

Bio-paraffin Mixture Production from Waste Lard

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The importance of bio-paraffins produced from waste is increasing nowadays. Bio-paraffins obtained from renewable sources can be used in cosmetics, pharmaceutical products, food industry, petrochemicals, lubricants and fuels. The aim of our research was the investigation of catalytic hydrogenation of pre-treated waste lard over different catalysts, such as, sulphided/non-sulphided CoMo/Al₂O₃ and NiMoP/Al₂O₃ to valuable bio-paraffin products. The effect of catalyst properties, process parameters – temperature: 300 – 360 °C, pressure: 4 MPa, liquid hourly space velocity: 1.0 – 3.0 h⁻¹, hydrogen/feedstock volume ratio: 550 Nm³/m³ – on the yield and quality of the paraffin mixture was investigated. The catalytic hydrogenation experiments were carried out in a high-pressure reactor system, which contained a tubular down flow reactor with 100 cm³ effective volume. Based on the results, it was concluded that every catalyst is suitable for the production of bioparaffins from waste lard. Yield of main products changed in function of catalyst compositions at favourable process parameters (temperature: 345 °C, liquid hourly space velocity: 1.0 h⁻¹): sulphided NiMoP/Al₂O₃ (75.1 %) > sulphided CoMo/Al₂O₃ (71.1 %) > non-sulphided NiMoP/Al₂O₃ (69.2 %) > non-sulphided CoMo/Al₂O₃ (67.0 %). Paraffin mixtures with relatively high isoparaffin content (8.9 %) were obtained over non-sulphided CoMo/Al₂O₃.

1. Introduction

The diesel fuel demand was around 210 million t in the European Union (EU) in 2016. The newest Renewable Energy Directive (RED) of the EU aims to increase the share of renewable and low-carbon fuels to 3.5 % in energy terms by 2030 (European Parliament, 2018). The amount of renewable, advanced diesel fuels estimated from RED and the diesel fuel demand in 2016 should reach ca. 6.3 million t/y. The most commonly used biofuel in diesel fuel is biodiesel. It is manufactured mainly by acid or base catalysed transesterification of edible vegetable oils e.g., rapeseed oil and alcohol such as methanol or ethanol. It has many disadvantages due to its molecular structure compared to crude oil based diesel fuel, such as lower energy content, lower storage stability, and higher NO_x emission, etc. Therefore, the EN 590:2017 diesel fuel standard limits its application to 7 V/V %. Regarding to the RED, EU member states will be obliged to reduce the share of food-based, i.e. first generation biofuels. The first generation plant-oil based biodiesel can be replaced by second generation biofuels i.e. bio-paraffins produced from different feedstocks (Srivastava and Hancsók, 2014). Biofuels should be produced from low-cost feedstocks due to economic considerations. The above mentioned amount of advanced diesel fuel (ca. 6.3 million t/y) can be partially covered by waste cooking oil (ca. 1 million t/y), fatty acid by-products (ca. 0.3 – 0.6 million t/y) or animal fat produced by protein processing plants (ca. 2.7 million t/y) which are good choices, because these low-cost feedstocks are permanently available in sustainable manner. In addition beside the disposal of wastes, products transformed from them are high value-added products. Among the listed raw materials, animal fat is the most promising feedstock for the production of bio-paraffins. It is biodegradable and completely renewable source; consists essentially fatty acids/triglycerides, its price is often more favourable than edible vegetable oils (Hachemi et al., 2017). From the negative aspect, it has high amount of solid contaminants, metal and phosphorus content which can shorten the catalyst lifetime. Therefore, pre-treatment is needed to decrease the concentration of impurities (Baladincz and Hancsók, 2015). Bio-paraffins

can be produced from lignocellulose through simple sugars (Xing et al., 2010); with integrated Fischer-Tropsch synthesis from biomass-derived syngas (Van Vliet et al., 2009), etc. The simplest production possibility of bio-paraffins is the catalytic hydrogenation of natural/waste fatty acids/fatty acid esters (Bezergianni and Kalogianni, 2009). In the literature there are many articles about the production of biodiesel from animal fat (Adewale et al., 2015). However, there is a lack which report about the production of bio-paraffins as second generation biofuel by catalytic hydrogenation of waste lard from protein processing plant over different hydrogenation catalysts.

2. Experimental part

Due to the above, the aim of our research was the investigation of production possibilities of valuable bio-paraffin mixtures by catalytic hydrogenation of pre-treated waste lard over different catalysts e.g., sulphided and non-sulphided NiMoP/Al₂O₃, CoMo/Al₂O₃ in one catalytic step. Figure 1 illustrates the main reactions of the catalytic hydrogenation of animal fat or waste lard: hydrogenation of olefinic double bounds in triglycerides, propylene splitting and its hydrogenation, oxygen removal reactions such as hydrodeoxygenation (HDO), decarbonylation/decarboxylation (DCO_x). Isomerization and cracking as side reactions occur only in a small extent. The target products are mixtures of mainly normal- and slightly iso-paraffins (Hancsók et al., 2018).

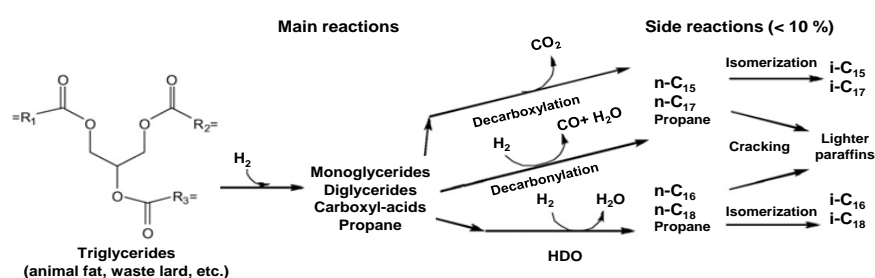


Figure 1: Reaction pathways of bio-paraffin mixture production (R_{1-3} = alkylene chains)

2.1 Feedstock

Waste lard from protein processing plant was used as feedstock in the catalytic experiments. Due to its high impurity pre-treatment was needed. The pre-treating steps were as follows, the mechanical impurities were removed by filtration which was followed by chemical treatment with citric acid, clarification, another filtering, and then it was washed with water to remove the alkali and alkaline earth metals, drying. The waste (2 – 4 %) formed during the treatment of the feedstock can be used as feedstock for biogas production. The properties of pre-treated waste lard are summarized in Table 1.

Table 1: Properties of feedstock

Properties	Pre-treated waste lard
Density (50 °C), g/cm ³	0.8991
Sulphur, content, mg/kg	< 10
Acid number, mg KOH/g	60.8
Free fatty acid content, %	32.4
Fatty acid composition (glycerides), %	
C14:0	1.3
C16:0	24.3
C16:1	2.1
C18:0	14.0
C18:1	45.9
C18:2	10.2
C18:3	1.4
C20:0	0.5
C20:1	0.3
C21+	<0.1
Other impurities (N, P, S, metals), mg/kg	13.9

*Average exp. results +/- std. dev.

2.2 Catalysts

Commercial “in situ” sulphided and non-sulphided CoMo/Al₂O₃ and NiMoP/Al₂O₃ catalysts (Table 2) were applied in the special hydrocracking of pre-treated waste lard. Straight run light gas oil was used for the pre-sulphidation of the catalysts. First of all, the light gas oil was desulphurized to remove the instable compounds which decrease the catalyst activity by poisoning the active sites. Then, its sulphur content was set to 2.5 % by dimethyl disulphide (DMDS). DMDS easily decomposes to H₂S and ensures the completion of the sulphidation process. To preserve the sulphided state of the catalysts during the experiments, sulphur content of the feedstock was adjusted to 500 mg/kg by DMDS. The non-sulphided catalysts were dried in hydrogen, and then treated at 400 °C for 6 h in hydrogen as well.

Table 2: The main properties of the applied catalysts

Properties	CoMo/Al ₂ O ₃	NiMoP/Al ₂ O ₃
Molybdenum content, %	13.2	13.7
Nickel content, %	-	2.4
Cobalt content, %	3.1	-
Phosphorus content, %	-	1.9
Specific area (BET), m ² /g	198	155

2.3 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. The hydrocarbon compositions were analysed with high-temperature gas chromatographic (HT-GC) method. Aromatic and olefin content was analysed with GC-MS.

Table 3: Applied analytical methods

Properties	Standard code	Standard deviation
Cold Filter Plugging Point	EN 116:2015	+/- 1 °C
Distillation properties	EN ISO 3405:2011	+/- 1 °C
Acid number	EN 11723-3:1967	+/- 5 mg KOH/g
Sulphur content	EN ISO 20846:2012	+/- 1 mg/kg
Derived Cetane number	ASTM D7170-16	+/- 2 units

2.4 Apparatus and process conditions

The catalytic hydrogenation experiments were carried out in a pilot scale, high pressure reactor system, which contained a tubular down-flow reactor with 100 cm³ effective volume. The length and diameter of the reactor was 470 and 25 mm, respectively. This reactor system contains all the equipment and devices applied in an industrial hydrotreating plant (Hancsók et al., 2007). The experimental work was performed in continuous mode at constant catalyst activity. The chosen process parameters were based on previous experimental results (Baladincz and Hancsók, 2015): temperature of 300 – 360 °C, liquid hourly space velocity (LHSV) of 0.75 – 3.0 h⁻¹, pressure of 4 MPa which is the most commonly used value in hydrosulphurisation, H₂/feedstock volume ratio of 550 Nm³/m³ which is 1.5 times more than the theoretical hydrogen consumption of the chemical reactions.

3. Results and discussion

The target products were bio-paraffins with boiling range of 180 – 360 °C. Lighter products e.g., cracking products and heavier products such as unconverted or partially converted fatty acids/fatty acid esters were separated from the target products by distillation if the conversion was not complete.

From the large number of experimental results only the yield and the approach of the theoretical yield values are presented. These yield data clearly illustrate the change in the activity and selectivity of the applied catalysts as a function of process conditions, i.e., characterize the catalytic conversion of fatty acids/fatty acid esters to bio-paraffin mixtures. Based on the feedstock composition, the theoretical yield was 82.28 %, calculated by taking into account the saturation of olefinic double bounds, the reactions resulting propylene splitting, its hydrogenation, oxygen and sulphur removal. The ratio of HDO and DCO_x oxygen removal reactions was suspected as 50 – 50 %, which was based on the previous working experiences.

The yield of the target products obtained at different process parameters over different catalysts is summarized in Table 4. The highest yield values were obtained over sulphided NiMoP/Al₂O₃ catalyst at every process parameter combination.

These values were clearly lower in case of using sulphided CoMo/Al₂O₃ or non-sulphided NiMoP/Al₂O₃ and CoMo/Al₂O₃. This is due to the fact that the reaction rate of heteroatom e.g., oxygen removal reactions on the sulphided NiMoP/Al₂O₃ is the highest compared to all the catalysts tested, furthermore the propylene splitting activity of the mentioned catalyst is high as well. Oxygen removal reactions are taken place at the lowest reaction rate among the reactions going parallel (Boda et al., 2010). The reaction rate of the hydrogenation of olefinic double bounds in fatty acids/triglycerides is nearly equal (Kubicka et al., 2013).

Table 4: Yield of the target products over different catalysts*

Catalysts	Yield of target products, %											
	300 °C				330 °C				360 °C			
	0.75	1.0	1.5	3.0	0.75	1.0	1.5	3.0	0.75	1.0	1.5	3.0
sulphided NiMo/Al ₂ O ₃	75.0	73.3	71.6	47.5	76.6	75.3	74.3	65.5	75.0	74.7	76.2	70.6
non-sulphided NiMo/Al ₂ O ₃	63.2	61.6	60.8	35.9	68.9	68.1	66.9	57.4	68.9	68.5	66.2	59.9
sulphided CoMo/Al ₂ O ₃	67.1	65.2	62.9	37.6	72.5	69.9	68.3	58.3	73.1	71.2	69.9	64.3
non-sulphided CoMo/Al ₂ O ₃	60.6	58.4	54.3	27.4	67.8	66.6	63.3	51.7	68.4	66.6	63.5	55.1

*Average exp. results +/- std. dev.

The approach of the theoretical yield (ATY) was calculated by according to the Eq(1):

$$ATY = \frac{\text{Experimental product yield}}{\text{Theoretical yield}} * 100 \quad (1)$$

The bio-paraffin production activity of catalysts is also supported by the approach of the theoretical yield values. Figure 2 demonstrates the approach of the theoretical yield of target products as a function of temperature and LHSV. LHSV values of 0.75/1.0 h⁻¹ were chosen based on the most favourable results presented in Table 4. It is noticeable that some of the ATY values are increasing only slightly or not changing, some of them even decreasing at 345 °C and above. This can be explained by the fact that the cracking reactions (Figure 1) are taken place in higher extents which decrease the yield of the target products. Increasing the LHSV (shorter residence time) resulted in lower ATY values, i.e. lower yields over all the catalysts tested. The approach of theoretical yield of target products obtained over sulphided NiMoP/Al₂O₃ catalyst was the highest, so this catalyst showed the highest activity. Applying lower LHSV (0.75 h⁻¹) did not result in significant yield improvement. Therefore, from the industrial implementation perspective, the use of 1.0 h⁻¹ LHSV value is more advantageous due to the higher plant capacity at the same catalyst volume.

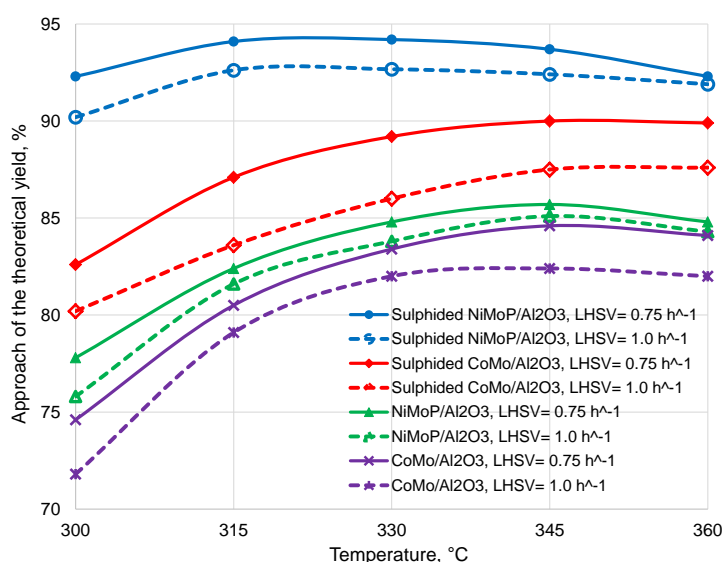


Figure 2: Approach of the theoretical yield of target products as a function of temperature and LHSV*
*Average exp. results +/- std. dev. (P: 4 MPa, H₂/feedstock ratio: 550 Nm³/m³)

The gas chromatographic results of target products obtained from the hydrogenation of pre-treated waste lard show that beside the conversion of fatty acids/fatty acid esters, the isomerization of n-paraffins also occurred, however only in a small extent (Table 5). This is due to the isomerization activity of molybdenum (Krár et al., 2011). Non-sulphided CoMo/Al₂O₃ showed the highest isomerization activity among the applied catalysts. The iso-paraffin content of the target product could reach 8.9 % at temperature of 360 °C and LHSV of 1.0 h⁻¹ over non-sulphided CoMo/Al₂O₃.

Table 5: Iso-paraffin content of target products over different catalysts (LHSV: 1.0 h⁻¹)*

Catalyst	Iso-paraffin content of main products %		
	330	345	360
NiMoP/Al ₂ O ₃	1.8	3.6	6.2
sulphided NiMoP/Al ₂ O ₃	1.6	3.1	5.8
CoMo/Al ₂ O ₃	3.1	5.2	8.9
sulphided CoMo/Al ₂ O ₃	0.9	2.7	5.1

*Average exp. results +/- std. dev.

Based on the detailed assessment of the results described above, it was concluded that for the conversion of pre-treated waste lard from protein processing plant to bio-paraffins, the sulphided NiMoP/Al₂O₃ showed the highest activity and selectivity among the tested catalysts. The properties of the target products obtained at favourable process parameters are summarized in Table 6.

Table 6: Summary of the most favourable results obtained over sulphided NiMoP/Al₂O₃*

Properties	Diesel fuel	Cosmetics, pharmaceutical products
Process parameters**		
T, °C	345	360
LHSV, h ⁻¹	1.0	1.0
Liquid products		
Yield, %	75.1	74.7
Approach of the theoretical yield, %	92.4	91.9
Paraffin content, %	> 99.9	> 99.9
Olefin content, %	< 0.1	no detectable
Aromatic content, %	no detectable	no detectable
Sulphur content, mg/kg	< 5	no detectable
Oxygen compound content, %	no detectable	no detectable
Derived Cetane number	94	-
Cold Filter Plugging Point	> 20	-

*Average exp. results +/- std. dev.

**P: 4 MPa, H₂/feedstock ratio: 550 Nm³/m³

Table 6 represents well that excellent diesel fuel blending components having very low sulphur and aromatic content can be obtained over sulphided NiMoP/Al₂O₃ at favourable process parameters. Cetane number of the products greatly exceeded (94) the value in the EN 590:2017 diesel fuel standard (min. 51). These products can be blended with low-cost components having cetane number lower than 51, therefore the final production cost of the diesel fuel can be decreased result in higher profitability. However, the cold filter plugging point (CFPP) of target products was high (> 20 °C); further isomerization in an existing middle-distillate isomerization plant is needed to improve the cold-flow properties. Applying stricter process parameters the target products due to their high purity and paraffin content (> 99.99 %) can be used in cosmetics and pharmaceutical industry.

4. Conclusions

Bio-paraffins can be produced by the presented special hydrocracking of pre-treated waste lard from protein processing plant over sulphided/non-sulphided transition metal/support catalysts. The application of waste lard seems to be a promising alternative feedstock for the production of high value-added bio-paraffins, because it has low cost, completely biodegradable, and permanently available which is important for the sustainability. The waste (2 – 4 %) formed during the treatment of the waste lard can be used as feedstock for biogas production. Among the tested catalysts, over the sulphided NiMoP/Al₂O₃ both the technical grade bio-paraffin mixture, cosmetic and pharmaceutical grade bio-paraffins could be obtained by using different process parameter combinations. The activity of the catalyst was nearly constant in the experiment having length of 400 h. Increasing the energy efficiency of the applied catalytic system can be one of the main tasks in the future work. The main goal is the recognition of novel catalysts which are suitable for the production of bio-paraffins from the mentioned feedstock at lower temperature, moreover, which are suitable to change the ratio of normal and iso-paraffins in the obtained bio-paraffin mixture depending on the demands.

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