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INVESTIGATION OF FUEL COMPONENTS PRODUCED BY THE ISOMERIZATION OF BIO-PARAFFIN MIXTURES

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The importance of biofuels becomes more acute, especially in the European Union. Beside them, the biogasoil is a promising product that is a fuel with high isoparaffin content in the gas oil boiling range, which can be produced by the catalytic hydrogenation of different natural triglycerides. In order to improve the cold flow properties of mixtures consist of mainly normal paraffins they have to be isomerized. In this paper the isomerization of paraffin mixture consists of only normal and iso-paraffin was studied on 0.5% Pt/SAPO-11 catalyst at 300–380 °C temperature, 40 bar pressure, 0.5–4.0 h^{-1} of liquid space velocity and 400 Nm^3/m^3 of H_2/feed ratio. It was found that CFPP value of the products can be tailored between -7 °C and -15 °C at a gas oil yield of 85–95%. During the conversion 2–5% of bio-jet fuel was obtained with CFPP value of between -55 °C and -45 °C. Bio-naphtha also formed with a yield of 2–5.5%, which can be used as a feedstock of naphtha isomerization. All of the products are free of aromatics, sulphur and nitrogen content, so they are environmentally sound blending component.

Keywords: biogasoil, bio-jet fuel, bio-naphtha, isomerization, Pt/SAPO-11

Introduction

In the last decade, the express population growth of the world and the increase of the living standard in the developing countries have increased significantly the energy demand of the World. Besides, the demand of fuels has constantly extended. In the developed countries of the World environmental regulations were made to protect the environment and to stimulate the economy. Because of these effects and environmental advantages the role of bio-fuels has become more and more important [1-5]. Bio-fuels are materials which are suitable for carrying energy and drive engines, and are produced by different ways from different biomass such as agricultural products and/or wastes.

Because of the several disadvantages of the currently used bio-fuels and those production technologies and of the different demands and incentives the research, development and market introduction of second or new generation bio-fuels came into front in European Union [6-8], USA [9] and on other part of the world [10]. Accordingly products of different composition have to be produced.

Because of these in the last few years intensive research-development activity started in the field of production and utilization of Diesel fuels produced from natural triglycerides via thermal or mainly catalytic processes. Beside these bio-fuels one of the most promising one is the so-called biogasoil, which can be produced from natural triglycerides by catalytic hydrogenation *(Fig. 1)* [11-15].

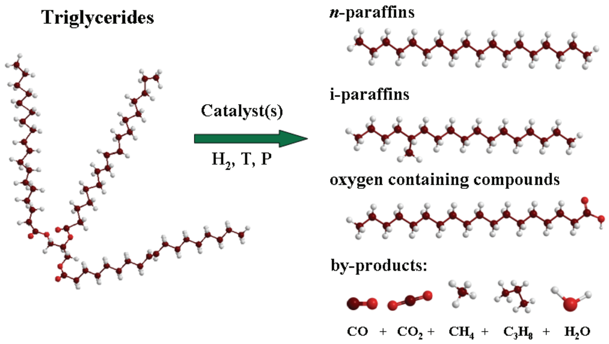


Figure 1: Reaction scheme of the biogasoil production

During the catalytic hydrogenation – as a function of the catalyst and process parameters – normal paraffins form which carbon number is the same or shorter by one than that of the carbon number of the fatty acid of the triglyceride [13, 16]. The concentration of iso-paraffins – as a function of the catalyst and process parameters – generally do not exceed 30%; often less than 10% [13]. The concentration of the intermediate oxygenic compounds (e.g. mono and diglycerides, carboxyl acids, esters, etc.) is often below 0.5% over the high activity heteroatom removal catalysts [14].

As a feedstock of biogasoils not only soy, palm, coconut, rapeseed and sunflower oils are suitable (which are cultivated currently in large quantities for biodiesel production), but the waste triglycerides such as used cooking oils, waste animal fats, greases from meat and leather processing industry, brown greases of sewage farms, saturated fatty acids of palm oil production, as well. In the last few years, in order to broad the feedstock supply the cultivation of such oil plants started which can subsist on unarable lands or salt water coasts, as well (jatropha, mahua, karanja, neem, jupati [17-19]). Furthermore the production of algae and fungal oils are intensively researched, as well [19-23].

The second step of the biogasoil production is the isomerization of paraffin rich mixture to improve the cold flow properties. During this process branched hydrocarbons form from linear paraffins, which freezing point is lower by 20–30 °C than that of the convenient normal paraffins *(Fig. 2)*, while their cetane number is still higher than it is specified in the current Diesel standard *(Fig. 3)* [24].

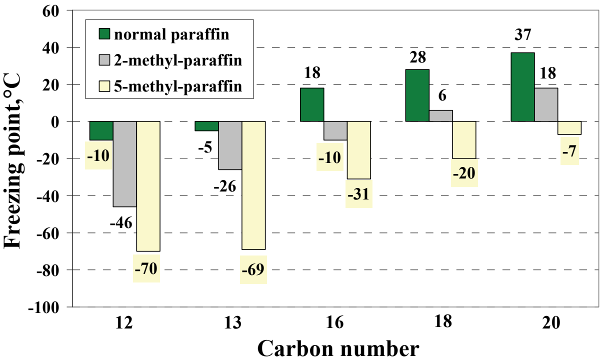


Figure 2: Freezing point of some iso and normal paraffin as a function of the carbon number

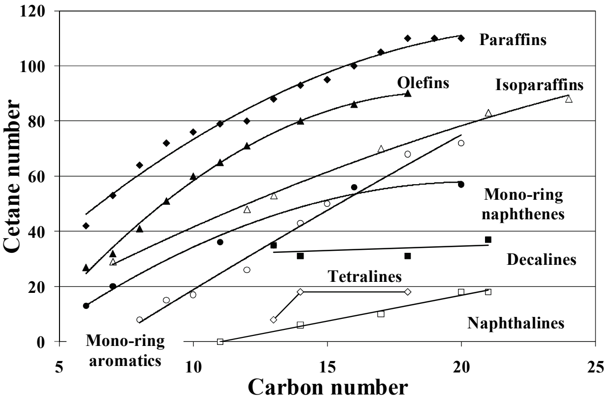


Figure 3: Cetane number of different hydrocarbons as a function of carbon number

During the catalytic hydroisomerization hydrocracking reactions also take place in different measure as a function of the applied catalyst and process parameters. During these reactions smaller molecule mass hydrocarbons form which have different number of branching. In the research field of isomerization of bioparaffins only a few research paper were published. These have not discussed the yield of the products and those performance properties in detail and with academic depth.

Accordingly the aim of our present contribution was the conversion of hydrocarbon mixture produced from sunflower oil in order to be suitable to use in Diesel engines as fuel or blending component. During this we investigated the change of yield and composition of the product over Pt/SAPO-11 catalyst found to be favourable in our pre-experiments.

Experimental

During the experiments the process temperature was varied between 300 and 380 °C, while liquid hourly space velocity (LHSV) was changed between 0.5 and 4.0 h^{-1}. The process pressure was 40 bar which was found to be favourable in our experiments over 0.5% Pt/SAPO-11 catalyst [11, 15]. Applying lower pressure resulted loss of yield and catalyst deactivation because of the intensifying cracking reactions, while the use of higher pressure did not have further beneficial effect on the product yield and composition.

The value of the H_2/feedstock ratio was unchanged; it was 400 Nm^3/m^3. During our pre-experiments it was found that the utilization of lower amount of hydrogen causes the increase of the cracking reactions which led to the decrease of the isoparaffin content of the product. The utilization of higher amount of hydrogen/feedstock ratio – higher than 400 Nm^3/m^3 – is unfavourable regarding economical aspects; moreover it could retard the degree of the isomerization [11, 15].

Apparatus

The experiments were carried out in an apparatus containing a tubular down-flow reactor of 100 cm^3 effective volume. It contains all the equipment and devices applied in the reactor system of an industrial heterogeneous catalytic plant [13]. The experiments were carried out in continuous operation with steady-state activity catalyst.

Materials and methods

Table 1 contains the properties of paraffin mixture produced from sunflower oil used as feedstock. The properties of the feedstock and the products were determined according to the test methods specified in EN 590:2009 Diesel fuel standard. The hydrocarbon composition was measured by Shimadzu 2010 GC using Zebron DB-1HT (30 m x 0.32 mm x 0.1 µm) column.

The catalysts were prepared as described and characterized according to HU 225 912 patent. The crystal structure and the purity of the catalyst were determined by X-ray diffraction (XRD). XRD characterization of the obtained powder confirmed that it was SAPO-11. The synthesized SAPO-11 microporous molecular sieve was impregnated with $Pt(NH_3)_4Cl_2$ solution. The platinum content of the catalyst was determined according to UOP-274 standard.

Table 1: The main properties of the feedstock

Properties		Value
Density at 40°C, g/cm^3		0.7697
Kinematical viscosity, 40°C, mm^2/s		3.714
Cold filter plugging point, °C		+23
Flash point, °C		50
Sulphur content, mg/kg		3.4
Nitrogen content, mg/kg		2.3
Acid number, mg KOH/g		1.9
Iodine number, g I_2/g		<1
Paraffin content, %	C_{17}-	7.0
	n-C_{17}	46.8
	i-C_{17}	0.8
	n-C_{18}	42.9
	i-C_{18}	0.9
	C_{18}+	1.7

The dispersity of the platinum was determined by H_2 chemisorption, which was 91%. The BET surface area of the catalyst was 100.1 m^2/g. The acidity of the catalyst determined by NH_3 adsorption was 0.66 mmol NH_3/g. Prior to activity measurements the catalysts were pretreated in situ, as described in our earlier publication [11].

Results and discussion

The products obtained during the isomerization of the paraffin rich feedstock were the mixtures of liquid and gas phase hydrocarbons. The gas products were generated by the hydrocracking side reactions. They contained mainly butane and isobutane (more than 40% of the gas phase). These can be used for several purposes in a refinery e.g. LPG production, alkylation of i-C_4 with olefins, dehydrogenation of i-C_4 to isobutylene, etc.

The liquid products were the mixtures of iso and normal paraffins. These were separated by distillation to gasoline (C_5-C_9 hydrocarbons; B.P.: 40–160 °C) and jet fuel fraction (C_{10}-C_{13} hydrocarbons; B.P.: 160–240 °C) as valuable side product and to the gas oil boiling range (C_{14}-C_{22} hydrocarbons; B.P.: 240–360 °C) main product.

The yields of products

The yield of the liquid product mixtures decreased by increase of the level of the conversion (by increasing the temperature and by decreasing the LHSV) *(Fig. 4)*. The reason of this was that the carbenium ions generated on the surface of the catalyst during the isomerization, having lower stability than that of the saturated hydrocarbons, could be cracked more easily at higher temperature [25]. In the investigated process parameter range, the yield of the product exceeded 85% in every case.

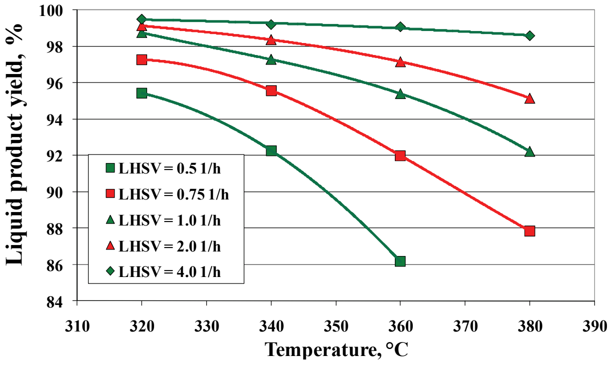


Figure 4: Product yields as a function of temperature and LHSV (P = 40 bar; H_2/HC ratio = 400 Nm^3/m^3)

The composition of the products

By increase the temperature up to about 360 °C the isoparaffin content of the products increased significantly, namely the degree of isomerization increased. However, at about 360 °C it reached a maximum, and then started to decrease. It was partly because of the thermodynamic inhibition (namely the isomerization is an exothermic reaction) and partly because of the increase of the cracking reactions *(Fig. 5)*. Cracking reactions not only decreased the yield of isoparaffins, but caused coke formation, that decreased the activity of catalyst, as well.

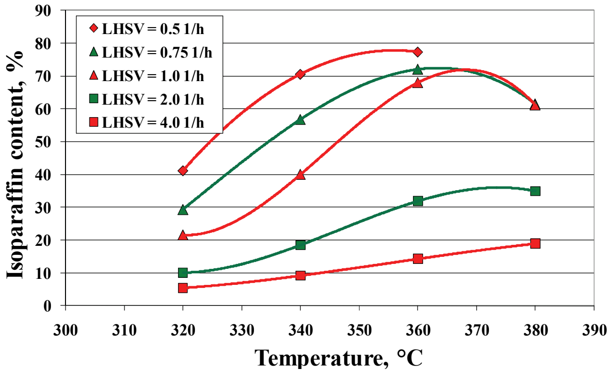


Figure 5: Isoparaffin content of the products as a function of temperature and LHSV
(P = 40 bar; H_2/HC ratio = 400 Nm^3/m^3)

The carbon number based fraction distribution and the faction composition of some products are given in *Fig. 6*. It presents well that the share of C_{14}-C_{19+} fractions decreased while that of C_3-C_{13} fractions increased by the increase of the conversion. Methane and ethane were not found in gas products. It suggested that cracking of hydrocarbons occurred by beta cracking, wherein cracked products having at least three carbon number *(Table 2)* [25]. The distribution of cracked products was not similar to that of the theoretical, modal cracked product distribution, it was shifted toward to lighter hydrocarbons. It indicated that the secondary cracking of long chain hydrocarbons took place as well.

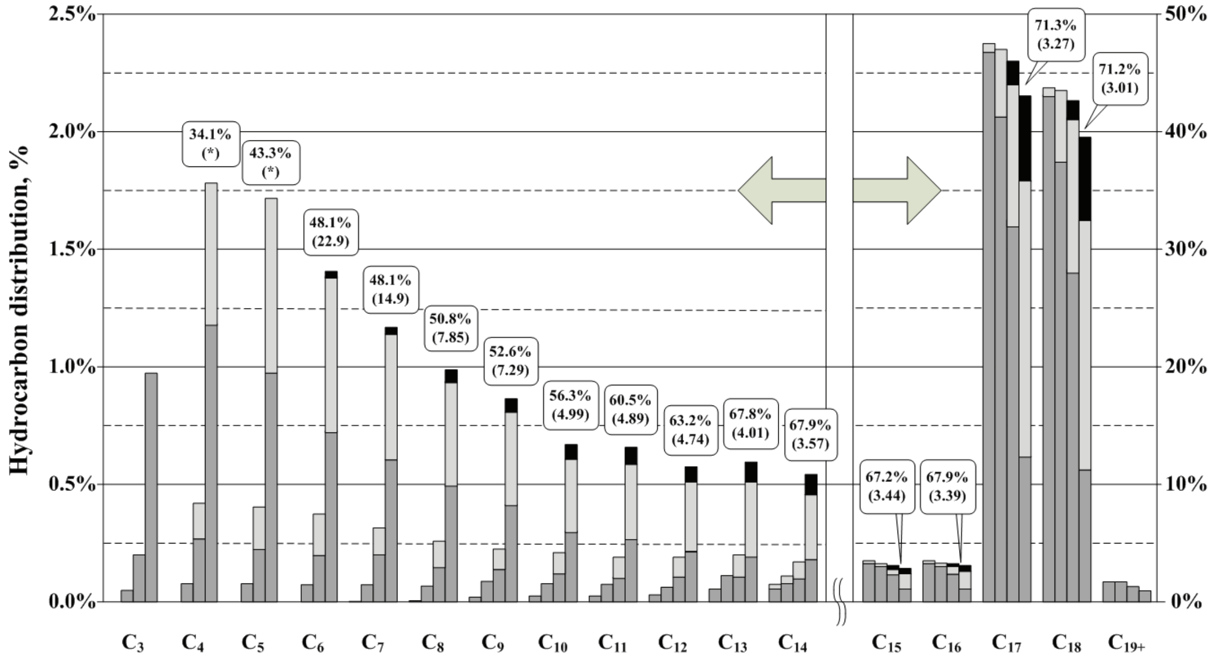
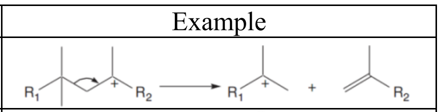
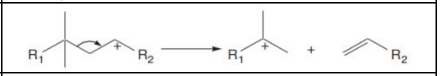
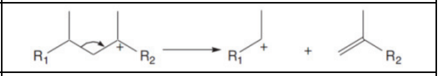
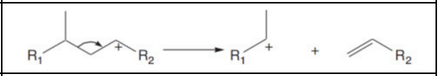
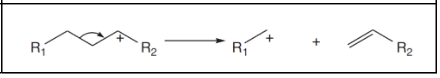


Figure 6: Hydrocarbon composition of the feedstock and products obtained at LHSV of 4.0, 2.0 and 0.75 h^{-1} respectively (Upper number in the bubble is isoparaffin content of the given carbon number fraction; while lower value is the ratio of mono and multibranched isoparaffins of the given carbon number fraction; T = 360 °C; P = 40 bar; H_2/HC ratio = 400 Nm^3/m^3); * - can not be measured, or no such a compound.

Table 2: Five types of β-cracking

Type	NCA_{min}	Example
A	≥8	
B1	≥7	
B2	≥7	
C	≥6	
D	≥5	

NCA_{min}: Minimal carbon number of carbenium ion

The isoparaffin content and the ratio of mono/multi branched paraffins of the different fractions obtained at LHSV of 0.75 h^{-1} are presented in Fig 6. It can be seen well that concentration of isoparaffins formed from the dominant fractions (n-C_{15} – n-C_{18}) and the ratio of mono/multi branched paraffins were significantly higher than those of the lower molecule weight hydrocarbons.

The reason of these effects was the special pore structure of Pt/SAPO-11 catalyst. Namely, during the isomerization of paraffins over SAPO-11 catalyst, mainly mono and multi branched methyl paraffins form. Their cracking could happen via C and D type beta cracking (Table 2), because between the branchings of these multibranced paraffins have at least 3 or 4 carbon number distance [25]. Accordingly during the cracking of mono-methyl paraffins two normal paraffins form, while from dibranched paraffins a normal and an isoparaffin generate.

Investigation of the performance properties

The cold filter plugging point (CFPP) of diesel fuels is an importance performance property, because at decreased temperature the precipitated paraffin crystals can cause operational disorders or unserviceability of the fuel supply system.

The CFPP values of the products decreased by the increase of the temperature and the decrease of the LHSV. Its reason was mainly the increase of the isoparaffin content of the products. The lower molecule weight compound formed in the cracking reactions also improved the CFPP value, as they have lower freezing point. Accordingly, at the favourable operational parameters (T = 360 °C, p = 40 bar, LHSV = 0.75–1.0 h^{-1} and H_2/feedstock ratio of 400 Nm^3/m^3) the CFPP value of the products was between -11 and -15 °C.

By the increase of the conversion the concentration of the multibranched paraffins increased. It had a positive effect on the cold flow properties of the products. However, another important performance property, the cetane number varied somewhat unfavourably. Consequently during the catalytic conversion the cetane number of the products decreased relative to that of the feedstock (101 unit) as a function of the conversion. However, products obtained at the favourable process parameters still had a cetane number of 76–88. These exceed significantly the standard value of 51.

Investigation of side products

During the isomerization about 1–3% of side-product having jet fuel boiling range was formed. In case of this fraction the key characteristics are the crystallization point and the smoke point. The obtained jet fuel fractions had an isoparaffin content of 40–70%, wherein 5–20% was the concentration of multi-branched isoparaffins. Consequently these fractions had a crystallization point of between -55 °C and -50 °C, so they could satisfy the standard value of at most -40 °C or -50 °C values. Since they are free of aromatics, sulphur and nitrogen they burn cleanly.

At the investigated parameter ranges 3–7% of light hydrocarbons having gasoline boiling range also formed in the cracking reactions. In case of this fraction the key characteristics is the octane number. In spite of that this fraction contained about 40–50% of isoparaffins, the octane number was low, because they were mainly mono-branched isoparaffins. We note that the multi-branched paraffins having high octane number cannot be formed over SAPO-11 catalyst because of the special pore structure. However these fractions were free of sulphur, aromatics, benzene and olefins, so they are good feedstock for naphtha isomerization plants.

The obtained propane-butane fraction can be used as heating gas, or might be used in alkylation plants because of its high isobutene content.

Summary

During our experiments the production possibilities of biogasoil with good cold flow properties was investigated using a mixture of n-paraffins over Pt/SAPO-11 catalyst.

Based on the results it was found that up to a limit the increase of the temperature and decrease of the LHSV were favourable for the conversion of n-paraffins. Regarding the yield, the CFPP value and cetane number of the products the most favourable parameter combination was the temperature of 360 °C, pressure of 40 bar, 1.0 h^{-1} of LHSV and 400 Nm^3/m^3 H_2/feedstock ratio.

At the favourable process parameters product had high yield (95.4%) and high iso-paraffin content (68.0%). At this parameter combination the CFPP of the product was favourable (-11 °C), which satisfy the summer grade quality (+5 °C) of diesel standard, and with some addition can satisfy the winter grade specification (-20 °C), as well. The cetane number of this practically heteroatom and aromatic free product was about 77 unit, which is significantly higher than that is specified in the Diesel fuel standard (51).

The jet fuel boiling range side-products had perfect freezing point (between -55 and -50 °C), and they can satisfy all of the specification of the standard. The gasoline boiling range compounds can be converted to excellent quality gasoline blending compounds by isomerization.

Acknowledgement

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