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Co-Processing of High-Sulphur Gas Oil and Waste with High Fatty Acid Content

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Energy consumption is continuously growing world-wide. Due to tightening environmental regulations and to reduce dependency on fossil fuels the demand for alternative fuels is increasing in the EU. At the same time the use of first generation biofuels is limited because of their inappropriate properties and feedstocks. First generation biofuels are mainly produced from edible feedstocks. So this is important to investigate the utilisation of waste based sources and new methods to produce new, alternative fuel components with better properties. Waste fatty acids can be promising feedstocks for alternative fuel production, since hydrocarbons can be produced from them with oxygen removal reactions. There is little information about the hydrogenation of fatty acid mixtures in the literature; most of the studies are about the conversion of model compounds. Real waste fraction with high fatty acid content (> 90 %) has high oxygen and olefinic double bond content (> 78 %). These are heat and oxidation sensitive compounds. Hydrocarbon fraction with mainly normal-paraffins can be produced with the hydrogenation of these compounds. These paraffins are good blending components of engine fuels with favourable performance properties. The aim of our work was to study the production of high quality diesel fuels with alternative component content from the different mixtures of waste fatty acids and high-sulphur, crude oil based light gas oil fractions. The quality improvement of mixtures of unrefined, winter grade gas oil fraction and fatty acids (10, 20 and 30 wt%) was carried out on a commercial, sulphided NiMo/Al_2O_3 catalyst. Our goal was to achieve the most complete hydrogenation of the unstable fatty acids (saturation and oxygen removal) and to practically remove the sulphur content of the gas oil fraction, furthermore, to saturate the aromatics (especially the polycyclic ones) as much as possible.

1. Introduction

Increased energy consumption is largely caused by the growth of transportation and shipping. Due to the continuous growth of road transportation, the use of diesel fuels is also increasing world-wide (World Oil Outlook, 2017). There are several ways to reduce the harmful environmental impact of energy consumption. Energy production from renewable energy sources instead of fossil ones and the production of engine fuels from renewable sources with the same characteristics as conventional fuels (Srivastava and Hancsók, 2014). First-generation biofuels, such as bioethanol and biodiesel, cannot replace crude oil-based engine fuels. They have inadequate properties, limited quantities and are mainly produced from edible feedstocks. The latest directives of the European Union already require a reduction in the use of first-generation biofuels while requiring increase in the total use of biofuels (EU, 2017). That is why it is important to deal with the production of fuels from non-edible, renewable or waste feedstocks. Such a bio-derived diesel fuel blending component is green diesel (Razak et al., 2017).

Fatty acids are derived from renewable sources. Because of the high amount of produced and consumed vegetable oil the quantity of vegetable oil originated fatty acid waste is significant. Furthermore, they are produced as forestry by-product as well. The deoxygenation reactions of fatty acids were mainly studied in inert atmosphere (Santillan-Jimenez and Crocker, 2012) and the possibility of biodiesel production from them was investigated (Islam et al., 2013).

Perígolo et al. (2017) studied fatty acids treatment with NaOH to produce hydrocarbons. Hossain et al. (2018) investigated the deoxygenation of oleic acid, as a model compound, on active carbon catalyst with subcritical

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water consumption. Hengst et al. (2015) studied the deoxygenation of oleic acid under mild pressure. Kim et al. (2016) investigated the catabolism of fatty acids to produce chemical compounds. During these researches no industrially viable solution was found.

Boonyasuwat and Tscheikuna (2017) studied the co-processing of palm fatty acid distillate and sulphur containing light gas oil on commercial CoMo/Al_2O_3. They found that the efficiency of oxygen removal was appropriate while the efficiency of sulphur removal decreased. Sági et al. (2017) concluded similar findings during the investigation of co-hydrogenation of vegetable oil-based fatty acid by-product and sulphur containing heavy gas oil on commercial NiMo/Al_2O_3 catalyst.

2. Experimental

2.1 Equipment

Single-through isothermal tube reactor with 100 cm^3 effective volume was used during the co-processing experiments in continuous mode. Our equipment contained all units and devices (pumps, separators, heat exchangers and controllers) which can also be found in an industrial gas oil hydrogenation plant (Hancsók et al., 2007).

2.2 Feedstocks

The main properties of the used unrefined light gas oil (LGO), waste fatty acid fraction (FAF) and the feedstock blends with 10, 20 and 30 wt% fatty acid fraction content are summarized in Table 1.

Table 1: Main properties of the feedstocks

Main property	LGO	FAF	LFA-1	LFA-2	LFA-3
Fatty acid fraction content, wt%	0	100	10	20	30
Sulphur content, mg/kg	5762	32	5240	4521	3876
Total aromatic content, wt%	36.4	0	32.7	29.2	26.2
PAH** content, wt%	8.3	0	7.5	6.7	5.6
Density, g/cm^3	0.8436	0.9215	0.8513	0.8591	0.8669
CFPP*, °C	- 31	20	- 13	- 7	- 2

*Cold Filter Plugging Point, **Polycyclic Aromatic Hydrocarbon

2.3 Analytical methods

The applied analytical methods for determining the properties of the feedstocks and products are summarized in Table 2.

Table 2: Analytical methods

Properties	Analytical methods
Hydrocarbon composition	GC method, Shimadzu GC 2010
Sulphur content	EN ISO 20846:2012
Aromatic hydrocarbon content	EN 12916:2016
Density at 15.6 °C	EN ISO 12185:1998
Cold Filter Plugging Point	EN 116:2016

3. Results and discussion

3.1 Yield

Based on the comparison of the yields of products form different feedstocks under the same conditions we found that with higher fatty acid fraction content in the feedstock the yield of the main products decreased (Figure 1). This is caused by the occurring losses during the deoxygenation of fatty acid fraction (H_2O, CO and CO_2 by-products). However, at the same time due to the inherently lower sulphur content of the feedstocks the losses occurring from the sulphur removal reactions are lower (H_2S by-product). In addition, the increase of yield was also due to the fact that the hydrocracking reactions were also less frequent. During the hydrogenation fatty acids occupy or cover the catalytically active sites, therefore they are only available in a smaller proportion for other reactions.

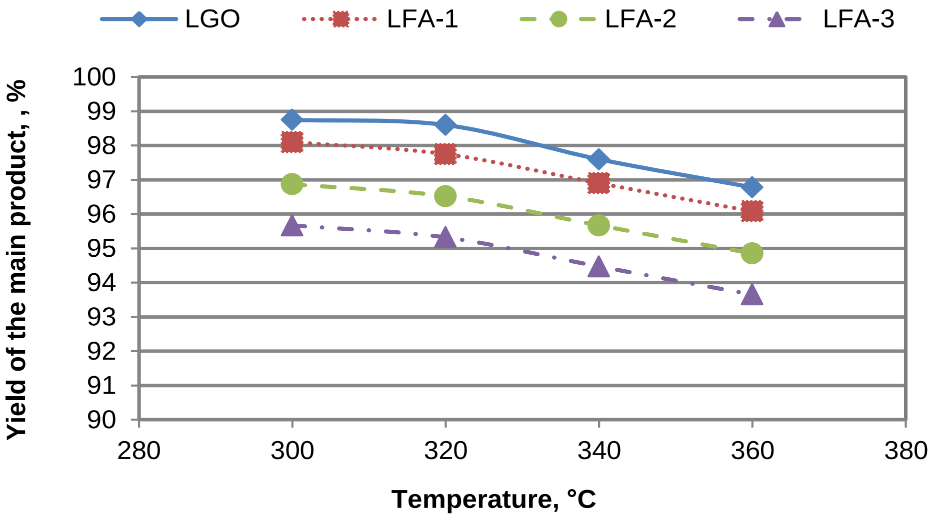

Figure 1: Yields of the products obtained from different feedstocks as a function of temperature (LHSV: 1.0 h^{-1}, P: 50 bar, H_2/HC: 600 Nm^3/m^3)

3.2 Fatty acid content

Figure 2 shows the share (%) of decarboxylation/decarbonylation (DCO_x) and hydrodeoxygenation (HDO) reactions as a function of feedstocks and process temperature. With higher fatty acid fraction content in the feedstock the share of DCO_x reactions increased compared to the share of HDO reactions. The higher the oxygen content of the feedstock the more difficult the hydrogenation reactions (HDO) occurred. The reason is that the number of available catalytically active sites on the catalyst surface was less. Furthermore, the excess hydrogen compared to the oxygen content is decreased (H_2/CH ratio: 600 Nm^3/m^3). With higher temperature the ratio of DCO_x reactions also increased while the ratio of HDO reactions decreased. The explanation for that is DCO_x reactions are endothermic reactions. Therefore increasing the temperature has a beneficial effect on them. HDO reactions are exothermic reactions so increasing the temperature has an opposite effect on them.

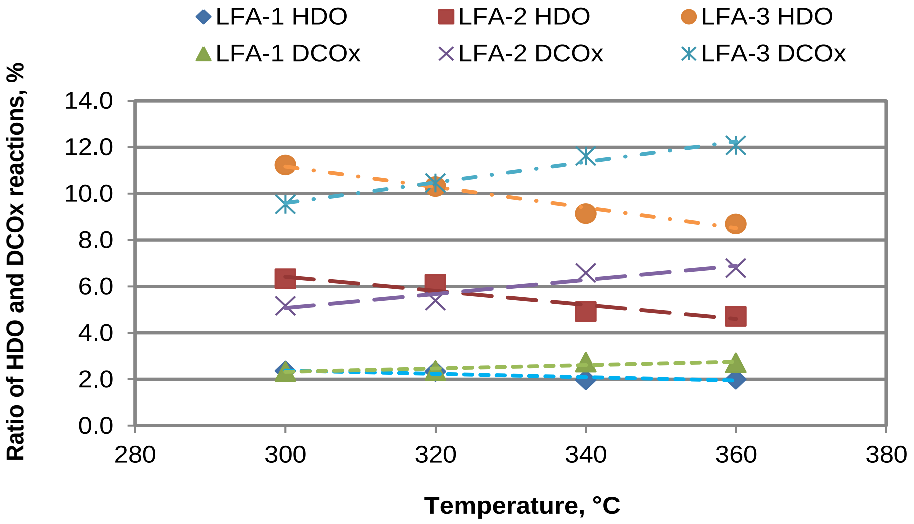

Figure 2: Ratio of the products obtained from different feedstocks as a function of temperature (LHSV: 1.0 h^{-1}, P: 50 bar, H_2/HC: 600 Nm^3/m^3)

3.3 Sulphur content

Due to the inherently low sulphur content of the fatty acid fractions (32 mg/kg) with increasing the FAF fraction content of the feedstocks their initial sulphur content has decreased. However, the sulphur content of the main products obtained at the same temperature and LHSV values changed inversely. The efficiency of sulphur removal was influenced by the fatty acid content of the feedstock (Figure 3). It decreased with higher fatty acid content of the feedstock. The reason is that the oxygen and sulphur removal reactions are competitive ones. At lower temperatures, the difference is bigger because with increasing the temperature the ratio of the reactions is higher. So the effect of the oxygen compounds is decreasing. EN 590:2017 diesel fuel standard sets max. 10 mg/kg sulphur limit. The products from the hydrogenation of the gas oil fraction by itself have reached this limit already at 300 °C and 1.0 h^{-1} while products from FAF containing feedstocks have reached this limit only at 340 °C and 1.0 h^{-1}.

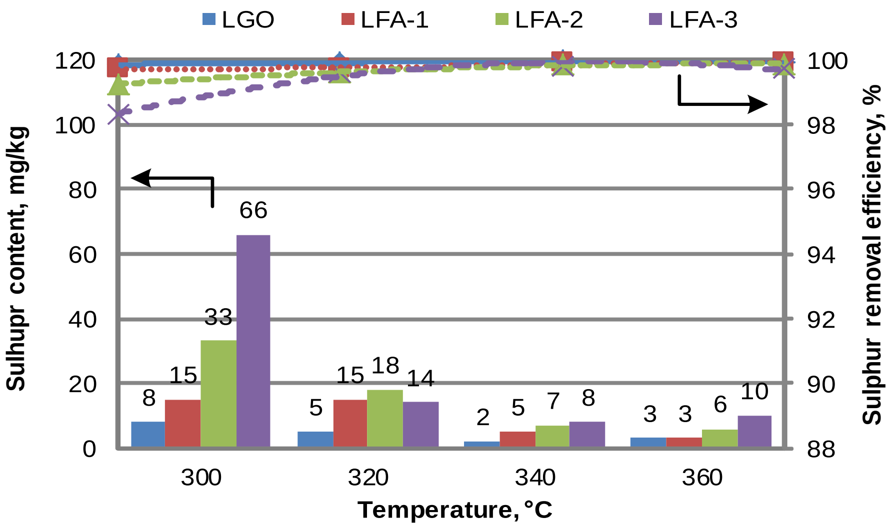

Figure 3: Sulphur content of the products and the sulphur removal efficiency as a function of feedstock and temperature (LHSV: 1.0 h^{-1}, P: 50 bar, H_2/HC: 600 Nm^3/m^3)

3.4 Aromatic content

Chapter 2 With higher FAF content the aromatic content of the feedstocks was proportionately lower because the FAF was practically aromatic free. The aromatic content of the products from higher FAF containing feedstocks was lower but not proportionally lower than products from petroleum based gas oil. So the fatty acid content of the feedstocks influenced the performance of the aromatic saturation reactions (Figure 4).

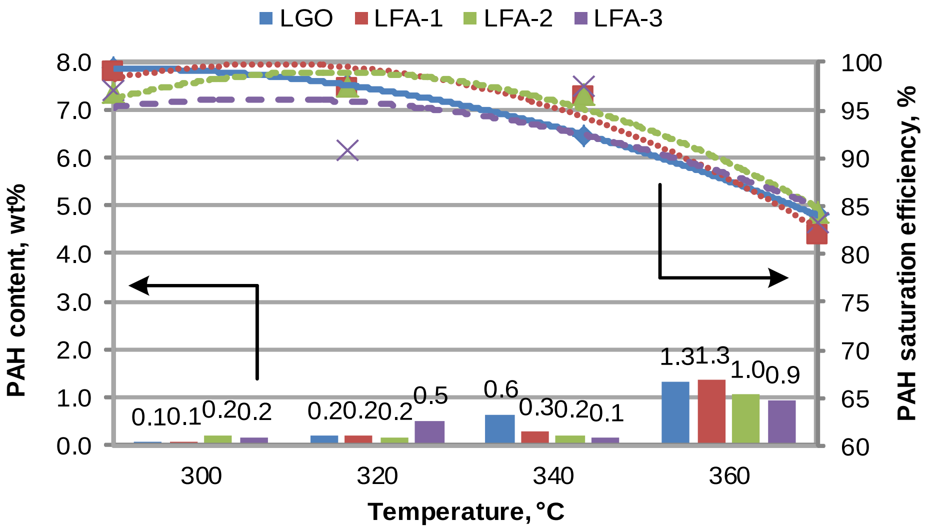

Figure 4: Polycyclic aromatic hydrocarbon content of the products and the saturation efficiency as a function of feedstock and temperature (LHSV: 1.0 h^{-1}, P: 50 bar, H_2/HC: 600 Nm^3/m^3)

Polycyclic aromatic hydrocarbon content decreased significantly already at 300 °C and decreased further with increasing the temperature until 340 °C. Above this there was a slight increase. This is due to the exothermic hydrogenation of polycyclic aromatic hydrocarbons (thermodynamic inhibition). The efficiency of polycyclic aromatics saturation has changed between 63 and 99 %. Its value increased with decreasing the LHSV. The effect of fatty acid presence was more significant at lower temperatures. It is true that at higher temperatures the polycyclic aromatics saturation efficiency was lower but the difference between the values obtained for the different feedstocks was also lower. The polycyclic aromatic hydrocarbon content of all main products was below the upper limit of the diesel fuel standard (maximum 8 wt%).

3.5 Cold filter plugging point

European diesel fuel standard has different summer and winter grade CFPP values. For countries in temperate zone in case of summer grade diesel fuel the limit is maximum + 5 °C (Class A) while in case of winter grade diesel fuel it is maximum - 20 °C (Class F). The CFPP values of our products can be seen on Figure 5. The composition of the feedstocks had significant effect on this property. With higher FAF content the CFPP value increased. During the hydrogenation of fatty acids long-chain normal-paraffins formed. They have high freezing point (n-C_{15}: 10 °C) and it increases with higher carbon number. At lower temperature and higher LHSV the conversion of triglycerides from FAF was lower. According to this the CFPP of the main products increased. The lower values obtained at 340 and 360 °C are the outcome of the higher ratio of the hydrocracking reactions. This causes the decrease of the yields of the liquid products and the CFPP values. The freezing point of the normal-paraffins decreases with the decrease of their carbon number. As it can be seen, only the product formed from 10 wt% FAF containing feedstock at 360 °C met the winter grade limit of the standard. However, other products derived from this feedstock are also close enough to this limit. With appropriate middle distillate flow improver and wax anti-settling additive CFPP could be improved. For other feedstocks, further quality improvement (isomerization) of the products, blending with other components and application of cold flow improvers could be necessary to achieve winter quality CFPP. Or their use as summer grade gas oil is recommended.

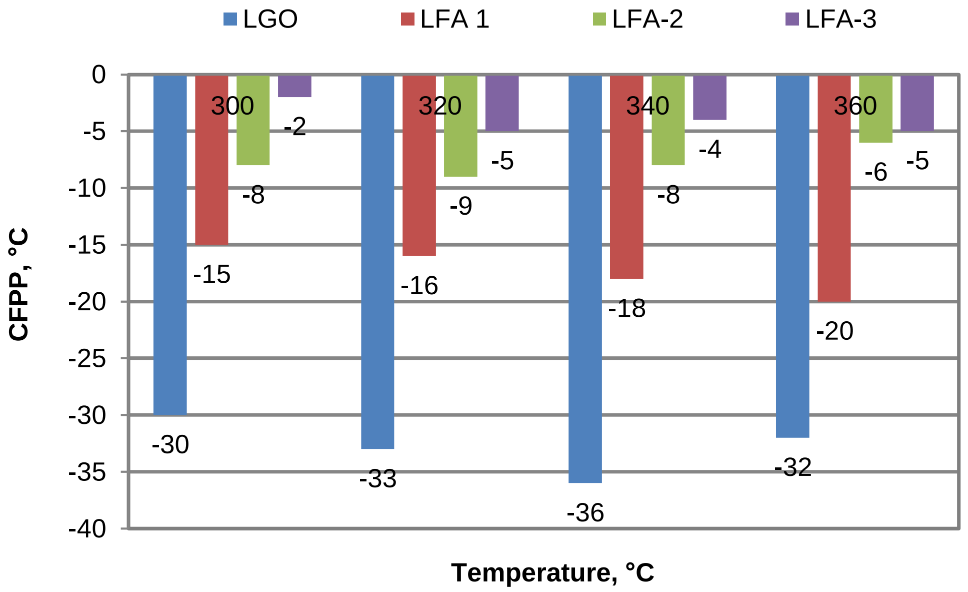

Figure 5: Cold filter plugging point of the products as a function of feedstock and temperature (LHSV: 1.0 h^{-1}, P: 50 bar, H_2/HC: 600 Nm^3/m^3)

4. Conclusions

We determined that the blending of fatty acids into the gas oil feedstock had a slightly unfavourable effect on the yield and on the efficiencies of the occurring hydrogenation reactions. During the quality improving step, the removal of oxygen and sulphur and the saturation of aromatics took place in a large extent. As a result of these reactions aliphatic hydrocarbon products with higher hydrogen content and high hydrogen: carbon ratio formed, so the paraffinic characteristic of the targeted products increased. The use of ultra-low polycyclic aromatic hydrocarbon containing fraction results in significantly less pollutant emissions when used as engine fuel due to lower flame temperature and cleaner combustion.

Based on the result of our experiments (T: 300 - 360 °C; H_2/CH ratio: 600 Nm^3/m^3; LHSV: 1.0 - 3.0 h^{-1}; P: 50 bar) we selected the favourable operation parameters to produce high quality winter grade diesel fuel blending components (e.g. 10 wt% fatty acid waste containing feedstock, 360 °C, 1.0 h^{-1} liquid hourly space velocity). At the same time the gas oil product from this feedstock at 340 °C has excellent, near standard quality and higher gas oil yield. The operation parameter combination must be selected to be economically optimal; in addition to the appropriate quality, the yield value should be sufficiently high. Overall, we found that high quality diesel gas oil blending component can be produced from fatty acid waste fraction and high-sulphur, crude derived gas oil fractions with co-processing, with the presented catalytic conversion. Co-processing with straight run gas oil with high sulphur content can be a favourable solution to improve the quality of the fatty acid fraction in an existing desulphurisation unit of a crude oil refinery. This can lead to significant savings in investment and operational costs.

For high quality, alternative diesel gas oil blending component production the effect of fatty acid fraction to the hydrogenation of other quality straight run gas oils need to be studied. In our future research work the co-processing of different alternative components with straight run gas oils will also be examined.

Acknowledgments

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