (hydroconversion) of natural and waste triglycerides and fatty acids (Hancsók et al., 2007) (Figure 1). Bio gas oil is an excellent gas oil blending component (high cetane number, aromatic and sulphur free, etc.) and the blending of it to diesel fuel is not limited by any regulations.
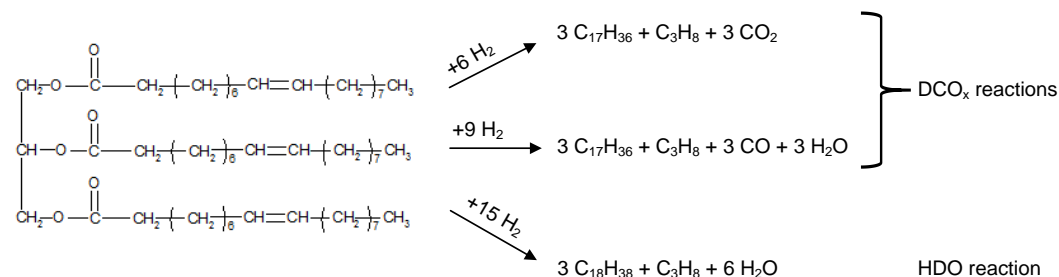

Figure 1: An example for production of bio gas oil from triglycerides

A lot of publications are available in the literature, which are about the hydrogenation of mixtures of triglycerides (from different sources) and gas oils. However, there are no publications available, which are especially about the hydrogenation of mixtures of waste fatty acids (FA) and gas oils. Furthermore, those publications investigating the hydrodeoxygenation of FA, used mostly only model compounds (oleic acid, palmitic acid, caprylic acid, etc.) (Boda et al., 2010). That is why, the aim of our research work was to investigate the hydrogenation of mixtures of FA by-products and heavy straight run gas oil (SRGO) to produce diesel fuel blending component.

2. Experimental

We investigated the fuel purpose hydrotreating of FA by-products and heavy straight run gas oil on a commercial, sulphided $NiMo/Al_2O_3$ catalyst. The effects of feed compositions and process parameters (temperature, liquid hourly space velocity, pressure, H_2/feedstock ratio) on the quality and quantity of the main product (gas oil fraction) were investigated.

2.1 Equipment

The experiments were carried out in an apparatus containing a tubular down-flow reactor of 100 cm^3 effective volume. It contains all the equipment and devices applied in the reactor system of an industrial heterogeneous catalytic plant (Sági et al., 2016).

2.2 Materials

Free fatty acids which are by-products of vegetable oil processing (Table 1) and heavy straight run gas oil (Table 2) produced from Russian crude oil were used to heterogeneous catalytic hydrogenation experiments. FA was blended into SRGO in different ratios: 0 %, 3 %, 5 %, 10 % and 20 %.

Table 1: Properties of fatty acid by-products (FA)

Density, 15.6 °C	g/cm^3	0.9212	Composition	%
Acid number	mg KOH/g	188	Myristic acid	0.09
Cold Filter Plugging Point	°C	+22	Palmitic acid	6.14
Kinematic viscosity (40 °C)	mm^2/s	24.05	Oleic acid	69.20
Simulated Distillation			Nonadecane	0.10
Initial boiling point	°C	296	Icosane	0.79
10 %		362	Mixture of esters	8.95
50 %		378	Monoglycerides	0.16
90 %		460	Diglycerides	1.02
Final boiling point		649	Triglycerides	2.98
			Unknown	6.54

2.1 Process parameters

Process parameters were chosen based on results of our previous experiments (Hancsók et al., 2012). Process parameters of current experiments were the following: P = 40 - 50 - 60 bar, T = 300 - 375 °C, LSHV = 1.0 - 2.0 h^{-1}, hydrogen/feedstock ratio = 400 Nm^3/m^3.

2.2 Applied analytical methods

The properties of feedstocks and products were measured and calculated according to the methods of EN 590:2013 standard (Table 3). We analysed the hydrocarbon composition of the products with a gas chromatograph (Shimadzu GC 2010). The applied column is stable at high temperatures (Restek MXT-1 (30m × 0.28mm × 0.1 μm)). The temperature program was the following: 40 °C (4 min), then 240 °C (10 °C/min heating speed), after that 400 °C (8 °C/min) and finally 16 minutes at 400 °C.

Table 2: Properties of heavy straight rung gas oil (SRGO)

Properties		SRGO
Density, 15.6 °C	g/cm^3	0.8667
Kinematic viscosity, 40°C	mm^2/s	6.131
Sulphur content	mg/kg	11,000
CFPP	°C	+10
Monoaromatics	%	21.1
Polyaromatics	%	11.5
Total aromatics	%	32.6
Boiling range	°C	184-352

Table 3: Standardized analytical methods for determining product properties

Properties	Standard code
Density	EN 12185:1998
Sulphur and nitrogen content	EN 20846:2004
Aromatic content	EN 12916:2000
Distillation properties	EN 3405:2000
Gas chromatography	Shimadzu GC 2010 (own method)
Kinematic viscosity	EN ISO 3104:1996
Cold Filter Plugging Point	EN 116:1999

3. Results and discussion

Figure 2 shows the yield of main product (180 - 360 °C boiling range) as a function of temperature, pressure and composition of feedstocks (results are shown only in case of the favourable feedstock compositions because of the length of this publication). The main product yields (or yield losses) were basically determined by the forming of H_2O, CO, CO_2 during the conversion of FA to n-paraffins, and the hydrodesulphurisation of gas oil (sulphur removal in the form of H_2S) at 40-50 bar. Yield loss (3.1 - 5.2 %) resulting cracking reactions took place significantly at only 60 bar (and above 345 °C). Main product yields (93.4 - 97.6 %) were in theoretical range (95.7 - 98.8 %), or they approached it well.

The ratio of HDO and DCO_x reactions can be easily tracked by observing the n-C_{18} and n-C_{17} paraffin content of main product. Figure 3 shows the change of mass ratio of n-C_{18} and n-C_{17} paraffins as a function of temperature and feedstock composition. After the hydrogenation of SRGO, this ratio was around constant value (1.12), so n-C_{18} and n-C_{17} paraffin content of main products were almost the same. That means only the n-paraffins produced from hydrodeoxygenation of FA could influence this ratio. The n-C_{18}/n-C_{17} ratio decreased in every case by increasing the reaction temperature, so DCO_x reactions came into the front. Furthermore, we observed that the ratio decreased too by increasing the FA content of the feedstock, consequently less HDO reactions occurred (in case of same process parameters). The explanation of this effect can be that the theoretical chemical hydrogen consumption of feedstocks increased by the higher FA content, which resulted less HDO reactions. HDO reactions consume more hydrogen than DCO_x reactions. By increasing the quantity of FA molecules in the feedstock, more and more FA molecules will occupy the active sites of the catalyst, so less hydrogen will be available for the reactions and absence of hydrogen may occur. These results are similar to Yang et al. (2013) findings. They investigated the hydrogenation of dodecane and C_{18} fatty acids. They reported that the C_{17} paraffin content of products were higher when they increased C_{18} fatty acid content of the feeds.
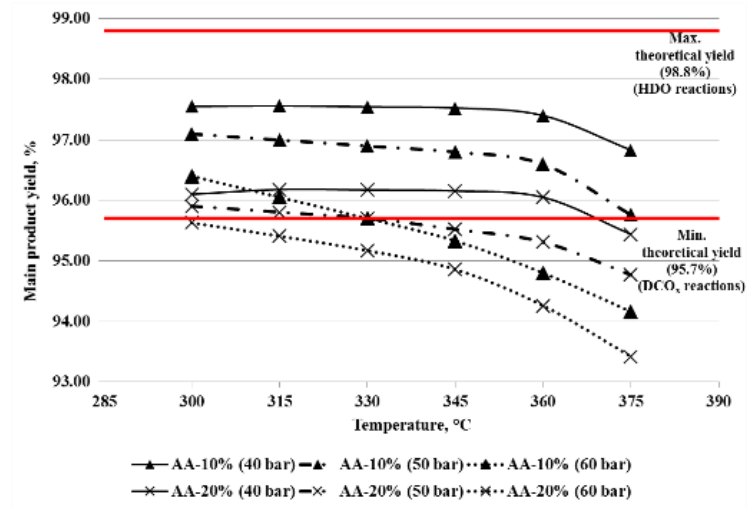
Figure 2: Main product yield as a function of temperature, pressure and feedstock compositions (LHSV=1.0 h^{-1}, H_2/feedstock ratio = 400 Nm^3/m^3)

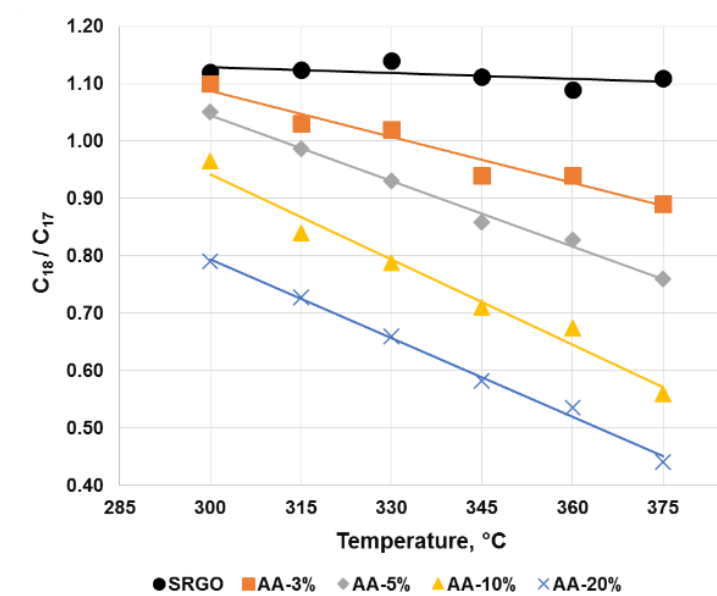*Figure 3: The ratio of C_{18} and C_{17} n-paraffins as a function of temperature and feedstock compositions (P=40 bar, LHSV=1.0 h^{-1}, H_2/feedstock ratio = 400 Nm^3/m^3)*

Figure 4 shows the sulphur content of main products as a function of temperature and feedstocks at 40 bar. SRGO had high sulphur content (11,000 mg/kg), thus the sulphur content of feedstocks changed between 8,800 - 11,000 mg/kg as a function of FA content.
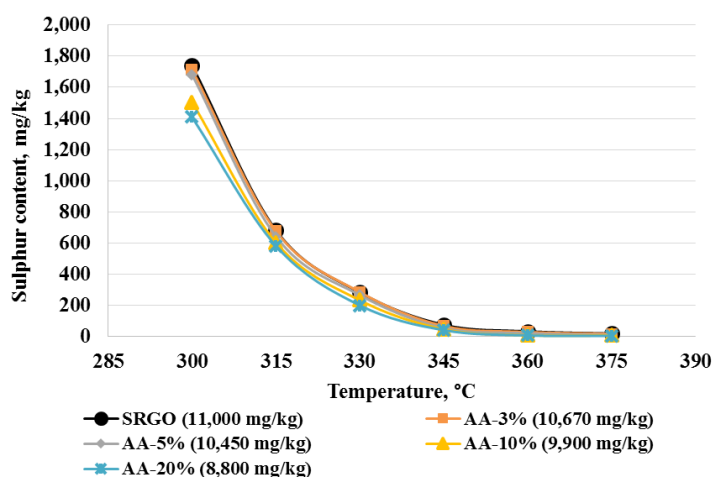
Figure 4: Sulphur content of main products as a function of temperature and feedstock compositions (P=40 bar, LHSV=1.0 h^{-1}, H$_2$/feedstock ratio = 400 Nm^3/m^3)

Increasing of temperature had the most significant effect on the sulphur content of main products. Besides that, lowering the LHSV and increasing the pressure were favourable, too. Products with the lowest sulphur content (6 - 33 mg/kg) were obtained from feedstocks with 10 - 20 % FA content at 360 °C and at all pressures (40 - 50 - 60 bar) and applying 1.0 - 1.5 h^{-1} LHSV. Benefits of higher pressure and lower LHSV showed significant effect only at lower temperature range (300 - 345 °C). Therefore, products with low sulphur content, which satisfies the diesel fuel standard of EU, (≤ 10 mg/kg) were already obtained at 40 bar. The sulphur content of the main products was lower with higher FA content. This can be explained by the fact that the feeds had already lower sulphur content. It is important to notice that this phenomenon was basically true at lower reaction temperature range (< 345 °C), but it was not true during the production of ultra-low sulphur (< 10 mg/kg) products. The reason of this could be that oxygen and sulphur removal reactions take place on the same active sites of the catalyst.

Total aromatic content of products was lower than the feedstock's one, and in function of temperature it changed as a minimum curve, which had equilibrium minimum value at 360 °C (Figure 5). This can be explained by the exothermic reactions of the hydrogenation of aromatics. Kinetic inhibition can be observed at lower temperature (< 360 °C), but thermodynamic inhibition occurs by increasing further the temperature. Total aromatic content of products was lower, too by increasing the pressure and FA content of feedstocks, and lowering the LHSV. FA is aromatic free, thus total aromatic contents of feedstocks and products decreased by increasing the FA concentration of feeds.
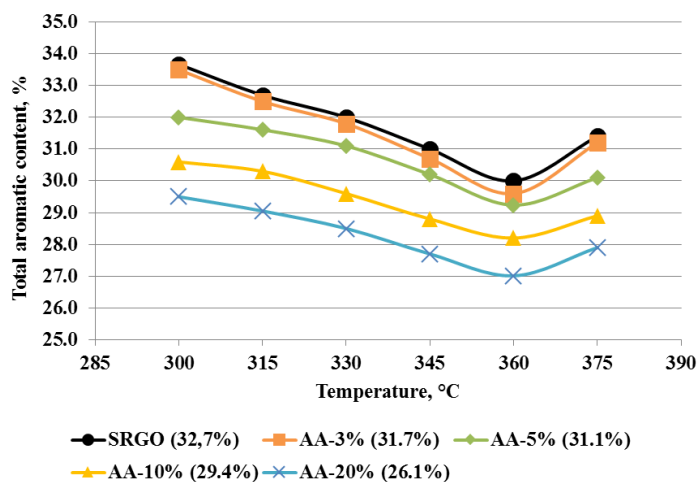

Figure 5: Total aromatic content of main products as a function of temperature and feedstock compositions (P = 40 bar, LHSV = 1.0 h^{-1}, H$_2$/feedstock ratio = 400 Nm^3/m^3)

The EU diesel fuel standard (EN 590:2013) limits only the polyaromatic content of diesel fuel (≤ 8.0 m/m %). Polyaromatic content of main products changed between 2.6-7.0 % in case of all process parameters, so they satisfied the requirements of the diesel fuel standard.

4. Conclusions

In this paper we have investigated the fuel purpose hydrotreating of mixtures of waste fatty acid by-products (0 %, 3 %, 5 %, 10 %, 20 % alternative component) and heavy straight run gas oil (sulphur content: 11,000 mg/kg, total aromatic content: 32.6 %) on a commercial, sulphided $NiMo/Al_2O_3$ catalyst. The effects of feed compositions and process parameters (P = 40 - 50 - 60 bar; T = 300 - 375 °C; LSHV = 1.0 - 2.0 h^{-1}; H$_2$/feedstock ratio = 400 Nm^3/m^3) on the quality and quantity of the main product (gas oil fraction) were investigated.

Based on our results we concluded that products in diesel fuel boiling range can be obtained with high yield (96.0 - 97.5 %) from 10 - 20 % waste fatty acids containing feedstocks, when favourable process parameters (P = 40 bar; T = 360 °C; LSHV = 1.0 - 1.5 h^{-1}; H$_2$/feedstock ratio = 400 Nm^3/m^3) are applied. Theoretical yields were well approached by applying favourable process parameters. The products with their low sulphur (< 10 mg/kg) and polyaromatic (< 7.0 %) content satisfy the requirements of the EU's diesel fuel standard (EN 590:2013).

Fuel purpose hydrotreating of fatty acids could be beneficial in this form; because milder process parameters (e.g. lower temperature) are sufficient and/or higher LHSV (1.1 - 1.5 h^{-1}) can be applied than in case of co-processing of triglycerides. Furthermore, we concluded that the hydrogen consumption was lower than when triglycerides are hydrogenated. The reasons for this could be the followings: there is no need for removing of propylene from triglycerides and hydrogenate it to propane (spontaneous reaction in the catalytic hydrogenation system), and fatty acids with the same structure have one more hydrogen than when they are in triglyceride bond. In addition we clearly concluded that, the ratio of HDO reactions compared to DCO$_x$ reactions was getting lower by increasing the fatty acid content of feedstock, because of the higher reaction rate of decarbonylation/decarboxylation reactions in the investigated catalytic system.

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