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Long-Term Performance of NiMo/Al_2O_3 Catalyst during the Co-processing of Fatty Acid By-Products and Gas Oil Fraction

Olivér Visnyei[a,*], Dániel Sági[a], András Holló[b], Róbert Auer[b], Jenő Hancsók[a]

[a]University of Pannonia, Department of MOL Hydrocarbon and Coal Proc., 10 Egyetem Street, H-8200, Veszprém, Hungary
[b]MOL Plc., 2 Olajmunkás Street, H-2440, Százhalombatta, Hungary
visnyei.oliver@almos.uni-pannon.hu

Internal combustion engines will play a major role in road transportation during the next decades. However, based on the legislative actions, the abatement of GHG emission is an important task in the production of future fuels. Waste and renewable based fuels can play an important role in the future. Though, there are many open questions in these fields. The main target in future is to develop new and economical technologies providing excellent quality advanced fuels, having low heteroatom, aromatic and olefin content. Nowadays, biodiesel is the most commonly used bio-component in diesel fuels. Bio gas oil is an alternative bio-fuel which can be produced from triglycerides/fatty acids by catalytic oxygen removal reactions. Diesel fuel blending components with bio-component can be obtained from the co-processing of fatty acids and different crude oil-based gas oil fractions. The aim of our experimental work was to monitor the long-term stability and performance of a commercial, sulphided NiMo/Al_2O_3P hydrotreating catalyst. We studied the catalytic hydrogenation of fatty acid mixture (5 %) and gas oil with high aromatic and sulphur content producing valuable diesel blending components. The effect of temperature, pressure and space velocity on the quality and quantity of the gas oil products were investigated in the long term tests. Based on the experimental results diesel fuel blending components with high hydrogen content can be economically produced in the studied catalytic system with minimal or negligible change in the activity of the catalyst after 472 h. The most favourable process parameters were the followings: P = 70 bar, T = 350 – 360 °C, LHSV = 1.2 – 1.5 h^{-1}, at hydrogen/feedstock ratio = 400 Nm^3/m^3.

1. Introduction

Among the various powertrain systems of road transportation vehicles, conventional internal combustion engines are the most commonly used. Over the next decade, they will still continue to play a key role in transportation. Nowadays the application of alternative fuels is getting more attention to protect the environment and decrease the emission of greenhouse gases and harmful pollutants. The mobility of people and the transportation of goods are continuously increasing; however, it is a huge challenge to ensure these in environmentally friendly way. Despite of the recent “Diesel Emissions Scandal” and the decreasing sales of diesel-powered passenger cars, diesel is still a popular fuel among consumers in the EU. Roughly 45 % of buyers select this engine type (among the new passenger cars) in West Europe (ACEA, 2017). Furthermore, diesel fuels play important role in the road transportation of goods and shipping all over the world, their consumption increases compared to gasoline by 2040 (ExxonMobil, 2016). The research and development of alternative fuels for diesel engines are important target. Currently, the most commonly applied bio-component is biodiesel (fatty acid methyl esters). The above-mentioned aims cannot be reached with conventional biodiesel because of its disadvantages (Datta et al., 2016). Biodiesel has lower heating value than diesel fuels (by 8 - 14 %), bad cold flow properties, because of the double bonds in its molecular structure it has weak thermal and oxidation stability (storage). Ester bonds in biodiesel are sensitive to hydrolysis (Srivastava and Hancsók, 2014). It is produced mainly from edible oils and it has unfavourable ILUC (Indirect Land Use Change) value. It is noteworthy that the European Union aims to increase the share of renewable and low-carbon fuels in energy terms. The actual target is 1.5 % and 6.8 % (including at least 3.6 % advanced biofuels) by 2021 and 2030, respectively. Furthermore, EU member states will be obliged to reduce the share of food-based biofuels

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according to EU’s renewable energy target, starting at 7 % in 2021 and going down progressively to 3.8 % in 2030 (European Parliament, 2016).

Bio gas oil could be a promising solution to replace biodiesel. Bio gas oil is a mixture of iso- and n-paraffins and it is produced from different feedstocks having high triglyceride content (and fatty acid content) by special type of hydrocracking. Because of its high cetane number and the absence of aromatic and sulphur compounds, bio gas oil is an excellent diesel blending component. Moreover, there is no regulatory restriction imposed on the blending of bio gas oil to diesel fuel. Bio gas oil can be produced in stand-alone mode (Hancsók et al., 2007) or during the co-hydrogenating (“co-processing”) of low cost feedstocks with different crude oil refinery streams (Sági et al., 2017). Low-cost biofuels should be produced from low-cost feedstocks as mentioned above, such as wastes of different origins (e.g. nonedible vegetable oils, fats of protein processing plant, wastes of slaughterhouses, etc.). The catalytic hydrogenation of natural (Kovács et al., 2010) and/or waste-derived esters and/or fatty acids has been studied by several authors (Aamen et al., 2017). Researchers investigating the catalytic hydrodeoxygenation of fatty acids used mostly model compounds (Coumans and Hensen, 2017). A large number of articles are available in the literature about bio gas oil production. These experiments were investigated the short-term (20 – 200 h) performance of the catalyst, but there is a lack, which reports about the long-term (> 400 h) stability or performance of the catalyst used for co-processing of fatty acids/esters with different gas oil fractions (e.g. light-, heavy-, vacuum gas oils).

2. Experimental

The objective of this study was to monitor the long-term performance of a commercial, sulphided $NiMo/Al_2O_3P$ catalyst during the co-processing of fatty acid mixture and untreated gas oil fraction with high sulphur content. The available fatty acid mixture in EU countries is less than 3 – 4 % of the diesel fuel consumption of the countries. Therefore, in our long-term experiment (> 400 h) the hydrogenation of high sulphur containing gas oil fraction with 5 % fatty acid content was investigated. The effects of the process parameters (temperature, liquid hourly space velocity, pressure, hydrogen/feedstock ratio) on the quality and quantity of the main products were investigated.

2.1 Materials

Fatty acid mixture and untreated gas oil fraction with high sulphur content were used in the long-term experiment. The properties of the feedstocks are summarised in Tables 1 and 2. A commercial $NiMo/Al_2O_3P$ (Ni: 2.4 %, Mo: 13.7 %, P: 1.9 %) was chosen for the long-term experiments which was sulphided with a straight-run gas oil. Sulphur content was set to 2.5 % by adding dimethyl disulphide (DMDS) to maintain the sulphide state of the catalyst. DMDS easily decomposes under the experimental process parameters and forms H_2S which ensures the completion of the sulphidation process.

Table 1: Properties of untreated gas oil fraction

Properties	
Density (15.6 °C), g/cm^3	0.8473
Kinematic viscosity (40 °C), mm^2/s	2.939
Sulphur content, mg/kg	7150
Total aromatic content, %	32.5
monocyclic	19.9
polycyclic	12.6
Cold Filter Plugging Point, °C	- 2
Boiling range, °C	178 - 374

Table 2: Properties of fatty acid mixture

Properties	
Density (15.6 °C), g/cm^3	0.9340
Kinematic viscosity (40 °C), mm^2/s	2.300
Sulphur content, mg/kg	8
Cloud point, °C	20
Pour point, °C	18
Cold Filter Plugging Point, °C	19

2.2 Equipment

Heterogeneous catalytic hydrogenation experiments were carried out in a reactor system which was equipped with all the accessories generally employed by industrial catalytic hydrogenation plants. The effective height of the reactor is 575 mm, while it has 15.9 mm inner diameter. 80 cm^3 catalyst was loaded into the middle section of the reactor, the height of the catalyst bed was 403 mm. Glass pearls were added under and above the catalyst bed as inert load.

2.3 Process parameters

Process parameters were chosen based on the industrial requirements such as low sulphur content (≤ 10 mg/kg). For the $NiMo/Al_2O_3$ catalyst the applied industrial pressure is commonly 65 – 70 bar, with the temperature range of 330 – 360 °C, thus during our long-term experimental work the reaction conditions were the following: P = 70 bar, T = 315 – 360 °C, LHSV = 1.2 – 1.5 h^{-1}, hydrogen/feedstock ratio = 400 Nm^3/m^3.

2.4 Analytical methods

The properties of feedstocks and products were determined according to the standard analytical methods with the given precisions as shown in Table 3. We analysed the hydrocarbon composition of the products with a gas chromatograph (Shimadzu GC 2010). The applied column is stable at even high temperatures (Restek MXT-1 (30 m x 0.28 mm x 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 min at 400 °C.

Table 3: Used analytical methods

Properties	Standard code
Density	EN ISO 12185:1998
Kinematic viscosity	EN ISO 3104:1996
Cold Filter Plugging Point	EN 116:2015
Sulphur content	EN ISO 20846:2012
Aromatic content	EN 12916:2006
Distillation properties	EN ISO 3405:2011
Hydrocarbon composition	Shimadzu GC 2010 (own method)

3. Results and discussion

During our long-term co-processing experiment the reactor effluent was separated into liquid and gaseous fractions in the phase separator of the reactor system. The gaseous reactor effluent consisted of hydrogen sulphide, hydrogen, ammonia, carbon dioxide, carbon monoxide and a small amount of C_1-C_4 hydrocarbons which were produced by various reactions during the hydrogenation of fatty acid mixture. The applied process parameter combinations promoted the conversion of fatty acid components to n-paraffins as well as the deep hydrodesulphurization (HDS) and the saturation of aromatic compounds. As a result, the final boiling points of the main products were lower than 360 °C, there was no residue left. The liquid-phase reactor effluent was separated into organic and aqueous (H_2O was generated during the hydrodeoxygenation) phases. Because of the full conversion of fatty acid molecules oxygen content could not be detected in the liquid products. After separating the water and liquid hydrocarbon products, the dissolved H_2S was stripped out with N_2 in a heated stripping unit. After the stripping process main products were separated from lighter (< 180 °C) hydrocarbons by atmospheric distillation. The main products were hydrocarbons in the boiling range of 180 – 360 °C (gas oil boiling range).

The maximum theoretical yield of the liquid products was calculated based on the composition of the raw material considering the weight loss due to the removal of heteroatoms such as sulphur from the untreated gas oil and oxygen from the fatty acid molecules during the HDO reaction. Moreover, the theoretical yield is somewhat lower if the carbon loss (as CO_2 and CO) due to the DCO_X reactions (decarboxylation and decarbonylation) is also accounted. Based on the calculations the maximum theoretical yield of the liquid products is 99 %. The yields obtained from the experiment were well-approached (96.8 – 98.8 %) the calculated theoretical yield. Table 4 shows the average yields of the main products and the lighter hydrocarbons (< C_{10}) of the obtained liquid fractions after the separation of water. The yield of the lighter hydrocarbons was 4.9 – 8.0 %, which shows that the hydrocracking reactions which produced light hydrocarbons took place only to a small extent, thus the cracking activity of the $NiMo/Al_2O_3P$ catalyst was low. The higher the temperature, the higher were the yields of the light hydrocarbons, because with increasing the reaction temperature the rate of cracking reactions increased, too.

Based on our previous work (Sági et al., 2017), we proved experimentally that the hydrogenation of fatty acids occurs under milder conditions than triglycerides. In fatty acids there is no need to cleave propylene and further hydrogenate it to propane. Therefore, more catalytically active sites remain for adsorption of further fatty acid molecules and for saturation of olefinic double bonds and oxygen removal. From the results obtained during the current long-term test, it was concluded that at sufficiently high (but lower than the industrial temperature) 315 °C ≤ and shorter but sufficient residence time (LHSV = 1.2 – 1.5 h^{-1}) gas oil boiling range products were obtained with high yield (92.0 – 95.1 % of liquid fractions).

Table 4: Average yields of gas oil and lighter hydrocarbons of the obtained liquid fractions (after the separation of water) T = 315 – 360 °C, LHSV = 1.2 – 1.5 h^{-1}

Temperature, °C	Yield of light hydrocarbons (< C_{10}), %	Yield of gas oil %
315	4.9	95.1
330	4.7	95.3
340	5.1	94.9
350	7.5	92.5
360	8.0	92.0

At the beginning of the long-term experiment, with the sulphur-containing straight run gas oil fraction containing the previously mentioned DMDS we adjusted the initial high activity of the catalyst to a near constant value. It was followed by the adjustment of the sulphur content of the gas oil product. After the activity decay of the catalyst, the long-term experiment was then carried out on a catalyst of constant activity. Figure 1 illustrates the change of sulphur content of the main products (gas oil) as function of temperature and time at 400 Nm^3/m^3 hydrogen/feedstock ratio. During the phase of catalyst activity setting the sulphur content of the targeted products changed between 307 and 347 mg/kg in 315 °C and 1.5 h^{-1} LHSV. After 72 h, the pressure was increased from 40 to 70 bar. The sulphur content of the products was ~ 200 mg/kg which was still too high. To reach the targeted sulphur content of the main products (10 mg/kg), the temperature was increased in a few steps from 315 to 350 °C. The sulphur content of the main products decreased significantly with the increase of reaction temperature, because it enhanced the efficiency of hydrodesulphurization (HDS).

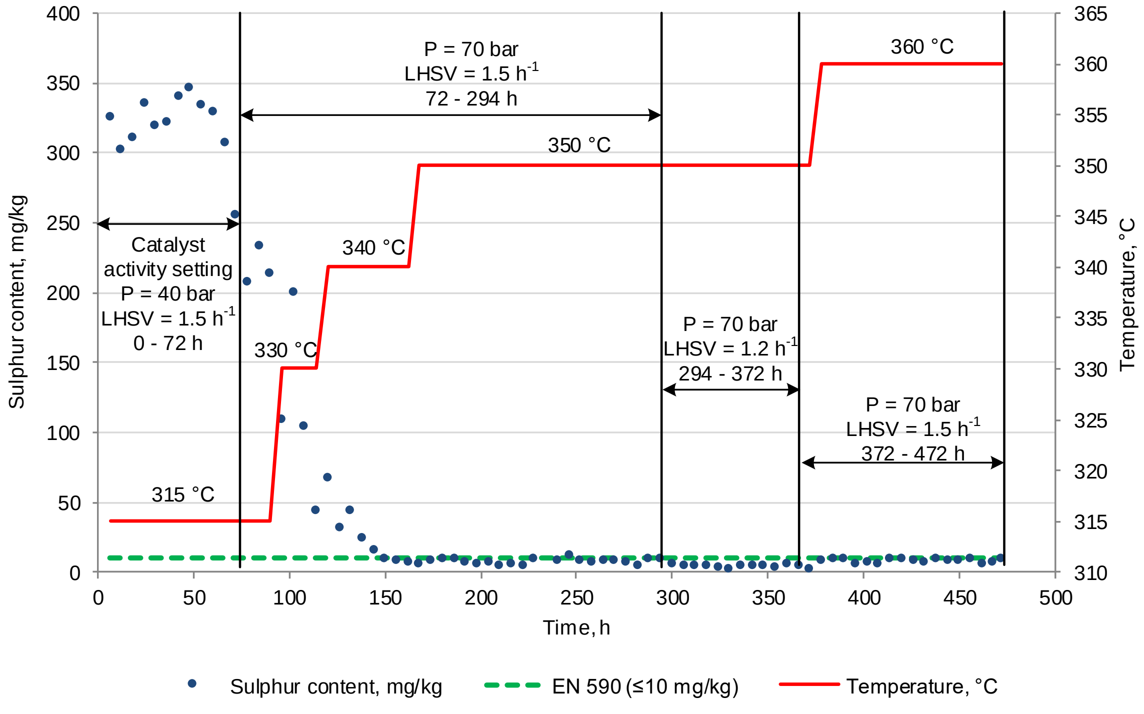

Figure 1: Change of sulphur content of the main products as function of temperature and time

After 294 h of reaction time the LHSV was decreased from 1.5 to 1.2 h^{-1} to achieve products with ≤ 5 mg/kg sulphur content without increasing hydrocracking side reactions. The longer residence time lead to deeper desulphurization. However, the lower LHSV may cause decrease in capacity. In the future the demand for diesel fuels will decrease; on the other hand the demand for better quality (lower sulphur and aromatic content) will increase to reduce the air pollution. At the 372nd h of reaction time the temperature was increased from 350 to 360 °C and the LHSV was increased from 1.2 to 1.5 h^{-1}. The sulphur content of the obtained product was slightly higher than before (T = 350 °C, LHSV = 1.2 h^{-1}), but still lower than 10 mg/kg. The authors concluded that at 360 °C the activity of $NiMo/Al_2O_3P$ catalyst was permanent.

Figure 2 demonstrates the change of total aromatic content of main products (gas oil) as function of temperature and time at 400 Nm^3/m^3 hydrogen/feedstock ratio. The concentration of aromatic compounds is an important property of diesel fuels, the polycyclic aromatic content is regulated by the EN 590:2017 diesel fuel standard (≤ 8 wt %). In the future this regulation could be stricter because of the fact that aromatic compounds, especially the polycyclic aromatic compounds have low cetane number, increased NO_X emission, also they pose a health hazard. The untreated gas oil fraction which was used as feedstock had 32.5 % total aromatic content, while the used fatty acid mixture was aromatic free. During the co-processing catalytic experiment, the highest total aromatic content of the products was produced at the temperature of 315 °C (31.5 %), when the reaction rate was not fast enough. The total aromatic content of the main products decreased significantly at higher pressure, since the mole number decreases in aromatic saturation, higher pressures are favourable for the reaction (principle of Le Chatelier and Braun). It is noteworthy that the polycyclic aromatic content of the main products was below the detection limit on the chosen process parameter combinations. It shows high efficiency of saturation, because the gas oil fraction used as feedstock contained 12.6 % of polycyclic aromatic compounds. A decrease in the LHSV and an increase in the temperature increased the efficiency of aromatic saturation too, because of the longer residence time of the aromatic compounds on the catalytically active sites. The product with the lowest aromatic content (17.9 %) was obtained at the temperature of 350 °C and at 1.2 h^{-1} LHSV. The aromatic contents in the products at 350 °C were lower than in 360 °C because at lower temperatures the aromatic saturation was limited by the kinetics of the reaction, whereas at higher temperatures (> 350 °C) the thermodynamic limit controlled the conversion. The saturation of aromatic compounds is highly exothermic reaction and has a chemical equilibrium state.

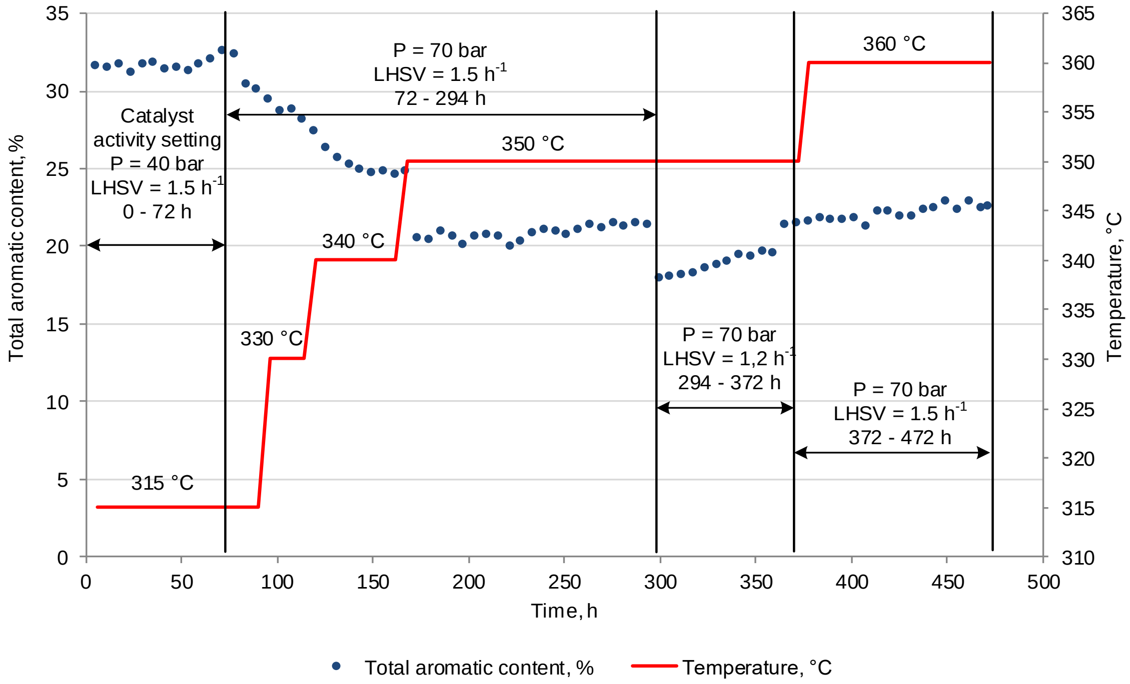

Figure 2: Change of total aromatic content of main products as function of temperature and time

The density of main products decreased by the increasing extent of hydrogenation reactions such as aromatic saturation and conversion of fatty acids to n-paraffins (higher hydrogen content). The hydrogen content of the products increased improving the hydrogen to carbon ratio of the products, too. Moreover, the carbon loss due to decarbonylation/decarboxylation (DCO_X) of fatty acids decreased the density of main products. By increasing the temperature, the density of the products was decreased, because the activity of catalyst was higher in higher temperature, thus the efficiency of aromatic saturation was enhanced. Applying lower liquid hourly space velocity (LHSV), the density of main products was decreased due to the longer residence time. The density of main products varied between 0.8269 – 0.8321 g/cm^3 depended on the applied process parameters. Targeted products with suitable kinematic viscosity (3.12 – 3.42 mm^2/s) of diesel fuel standard (2.0 – 4.5 mm^2/s) were produced. The CFPP of targeted products varied between – 1 °C and +1 °C. The fatty acid mixture had high CFPP value, but the feedstock contained only 5 % of it, so it had minor effect on the CFPP value of the main products. Every product fulfilled the regional summer CFPP limits of diesel fuel standard (EN 590:2017, max + 5 °C). Products did not satisfy the winter CFPP requirements of the standard. Beside the application of appropriate cold flow additives, one can blend the gas oil products with lighter components or convert to obtained n-paraffins to iso-paraffins in a catalytic isomerization process.

4. Conclusions

In our experimental work, the long-term performance of a commercial, sulphided NiMo/Al_2O_3P catalyst was studied during the co-processing of fatty acid mixture (5 %) and untreated gas oil fraction. The effect of process parameters (T = 315 – 360 °C, P = 70 bar, LHSV = 1.2 – 1.5 h^{-1}, hydrogen/feedstock ratio = 400 Nm^3/m^3) on the quality and quantity of the main products were investigated. Based on the experimental results it was concluded that alternative component containing (approx. 4 %) diesel fuel blending components with high hydrogen content can be produced with high yield (92.0 – 95.1 % of liquid products), which meet the requirements of diesel fuel standard (EN 590:2017, summer period) under the favourable process parameters: P = 70 bar, T = 350 – 360 °C, LHSV = 1.2 – 1.5 h^{-1}, hydrogen/feedstock ratio = 400 Nm^3/m^3. The performance of the catalyst practically was not affected by the feedstock's fatty acid content during the long-term experiment (472 h). With this feedstock higher liquid hourly space velocity can be used to convert fatty acids to n-paraffin molecules in an industrial hydrotreating plant, than in case of different triglycerides.

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