

## Sustainable Production of Bioparaffins

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Most prevalent fuels of Diesel engine vehicles are the gas oils produced on crude oil bases. According to some disadvantages of fatty acid-methyl-esters (biodiesels), bioparaffins (mainly isoparaffins) are able to substitute them partially or totally. The production of bioparaffins can be carried out on a wide raw material base. This means the natural triglycerides (different origin non-food vegetable oils, "brown fat" of sewage works, fat of protein processing, algae oils, etc.), lignocelluloids etc.. In this paper catalytic systems (NiMo/Al<sub>2</sub>O<sub>3</sub>; Pt/SAPO-11; Pt/AISBA-15) for the production of bioparaffins from different triglycerides (oils and fats) and high molecular weight Fischer-Tropsch (heavy) hydrocarbons (produced from biobased synthesis gas) are introduced. After the proper pretreatment of natural triglyceride feedstocks the suggested two-step technologies (deoxygenation and isomerisation) are able to produce n- and isoparaffins with yield that approaches the 93-99 % of the theoretical value. Properties of the two bioparaffin fractions produced with these methods satisfy the requirements of EN 590:2009+A1:2010 standard. Their cetane number is in the range of 65-75, which makes it possible to blend lower quality blending components in higher quantity, which is the source of significant profit increase. The integration possibilities of the suggested technologies in to crude oil refineries are introduced, too.

### 1. Introduction

One of the main pillars of sustainable development is the mobility. To realize mobility (road, air and water transport) more and more quantities of engine fuels are required. Furthermore, several quality parameters have become stricter and stricter recently, and many of them will be tightened further in the near future. Based on the abovementioned, it is very important to produce an even higher share of these fuels from alternative sources. One of the promising solutions is the production and use of fuels on agricultural bases in an economic and environmentally friendly way.

Biofuels can be classified – according to arbitrary principles – on the basis of multiple aspects. Our recommendations are:

- Based on feedstocks
  - First generation (edible)
  - Second generation (non-edible)
  - Third generation, ...
- Based on product quality (independent from the feedstock)
  - First generation (conventional; more or less application disadvantages)
  - Second generation (new or developed molecular structure, enhanced quality)
  - Based on feedstocks and product quality too
- Based on the time of recognition and application (Hancsók, 2007).

Nowadays, most prevalent fuels of Diesel engine vehicles are still the gas oils produced on crude oil base. Due to some disadvantages of fatty acid-methyl-esters (biodiesels), bioparaffins (mainly isoparaffins) are able to substitute them partially or totally. The reason is that isoparaffins the gas oil boiling point range have excellent performance properties; e.g. relatively high cetane number (ca. 20-70) by low methyl-branching and low freezing point (Murphy, 2004). Because of their high hydrogen content (composition: C<sub>n</sub>H<sub>2n+2</sub>) they have high energy content too and their burning is relatively clean. Products with high

isoparaffin content can be produced from the following biomass based feedstocks: natural triglycerides (non-edible vegetable oils, waste cooking oils/fats, rendering fats, brown greases, algae oil, etc.) (Mohammad, 2013), high molecular weight hydrocarbons of the biomass based Fischer-Tropsch synthesis (high carbon number: >22) (isomerizing hydrocracking to gas oil boiling point range 180–360 °C; C11–C22 hydrocarbons) (Calemma 2010), lignocellulose, carbohydrates (Xing, 2010), biomass pyrolysis oils (Czernik, 2004), wastes with carbon and hydrogen content (Ofoma, 2006), etc. These feedstocks are available in high volume, and do not endanger the food and fodder supply, their application has no negative effect on the land use being mainly wastes. Of course the production of bioparaffins from different feedstocks takes place on different reaction pathways. In case of every feedstock their proper pretreatment is needed. (The description of these methods is not subject of this paper).

Table 1: Categorization of biofuels based on the chronology of their development and application

First	Second	Third	Fourth
<b>GENERATION</b>			
<ul style="list-style-type: none"> <li>bioethanol</li> <li>vegetable oils</li> <li>biodiesels</li> <li>blends of the previous and conventional petroleum-based fuels</li> </ul>	<ul style="list-style-type: none"> <li>bio gas oils (hydrogenation / isomerization of vegetable oils)</li> <li>bioethanol from lignocelluloses</li> <li>biobutanol</li> <li>biocomponents as molecular constituents</li> <li>biomethan (bio gas)</li> </ul>	<ul style="list-style-type: none"> <li>synthetic biofuels from bio synthesis gas</li> <li>biogasoline and biogasoil (hydrocracking of biooils produced by biomass pyrolysis)</li> <li>bio-paraffins from carbohydrates</li> <li>biodimethyl ether (DME)</li> </ul>	<ul style="list-style-type: none"> <li>biohydrogen</li> <li>synthetic biomethane</li> <li>biomethanol</li> <li>bio electricity (indirectly for fuel cells)</li> <li>γ-valero-lactone</li> <li>as yet unknowns</li> </ul>

In this paper we present our solutions (catalytic systems) to produce product mixtures rich in isoparaffins from natural triglycerides and biomass based high molecular weight Fischer-Tropsch (heavy) hydrocarbons with isomerization and hydrocracking. Therefore we focus on the chemistry of the before mentioned bioparaffin production pathways. Product mixture rich in isoparaffins can be produced in two steps from the natural triglycerides: 1. saturation of olefinic double bonds and oxygen removal; 2. isomerization of the formed n-paraffin mixture (Figure 1) (Hancsó 2012).

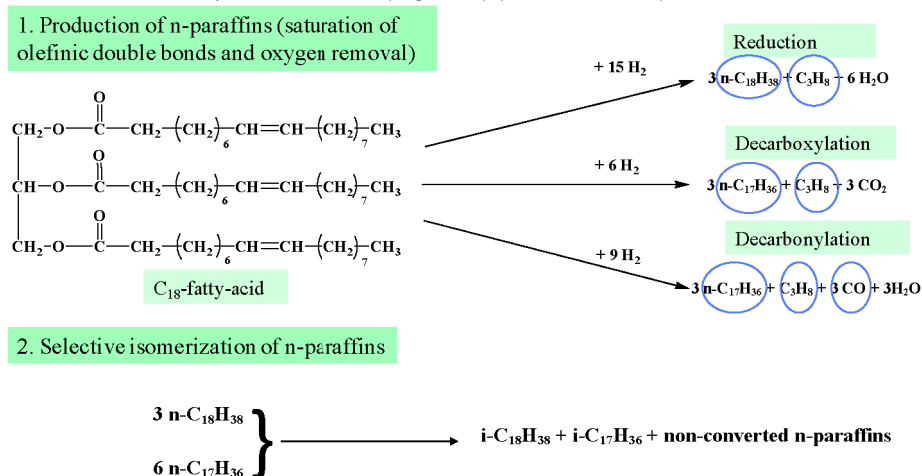


Figure 1: Possible gross reactions of triglyceride conversion

The main reactions taking place during the isomerization and hydrocracking of biomass based Fischer-Tropsch heavy paraffin mixture are as shown in Figure 2.

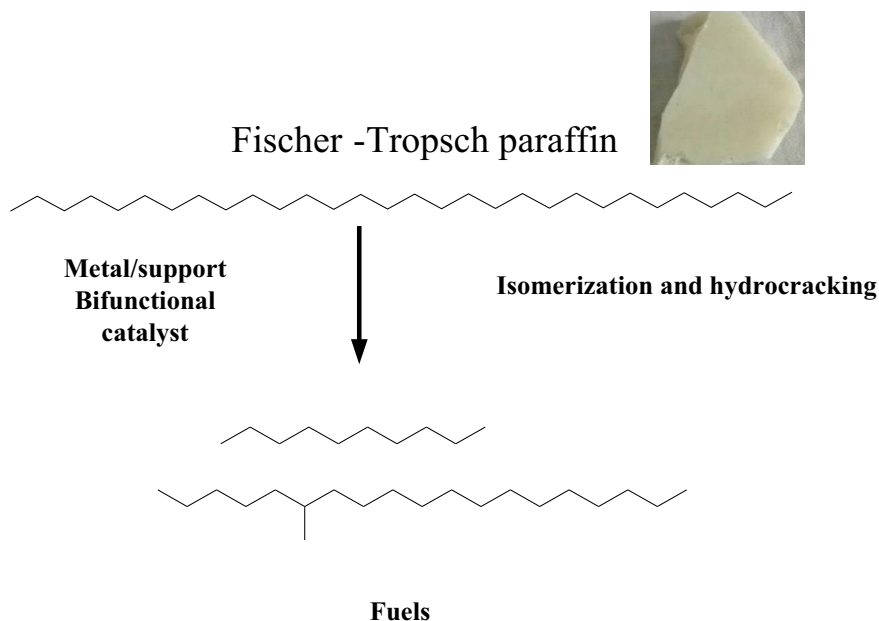


Figure 2: The main reactions taking place during the isomerization and hydrocracking of biomass

Several processes were proposed and developed to produce bioparaffins from triglycerides (Toba 2011), but few of them are applied in the industry (Hancsók, 2012). Their disadvantages are: the level of the approach of theoretical yields of the target products is not good enough (<90%) in case of the applied n-paraffin production and consecutive isomerization catalytic systems [feedstocks, reactor(s) and internals, catalyst(s), process parameters (T,P, etc.), intermediates and final products]; additionally the feedstock flexibility is not adequate too.

In case of isomerization and hydrocracking of high molecular weight Fischer-Tropsch heavy paraffins the recommended catalytic systems are not selective enough to produce isoparaffin-rich gas oil product mixtures (too many non-gas oil products with lower or higher carbon numbers).

In view of the aforementioned, the aim of our experiments was to recognize new catalytic systems and to determine advantageous process parameters to produce biooriginated gas oil components (mainly isoparaffins) with a high yield and selectivity. Additionally our aim was to find solutions which can be integrated into the structure of an existing crude oil refinery, so the solution is feedstock and energy saving and economic.

## 2. Experimental

To reach the presented goals, we carried out our experiments with the following conditions.

### 2.1 Catalytic tests

Catalytic reactions were carried out in a bench-scale, high-pressure reactor system that containing a fixed-bed flow-through reactor with 100 cm<sup>3</sup> catalyst volume. The reactor system contained all the equipments and devices those used in the reactor system of a hydrotreating and isomerisation plants respectively. The reaction conditions with respect to the results of preliminary experiments were selected. The product mixtures for the heterogeneous catalytic transformation of natural triglycerides were separated into gaseous, water and organic phase. The main products (mixtures of gas oil boiling-range normal- and isoparaffins) were obtained by the distillation of the organic fraction produced by the conversion of natural triglycerides and the isomerisation-hydrocracking of the high molecular weight Fischer-Tropsch heavy paraffins.

## 2.2 Catalyst and feedstocks

We used a sulphided Ni(3.2 %)/Mo(13.4 %)/P(1.1 %)/Al<sub>2</sub>O<sub>3</sub> catalyst for the conversion of natural triglycerides to n-paraffins. (Hancsók, 2012). For the isomerization of the product n-paraffin mixture a Pt(0.5 %)/SAPO-11 catalyst was applied (Kasza, 2010). For the isomerisation of the high molecular weight Fischer-Tropsch paraffin mixture we chose the self developed Pt(0.5 %)/AISBA-15 catalyst (Pölcsmann, 2010) with a new composition.

Natural triglyceride feedstocks were the following: used cooking oil, waste lard, non-food rapeseed oil (euric-acid content: >50%). The n-paraffin content of the high molecular weight (to nC50) product mixture from biowaste based Fischer-Tropsch synthesis was 97.4 %, C22+ content was 64 %, i-/n-paraffin mass ratio was 0.03, aromatic and olefin content was <0.8% (Pölcsmann, 2011).

## 2.3 Analytical methods

In every case, if it was possible, we used standard test methods (EN, EN ISO, ASTM D). In every other case, we used our methods (eg. for the determination of feedstock and product composition we used gas chromatographs).

## 3. Results and discussion

We carried out the systematic experimental series with well-pretreated natural triglycerides from different origins on the sulphided NiMo/P/Al<sub>2</sub>O<sub>3</sub> catalyst in a wide process parameter range (temperature: 280-380 °C, pressure: 20-80 bar, liquid hourly space velocity: 0.75-3.0 h<sup>-1</sup>, H<sub>2</sub>/feedstock volume ratio: 450-700 Nm<sup>3</sup>/m<sup>3</sup>). To keep the sulphur on the catalyst surface we blended 1,000 mg/kg dimethyl-disulphide in each feedstock. This disintegrates quickly in the applied reaction conditions.

From the great number of the experimental results with each feedstocks in this paper we publish only the preferable process parameters and the yield of the obtained target products (the theoretical yield also shown) and the main quality properties (upper part of Table 2). The data of this Table shows well that we found process parameter combinations in case of each feedstock where the yield of the target products (gas oil boiling range products) approaches the theoretical yield well. From this aspect the order of the feedstocks was the following: high euric acid containing rapeseed oil (non-food) > used cooking oil > waste lard. The reasons are: the longer chain of fatty acid component of the triglyceride has a positive effect on the yield, this is true in reverse too (e.g. waste lard), and of course the catalyst poisons still in the pretreated feedstock (e.g. sulphur and nitrogen content compounds, polycyclic hydrocarbons).

There was no significant difference in the properties of the different target products; the n-paraffin content was higher than 92 % in every case, the share of i-paraffins did not reach 65 %; the sulphur and nitrogen content was the highest in case of n-paraffin produced from waste lard; this can be explained with the relatively high sulphur and nitrogen content of this feedstock; neither of the products contained mono-, di- and triglycerides; the concentration of fatty acids was lower than 0.5 %. This is important because during the catalytic isomerisation water is formed from these compounds, which reduces the skeletal isomerisation activity of the acid catalyst. The cetane number of the products was very high, but they were solid at room temperature (20 °C) (the freezing point of each hydrocarbon is high), so they are not able to drive Diesel-engines.

This property can be improved with the transformation of n-paraffins to branched chain compounds (isoparaffins) with catalytic isomerisation. The catalyst of this transformation was a self developed Pt/SAPO-11 catalyst. We chose the process parameters on the basis of our previous experimental results (Hancsók, 2011).

Based on the obtained results (lower part of Table 2) good flow property (CFPP: Cold Filter Plugging Point) products with a good cold flow property can be produced with a high yield (>95 %) from n-paraffin rich feedstocks. Products from waste lard have the lowest CFPP value. The reason is that the hydrocarbon components have the lowest average chain length, so these compounds have the lowest freezing point. This is determined by the fatty acid composition of the feedstock.

According to the previous results a two-step technology can be recommended, which can be integrated well in the existing crude oil technologies. The olefin saturation and oxygen removal reactions of natural triglycerides (experimental experiences) are exothermic, so they should be carried out in a split bed reactor, or a reactor with quench hydrogen. The isomerisation step can be carried out in a new fixed bed reactor or in a catalytic isomerisation plant (application of more active and selective catalyst and/or dense catalyst loading) after the desulphurizer plants or the application of more reactors.

Table 2: Main properties of product mixtures obtained from different natural triglycerides

Appellation	Feedstock		
	Used cooking oil	Waste lard	Non-food rapeseed oil
Paraffin mixture (NiMoP/Al <sub>2</sub> O <sub>3</sub> ) <sup>a</sup>			
yield, %	80.1	77.4	82.8
theoretical yield <sup>b</sup> , %	86.4-81.6	85.55-80.65	89.7-80.3
approaching of theoretical yield <sup>c</sup> , %	95.4	93.1	97.4
n-paraffin content, %	96.2	97.1	95.6
isoparaffin content, %	3.5	2.1	3.9
S, N concent, mg/kg	2/3	8/10	2/1
mono-, di- triglyceride content, %	<0.5	<0.5	<0.5
aromatic and cycloparaff. content, %	<0.2	<0.1	<0.1
cetane number	90	93	90
CFPP, °C	>20	>20	>20
Isomerized product (Pt/SAPO-11) <sup>d</sup>			
yield, %	97.0	97.5	96.5
isoparaffin content, %			
cetane number	76	79	74
CFPP, °C	-18	-17	-19

<sup>a</sup>) Preferable process parameters: T=340 °C, P=40 bar, LHSV=1.0 h<sup>-1</sup>, H<sub>2</sub>/feedstock ratio: 600 Nm<sup>3</sup>/m<sup>3</sup>

<sup>b</sup>) The first number supposes only HDO reaction, while the second supposes only DCO reactions

<sup>c</sup>) Counted to the middle of the two theoretical yields.

<sup>d</sup>) Preferable process parameters: T=350 °C, P=50 bar, LHSV=1.5 h<sup>-1</sup>, H<sub>2</sub>/feedstock ratio: 300 Nm<sup>3</sup>/m<sup>3</sup>

We carried out the isomerisation hydrocracking of the biooriginated high molecular weight Fischer-Tropsch (heavy) paraffin mixture in more catalytic systems (Valyon, 2011). According to our new research results, the Pt(0.5 %)/AISBA-15 containing system was the most selective to produce gas oil boiling-range (ca. 200-360 °C) isoparaffinrich fractions (Table 3; it contains two other catalysts for comparison). The highest product yield and isoparaffin content was obtained on the Pt/AISBA-15 catalyst. From the aspect of product quality, we obtained the best results on this catalyst.

Table 3: Results from isomerization hydrocracking of Fischer-Tropsch heavy paraffins

Product properties	Pt(0.5%)/AISBA-15	Pt(0.5%)/SAPO-11	Pt (0.5%)/ β-zeolite
Reaction temperature, °C*	325	345	275
Gas oil fraction			
yield, %	31.1	61.9	14.0
isoparaffin content, %	84.2	78.0	20.7
isoparaffin yield, %	26.2	43.8	
cetane number	72	68	65
Distillated share to 300°C, v/v%	58	71	74
CFPP, °C	-15	-19	-18
Mono-branched paraffin cont./share, %	49/20.5	58/34	54/22
			63/30

\*other parameters: P = 50 bar, LHSV: 1.0 h<sup>-1</sup>, H<sub>2</sub>/feed ratio: 450 Nm<sup>3</sup>/m<sup>3</sup>

The reason of the lower cetane number of the products obtained at higher temperature on the Pt/AISBA-15 catalyst was that the share of lower carbon number hydrocarbons was higher (see: distillation data) by the higher cracking. The lower carbon number paraffin hydrocarbons have lower cetane number. At the same time, this latter product has a better low temperature property (CFPP value is -19 °C as opposed to -15 °C). Additionally, besides the aforementioned, the reason is not just that the CFPP of multibranched isoparaffins is generally lower than that of one-branched isoparaffins, but the share of internal single methyl branches (e.g. on the fifth carbon atom) from the one-branched isomers was higher than terminal branches (e.g. on the second carbon atom). The freezing point of the latter ones is clearly higher. Based on the obtained experimental results the isomerization hydrocracking of high molecular weight Fischer-Tropsch mixture can be integrated easily in the middle pressure technologies (40-80 bar) of an average structure crude oil refinery with regard to the process parameters.

#### 4. Conclusions

Excellent quality (high isoparaffin containing) gas oil boiling-range hydrocarbon mixtures (fractions) can be produced from natural (waste too) triglycerides and from high molecular weight Fischer-Tropsch paraffins in a targeted catalytic system. Considering the process parameters and the average technologies in a crude oil refinery, the recommended processes can be integrated easily in the structure of the refinery.

According to the previously detailed results we determined that the biooriginated, gas oil boiling-range, high isoparaffin containing fractions have excellent application properties (e.g. cetane number is higher with 18-30 unit than the requirement of the actual standard (EN 590:2009+A1:2010), which is minimum 51. So they make it possible to blend lower cost stream(s) in the gas oil pool (including hydrogenated and isomerized product obtained by cracking of waste polyolefins), which can be a source of significant profit. The raw material base is partially ready for the sustainable production of isoparaffin rich bioparaffin fractions. From the natural (including wastes) triglycerides 10-15 % of the actual gas oil demand and further ca. 30-60 % can be fulfilled with biomass (including biogas) and biowastes and other wastes (e.g. hydrocarbon residues, plastic wastes) based Fischer-Tropsch synthesis which produces directly or indirectly products rich in isoparaffins.

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