

## Investigation of Quality Improving of Waste Origin Bio-Paraffins

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The liquid engine fuels are the main power source of the transportation in the passenger sector. Within this, the waste originated engine fuels can play the main role to achieve the prediction of EU, to reach the 10 % ratio of the renewable fuels until 2020. Thus the sustainable and environmental friendly production of this components is momentous. To achieve all this goals the European Union created the 2003/30/EC and further the 2009/28/EC Directives to encourage the bio components blending in the engine fuels. Nowadays the research, development and market entry of the second generation or new generation biofuels are under introduction. The main reason is the demand for better quality fuels and wider raw material basis. All of these above mentioned reasons explain the investigation of unconventional feedstocks which do not endanger the security of food supplement and/or can be processed with lower operation costs. For example these feedstocks can be non-edible hybrids such as rapeseed oils with high euric acid content obtained from special hybrids of rape (e.g. Brassica Napus) or high oleic acid containing oil sunflowers (Saaten Union Capella) waste lards (used cooking oil, slaughterhouse lards) or raw materials from long term unused agricultural area (abandoned area). The precondition of availability is the sustainable and the technical compatibility with running engine and vehicle construction, thus this bio components can be blended in the motor fuels unlimited quantity. Considering the utilization properties of currently used first generation biofuels, the maximum amount of biocomponent in the applied motor is 10 % bioethanol in the case of gasoline and 7 % fatty acid methyl ester in the case of diesel fuels. One of the reliable production technology of second generation biofuels which can be blended into diesel fuels is the heterogenic catalytic hydrogenation of triglycerides and waste lards. In this context we studied the heterogeneous catalytic hydrogenation of used cooking oils on aluminium-oxide supported transition metal catalyst. The applied operation parameters were the following: temperature: 320 – 380 °C, pressure: 20 - 80 bar, LHSV: 1.0 h<sup>-1</sup>, H<sub>2</sub>/hydrocarbon ratio: 600 Nm<sup>3</sup>/m<sup>3</sup>. The yield of gas oil boiling range products at the favourable operation parameters was close to the theoretical yield (80 – 90 %). The quality characteristics of these products were very favourable; for example the cetane number was higher than 75, the aromatic content was lower than 0.1 % and the sulphur content was lower than 5 mg/kg. To sum it up, the quality characteristics satisfied the CWA 15940:2009 (9th March) NSAI standard's (Automotive fuels – Paraffinic Diesel from synthesis gas hydrotreatment – Requirements and test methods) requirements. The actual EN 590:2013 standard does not limit the blending rate of these bio components, while on the other hand the blending of biodiesel (fatty-acid-methyl ester) is limited (max 7 v/v%). Consequently these products which were obtained by catalytic hydrogenation of vegetable oils can be blended in gasoil up to 10 %, and this way we can meet the requirements of the EU which prescribe at least 10-80 % bio component blending in motor fuels by 2020.

### 1. Introduction

The interest on alternative fuels is on the rise due to the unequal presence of the fossil energy carriers, the periodic rise of the price of fossil fuels, the need for decreasing the dependence of crude oil and the regulations of European Union. Thus, the liquid fuels (included the alternative fuels) as the main power

source both of the commercial and public transportation. The alternative fuels can play significant role to achieve of the plan of the EU, to reach the 10 % energy ratio of total fuel consumption until 2020. Based on these reasons the application of the bio-fuels can be increased in large degree in long and middle term, for example: in some countries of the domestic demand on bio-fuels can be increased to 20 % until 2030, along with the decreasing of engine fuels demand it can be up to 70 % until 2030, the world's biomass based energy production can reach 5 % until 2050 (Shell report, 2012) and also (Schollnberger, 2012). Sustainable and environmental friendly production of these compounds are very important. Accordingly to ensure the availability of this feedstock can decrease the production costs. To achieve all this goals the European Union created several directives (1998/70/EC, 2001/77/EC, 2003/17/EC, 2003/30/EC, 2003/87/EC, 2009/28/CE, 2009/30/CE). Natural triglycerides like vegetable oils (edible or non-edible/waste) can be feed stocks of bio-fuels as alternative energy sources. Consequently, production of second generation bio fuels from alternative sources (mainly hydrotreated vegetable oils) is widely investigated. Using of these raw materials can decrease the CO<sub>2</sub> emission and dependence of crude oil. Beside the sustainability and the technical compatibility of these compounds with the current engine and vehicle constructions should be ensured, thus this bio-components can be blended in the engine fuels with unlimited quantity. Due to the low utilization properties of the present by applied first generation bio-fuels these compounds are limited in the fuels. The maximum amount of bio-component can be applied in motor fuels is 10 % bio-ethanol in gasoline and 7 % fatty acid-methyl-ester in diesel fuel. Disadvantages of the first generation bio-fuels, are:

limited blending ratio of the engine fuels, storage problems, (FAME), endangering the safety of food supply

The second generation of bio-fuels can be the hydrogenated vegetable oils or hydrogenated triglycerides from other source, bio-ethanol from lignocelluloses. These compounds can be blended into engine fuels higher quantity due to their better utilization properties. The second generation bio gas oil (mixture of iso- and normal-paraffins) is among the bio-fuels for Diesel engines, it's utilization properties are the followings: good quality, blending into fuels in unlimited quantity, fitting for the aviable refinery structure (in case of hydrogenation of natural triglycerides). The actual EN 590:2013 standard does not limit the blending ratio of second generation bio-components, and the blending of biodiesel is limited (max 7 v/v%). Consequently these products can be blended into diesel fuel up to 10-20 %, and this way we can meet the requirements of the EU which prescribe until 2020. All of these above mentioned reasons explain the investigation of unconventional feedstocks which do not endanger the safety of food supplement and/or can be processed with lower operation costs. For example these feedstocks can be oils which are obtained non edible special hybrids [rapeseeds with high euric acid content (e.g. Brassica Napus) or high oleic acid containing oil of rapeseeds (Pioneer Hi-Bred 45A37) or sunflowers (Saaten Union Capella)] waste triglycerides (slaughter-house waste lard, used cooking oil) or oil seeds that grow on long term unused agricultural area (waste land). Engine fuels purpose application of waste origin raw materials is important because the waste origin raw materials is recognized in double weight.

On the basis of the above mentioned facts it is necessary to investigate the hydrogenation of non edible (used cooking oil) originated triglyceride sources for production of diesel fuel blending components which has good flow properties in colder conditions. It is because the aim of our experimental work was the production of diesel fuel blending component via isomerization of bio-paraffin mixture which was obtained catalytic hydrogenation of used cooking oil. The freezing point of generated iso-paraffin mixture is significantly lower than the equal chain length normal-paraffins. Thus the flow properties (cold filtering plugging point, cloud point) of obtained fraction is more favourable in colder conditions (Figure 1).

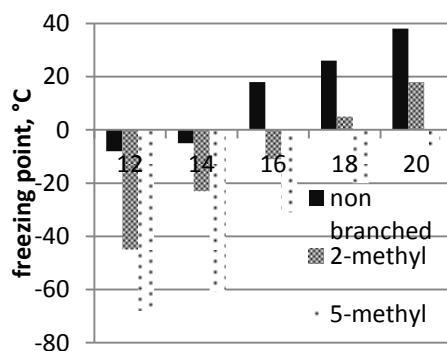


Figure 1: Freezing point of iso- and normal-paraffins in the function of chain length and the place of branch

## 2. Experimental

### 2.1 Catalytic test

During our experimental work the isomerization of bio-paraffin mixture was investigated on inhouse upgraded Pt-SAPO-11 catalyst. The bio-paraffin mixture was obtained with heterogenous catalytic oxygen removal of properly prethreated (filtered) used cooking oil which was collected in Hungary.

### 2.2 Feedstocks

The feedstock of the catalytic tests was bio-paraffin mixture which was obtained used cooking oil which was collected in Hungary and it was properly pre-treated (filtered). The main properties of the feedstocks are shown in the Table 1. The catalyst was Pt-SAPO-11 (0.5 % Pt), the main properties of this can be found in Table 2.

### 2.3 Experimental apparatus and product separation

The experimental tests were carried out in one of the measure sections of a high pressure reactor system containing two tubular reactors (isothermal catalyst volume: 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 keeping the main process parameters with such precision at least as used in the industry (Nagy et al, 2007).

### 2.4 Process parameters

The range of the applied process parameters – based on our earlier experimental results – were the following: temperature 300 – 360 °C, total pressure 20 – 80 bar, liquid hourly space velocity (LHSV): 1.0h<sup>-1</sup> and H<sub>2</sub>/used cooking oil volume ratio: 400 Nm<sup>3</sup>/m<sup>3</sup>.

### 2.5 Analytical methods

The main properties of the feedstocks and products was determined by standard methods (Table 2.) The hydrocarbon composition of the bio-paraffin mixture was determined by high temperature gas chromatography (Shimadzu 2010 GC [column: Phenomenex Zebron MXT]).

Table 1: Main properties of the feed stocks

Quality properties	used cooking oil	bio-paraffin mixture	
kinematic viscosity, 40°C, mm <sup>2</sup> /s	42.6	3.427	
density (15°C) g/cm <sup>3</sup>	0.9432	0.7776	
cloud point, °C	9	26	
iodine number, g I <sub>2</sub> /100g	128	0.51	
cetan number	32	101	
Fatty acid composition , %	paraffin composition, %		
C16:0	5.0	C <sub>14</sub> -	0.1
C16:1	0.1	nC <sub>14</sub>	0.2
C18:0	3.0	iC <sub>14</sub>	0
C18:1	28.0	nC <sub>15</sub>	2.5
C18:2	54.8	iC <sub>15</sub>	0
C18:3	0.3	nC <sub>16</sub>	4.7
C20:0	0.2	iC <sub>16</sub>	0.3
C20:1	0	nC <sub>17</sub>	32.9
C22:0	0.5	iC <sub>17</sub>	3.2
C22:1	0	nC <sub>18</sub>	47.3
other	8.1	iC <sub>18</sub>	5.4
		C <sub>18+</sub>	3.5

Table 2: List of analytical methods

Properties	Standard method
Kinematic viscosity	EN ISO 3104:1996
Density	EN ISO 3675:2000
Acid number	EN 14104:2004
Iodine number	EN 14111:2004
CFPP	EN 116:1999
Fatty acid composition	EN ISO 5509:2000; EN 14103:2004

### 3. Results and discussions

The feedstock of the isomerization tests was a bio-paraffin mixture which was obtained by heterogen catalytic hydrogenation of used cooking oil. During the hydrogenation tests commercial available NiMo/Al<sub>2</sub>O<sub>3</sub>, CoMo/Al<sub>2</sub>O<sub>3</sub>, NiW/Al<sub>2</sub>O<sub>3</sub> catalysts were applied. The operation parameter range of the test were the following: temperature: 300 °C – 360 °C. pressure: 20 bar – 80 bar, H<sub>2</sub>/CH: ratio: 600 Nm<sup>3</sup>/m<sup>3</sup> (Solymosi, 2013). Based on the experimental results, it was concluded that the tested NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst is applicable for produce bio-gas oil (mixture of iso- and normal-paraffins) with high yield applying the favourable operation parameters (temperature: 340 °C, pressure: 40 bar, LHSV: 1.0 h<sup>-1</sup>, H<sub>2</sub>/CH ratio: 600 Nm<sup>3</sup>/m<sup>3</sup>). The approach of the theoretical paraffin yield (84 %) was 95 %. The cracking activity (<0.1 %) was low degree due to the moderate acidity of the catalyst. Furthermore the yield of iso-paraffins (5 %) was lower also the lower acidity of the used catalyst. Thus CFPP value of the products is high (+24 °C). The target fraction that was produced this way, cannot be blended into diesel gas oils in temperate zone area without isomerization quality improving. Consequently, the quality improving of high normal-paraffin content mixtures via catalytic isomerization is essential. In this context on the based of the abovementioned experimental results, large amount of bio-paraffins was produced in the 500 hours long term experiment. The main properties of obtained bio-paraffin mixtures can be found in the Table 1.

The 180 °C – 360 °C boiling range fraction was considered to be the target fraction (gas oil boiling range fraction). The yield of the target fraction in all operation parameter combination was higher than 96 % (Figure 2.). The formed light fraction boiling up to 180 °C (contains mainly C<sub>13</sub>. iso- and normal-paraffins) can be outstanding gasoline blending component due to the high octane number (>85). Based on the experimental result it was concluded that the yield of the target fraction is decreasing with the severing of the operation parameters (increasing the temperature and decreasing the LHSV), due to the increasing rate of the cracking reactions. The obtained target fraction mainly (80 % - 92 %) contains C<sub>17</sub> – C<sub>18</sub> hydrocarbons and depends on the operation parameters arose other gas oil boiling range hydrocarbons C<sub>13</sub> – C<sub>16</sub> and C<sub>19</sub> – C<sub>22</sub>. The iso-paraffin content of the target fraction increased significantly with the increasing temperature (Figure 3.) and over 360 °C the iso-paraffin content began to decrease.

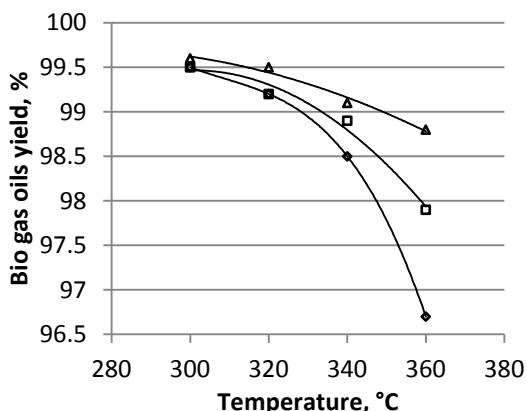


Figure 2: Yield of the bio gas oil fraction in the function on operation parameters. Pressure: 40 bar, H<sub>2</sub>/feed volume ratio : 400 Nm<sup>3</sup>/m<sup>3</sup> (◇ LHSV = 1.0 h<sup>-1</sup>, □ LHSV = 2.0 h<sup>-1</sup>, △ LHSV = 3.0 h<sup>-1</sup>)

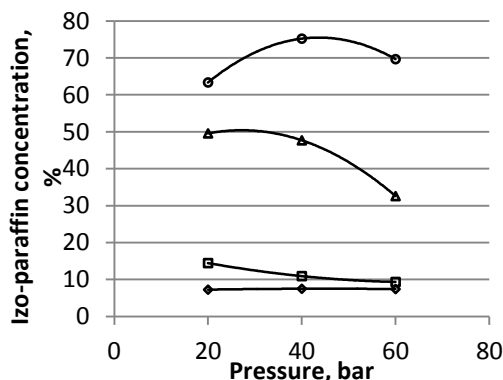


Figure 3: The iso-paraffin concentration of the target fraction in the function of operation parameters. LHSV = 1.0 h<sup>-1</sup> (◇ 300°C, □ 320°C, △ 340°C, ○ 360°C)

This is because the thermodynamic hindrance due to the exothermic nature of the isomerization reactions and the other hand the increasing rate of the cracking reactions. Until 320 °C mono-branched paraffins, were formed, most of these were mono-ethyl paraffins. Freezing point of these compounds are much lower than the normal-paraffins and the cetane number of there are enough high. The significant yield of the mono-methyl branched isomers can be explained other experiment of analogs of SAPO-11 catalyst. It was concluded that formation of longer branch than one carbon number is not potential due to the steric hindrance (Claude, 2000, Claude, 2001).

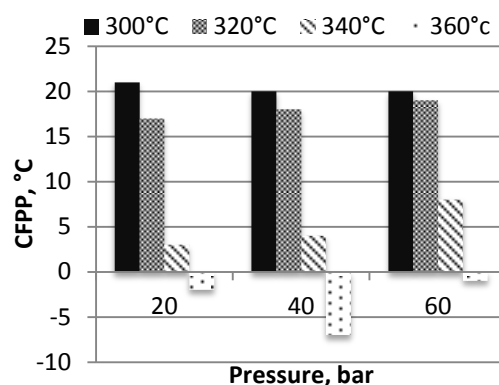
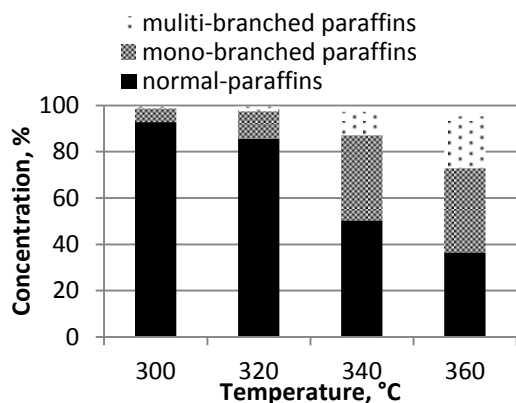


Figure 4: The iso-paraffins structure in the target fraction in the function of operation parameters (pressure: 20 bar, LHSV = 1.0 h<sup>-1</sup>)

Figure 5: CFPP of the target fraction as the function of operation parameters

Above 360 °C the formation of multi-branched paraffins was higher (Figure 4.). Cold flow properties of these compound are very favourable but the cetane number is too low. The cold filtering plugging point of the obtained fraction decreased with the increasing operation temperature and decreasing LHSV, ergo with the increasing iso-paraffin concentration. On the favourable operation parameters in terms of bio gas oil yield and iso-paraffin concentration can be produce bio gas oil that fit for the valid gas oils standard (EN590:2013). Additionally it was concluded that the minimal required iso-paraffin concentration is 50 % to satisfaction of the gas oil standard's requirement (max. CFPP: +5 °C), with the applied feedstock that contains mainly C<sub>17</sub>, C<sub>18</sub> normal paraffins (Figure 5. and Figure 6.).

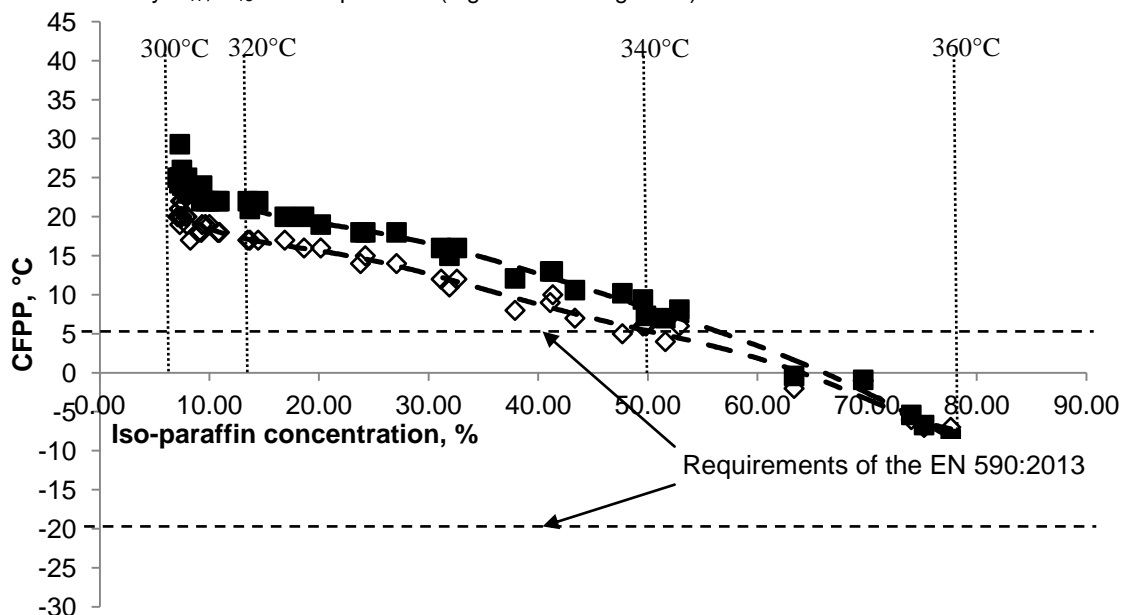


Figure 5: The cold flow properties as the function of operation parameters (◇ cold filtering plugging point, ◆ cloud point)

#### 4. Summary

Based on our experimental results it was concluded Pt-SAPO-11 catalyst is suitable for isomerization quality improving of bio-paraffin mixture which was produced heterogen catalytic deoxygenation of used cooking oil. The bio gas oil that was produced on the favourable operation parameters (temperature: 340

°C, LHSV: 1.0 h<sup>-1</sup>, H<sub>2</sub>/CH ratio: 400 Nm<sup>3</sup>/m<sup>3</sup>) can be blended into gas oils up to 10 % or higher amount due to the favourable utilization properties such as high cetane number (76), CFPP (-5 °C).

### Acknowledgements

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