

## FUEL PURPOSE HYDROTREATING OF VEGETABLE OIL ON NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> CATALYST

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The application of biofuels has become more important in the whole world since the last decades. Intensive research has been started for the production of biofuels which can be applied in Diesel engines and has different chemical composition from the previously used ones. Among these fuels the most important one is biogasoil (normal and iso-paraffins) produced from triglycerides with catalytic hydrotreating (special hydrocracking). The aim of present study was to investigate the applicability of commercial NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst for conversion of specially pretreated Hungarian sunflower oil to produce motor fuel components. The change in the hydrotreating activity of applied catalyst, the pathways of hydrodeoxygenation reactions and the effect of process parameters ( $T = 300\text{--}360\text{ }^{\circ}\text{C}$ ,  $p = 20\text{--}60\text{ bar}$ ,  $\text{LHSV} = 0.5\text{--}2.0\text{ h}^{-1}$ ,  $\text{H}_2/\text{sunflower oil volume ratio: } 400\text{ Nm}^3/\text{m}^3$ ) on the yield and composition of the products were also investigated. It was concluded that on the investigated NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst products with relatively high (>50%) paraffin content ( $T = 360\text{--}380\text{ }^{\circ}\text{C}$ ,  $p = 60\text{ bar}$ ,  $\text{LHSV} = 0.5\text{--}1.0\text{ h}^{-1}$ ) could be produced. The yield of the produced target fraction was 50.7–54.5% at these advantageous process parameters. So it is necessary to separate and recirculate the heavy fraction. In case of every investigated process parameter C<sub>18</sub>-, C<sub>17</sub>-, C<sub>16</sub>- and C<sub>15</sub> normal paraffins were formed, i.e. both the HDO and the decarboxylation/ decarbonylation reactions took place. The cetane number of the target fractions, are very high (>80, EN standard:  $\geq 51$ ), but the cold flow properties of this fraction are disadvantageous. To improve this disadvantageous property it is necessary to carry out selective isomerization of the target fraction.

**Keywords:** sunflower oil hydrotreating, biogasoil, paraffinic hydrocarbons

### Introduction

The application of biofuels has become more important in the whole world since the last decades. In Europe the production and application of diesel fuels and/or blending components derived from biomass have been emerged into the focus due to the climate, geographical conditions and the increasing demand for diesel fuel [1].

Actually the biodiesel (fatty acid methyl esters) is practically the only bio derived component used in crude oil derived diesel fuels, however it and the biodiesel technologies, which applied alkali catalyst, have numerous disadvantages [2-6]. Because of these facts and to reach better quality, intensive research has been started for the production of biofuels, which can be applied in Diesel engines and has different chemical composition from the previously used ones [6-13]. Among these fuels the most important ones are in the near and medium future the biogasoils produced from triglycerides with catalytic hydrotreating (special hydrocracking). The biogasoil is a second generation biofuel, therefore their research, production and use are strongly supported by the European Union.

The biogasoil contains mainly normal and isoparaffins having similar boiling point range as the conventional gas oil [6, 10, 11].

The normal and isoparaffins are the most advantageous components of crude oil derived diesel fuels because of their chemical structure, as they have cetane number and advantageous application technology properties at low temperature, too [15, 16].

Through the reactions of special hydrocracking of triglycerides primarily normal and isoparaffins, propane, CO<sub>2</sub>, CO, water and oxygenate compounds are formed on the applied catalyst(s) and process parameters.

Through this process the triglyceride molecules transform according to the following reactions [17-19]:

- saturation (hydrogenation) of double bonds,
- heteroatom removal,
  - deoxygenation,
    - hydrodeoxygenation (HDO reaction, reduction),
    - (hydro)decarboxylation,
    - (decarbonylation),
- different side reactions:
  - hydrocracking of fatty acid chain of triglycerides,
  - water-gas-shift, etc.
- isomerization of produced normal paraffins from deoxygenation.

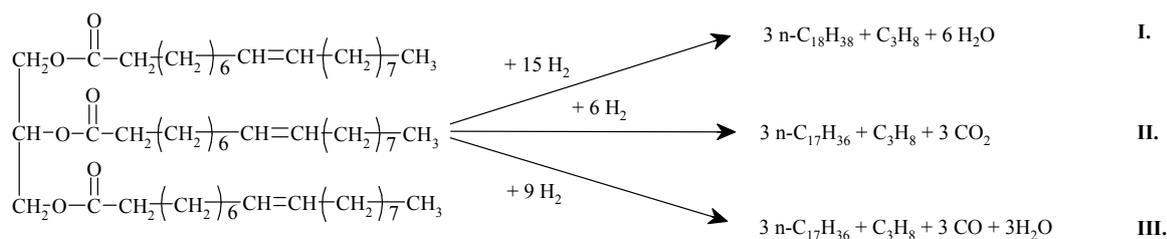


Figure 1: Possible reaction pathways for oxygen removal from trioleic triglycerides

Through the deoxygenation (Fig. 1) of triglycerides in the HDO reaction (reaction route I.) 1 mol triglyceride molecule is converted to 3 mol n-paraffins having the same chain length as the fatty acid. The carbon number of the produced normal paraffins by decarboxylation (reaction route II.) and decarbonylation (reaction route III.) reactions are lower by one compared to the fatty acid chains of triglycerides [17, 19].

The produced mixture having high n-paraffin content (cold filter pluggin point – CFPP: 18–28 °C) has to be isomerized after separation to the necessary level to improve the flow properties.

The biogasoil can be also used alone in Diesel engines, but in conventional utilization it is unnecessary to apply this excellent product. Furthermore, due to the limited availability of the currently used feedstock and the amount of the produced biogasoil allows limited application. Therefore the application of biogasoil as gas oil blending components will be primarily of practical significance.

For the production of biogasoil several technologies are proposed in the literature: Neste Oil NExBTL [20], UOP/Eni Ecofining<sup>TM</sup> technology [18] and the SuperCetane process [9].

In the last couple of years our widespread and systematic research and development activity has been focused on the field of conversion of natural triglycerides to diesel fuels. In this paper the most important results of triglycerides hydrotreating obtained on commercial NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst are presented.

### Experimental work

Based on the introduction the aim of our experimental work was to determine the applicability of the commercial NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst in the fuel purpose (hydrocarbons with high n-paraffin content in gas oil boiling range) hydrotreating (special hydrocracking) of properly pretreated Hungarian sunflower oil.

Our objective was to study the change of the hydrocracking activity (deoxygenation activity) and the effect of the operating parameters (temperature, pressure, LHSV) on the yield and the composition of products.

### Apparatus

The experiments were carried out in an apparatus containing a tubular down-flow reactor of 100 cm<sup>3</sup> effective volume. It contains all the equipment and devices applied in the reactor system of an industrial heterogeneous catalytic plant. The experiments were carried out in continuous operation [21].

The products of the experiment were fractionated to three main fractions: gaseous-, water- and liquid organic fractions. The liquid products which were separated in the separator of the apparatus contained water, hydrocarbons (C<sub>5</sub> and larger) and compounds with oxygen content. The organic phases were separated from the water phase and analyzed without phase separation.

### Feedstock and catalyst

The feedstock of the hydrotreating experiments was properly pretreated Hungarian sunflower oil (Table 1).

Table 1: The main properties of the feedstock of hydrotreating

Properties	Value
Density (15°C) g/cm <sup>3</sup>	0.9252
Acid number, mgKOH/g	2.2
Iodine number, g I <sub>2</sub> /100g	136
Water content, mg/kg	244
Fatty acid composition, %	
C16:0	6.5
C18:0	3.8
C18:1	20.7
C18:2	68.4
C22:0	0.6

The catalyst was an expediently chosen and commercial NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. The BET surface area of the catalyst was 115 m<sup>2</sup>/g, Mo-content was 2.9% and the Ni-content was 1.5%. Before the experiments we increased the temperature of catalyst “in-situ” with 25 °C/hour to 400 °C, then we held the temperature at 400 °C for 2 hours at a gas flow-rate of 40 dm<sup>3</sup>/h. Thereafter we decreased the temperature of the catalyst to the temperature of the first experimental point.

### Process parameters

The range of the chosen process parameters – based on our pre-experimental results – were the following: temperature 300–360 °C, total pressure 20–60 bar, liquid hourly space velocity (LHSV): 0.5–2.0 h<sup>-1</sup> and H<sub>2</sub>/sunflower oil volume ratio: 400 Nm<sup>3</sup>/m<sup>3</sup>.

### Analytical methods

The properties of the feedstock and the products were measured according to standard methods (Table 2). The compounds of the products were determined with high temperature gas chromatograph on special column (6m x 0,53mm x 0,1 μm, DB5-HT AluClad column).

Table 2: The applied analytical methods

Properties	Method
Density	EN ISO 12185:1996
Iodine number	EN ISO 3961:2000
Acid number	EN 14104:2003
Water content	EN ISO 12937:2001
Hydrocarbon composition	EN 15199-2:2007
Fatty acid composition	EN ISO 5509:2000 EN 14103:2003

### Results and discussion

The main aim of the fuel purpose hydrotreating experiments of sunflower oil was – besides the saturation of double bonds – the removal of the oxygen atom from the sunflower oil and the production of the target fraction (primary C<sub>15</sub>-C<sub>18</sub> n- and i-paraffins) in gas oil boiling range with the highest yield.

Based on our results it can be concluded that the yield of the liquid organic fraction was higher than 88% in every case related to the weight of the feedstock (depending on the process parameters). The cause of this is the conversion of the oxygen content of the sunflower oil to water and CO<sub>2</sub> (and CO) in different amounts, the elimination of propane and the lower carbon number (≤4) gas products formed by cracking reactions.

The conversion of triglycerides increased with increasing temperature. The amount of the not converted triglyceride was below 10% at 380 °C temperature, at 60 bar pressure and at every LHSV (Fig. 2).

The conversion of triglycerides significantly increased with increasing pressure (if the other process parameters were constant) (Fig. 3). But at 300 °C the hydrocrack reactions took place only to produce carboxylic acids. Accordingly the organic fraction contained primarily carboxylic acids (methyl esters) and other esters, diglycerides and triglycerides and the amount of the target fraction was below 5%.

The conversion of triglycerides decreased with increasing the LHSV (and decreasing the time on stream)

so the content of triglyceride was higher in the product mixture (Fig. 4).

But at 300 °C and 60 bar the deoxygenation reactions took place only in a little extent because the target fraction was formed in a small amount.

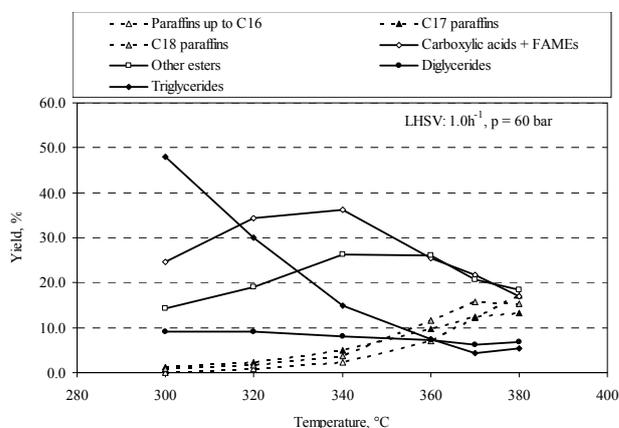


Figure 2: The yield of important compounds in organic phase as a function of the temperature (LHSV: 1.0 h<sup>-1</sup>; p = 60 bar)

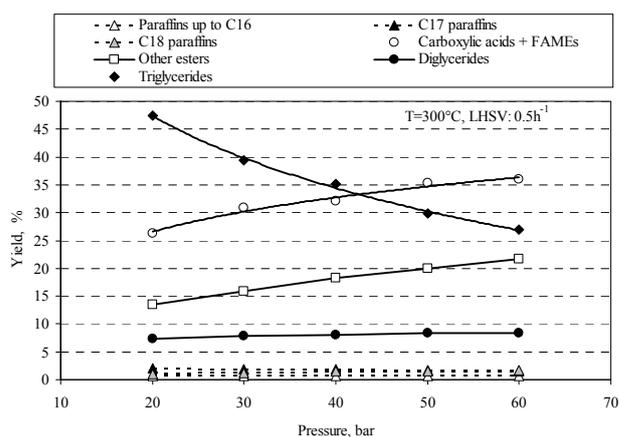


Figure 3: A The yield of important compounds in organic phase as a function of the pressure (LHSV: 0.5 h<sup>-1</sup>; T = 300 °C)

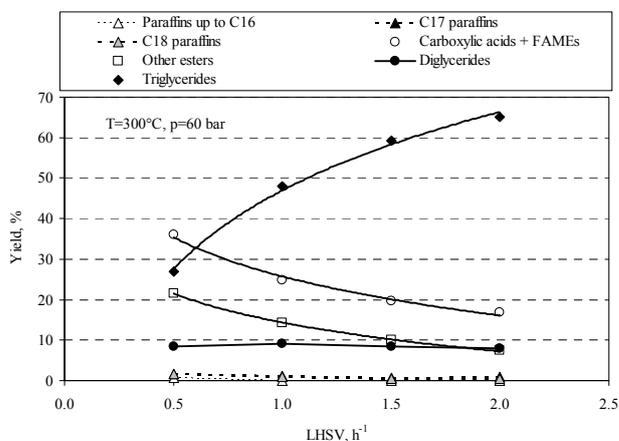


Figure 4: The yield of important compounds in organic phase as a function of the LHSV (p = 60 bar; T = 300 °C)

The yield of the target fraction (50.7–54.5%) was significantly lower at advantageous process parameters (370–380 °C, 60 bar, 0.5 h<sup>-1</sup>) than the theoretical values (82–86%). So it is necessary to separate the target fraction from the not converted triglyceides and from the produced intermediates. The heavy fraction has to be recirculated to the reactor after the separation.

One of the intermediates, which were formed by the special hydrocracking reactions, is the different carboxylic acids. The yield of this intermediate at the applied pressure and LHSV changed according to maximum curve as a function of temperature. The maximal yield of carboxylic acids were between 320–340 °C (LHSV: 0.5 h<sup>-1</sup>), about 340 °C (LHSV: 1.0 h<sup>-1</sup>), and about 360 °C (LHSV: 1.5 h<sup>-1</sup> and 2.0 h<sup>-1</sup>) (Fig. 5).

Consequently it is necessary to apply properly high temperature in order to convert the intermediates to valuable components (target fraction) in further reactions.

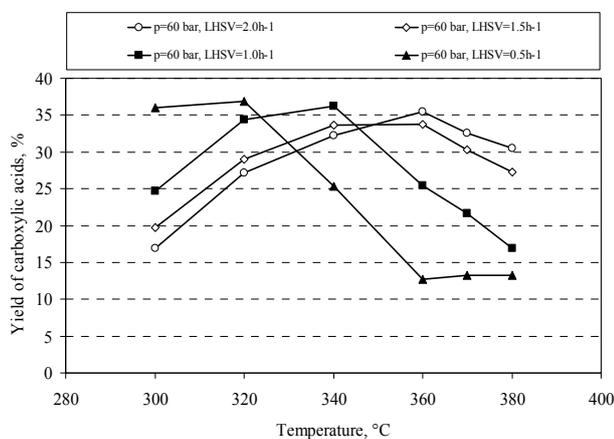


Figure 5: The yield of the produced carboxylic acids as a function of the temperature (p = 60 bar)

Based on the hydrocarbon composition (determined by gas chromatograph) it can be concluded that these intermediates are converted primarily to C<sub>16</sub> and C<sub>18</sub> paraffins in HDO reaction and to C<sub>15</sub> and C<sub>17</sub> paraffins in the decarboxylation/decarbonylation reaction and in a lower amount to C<sub>14</sub> and shorter hydrocarbons (with cracking of C–C bonds)

The yield of the C<sub>18</sub> paraffins which were formed in HDO reaction – similarly to the yield of carboxylic acids – changed according to maximum curve as a function of temperature (Fig. 6) so the amount of C<sub>18</sub> paraffins significantly decreased with further strictening of the process parameters due to the chain cracking reactions.

The yield of C<sub>17</sub> paraffins which were obtained by decarboxylation/decarbonylation reactions changed similarly to the yield of C<sub>18</sub> paraffins for example at the lowest LHSV (0.5 h<sup>-1</sup>) (Fig. 7). The yield of C<sub>17</sub> paraffins increased with increasing the temperature at higher LHSVs. The further increase of the temperature will probably increase the rate of chain cracking reactions and the yield of C<sub>17</sub> paraffins will be lower, too.

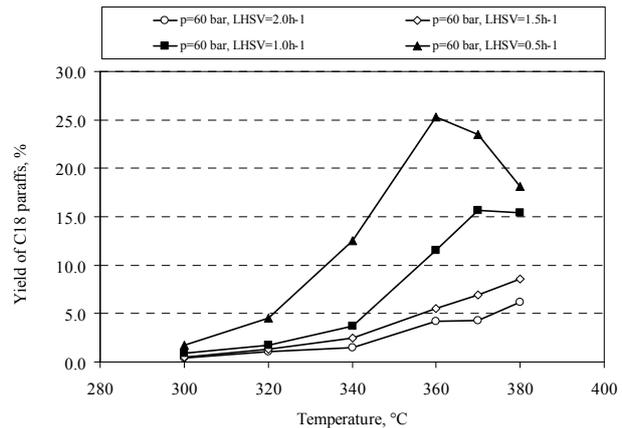


Figure 6: The yield of the C<sub>18</sub> paraffins as a function of the temperature (p = 60 bar)

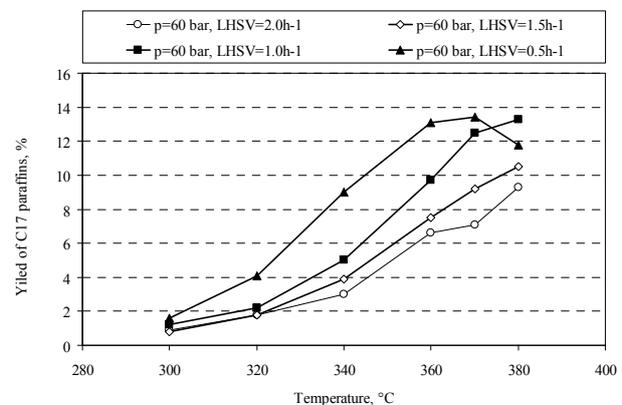


Figure 7: The yield of the C<sub>17</sub> paraffins as a function of the temperature (p = 60 bar)

To summarize the results we concluded that in case of every investigated process parameter the C<sub>18</sub>-, C<sub>17</sub>-, C<sub>16</sub>- and C<sub>15</sub> paraffins were formed, i.e. on the applied catalyst both the HDO and the decarboxylation/decarbonylation reactions took place.

We obtained the target fraction (gas oil boiling range fraction) with distillation of organic fractions. These target fractions, which were produced under optimal process parameters (360–380 °C, 60 bar, 0.5 h<sup>-1</sup>, 400 Nm<sup>3</sup>/m<sup>3</sup>), contained more than 95% normal paraffins (from this 5.3–6.9% n-C<sub>15</sub>, 19.2–29.1% n-C<sub>16</sub>, 16.5–18.0% n-C<sub>17</sub>, 20.3–34.0% n-C<sub>18</sub>) and <5% isoparaffins.

The use of the target fraction as engine fuels (diesel) is limited, because its cetane number is high (>80) but its CFPP value is also high (>20 °C).

So to improve this disadvantageous property it is necessary to carry out selective isomerization of the target fraction.

## Summary

To summarize the results, it can be concluded that with the hydrotreating (special hydrocracking) of sunflower oil high paraffin containing (>50%) product mixtures

(target fraction) with high yield can be produced on the applied NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.

But it is necessary to apply high pressure ( $p = 60$  bar), high temperature ( $T = 360\text{--}380$  °C) and low LHSV (LHSV =  $0.5\text{--}1.0$  h<sup>-1</sup>); for example  $370\text{--}380$  °C, 60 bar,  $0.5$  h<sup>-1</sup>. The yield of the produced target fraction (gas oil boiling range fraction) was significantly lower (50.7–54.5%) at advantageous process parameters ( $370\text{--}380$  °C, 60 bar,  $0.5$  h<sup>-1</sup>) than the theoretical values (82–86%). That is why it is necessary to separate and recirculate the heavy fraction.

The conversion of triglycerides significantly increased with increasing pressure, but at lower temperature (300 °C) the hydrocracking reactions took place only until the formation of carboxylic acids. The yield of produced intermediates (esters, carboxylic acids) and the target fraction changed according to maximum curve as a function of temperature in every LHSV.

In case of every investigated process parameter the C<sub>18</sub>-, C<sub>17</sub>-, C<sub>16</sub>- and C<sub>15</sub> paraffins were formed, i.e. on the applied catalyst both the HDO and the decarboxylation/decarbonylation reactions took place.

The cetane number of the target fractions which were obtained from organic fraction with distillation are very high (>80, EN standard:  $\geq 51$ ), but the cold flow properties of this fraction are disadvantageous. So to improve this disadvantageous property it is necessary to carry out selective isomerization of the target fraction [8, 11].

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