

## INVESTIGATIONS OF BIO-GASOIL PRODUCTION

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Liquid engine fuels are the main source of power for transportation in the passenger sector. It is the projection of the European Union (EU) to reach 10% utilisation of renewable fuels by 2020. To achieve this goal the EU created the 2003/30/EC and furthermore the 2009/28/EC Directives. For example, the feedstocks of these renewable engine fuels can be non-edible oil plant hybrids, such as rapeseed oils with high erucic acid content obtained from special hybrids of rape (e.g. *Brassica napus*) waste lards (used cooking oil and slaughterhouse lards). If the preconditions of utilisation are given with respect to the sustainability and technical compatibility of motor engines and vehicle construction, these bio components can be blended with motor fuels in large quantities. Considering the properties of currently used first generation biofuels, the maximum amount of bio-component in engine fuels is approximately 7 (v/v)% fatty acid-methylester in diesel fuels. A reliable production technology of second generation biofuels, which can be blended into diesel fuels is the heterogenic catalytic hydrogenation of triglycerides and waste lards. Furthermore, isomerisation can improve the quality of a bio-paraffin mixture. In this context, we studied the isomerisation of bio-paraffin mixtures, which were obtained from the hydrodeoxygenation of vegetable oil. The characteristics of these products were favourable, such as their cetane number being higher than 75, for example. The actual EN590:2013 standard does not limit the blending ratio of the paraffinic bio-component in diesel fuels. Consequently, these products obtained by the catalytic hydrogenation of vegetable oils can be blended into gasoil by up to 10 % or even more to meet the above EU requirements with respect to the utilisation of renewable fuels.

**Keywords:** bio gasoil, hydrodeoxygenation, catalytic conversion, biofuels, blending diesel fuels

### Introduction

Interest in alternative fuels is on the rise due to the unequal presence of the fossil energy carriers, the periodic rise in the price of fossil fuels, the need for decreasing dependence on crude oil, and the regulations of the European Union. They can play a significant role in achieving the EU plan to reach a 10% energy ratio of total fuel consumption using alternative fuels by 2020. Thus, the application of the biofuels can be increased to a large degree in the long- and medium-terms. For example, in some countries the domestic demand on biofuels could increase to 20% by 2030, along with the decrease in the demand for engine fuels that could be up to 70%. The world's energy production from biomass could reach 5% by 2050 [4, 5]. Accordingly, to ensure the availability of this feedstock the production costs could decrease. To achieve these goals, the EU created several directives (1998/70/EC, 2001/77/EC, 2003/17/EC, 2003/30/EC, 2003/87/EC, 2009/28/CE, and 2009/30/CE). Natural triglycerides like vegetable oils (edible or non-edible/waste) can be feedstock for biofuels as alternative energy sources [6, 7], such as special breeding non-edible oil plants [8, 9], animal fats or waste cooking oil [10, 11]. During the conversion of natural triglyceride molecules to bio-gasoil the following reactions take place [1, 2, 3]:

- full saturation of double bonds (hydrogenation),
- heteroatom removal
  - oxygen removal
    - hydrodeoxygenation (HDO reaction, and reduction)
    - decarboxylation,
    - decarbonylation
  - removing of other heteroatoms (sulphur, nitrogen, phosphorous, and metals),
- isomerisation of *n*-paraffins that are formed during the removal of oxygen
- different side reactions
  - hydrocracking of the fatty acid chain of triglyceride molecules,
  - water-gas shift reaction
  - methanisation,
  - cyclisation, aromatisation, etc.

During the HDO reduction reaction normal paraffins are formed with carbon numbers that are equal to the fatty acids in triglycerides. In the case of decarboxylation and decarbonylation reactions (HDC) normal alkanes are produced, where the carbon number is one less than that of fatty acids of the original vegetable (*Fig. 1*).

Bio-gasoil is a mixture of gasoil with the boiling range of *iso*- and *normal*-paraffins. It can be obtained by the hydrogenation of vegetable oils and natural triglycerides

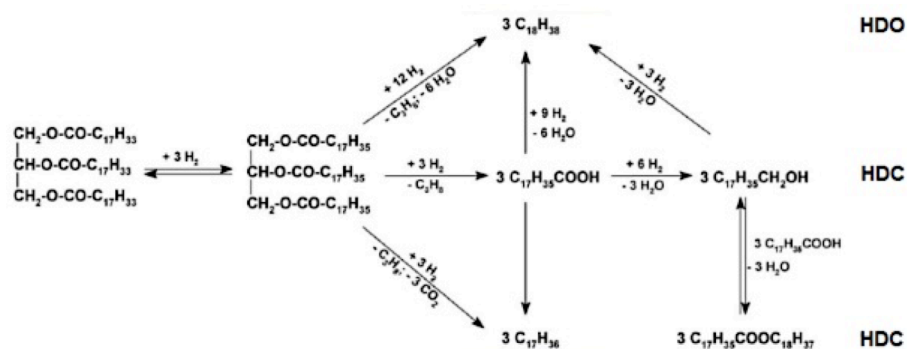


Figure 1: Pathways for the removal of oxygen from vegetable oils

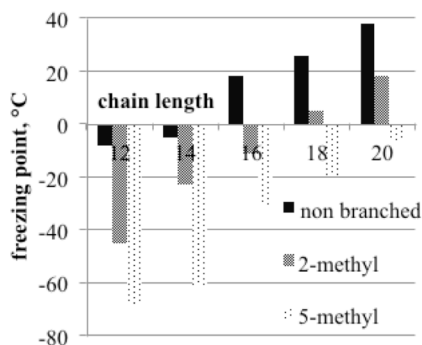


Figure 2: The freezing point of *iso*-paraffins as a function of the branch position

from other sources. These constitute the second generation biofuel components of diesel engines. They have good quality characteristics, such as high cetane number, good flow properties, unlimited mixability with engine fuels, and the a production line compatible with existing refinery structures [18, 19]. The actual EN 590:2013 standard does not limit the blending ratio of second generation bio-components, while the blending of biodiesel is limited to 7 v/v%. All the above mentioned aspects of alternative fuels can rationalise the investigation of the hydrogenation of non-traditional feedstock sources. These are the vegetable oils that can be obtained from non-edible hybrid oil-plants, rapeseed oil from *Brassica napus* with high erucic acid content to produce diesel fuel blending components with good flow properties in colder conditions (below +5 °C). The freezing point of *iso*-paraffins from bio-sources is lower than for equal chain length *normal*-paraffins (Fig.1) [12-15, 17]. Thus, products with high *iso*-paraffin contents have more favourable cold flow properties (CFPP) with cloud points at lower temperatures (Fig.2). The aim of our work was the production of diesel gasoil blending components *via* the isomerisation of paraffin mixtures obtained from the hydrodeoxygenation of rapeseed oil with high erucic acid content.

## Experimental

In this work, a diesel gasoil bio-blending component production technique was investigated that meets the requirements of the EN:590 Standard with the possibility of blending it with engine fuels in unlimited quantities. Thus, the hydrodeoxygenation of natural

triglycerides and further the isomerisation of the obtained bio-paraffin mixture were investigated over the Pt-SAPO-11 catalyst [16] developed in-house. The effect of the operation parameters, such as temperature, pressure, and liquid hourly space velocity (LHSV) was studied on the yield, composition, and utilisation properties of the products.

### Experimental Apparatus and Product Separation

The experimental tests were carried out in one of the measured sections of a high-pressure reactor system containing two tubular reactors with a isothermal catalyst volume of 100 cm<sup>3</sup>. The reactor system contained all the equipment and devices applied in the reactor system of a hydrotreating plant. The apparatus is suitable for maintaining if not succeeding the industrial precision of main process parameters.

### Analytical Methods

The main properties of the feedstock materials and products were determined by standard methods. The hydrocarbon composition of the bio-paraffin mixture was determined by high temperature gas chromatography (Shimadzu 2010 GC [column: Phenomenex Zebron MXT]).

### Process Parameters

The ranges of the applied process parameters in the isomerisation test on the basis of our earlier experimental results [13, 14, 17, 20-23] were as follows: temperature 300–360 °C, total pressure 20–80 bar, liquid hourly space velocity (LHSV) 1.0 h<sup>-1</sup>, and H<sub>2</sub>/feed volume ratio of 400 Nm<sup>3</sup> m<sup>-3</sup>.

### Feedstock materials

The feedstock of the catalytic tests was a bio-paraffin mixture, which was obtained from the hydrodeoxygenation of rapeseed with erucic acid produced in Hungary. It was properly filtered as a pre-treatment. The main properties of the feedstock material are shown in Table 1. The catalyst was Pt-SAPO-11 (0.5 % Pt), the main properties of this can be found in Table 2.

Table 1: Selected properties of the feedstock materials

Properties	rapeseed oil	Bio-paraffin mixture
kinematic viscosity at 40 °C, mm <sup>2</sup> s <sup>-1</sup>	46.56	3.493
density at 15 °C, g cm <sup>-3</sup>	0.9804	0.7923
cloud point, °C	16	32
cetane number	42	104
compositions, %	Fatty acid	Paraffin
	C16:0 2.3	C <sub>14</sub> 0.2
	C16:1 0.1	C <sub>14</sub> 0.1
	C18:0 1.2	C <sub>15</sub> 0
	C18:1 28.8	C <sub>16</sub> 2.3
	C18:2 12.4	C <sub>17</sub> 29.5
	C18:3 8.3	C <sub>18</sub> 28.8
	C20:0 0	C <sub>19</sub> 6.1
	C20:1 4.8	C <sub>20</sub> 5.6
	C22:0 0.1	C <sub>21</sub> 14.8
	C22:1 41.8	C <sub>22</sub> 12.5
	other 0.2	C <sub>22+</sub> 0.1

## Results and Analysis

The first step was to produce a bio-paraffin mixture with a boiling range of gasoil from rapeseed with a high euristic acid content. The properties of the bio-paraffin are summarised in Table 1. The commercially available NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst was utilised for the production of the bio-paraffin mixture. During the catalytic test the employed operation parameters were as follows: 320–380 °C, 20–80 bar, LHSV = 1.0 h<sup>-1</sup>, and H<sub>2</sub>/CH ratio of 600 Nm<sup>3</sup> m<sup>-3</sup> [8]. It was found that the favourable operation parameters are 340 °C, 40 bar, LHSV=1.0 h<sup>-1</sup>, and H<sub>2</sub>/CH ratio of 600 Nm<sup>3</sup> m<sup>-3</sup>. The tested catalyst is suitable for the production of bio-paraffin mixtures with

Table 2: Selected properties of the isomerisation catalyst used

Properties	Pt/SAPO-11
Pt content, w%	0.5
Pt dispersity, %	69
BET surface area, m <sup>2</sup> g <sup>-1</sup>	105
average pore size, nm	0.61
micropore volume, cm <sup>3</sup> g <sup>-1</sup>	0.06
macropore volume, cm <sup>3</sup> g <sup>-1</sup>	0.20
total pore volume, cm <sup>3</sup> g <sup>-1</sup>	0.26
acidity, mmol NH <sub>3</sub> g <sup>-1</sup>	0.13
acidity (rel.), mmol NH <sub>3</sub> m <sup>-2</sup> cat.	0.0012

high yields from natural triglycerides. Due to the moderate acidity of this catalyst, the formation of *iso*-paraffins was lower (5 wt%, Fig.3). Accordingly, the CFPP of the products was found to be high (27 °C). The product fraction produced in this way, in practice, cannot be blended into diesel fuels in low temperate zone countries. It is necessary then for the improvement of CFPP *via* the catalytic isomerisation of this mixture with high *normal*-paraffin content [10, 11]. A large amount of bio-paraffin mixture was produced in a thousand hour, long-term catalytic test. The target fraction of the isomerisation tests was the 180–360 °C boiling range, which is the boiling range of gasoil. The yield of the target products was higher than 94 % in all operation parameter combinations (Fig.4). The lighter fraction with a boiling range of up to 180 °C contains mainly *iso*-paraffins, which can be outstanding gasoline blending components due to their high octane numbers (>85).

We found that by adjusting the operation parameters, such as increasing the temperature, and decreasing the LHSV, the yield of the target fraction was decreased due to the higher yield of the cracking reaction. The target fraction obtained between 70% and 80%

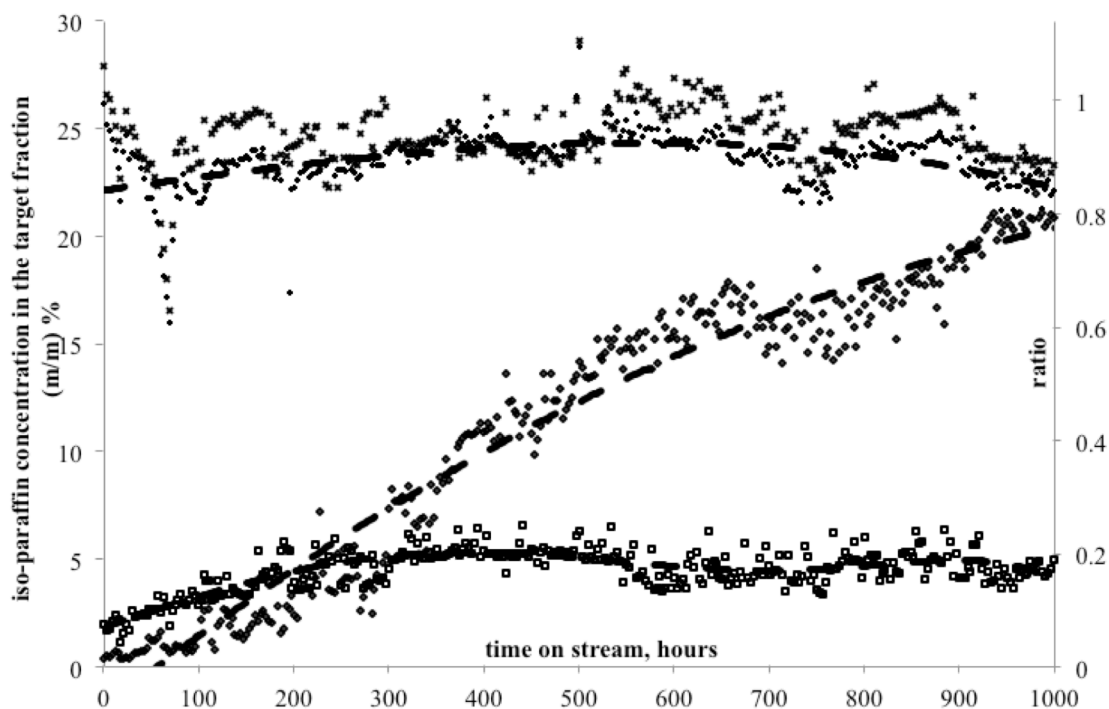


Figure 3: Hydrogenation of rapeseed oil with high euristic acid content (diamond: residual triglyceride, square: *iso*-paraffin content, cross C<sub>21</sub>/C<sub>22</sub> ratio)

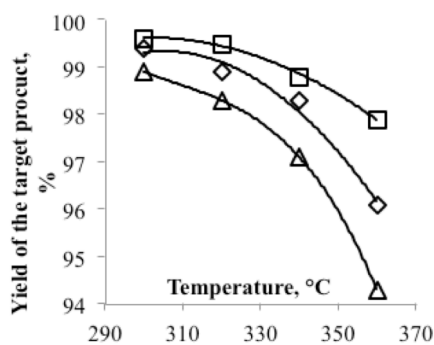


Figure 4: The yield of the target fraction as a function of operation parameters (pressure: 40 bar, liquid hourly space velocity square: 1.0 h<sup>-1</sup>, diamond 2.0 h<sup>-1</sup>, triangle 3.0 h<sup>-1</sup>)

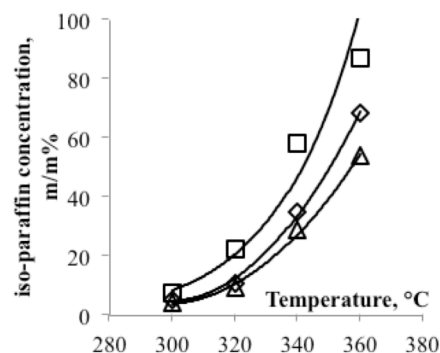


Figure 5: The *iso*-paraffin concentration of the target fraction as a function of operation parameters (pressure: 40 bar, liquid hourly space velocity: square 1.0 h<sup>-1</sup>, diamond 2.0 h<sup>-1</sup>, triangle 3.0 h<sup>-1</sup>)

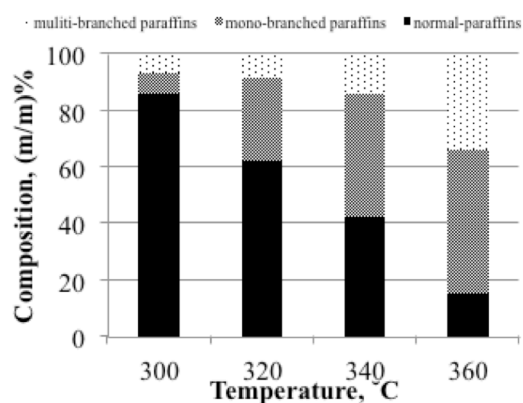


Figure 6: The composition of the products as a function of operation parameters (pressure: 40 bar, liquid hourly space velocity: 1.0 h<sup>-1</sup>)

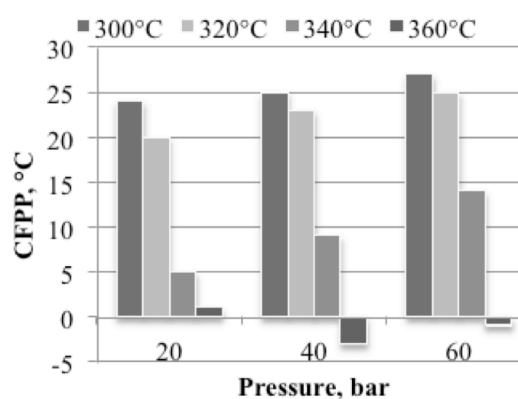


Figure 7: CFPP of the products as a function of operation parameters (liquid hourly space velocity: 1.0 h<sup>-1</sup>, H<sub>2</sub>/feed ratio: 400 Nm<sup>3</sup> m<sup>-3</sup>)

contained C<sub>17</sub>–C<sub>22</sub> hydrocarbons, as well as other (C<sub>13</sub>–C<sub>16</sub>) hydrocarbons from the boiling range of gasoil. The *iso*-paraffin content of the target fraction increased significantly with the operating temperature (Fig. 5). The increase of the *iso*-paraffin concentration occurred at 360 °C then at higher temperatures it started to decrease, due to the thermodynamic hindrance of the exothermic reactions, and the higher rate of cracking reactions.

Up to ca. 320 °C, mainly mono-branched *iso*-paraffins were formed and were by in large mono-ethyl-paraffins (Fig. 6). The freezing points of these products are much lower than *normal*-paraffins and the cetane number is high enough for a fuel additive. The greater formation of mono-methyl-paraffins over the SAPO-11 catalyst can be explained by the reduced formation of *iso*-paraffins due to steric hindrance. At 340 °C or higher, the formation of multi-branched isomers was significant (Fig. 6). These compounds have better cold flow properties (below -20 °C), but their cetane numbers are high enough (30–45) as shown in Fig. 2. The favourable operation parameters in terms of bio-gasoil yield and *iso*-paraffin concentration were as follows: T = 360 °C; p = 40 bar; and H<sub>2</sub>/feedstock ratio = 400 Nm<sup>3</sup> m<sup>-3</sup>. The CFPP values of the products as a function of temperature and operation pressures are shown in Fig. 7. These components have low enough CFPP values to blend into diesel gasoil in moderate amounts. On the basis of the experimental results, it was

concluded that the production of bio-gasoil meets the standard's requirements with a CFPP value of max. +5 °C and 70% *iso*-paraffin content (Fig. 8) in the case when the raw material contains 8% C<sub>17</sub>–C<sub>22</sub> *iso*-paraffins.

## Conclusions

Based on our experimental results, it was concluded that the NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst is suitable for the long-term production of bio-paraffin mixtures from natural triglycerides *via* catalytic hydrodeoxygenation. Furthermore, the investigated Pt-SAPO-11 catalyst is suitable for improving the quality of a bio-paraffin mixture that was obtained from the hydrodeoxygenation of rapeseed oil with high erucic acid content. During the isomerisation with optimised operation parameters, the yield of the target fraction was higher than 94%. At 340 °C or higher the *iso*-paraffin content is close to 70%. Consequently, the cold flow property of the cloud point is lower than +5 °C. Therefore, this approach can produce gasoil bio-blending components with good utilisation properties, such as high cetane number, and low temperature values for cold flow properties. Overall, the products described here are suitable for blending components of diesel fuels with concentrations of 10% or higher.

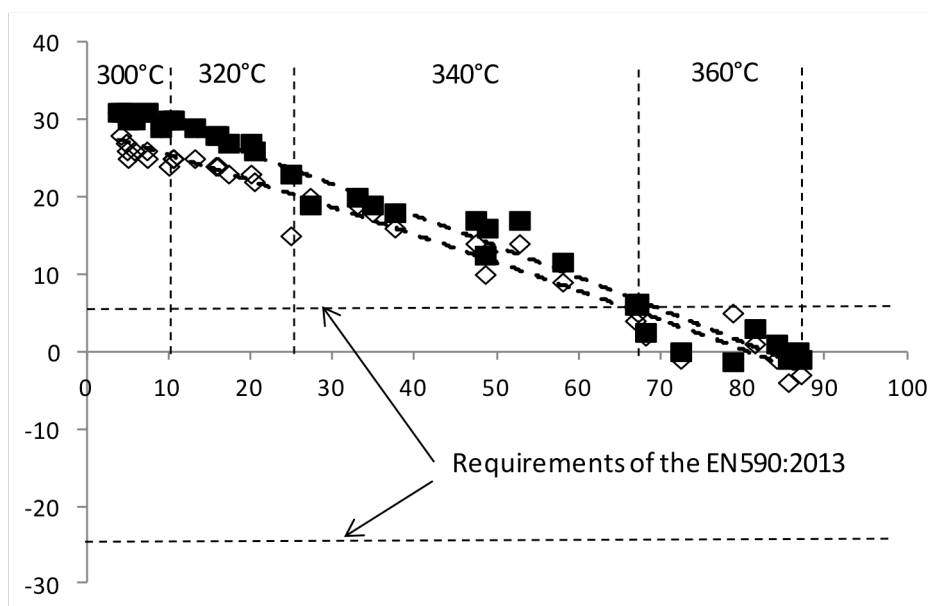


Figure 8: Cold flow properties as a function of *iso*-paraffin concentration (solid squares: cold filtering clugging point, hollow diamonds: cloud point)

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