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Bio-Paraffin Mixture Production from Waste Fatty Acid Mixture

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As the result of the European Union (EU) directives, the amount of alternative components used in fuels is continuously growing in Europe. One of the most common used biofuel is biodiesel which is produced by base- or acid-catalysed transesterification of triglycerides with an alcohol (usually methanol). Biodiesel has lot of drawbacks such as low thermal and oxidation stability, unfavourable cold flow properties, lower energy content, etc. Due its disadvantages the EU diesel standard (EN 590:2013) limits its blending rate to 7 V/V %. Fatty acids are derived from renewable sources; bio-paraffins in gas oil boiling range can be produced from them by catalytic oxygen removal reactions. The obtained bio-paraffins can be promising alternative fuel blending components or valuable petrochemical feedstock. Thus during our experimental work we demonstrated the bio-paraffin purpose hydrotreating of waste fatty acid mixture from vegetable oil processing on sulphided $NiMo/Al_2O_3$-P catalyst. The effects of process parameters (temperature: 300 – 345 °C, pressure: 40 bar, liquid hourly space velocity (LHSV): 0.75 – 3.0 h^{-1}, H_2/feedstock ratio: 450 – 600 Nm^3/m^3) on the quality and quantity of the main products were investigated. Based on the results we have determined the favourable process parameters for the production of bio-paraffins. The theoretical yields were approximated over 90%. Utilization ideas were proposed for the produced bio-paraffin mixture.

1. Introduction

During the environmentally-friendly mobility, the engine fuel components whose total life-cycle emission is significantly lower than fuels from crude oil are becoming increasingly important. In addition, it is expected that the cost of production and distribution of these components throughout the value chain cannot be higher than that of products from fossil feedstock. Therefore, it is particularly important to produce fuels from different sources of waste materials (Srivastava and Hancsók, 2014). The latest EU Renewable Energy Directive introduced an obligation on European transport fuel suppliers to provide an increasing share of renewable and low-carbon fuels, the level of this obligation is progressively increasing from 1.5 % in 2021 (in energy terms) to 3.6 % in 2030. Furthermore, they are obliged to reduce the share of food-based biofuels towards the EU renewable energy target, starting at 7 % in 2021 and going down progressively to 3.8 % in 2030 (European Parliament, 2016).

Fatty acids are derived from renewable sources and can be produced in larger quantities; they are carboxyl acids with long unsaturated or saturated aliphatic chains. Unsaturated fatty acids contain one or more carbon-carbon double bonds in their molecular structures such as oleic acid. Saturated fatty acids are fatty acids without carbon-carbon double bond for example: stearic acid. Fatty acids can be manufactured from vegetable oils and animal fats at a sufficiently high rate. Bio-paraffin mixture can be produced from them by catalytic oxygen removal reactions. These hydrocarbons are mostly in gas oil boiling range; therefore they can be promising alternative fuel feedstock, also they can be used in petrochemicals production (individual paraffins). Due to economic considerations, low-cost bio-fuels should be produced from low-cost feedstocks such as wastes of different origins for example: non-edible oils, protein processing plant grease, waste of slaughterhouses, etc. Tall oil fatty acid (which mainly consists of linoleic acid, oleic acid and palmitic acid) can be obtained from the vacuum distillation of crude tall oil. Crude tall oil is side stream from pulp and paper industry (Hermida et al., 2015). Palm fatty acid distillate (which mainly consists of palmitic acid) is the by-product of palm oil processing. Both of these fatty acids have various applications in biofuel industry, laundry soap industry etc.

Several publications have been published during the last few years about the hydrogenation of individual fatty acids (e.g. Szarvas et al., 2015). The catalytic oxygen removal reactions can be performed either in hydrogen or inert atmosphere over conventional hydrodesulphurization catalysts such as CoMo- and NiMo/Al_2O_3 or noble metal supported catalysts for example: Pd- or Pt supported on active and mesoporous carbon.

In a study (Rozmyszowicz et al., 2011) the influence of hydrogen on catalytic deoxygenation of a model lauric acid was investigated in a semi-batch reactor over a mesoporous 5 wt % Pd/C catalyst under inert and hydrogen rich atmosphere (T = 300 °C, P = 20 bar). They revealed that after 300 min of the reaction under hydrogen pressure a higher yield of C_{11} and C_{12} hydrocarbons (59 mol %) was obtained compared to the experiment under argon atmosphere where the yield of hydrocarbons was obtained with only 39 mol %. They concluded that the hydrogen has an influence on the reaction pathways: in the presence of hydrogen the transformation of fatty acid occurred via reduction to intermediates (aldehyde and alcohol) which further decarbonylate to hydrocarbons while under inert atmosphere hydrocarbon formation occurred via decarboxylation of lauric acid. In another publication (Coumans and Hensen, 2017) researchers studied the hydrodeoxygenation of model compounds (methyl oleate, oleic acid, triolein) for diesel-like hydrocarbon production on sulphided NiMo/Al_2O_3 in a single-pass micro flow reactor (T = 260 °C, P = 60 bar). Hydrolysis of the methyl oleate resulted in fatty acid intermediates which are converted by the HDO reaction to C_{18} or by the DCO_X (decarbonylation and decarboxylation) reactions to C_{17} paraffins. The hydrodeoxygenation of stearic acid to hydrocarbons was studied too (Santillan-Jimenez et al., 2013) in a semi-batch autoclave over 5 wt % Pd/C and 20 wt % Ni/C catalysts. On both of the catalysts they obtained good yields of fuel-like hydrocarbons, although the Pd/C catalyst showed higher selectivity to C_{17}. Ni/C catalyst is more acidic both in terms of the strength and the amount of its acid sites, in this way it decreased both the selectivity and conversion to hydrocarbons with long chain.

Influence of hydrogen pressure (7 – 30 bar) was investigated in the hydrodeoxygenation of stearic acid over 5 wt % Ni-γ-Al_2O_3 catalyst (Jeništová et al., 2017). The results revealed that after 300 min of the reaction (T = 300 °C, P = 30 bar) temperature both high conversion (99 %) and selectivity (97 %) to heptadecane were obtained. Under lower pressures both the conversion and the selectivity were lower. As comparison to stearic acid hydrodeoxygenation of tall oil fatty acid under the same conditions was demonstrated. In this case the conversion was 94 % and the selectivity was 96 % to heptadecane.

We concluded that the publications investigating the catalytical hydrodeoxygenation of fatty acids, used mostly only model compounds (lauric acid, oleic acid, stearic acid, etc.) Because of that, the aim of our research work was to investigate the catalytical hydrodeoxygenation of waste fatty acid mixture to produce valuable gas oil blending components or petrochemicals feedstock.

2. Experimental

Bio-paraffin purpose hydrotreating of waste fatty acid mixture from vegetable oil processing was investigated on a specifically selected, commercial, sulphided NiMo/Al_2O_3-P catalyst. The effects of process parameters (temperature, pressure, LHSV, hydrogen/feedstock ratio) on the quality and quantity of the main products were investigated.

2.1 Apparatus

The hydrogenation experiments were carried out in an apparatus containing a back-mixing free tubular reactor of 100 cm^3 effective volume in continuous way. It contains all the equipment and devices applied in the reactor system of an industrial catalytic hydrogenation plant (Baladincz et al., 2014).

2.2 Feedstock

Waste fatty acid mixture from vegetable oil processing was used in the experiments. The properties of the feedstock are shown in Table 1, its composition summarized in Table 2.

Table 1: Properties of the waste fatty acid

Properties	
Density (15.6 °C), g/ cm^3	0.9212
Kinematic viscosity (40 °C), mm^2/s	24.05
Cloud point, °C	18
Cold Filter Plugging Point, °C	22
Acid Number, mg KOH/g	188

Table 2: Composition of the waste fatty acid mixture

Composition	%
Fatty acids	
Oleic acid	76.9
Palmitic acid	6.9
Myristic acid	0.1
Fatty acid esters	
Monoglycerides	0.2
Diglycerides	1.1
Triglycerides	3.3
Mixture of other esters	9.9
n-paraffins	
n-C_{19}	0.1
n-C_{20}	0.9
Unknown	0.6

2.3 Catalyst and process parameters

The heterogeneous catalytic experiments were investigated on a commercial sulphided NiMo/Al_2O_3-P (Ni: 2.4 %, Mo: 13.7 %, P: 1.9 %) catalyst. Based on our previous experimental results we specifically selected the catalyst. The sulphur content of the feedstock was 500 mg/kg, adjusted with dimethyl-disulphide (DMDS) to maintain the sulphide state of the catalyst. This chemical compound easily decomposes under the experimental conditions and forms H_2S which ensures the completion of the sulphidation process. Experiments were carried out in continuous operation, the process parameters were chosen based on the results of our previous experiments, which are the following: T = 300 - 345 °C, P = 40 bar, LHSV = 0.75 – 3.0 h^{-1}, H_2/feedstock ratio = 450 - 600 Nm^3/m^3. The H_2/feedstock ratio was chosen based on the industrial experience so that hydrogen would be present in significant excess.

2.4 Analytical methods

The properties of feedstock 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: Analytical methods

Properties	Standard code
Density	EN ISO 12185:1998
Kinematic viscosity	EN ISO 3104:1996
Cold Filter Plugging Point	EN 116:1999
Sulphur content	EN ISO 20846:2012
Distillation properties	EN ISO 3405:2011
Hydrocarbon composition	Shimadzu GC 2010 (own method)

3. Results and discussion

The cracked gases in the experiments mainly consisted of hydrogen, hydrogen sulphide, carbon monoxide, carbon dioxide, very small amounts of propane (produced during hydrogenation of triglycerides of the feedstock) and lower carbon number hydrocarbons ($\leq C_3$) depending on the experimental conditions. These gaseous components are produced by various reactions during the hydrogenation of the waste fatty acid mixture. Figure 1 shows the reactions and products of fatty acid hydrogenated by the example of oleic acid. The main components of liquid products were n-C_{17}, n-C_{18} and n-C_{15}, n-C_{16} paraffins.

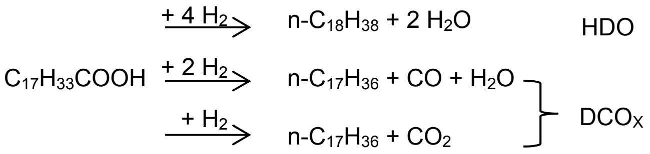

Figure 1: Reaction pathways of the hydrogenation of oleic acid

Figure 2 illustrates the yield of targeted products as a function of temperature and liquid hourly space velocity at 450 Nm^3/m^3 H_2/feedstock ratio. Liquid products did not contain gasoline boiling range components under the strictest parameters (operating conditions: T = 345 ° C, P = 40 bar, LHSV = 0.75 h^{-1}, H_2/feedstock ratio = 600 Nm^3/m^3). This means that the hydrocracking side reactions have taken place only in very small extent. The maximum theoretical yield of liquid products (87.5 %) was calculated on the basis of the composition of the raw material. In the calculations only the loss of yield due to hydrodeoxygenation (HDO) of free fatty acids (C16: 0 and C18: 1) and desulphurisation (HDS) were considered. In reality, the theoretical yield is somewhat lower, as with the HDO reaction, decarbonylation and decarboxylation also occur, resulting in carbon monoxide and carbon dioxide as by-products. Based on this, the range of theoretical yield was 83.8 - 87.5 %, which was well-approached by the experimental results. The yield of the targeted products changed between 68.6 % and 85.9 %. Increasing the temperature and reducing the LHSV resulted in an increase on the yield of the targeted products. Increasing the temperature at 3.0 h^{-1} LHSV in the whole temperature range significantly increased the yield of the targeted products, but at lower LHSVs it was not significant above 315 °C. This can be explained by the fact that the rate of theoretical yield was relatively high at 315 °C in the case of 2.0 h^{-1} and lower LHSVs. It is important to emphasize that the hydrogenation of fatty acids occurs under milder conditions than triglycerides, as in the case of 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, it was concluded that at sufficiently high (but lower than those of industrial heteroatom removal plants) temperature (315 °C ≤) and shorter but sufficient residence time (1.2 - 1.5 h^{-1} LHSV) gas oil boiling range products were produced with high yield (84.9 - 86.3 %). The application of lower LHSV (0.75 - 1.0 h^{-1}) did not result in significant yield improvement. Based on these, it has been concluded that higher LHSV can be used (1.2 - 1.5 h^{-1}), with which significant capacity increase can be achieved in a particular case. The effect of changing the hydrogen hydrocarbon ratio on the yield of targeted product was only very limited.

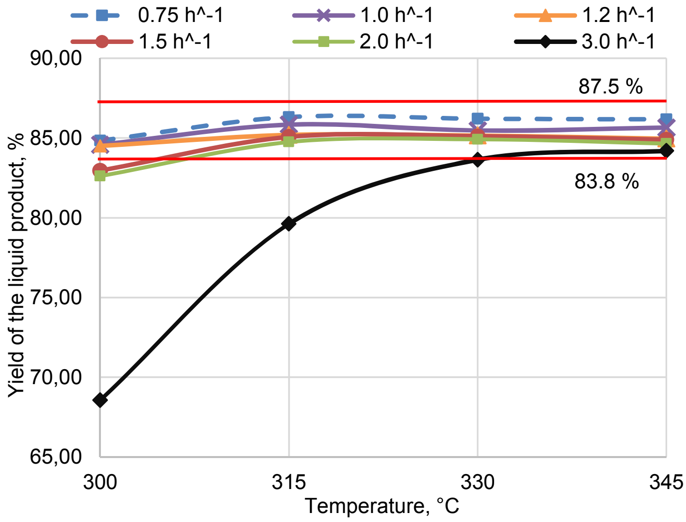

Figure 2: The yield of targeted products as a function of temperature and LHSV (H_2/feedstock = 450 Nm^3/m^3)

Monitoring the ratio of HDO and DCO_X reactions can be observed by changing the ratio of C_{18} and C_{17} paraffins. The change in the weight ratio of C_{18}/C_{17} paraffins to temperature and liquid hourly space velocity is shown in Figure 3 at 450 Nm^3/m^3 H_2/feedstock ratio. By reducing the LHSV, the proportion of HDO reaction increased in each case due to the higher residence time. Applying 0.75-1.5 h^{-1} and 2.0 h^{-1} LHSV, the C_{18} paraffin ratio varied according to a maximum curve, with a maximum value of 315 °C in case of 0.75-1.5 h^{-1} and a maximum of 330 °C for 2.0 h^{-1}. This can be explained with the fact that, at 0.75-1.5 h^{-1} LHSV, the residence time was sufficient at a lower temperature (315 °C) to allow the HDO reaction to be the most beneficial reaction. For 2.0 h^{-1} LHSV, the shorter residence time was compensated by the higher temperature (330 °C). At 3.0 h^{-1} LHSV, the short-term residence time did not show the aforementioned maximum curve. By increasing the temperature, the C_{18}/C_{17} ratio increased slightly, almost linearly. With the application of higher excess hydrogen, the reduction of the LHSV also resulted in a higher proportion of HDO reactions. By raising the temperature, DCO_X reactions began to dominate. The change in the sulphur content of the targeted products depending on the temperature and the LHSV is shown in Figure 4. The sulphur content of the feedstock was 500 mg/kg, adjusted with DMDS to maintain the sulphide state of the catalyst. Increasing the temperature in all cases greatly reduced the sulphur content of the products compared to the feedstocks. At higher excess of hydrogen, at least 300 °C and 0.75-2.0 h^{-1} LHSV resulted in 6 mg/kg or less sulphur-containing targeted products. Decrease of the liquid hourly space velocity resulted in a lower sulphur content of the products, as the longer residence time lead to more efficient desulphurisation.

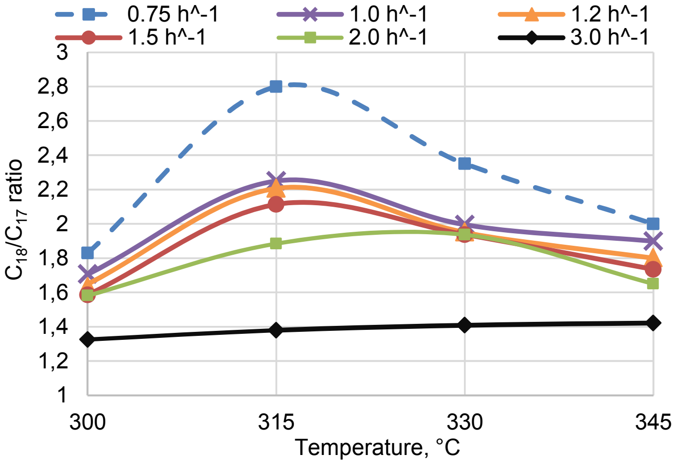

Figure 3: *The ratio of C_{18}/C_{17} paraffins depending on temperature and LHSV (H_2/feedstock = 450 Nm^3/m^3)*

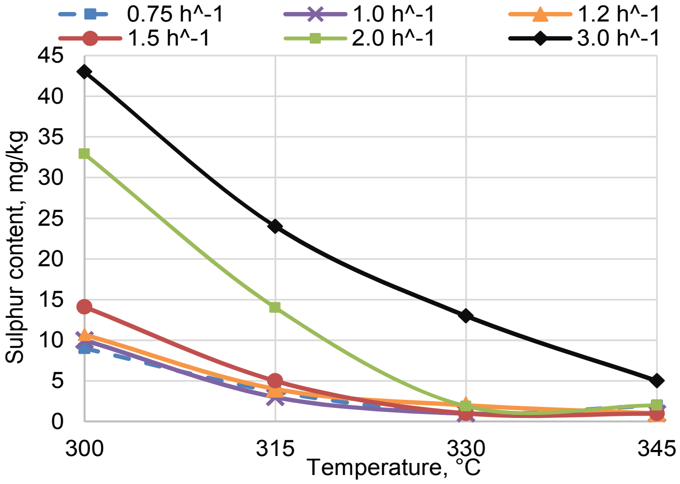

Figure 4: *Change of sulphur content of targeted products depending on temperature and LHSV (H_2/feedstock = 450 Nm^3/m^3)*

The density of the products was primarily determined by the product composition. At 3.0 h^{-1} LHSV, the density of the products varied between 0.8079 - 0.8110 g/cm^3. By reducing the liquid hourly space velocity, the density of the products was lower, which is due to the higher hydrogenation due to the longer residence time. At 0.75 - 2.0 h^{-1} LHSV, the density of the products varied between 0.8025 - 0.8055 g/cm^3. Applying higher excess of hydrogen, the density of the products decreased slightly due to the higher hydrogenation. Targeted products with suitable viscosity (4.300 - 4.496 mm^2/s) of diesel fuel standard (2.0 - 4.5 mm^2/s) were produced at 1.2 h^{-1} or lower LHSV for all test temperatures, at 1.5 h^{-1} LHSV on 315 °C and at a higher temperature and at 2.0 h^{-1} LHSV on 330 °C or on above temperature.

4. Conclusions

In our experimental work, the transformation of waste-derived fatty acid mixtures into petroleum and petrochemical products was investigated on a pre-sulphided NiMo/Al_2O_3-P catalyst. The effects of process parameters (T= 300 - 345 °C, P = 40 bar, LHSV = 0.75 - 3.0 h^{-1}, hydrogen/feedstock = 450-600 Nm^3/m^3) on the quality and quantity of the main products were investigated. Based on our research results we concluded that bio-paraffin mixture can be obtained from waste fatty acid mixture with high yield (experimental: 85.1 - 86.3 %; theoretical: 83.8 - 87.5 %) and with good quality (sulphur content ≤ 5 mg/kg; density (15,6 °C) = 0.8032 - 0.8040 g/cm^3; kinematic viscosity (40°C) = 4.346 - 4.451 mm^2/s) when favourable parameter combinations were the followings: temperature = 315 - 330 °C; pressure = 40 bar; liquid hourly space velocity = 0.75 - 1.2 h^{-1}; hydrogen/feedstock ratio = 450 Nm^3/m^3.

We concluded that the hydrogenation of fatty acids occurs under milder conditions than triglycerides and higher product yield can be obtained. Furthermore, it has been concluded that a higher LHSV can be used (1.2 - 1.5 h^{-1}), than in the case of triglycerides (1.0 h^{-1}), as in the case of 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. With which significant capacity increase can be achieved in a particular case.

The main products of our research consisted of n-C_{17} (22.42 - 32.15 %), n-C_{18} (32.05 - 62.91 %) and n-C_{15} (1.98 - 3.94 %), n-C_{16} (3.32 - 6.72 %) (there were no oxygen in the product).

The obtained bio-paraffin mixture can be used in direct or indirect (after isomerization) as gas oil blending components or as petrochemicals feedstock (for example it can be used for detergent production after dehydrogenation; depending on its molecular structure it can be used in the detergent industry and/or for petroleum industry as additives).

Acknowledgments

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