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ISOMERIZATION OF PARAFFIN MIXTURES PRODUCED FROM SUNFLOWER OIL

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The importance of biofuels becomes more acute, especially in the European Union. Beside them, the bio gas oil 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 triglycerides. In this paper the isomerization of different intermediate products obtained over different hydrogenation catalysts and having high n-paraffin content was studied on SAPO-11 catalyst at 300–380 °C temperature, 20–80 bar pressure, 0.5–3.0 h^{-1} of liquid space velocity and 400 Nm^3/m^3 of H_2/feed ratio. It was found that the oxygen containing intermediate products significantly changed the degree of isomerization, but the hydrocarbon composition and the aromatic content of the n-paraffin mixtures had no noticeable effect on the conversion. During the experiments excellent quality diesel gas oil blending components were produced with high i-paraffin content and they were practically free of heteroatom content.

Keywords: bio gas oil, isomerization, Pt/SAPO-11, oxygen containing compounds, hydrocarbon composition, aromatics

Introduction

Biofuels and bio blending components have higher and higher importance because of their economical and environmental advantages both in Europe and on the other parts of the World [1-2]. Mainly the second generation ones have very favourable composition, since they are practically free of sulphur and nitrogen, and their olefin and aromatic content is close to zero. They contain mainly iso and normal paraffins which have very favourable performance properties. Consequently during their combustion environmentally and toxicologically harmful compounds (SO_x and NO_x) do not form, their combustion is clear (low particle emission), furthermore the greenhouse gas emission is significantly lower relative to the whole life cycle [3].

Nowadays mainly the mixture of fatty acid methyl esters (biodiesels) are used as biocomponents of Diesel fuels which are produced from different vegetable oils and used cooking oils by transesterification with generally methanol. But these have numerous disadvantages such as they form deposits in the fuel supply system and the combustion chamber, they have poor storage (heat and oxidation) stability because of the olefinic double bonds of the molecules, they tend to water uptake, the esters bond tend to be hydrolysed resulting corrosive acids, they shorten the oil change interval, etc. [4].

Consequently in the European Union the maximum blending quantity of fatty acid methyl esters into Diesel fuels was limited to 7.0 v/v% by the EN 590:2009 standard based on the proposition of the vehicle manufacturers. At the same time the use of at least 10% of bio origin component is a target up to 2020 in the EU.

Because of these disadvantages and of the quantity of bio-origin fuels can be increased from the natural triglycerides (conventional and improved vegetable oils, used cooking oils and fats, greases from meat and leather processing industry, “brown grease” of sewage farms, etc.) such kind of fuel components have to be produced which molecular structure differs from that of the fatty acid methyl esters. This kind of compounds are hydrocarbons produced by heterogeneous catalytic hydrogenation of triglycerides, consisting mainly from mixtures of normal paraffins, consequently they have not possess with the disadvantageous properties of biodiesels [4].

However the cold flow properties of these mixtures rich (>95%) in normal paraffins (mainly n-C_{12}-n-C_{20}) are unfavourable (the freezing point of normal paraffins is high, e.g. n-C_{18}: +28 °C). This characteristic generally can be improved by additivation and/or isomerization. But the currently used flow improver additives were not effective enough in case of these products of new composition [5]. Accordingly the isomerization seems to be the suitable finishing process step to produce mixtures with good cold flow properties and high cetane number [4, 6-7].

The composition of the mainly n-C_{12}-n-C_{20} mixtures obtained by the fuel purpose hydrogenation of triglycerides can be significantly different depending on the used feedstock and catalytic system (catalyst, process parameters) [4, 8-12]. The oxygen removing reactions change as a function of the catalyst and process parameters. For example at elevated temperature and on higher acidity catalyst the decarboxylation reaction became dominant resulting shorter hydrocarbon chain by one carbon number than that of the fatty acid. Side reactions also take place during the oxygen removal. For example by increasing the severity of operational parameters the cracking reactions become dominant, furthermore the aromatization may also take place over high activity catalysts or at high temperature.

Accordingly the aim of present paper was the investigation of the effect of feedstock on the hydro-isomerization of normal paraffin rich (>95%) mixtures (produced from sunflower oil) over 0.5% Pt/SAPO-11 catalyst.

Experimental part

Experiment were carried out at the operational parameter combinations found to be favourable in our pre-experiments over 0.5% Pt/SAPO-11 catalyst [6, 7], which were the following: temperature = 300–380 °C, pressure = 20–80 bar, liquid hourly space velocity (LHSV) = 0.5–3.0 h^{-1}. The value of the H_2/feedstock ratio was unchanged; it was 400 Nm^3/m^3.

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. The experiments were carried out in continuous operation with steady-state activity catalyst.

Materials and methods

During our heterogenic catalytic experiments paraffin mixtures produced from two different sunflower oil (“A”: palmitic acid 4.5%, stearic acid: 2.1%, oleic acid: 63.2%, linoleic acid: 20.6%, linolenic: 6.8%, other carbon acids: 2.8%; “B”: palmitic acid: 6.6%, stearic acid: 3.7%, oleic acid: 26.4%, linolic acid: 62.2%, other fatty acids: 1.1%) were used, which main properties are summarized in *Table 1*.

Feedstock “A1” was produced from sunflower “A” over sulphided NiMo/Al_2O_3 catalyst (nickel content: 3.2%, molybdenum content 13.4%; BET specific surface area: 214 m^2/g; acidity: 0.489 mmol NH_3/g) having high activity, so it practically contained only paraffins. Feedstock “A2” was blended from “A1” and 0.5% oleic acid to investigate the effect of oxygen content. Feedstock “B1” was produced from sunflower “B” over Raney-Nikkel catalyst (nickel content: 65.3%, aluminium content: 34.4%; BET surface area: 68 m^2/g) having very high activity; however beside the cracking reaction the aromatization took also place because of the high reaction heat. Feedstock “B2” was obtained by the distillation of “B1” at 330 °C, while the most of the C_{18} fatty acids which were the most dominant oxygen containing compounds were removed.

As catalyst we used Pt/SAPO-11, which contained micro and mesopores as well (platinum content: 0.5%; Pt-dispersity: 69%; BET surface area: 105 m^2/g; acidity: 0.661 mmol NH_3/g). It was prepared according to HU 225 912 patent [13]. Prior to the activity measurements the SAPO-11 catalyst were pre-treated in situ, as described in our earlier publication [13].

Table 1: The main properties of the used paraffin mixtures (the type of the used hydrogenation catalyst)

Property	Sign of the feedstock, (hydrogenation catalyst)				Analytical method
	“A1” (sulphided NiMo)	“A2” (sulphided NiMo)	“B1” (Raney Nickel)	“B2” (Raney Nickel)	
Composition, %					Shimadzu 2010 GC
$i\text{-}C_{15}$	0.05	0.05	0.09	0.10	
$n\text{-}C_{15}$	3.10	3.10	6.00	6.70	
$i\text{-}C_{16}$	0.04	0.04	0.22	0.24	
$n\text{-}C_{16}$	3.15	3.15	4.40	4.90	
$i\text{-}C_{17}$	0.26	0.26	2.45	2.70	
$n\text{-}C_{17}$	47.30	47.10	64.70	72.00	
$i\text{-}C_{18}$	0.33	0.33	1.05	1.10	
$n\text{-}C_{18}$	43.90	43.70	13.60	9.10	
Total isoparaffin content,%	0.75	0.75	4.30	4.75	
Oxygen containing intermediate products, %	0.06	0.55	4.95	0.60	
CFPP, °C	23	23	22	21	EN 116:1997
Aromatic and naphthenic content, %	<0.1	<0.1	2.3	2.1	EN 12916

CFPP: Cold Filter Plugging Point

Test and calculation methods

The characteristics of the feedstock and the products of gas oil boiling range were determined according to test methods specified in EN 590:2009 diesel fuel standard, while the hydrocarbon composition was measured by Shimadzu 2010 GC using Zebron DB-1 high temperature (30 m x 0.32 mm x 0.1 µm) column.

The repeatability of measurements for determination of hydrocarbon composition was the following:

Hydrocarbon concentration range, %	Repeatability*, abs%	Relative error**, rel%
≥30	0.3	≤1
≥5–30	0.2	1–4
≥2–5	0.15	4–7.5
≥0.5–2.0	0.1	7.5–20
≥0.1–0.5	0.03	20–30

* maximum deviation of two parallel GC test results

** maximum relative deviation of two parallel GC test results

The crystal structure and the purity of the SAPO-11 catalyst were determined by X-ray diffraction (XRD). XRD characterization of the obtained powder confirmed that it was SAPO-11. The platinum content of the catalyst was determined according to UOP-274 standard. The platinum dispersion was determined by H_2 chemisorption. The surface properties of the catalyst were determined by ASAP 2000 equipment (Micromeritics) and mercury penetration method using CARLO-ERBA equipment. The acidity of the SAPO-11 catalyst was measured by NH_3 adsorption.

Results and discussion

During the heterogeneous catalytic experiments we investigated the effect of the composition of paraffin mixture, namely the indirect effect of process parameters and the used catalyst of the hydrogenation on the activity, selectivity and performance of the 0.5% Pt/SAPO-11-Al_2O_3 isomerization catalyst.

The products obtained during the isomerization of the paraffin rich feedstocks were the mixtures of liquid and gas phase hydrocarbons at every investigated operational parameter. The gas products generated by the hydrocracking side reactions contained mainly butane and isobutane (>40% in the gas phase). These could 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 feedstocks of the isomerization contained in the highest concentration (91–98%) C_{15} and C_{18} hydrocarbons and gasoil boiling range, smaller molecule mass hydrocarbons (C_{11}-C_{14}) in different concentration, furthermore higher molecule mass compounds (C_{19+}) in a small quantity (<2.0%; which were mainly C_{19}-C_{22} paraffins and different oxygenic compounds). In the C_{10}-C_{18} fractions the alteration of the concentration of the normal and isoparaffins could be detected exactly by the used gas chromatography method, so the degree of the structure conversion could be observed as a function of the operational parameters.

The yield of the products

The yields of the products decreased by increasing the temperature and decreasing the LHSV *(Fig. 1)*, furthermore by decreasing the pressure *(Fig. 2)* in case of every feedstock. This was because of the increasing rate of cracking reactions took place beside the isomerization and because of the longer contact time of hydrocarbons.

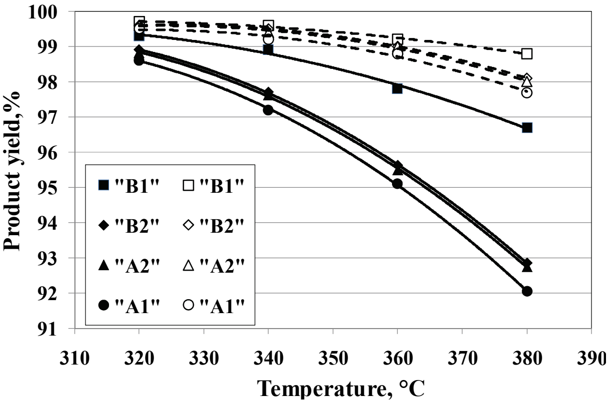

Figure 1: The product yields as a function of the temperature (P = 40 bar; continuous line: LHSV = 1.0 h^{-1}; broken line: LHSV= 3.0 h^{-1})

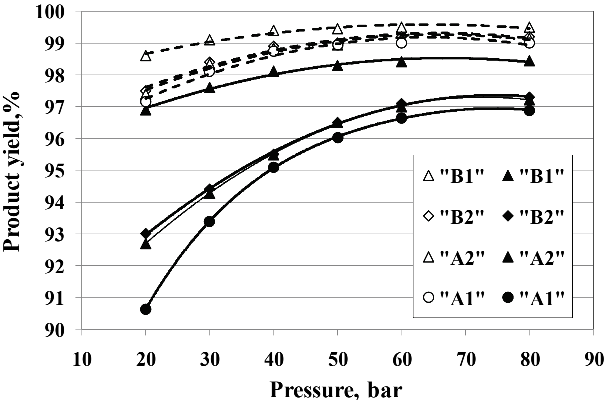

Figure 2: The product yields as a function of the pressure (LHSV = 1.0 h^{-1}; continuous line: T = 360°C; broken line: T = 320°C)

By decreasing the LHSV the flow rate of the molecules slowed down on the surface of the catalyst particles resulting increased degree of cracking. By decreasing the pressure the partial pressure of the hydrogen decreased, accordingly the hydrogenation rate of the unstable iso-carbenium ions formed during isomerization decreased. Consequently they could be cracked easier. The yields of the products decreased in the order of "B1" >> "B2" ≈ "A2" > "A1" as a function of the feedstock. It was because the more oxygen containing intermediate was in the feedstock the higher inhibition of the cracking reactions was manifested by these components and the forming water [14, 15].

The composition of the products

By increasing the temperature the isoparaffin content of the products increased significantly above 320 °C in case of all feedstock, namely the degree of isomerization increased. However, at about 360–380 °C it reached a maxima 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. This effect was intensified by the decrease of the liquid space velocity *(Fig. 3)*.

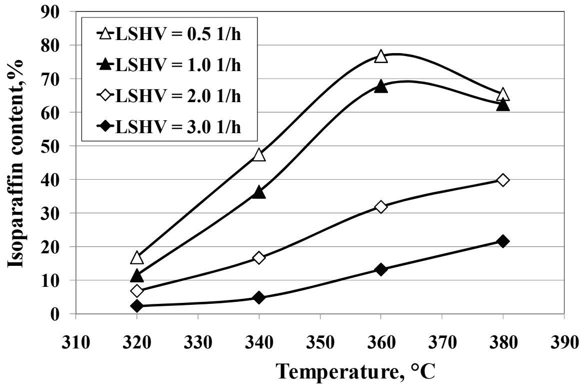

Figure 3: Isoparaffin content of the product as a function of the temperature (Feedstock „A1"; P = 40 bar)

The isoparaffin content of the products obtained from feedstock "B1" was significantly lower than the other feedstock. *(Fig. 4)*. It was because feedstock "B1" contained relatively high amount of oxygen containing intermediate products (mainly fatty acids). These compounds partly cover the active sites of isomerization; the water formed from them can react with the Brønsted acidic sites of the catalyst resulting irreversible structure damage [4, 16] and decreased acidity; the forming CO can adsorb on the surface of the platinum [17, 18], which decrease the hydrogenation activity, so thus induce cracking or coking, as well.

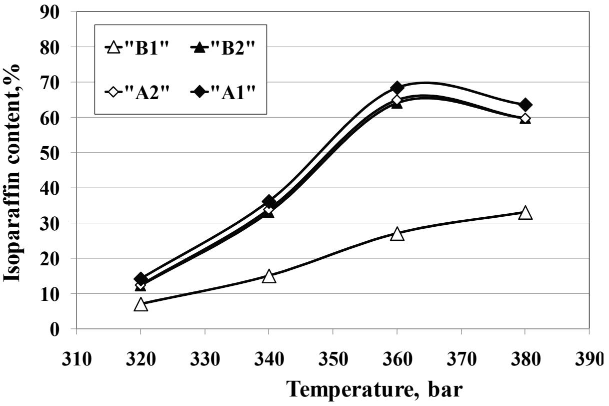

Figure 4: Isoparaffin content of the product as a function of the feedstock (LHSV = 1.0 h^{-1}, P = 40 bar)

These harmful reactions decreased the degree of isomerization. Consequently, by the decrease of the intermediate concentration of the feedstock the isoparaffin concentration of the product ("A1" > "A2" ≈ "B2" >> "B1") increased.

It was also concluded, that the carbon number change of the hydrocarbons caused by the different degree of decarboxylation/decarbonylation and hydrodeoxygenation reactions took place on different hydrogenation catalysts had no demonstrable effect on the isomerization, namely in case of "A2" and "B2" feedstock the isoparaffin content of the product was practically the same.

Furthermore, in the investigated concentration range (0.1–2.3%) the aromatic compounds did not inhibit the isomerization reactions in higher degree than the limit of the measure. This and that the aromatic content of feedstock "B1" and "B2" significantly decreased during the isomerization proved the high hydrogenation activity of the platinum containing catalyst [19].

The performance properties of the products

As by the increase of the temperature and decrease of LHSV the isoparaffin content of the product increased the cold filter plugging point (CFPP) of the products decreased. It was because the freezing point of the isoparaffins is lower than that of the normal paraffins and the lighter gas oil boiling range compounds (B.P. > 180 °C) formed by cracking in small quantity (<10%) also improved the CFPP value. Above 360–380 °C the CFPP values were not decreased further (between -15 and -5 °C), because the isoparaffins were decomposed by the intensive cracking. In case of the investigated mixtures the hydrocarbon composition and the aromatic content of the feedstock did not influenced noticeably the CFPP value. But the oxygen containing intermediate products remarkably hindered the improvement of cold flow properties.

The cetane number of the products decreased as a function of the conversion relative to the feedstock (97–101). Anyway the derived cetane number of the products (determined with a CID 510 Derived Cetane Number Analyzer according to ASTM D7668 standard) with favourable cold flow properties was about 71–83 unit (the shorter or branched hydrocarbons have lower cetane number [20]). These values were significantly higher than the specified values of at least 51 (EN 590 Diesel standard).

Conclusion

It was concluded that the oxygen containing intermediate products had significant effect on the isomerization of different paraffin mixtures (produced from sunflower oil) over 0.5%Pt/SAPO-11 catalyst. Because of the good hydrogenation activity of the platinum containing catalyst the aromatic compounds did not inhibit the isomerization reactions. Due to the difference in the reactivity of long alkanes (C_{15}-C_{18}) is relatively small the hydrocarbon composition had no notable effect on the degree of conversion.

The main product having gas oil oiling range reached had the highest isoparaffin content at 360 °C and LHSV of 0.5–1.0 h^{-1} (65–70%) *(Table 2)*. At higher temperature the degree of cracking was significant. The cold filter plugging point of the products decreased with the increase of the isoparaffin content. These isoparaffin rich products satisfy the summer grade regulation of CFPP value (at most +5°C; EN 590:2009 diesel fuel standard) and are above just a few the winter grade specification (CFPP at most -20 °C).

Table 2: The main properties of the product obtained from feedstock “A1” over Pt/SAPO-11 at 360 °C, p = 40 bar; LHSV = 1.0 h^{-1}, H_2/HC ratio: 400 Nm^3/m^3

Property	Value
Hydrocarbon composition, %	
i-C_{15}	1.73
n-C_{15}	1.42
i-C_{16}	2.45
n-C_{16}	2.10
i-C_{17}	34.00
n-C_{17}	19.50
i-C_{18}	24.80
n-C_{18}	9.40
Total isoparaffin content,%	67.80
Oxygen content, %	<0.05
CFPP, °C	-11
Derived Cetane Number	78
Aromatic and naphthenic content, %	<0.1

To sum it up over the selected 0.5% Pt/SAPO-11 catalyst and at the favourable process parameters (T = 360 °C, p = 40–60 bar; LHSV = 1.0 h^{-1}, H_2/HC ratio: 400 Nm^3/m^3) excellent quality (cetane number: 71–83), environmentally sound (sulphur and nitrogen content below 10 mg/kg, aromatic content <1%) gas oil blending component was produced from natural feedstock.

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