Different Pathways to Preserve the Sulphid State of the Catalyst During the Hydroprocessing of Triglycerides

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During the experimentals a special case of the hydrogenation of triglycerides was studied on a sulphided NiMo/Al$_2$O$_3$ catalyst (P = 40 and 80 bar, T = 320-380 °C, LHSV = 0.75-2.0 h^{-1}, H$_2$/feed ratio = 600 m^3/m^3). The sulphur containing compounds were covered with a small amount (10 %) of sulphur containing (0.9 %) gas oil in the sunflower oil to ensure the sulphided state of the catalyst. In comparison, the hydrogenation of another feedstock was examined, which sulphur content was adjusted approx. to the same concentration (905 mg/kg) with an easily decomposable sulphur compound (dimethyl disulphide). In case of the both feedstocks, by applying the favourable process parameters (T = 360-380 °C, P = 80 bar, LHSV = 0.75 to 1.0 h^{-1}, H$_2$/feed ratio = 600 m^3/m^3) the properties of the products - obtained in high yield - satisfied the requirements of the EN 590:2013 standard except their CFPP value and density. The composition of the feedstocks had a significant impact on the quality of products, but the difference is reduced by increasing temperature. Based on these results, we concluded that to preserve the sulphide state of the catalyst in case of the catalytic hydrogenation of triglycerides a suitable and cost-effective solution to increase the sulphur content of the feedstock with straight run (high sulphur containing) gas oil. With the blending of the high cetane and low density products they were able to improve the quality of low-quality gas oil streams to produce better quality diesel fuel with bio-component content.

1. Introduction

The composition of motor fuels is defined by different product standards. This can be done with direct restrictions of the composition (e.g. sulphur content up to 10 mg/kg, fatty acid methyl ester content up to 7 v/v %), or by the specified values of performance characteristics (e.g. flash point requirement to limit the quantity of light components). The use of alternative and bio derived components in higher amount are encouraged by the European Union with the help of its directives. Until 2020, the use of bio fuels is determined in 10 % referred to the energy content of motor fuels used in the transportation sector (Renewable Energy Directive, 2009/28/EC). In addition, they urge to take in account in case of calculation of greenhouse gas (GHG) emissions the impacts of the indirect land use change (ILUC) (2009/30/EC). The EU has supported the production of fuels derived from waste from the beginning. Nowadays they have also discussed the limitation of the first generation bio fuels based on edible feedstocks. Currently the first generation motor fuels produced from edible feedstocks are in use simultaneously with the waste derived fuels. The aim of further developments is the use of algae oil and lignocelluloses as feedstock (Liew et al., 2014).

Nowadays, because of the efforts of the EU and the several disadvantages (hydrolysis sensitivity, polymerization, etc.) of first generation fatty acid methyl esters obtained by transesterification of triglycerides (vegetable oils, fats, etc.) the demand on these products constantly decreases. Their place will be taken over by the second generation bio gas oils (HVO, mixture of normal and isoparaffins) produced by catalytic hydrogenation (Srivastava et al., 2014).

For the special hydrogenation of the triglyceride (preferably waste derived) containing feedstocks researchers investigated multiple catalysts with different compositions. Chistyakov et al. (2013) studied platinum and palladium containing Al$_2$O$_3$ and zeolite supported catalysts for converting rapeseed oil.

Platinum (as active metal) catalysts were used to convert triglycerides on Al_2O_3 (Madsen et al., 2011) and SAPO-11 (Herskowitz et al., 2013) support too. Krár et al. studied the conversion of sunflower oil on reduced state (non-sulphided) conventional $CoMo/Al_2O_3$ (2010), and in addition on $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ (2011) catalysts. Hancsók et al. (2012) found that the hydrogenation activity of the catalysts in elemental state increasing by the following order NiW/Al_2O_3 < $NiMo/Al_2O_3$ << $CoMo/Al_2O_3$. The triglyceride containing feedstocks on sulphided catalysts can be converted, for which are suitable e.g. $NiMo/Al_2O_3$ (Srifa et al., 2014) and NiW containing (Mikulec et al., 2009) catalysts. Veriansyah et al. (2012) compared several catalysts for hydrogenation of soybean oil; they achieved the highest conversion using a sulphided $NiMo/Al_2O_3$ catalyst.

In summary, the noble and transition metal catalysts on various supports are suitable for the processing of the triglyceride containing feedstocks. Catalysts containing noble metal have high activity, but they are expensive and quickly lose their activity. Transition metal catalysts in reduced state - like the noble metal catalysts – do not require the increasing of the sulphur content of the feedstock, but they have less activity than in their sulphided state.

Beside of the processing of feedstocks in themselves, it is increasingly significant to co-process the different origin triglycerides with straight run gas oils in existing refinery plants with catalytic hydrogenation directly into bio component containing diesel fuel (Tóth et al., 2011) and more recently (Bezergianni et al., 2014a)

Among the catalysts investigated by researchers and applied in the industry, the transition metal/support catalysts in sulphide state have proven to be the most suitable for the processing of the triglycerides by themselves and combined with gas oils. To maintain the activity of the catalyst in sulphide state the sulphur, which is continuously "washing down" (balance between the catalyst and the fluid) is required to be made up from external source (approx. 400 - 2,000 mg/kg of hydrogen sulphide in the reactor). In case of processing of triglycerides alone the necessary sulphur can be added into the catalytic system with the feedstocks: easily decomposable sulphur compounds (e.g. DMDS) are added to the liquid feed, or hydrogen sulphide is added to the hydrogen feed. In the case of co-processing, triglycerides (in the sufficient amount) are usually added to the gas oil to ensure the second-generation bio-component content of products. The sulphur content of these gas oils are as high to provide the required concentration of sulphur.

During processing triglycerides in themselves the application of a special case of co-processing has not been studied yet, in which only a small amount (5-15 %) of straight run (high sulphur containing) gas oil is added to the feedstock to cover the required sulphur content, maintaining the active state of the catalyst. The external addition of sulphur is required because even in case of using gas recirculation a part of the product gases has to be purged, which reduces the amount of sulphur in the system as well.

2. Experimental

During the experiments the hydrogenation of a small amount (10 %) of high-sulphur (0.9 %) gas oil containing sunflower oil (900 mg/kg S) was studied on a commercial sulphided $NiMo/Al_2O_3$ catalyst (P = 40 and 80 bar, T = 320-380 °C, LHSV = 0.75 - 2.0 h^{-1}, H_2/feed ratio = 600 m^3/m^3). In comparison, the hydrogenation of an other feedstock was examined, which sulphur content was adjusted approx. to the same concentration (905 mg/kg) with dimethyl disulphide (DMDS) (Table 1). Properly pretreated sunflower oil (originated from Hungary) and straight run gas oil produced from Russian crude oil were used to prepare the feedstocks.

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 hydrogenation plant (Tóth et. al. 2009). The experiments were carried out in continuous operation.

The properties of the feedstocks and the products were as analyzed by the specifications of the EN 590:2013 standard, relevant for diesel fuels and with standardised calculation methods.

3. Results and discussions

The products were separated into a gas phase, a water phase and an organic liquid phase. The gas phase was separated in the separator unit of the experimental equipment contained (besides of hydrogen) carbon-monoxide and carbon-dioxide formed in the deoxygenation reactions (hydrodeoxygenation, decarbonylation, decarboxylation), propane formed from the triglyceride molecule, hydrogen-sulphide and ammonia formed in the heteroatom removing reactions, and in addition it contained light hydrocarbon by-products (C_1-C_4) formed in the cracking reactions (as a valuable by-product). The liquid phase contained

water (formed in deoxygenation), hydrocarbons and different oxygen containing compounds. After the separation of the aqueous phase, we separated the main product fraction (gas oil boiling point range fraction – mainly C_{10}-C_{22} hydrocarbons until boiling point of 360 °C) from the residue via vacuum distillation. By applying gas chromatographic analysis we found that products in each case did not contain liquid components with boiling point less than 180 °C (gasoline) in detectable amounts, due to the selective hydrogenation activity of the catalyst. The residual fraction contained the not converted triglycerides, and the intermediate product hydrocarbons with higher carbon numbers.

Table 1: Properties of the raw materials and the feedstocks

Properties	Gas oil (GO)	Sunflower oil (SO)	TUE1 SO + 900 mg/kg S	TUE2 90 % SO + 10 % GO
Density (15.6°C), g/cm^3	0.8661	0.9211	0.9209	0.9152
Viscosity (40°C), mm^2/s	6.32	38.47	38.46	34.17
Acid number, mg KOH/g	0.04	0.23	0.23	0.21
Iodine number, g I_2/100 g	2	134	134	121
Aromatic content, %				
monoaromatic	25.3	0.0	0.0	2.5
diaromatic	15.1	0.0	0.0	1.5
total	40.4	0.0	0.0	4.0
CFPP, °C	8	19	18	15
Sulphur content, mg/kg	9010	15	905	900
Nitrogen content, mg/kg	245	6	244	218
Oxygen content, %	-	11.4	11.4	10.3
Flash point, °C	81	>300	>300	82
Distillation characteristics				
IBP	207	*	*	*
10 v/v%	278	*	*	*
50 v/v%	326	*	*	*
90 v/v%	372	*	*	*
FBP	388	*	*	*

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

The yield of the main products increased typically with increasing the temperature as well as with decreasing the LHSV in case of both feedstocks (Figure 1). At 40 bar pressure with the use of the other stricter process parameters the yields of the main products were less than the lower limit of the theoretical yield range, so in the further we present only the properties of products obtained at 80 bar pressure. In case of application LHSV = 0.75 h^{-1} at 360 °C the conversion was complete already, and the further increase in temperature caused small reduction in the yield of the main products due to cracking reactions. In case of feedstock containing gas oil (TUE2) the available theoretical yield was higher, because during the hydrogenation the gas oil component is converted almost totally to main product, in contrast the high yield loss during the conversion of triglycerides (the removed oxygen is 10-12 % of the feedstock). The approach of the theoretical yield was nearly the same for both feedstocks.

In case of LHSV = 2.0 h^{-1} and even using the highest temperature (380 °C) the conversion was not complete (the products contained more than 2 % residue). When lower LHSV was applied at 380°C the amount of residue in the products was under 0.2 %. The products obtained by using the highest LHSV may not be used as a diesel fuel blending component without separation (because of its residual content), so the properties of the obtained products only in case of LHSV = 0.75 to 1.0 h^{-1} are will be shown in the following.

The density of the main products by increasing the temperature and decreasing the LHSV become smaller because by applying stricter process parameters the cracking reactions resulted more components with lower density (Figure 2 "A"). The density of products obtained from TUE2 (gas oil containing) feedstock was higher compared to the density of products derived from TUE1 feedstock. The reason was that low density components (e.g. n-octadecane, density at 15.6 °C: 0.777 g/cm^3) were formed from the triglycerides of sunflower oil during the hydrogenation and the density of gas oil component (0.8661 g/cm^3 at 15.6 °C) is only slightly reduced by the hydrogenation, which increased the density of the main products. The densities of the products did not satisfy the requirements of the diesel fuel product standard (0.820-

0.845 g/cm^3 at 15.6°C; 0.796-0.822 g/cm^3 calculated to 50 °C), so they can be used only as a blending component.
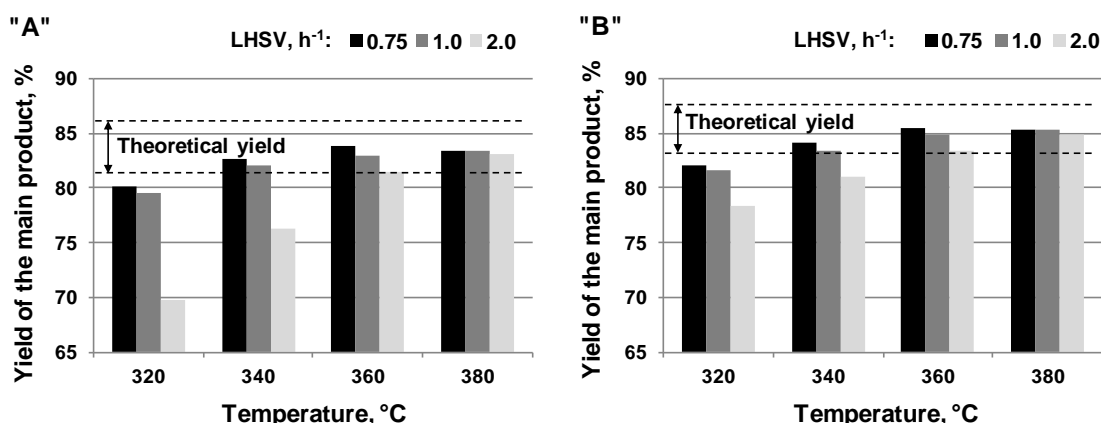

Figure 1: The yield of the main products as a function of the temperature and the LHSV ("A": TUE1 feedstock, P = 80 bar; "B": TUE2 feedstock, P = 80 bar)

The sulphur content of the main products were relatively small in case of the mildest process parameters, but - depending on the LHSV - the sulphur content of the products were lower than 10 mg/kg only above 340-360 °C (EN 590:2013) (Figure 2 "B"). As expected, the reduction of the sulphur content was more difficult in the case of gas oil containing feedstock, because the sulphur atoms bonded in the hydrocarbons (e.g. dibenzothiophenes) are more difficult to remove than the dimethyl disulphide. However, with increasing the temperature, this difference is getting smaller. Over 360 °C, the degree of difference was so small that it was close to the error arising from the repeatability of the experimental method. Based on the sulphur contents of the products we concluded that an appropriate solution is the use of high-sulphur straight run gas oils - available in refineries - to ensure the sulphur content of the feedstocks to maintain the activity (sulphided state) of the catalysts. This solution is economically more advantageous compared to the use of sulphur containing model compounds, or external hydrogen sulphide.

In case of diesel fuels the two most important performance characteristics are the cetane number and cold filter plugging point (CFPP). The determination of cetane number is a very expensive. Therefore, the change in an other characteristic for the autoignition - as required by the standard - the cetane index was examined. The values of the cetane index decreased by increasing the temperature and the LHSV (Figure 3 "A"). According to the mathematical formula (EN ISO 4264) the cetane index varies inversely with the density, so because of the lower density components formed in the cracking reactions (which are coming to the front by stricting the process parameters), the result is a higher cetane index value. Due to the low density and high normal paraffin content of the products their cetane index was significantly higher than the minimum 46 value required by the standard. Because of this property the obtained product is capable to improve the quality of lower quality (high density and aromatic content, and low cetane number) gas oil streams and to cover the second generation bio-component contents of diesel fuels.
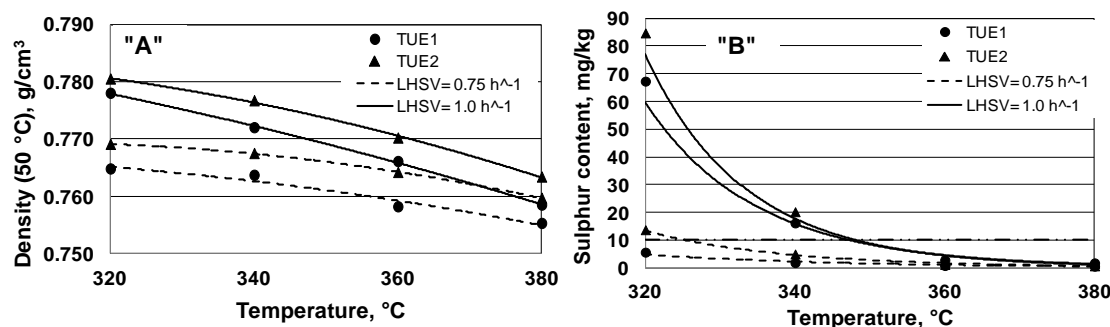

Figure 2: The density ("A") and the sulphur content ("B") of the main products as a function of the temperature, the LHSV and the composition of feedstocks
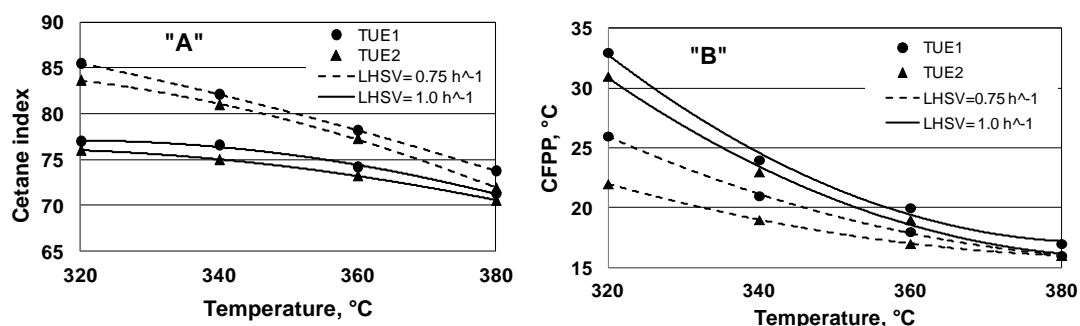
Figure 3: The cetane index ("A") and the CFPP value ("B") of the main products as a function of the temperature and the LHSV

The CFPP value of the motor fuels gives information about its cold flow properties. Due to the high n-paraffin content of the main products and their high freezing point, the CFPP values in the whole investigated process parameter range were very high (16-33 °C) respectively. The CFPP value of the main products became smaller by increasing the temperature and decreasing the LHSV (Figure 3 "B"). The reason is that due to the more stricter process parameters more cracked products were formed and a part of the obtained n-paraffins were isomerized. From the TUE2 feedstock products with lower CFPP value were obtained because the aromatic, naphthenic and i-paraffin hydrocarbons in the gas oil have lower freezing point than n-paraffins. This unfavorable property of the products limits their usability. For the production of summer grade diesel fuel (in the temperate zone CFPP < 5 °C) it can be blended in about 5-15 %. For the production of winter grade diesel fuel the cold flow properties of the main products may be improved, with eg. isomerization (Kasza et al., 2014, Bezergianni et al., 2014b).

4. Conclusions

During the experiments we investigated the applicability of straight run gas oil as sulphur source in the processing of triglyceride-containing feedstocks to maintain the activity of the catalyst in sulphided state. We investigated the hydrogenation of two, different sulphur source containing sunflower oil in the wide range of operating parameters (P = 40 and 80 bar, T = 320 - 380 °C, LHSV = 0.75-2.0 h^{-1}, and H_2/feed = 600 m^3/m^3). From the feedstocks containing gas oil could be produced main product in the diesel fuel boiling range with higher yield compared to the sulphur model compound (DMDS) containing feedstock. However, the theoretical yield approach was nearly the same for both feedstocks. In case of applying the favorable operational parameters (T = 360-380 °C, P = 80 bar, LHSV = 0.75 to 1.0 h^{-1}, H_2/HC = 600 m^3/m^3) the main properties of the high yield obtained products - except to the CFPP value and density - satisfy the requirements of the EN 590:2013 standard. The composition of the feedstocks had a significant impact on the quality of products, but the difference by raising the temperature became lower. Products obtained from gas oil containing feedstocks had higher sulphur content, and their cetane number and the CFPP value were lower.

Based on these results, we concluded that in order to preserve the sulphide state of the catalyst in the catalytic hydrogenation of triglycerides the suitable and cost-effective solution to increase the sulphur content of the feedstock with straight run gas oil. Because the straight run gas oil is available in refineries and will be converted into diesel fuel anyway. Due to the high cetane number and low density of the obtained products they were able to improve the quality of low-quality gas oil streams to produce diesel fuel with bio-component content.

Acknowledgement

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