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PRODUCTION OF BIO-ISOPARAFFINS BY HYDROISOMERISATION OF BIOPARAFFINS

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The importance of biofuels becomes more acute, especially in the European Union. Beside them, those second generation products are spreading increasingly which have better product and performance properties relative to the first generation biofuels. 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 isomerisation of an intermediate product with high n-paraffin content was studied on SAPO-11 catalyst at 300–360 °C temperature, 20–40 bar pressure, 1.0–3.0 liquid space velocity and 400 Nm^3/m^3 H_2/feed ratio. During the experiments we succeeded to produce an excellent quality diesel gas oil blending component with high i-paraffin content which is practically free of heteroatom content. This product satisfies with some addition all the requirements of the European diesel fuel standard.

Keywords: bio gas oil, catalytic hydroisomerisation, SAPO-11 catalyst.

Introduction

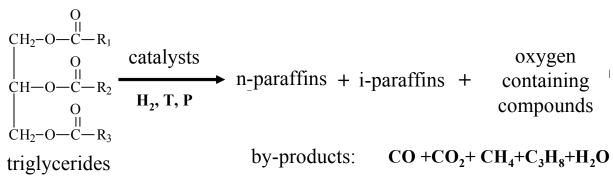
The continually increasing quantity demand, the efforts to decrease the crude oil dependency of several countries all over the world, the prediction exhaust of crude oil reserves, the increasing crude oil price, the environmental regulations and the requirements of the European Union induce the increasing importance of biofuels which can be produced from agricultural products and wastes, and this tendency will go on in the close future [1-6].

The different vegetable oils, and the different esters of them, furthermore the products obtained from the previous ones by catalytic hydrogenation belong to biofuels. As unconverted vegetable oils did not come up to the expectations as Diesel fuel, the chemical conversion of these vegetable oils is necessary in order to produce proper quality fuels and fuel blending components [7-8].

Nowadays among biofuels the biodiesel has been used in the highest degree which is produced by the transesterification of vegetable oils. It has numerous disadvantages, for example: poor heat and oxidation stability, hydrolysis sensitivity (corrosion), low energy content, unfavourable cold start properties, high viscosity, etc [7-8].

In the near future the bio gas oil which is biofuel with high isoparaffin content in the gas oil boiling range produced by the catalytic hydrogenation of different triglycerides (conventional and ennobled vegetable oils, used cooking oils and fats, greases from meat-packing and leather-work, “trap grease” from sewage farm, etc.) [8-12] provides a good solution to satisfy the bio component demand in gas oil.

During the reactions of catalytic hydrogenation of triglycerides mainly normal and isoparaffins, propane, carbon-oxides (CO_2, CO), water and other oxygen containing compounds are generated according to next gross reaction equation [8-15]:



The diesel fuel requirements can be satisfied by high n- and i-paraffin containing blending components with reduced aromatic content (which are practically free of sulphur and nitrogen). At arctic climate and at winter time in the temperate zone the normal paraffins with high carbon number in the diesel fuel are unfavourable regarding the cold flow properties, which affect unfavourably the freezing point, cloud point and cold filter plugging point (CFPP). Consequently, to improve the cold properties, the catalytic paraffin conversion technologies are becoming more and more important [12-15].

During the production of bio gas oils by catalytic hydrogenation the products have generally high n-paraffin content. So the catalytic paraffin conversion has high significance, because the cold properties (for example the cold filter plugging point) could not satisfy the specifications of diesel fuel quality standard. With the newest improved high activity catalyst high isoparaffin containing products can also be produced, by this way the CFPP values are more favourable, because of the lower freezing point of isoparaffins relative to normal paraffins [12-15].

Experimental work

The aim of our experimental work was the investigation of production possibilities of bio gas oil with good flow properties by catalytic paraffin conversion from high n-paraffin containing mixture produced from sunflower oil by catalytic hydrogenation.

Besides, our objective was to determine the effects of the favourable operational parameters (temperature, pressure, space velocity, hydrogen/feed ratio) on the yield and quality of the products on the used Pt/SAPO-11 catalyst.

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 [9].

Materials

The main properties of feedstock used in these heterogen catalytic experiments are presented in *Table 1*. The catalyst was an expediently chosen Pt/SAPO-11 catalyst [10].

Table 1: The main properties of the high n-paraffin containing 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

Analytical and calculation methods

The properties of the feedstock and the products were measured according to the methods of the EN 590:2004 standard and those were calculated according to the standard methods. These methods and the standard deviations of these analytical methods are summarized in *Table 2*.

Table 2: The applied analytical methods and theirs standard deviations

Properties	Method/device	Standard deviations*
Density, g/cm^3	EN ISO 12185:1998	± 0.0015
Viscosity, at 40°C, mm^2/s	EN ISO 3104:1996	± 0.03
Cold Filter Plugging Point, °C	EN 116:1999	± 1
Sulphur content, mg/kg	EN ISO 20846:2004 (Multi EA 3100 /Greenlab)	± 1.5
Nitrogen content, mg/kg	ASTM-D 6366-99 (Multi EA 3100 /Greenlab)	± 1.5
Hydrocarbon composition	gas chromatography (Trace GC 2000)	± 1 % rel

* In the investigated parameter range

Results and discussion

During our experiments we investigated the catalytic transformability of the high n-paraffin containing mixture produced by catalytic hydrogenation of Hungarian sunflower oil on Pt/SAPO-11 catalyst at 300–360 °C temperature, at 20–40 bar pressure, at 1.0–3.0 h^{-1} liquid space velocity and at 400 Nm^3/m^3 H_2/feed ratio. In this paper we present the major results of this experiment.

Product yields

During the experiments using this catalyst the yields of the products decreased by increasing the temperature and by decreasing the pressure and the liquid space velocity (*Fig. 1* and *2*) which was caused by the hydrocracking reactions which took place in an increasing degree beside the isomerisation reactions. In the ranges of the operational parameters the product yields were higher than 80% in all cases.

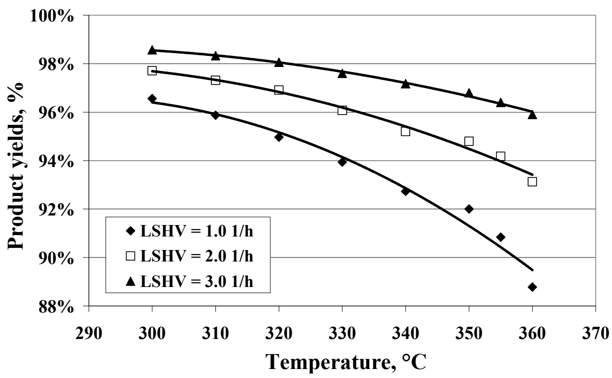


Figure 1: Product yields as a function of the temperature and the LHSV (p = 40 bar)

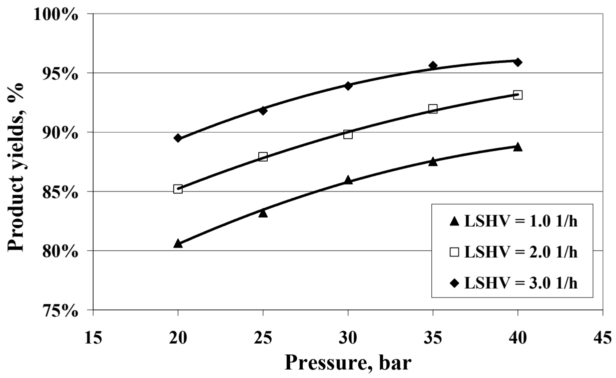


Figure 2: Product yields as a function of the pressure and the LHSV (T = 360 °C)

The composition of the products

The composition of the products was determined by gas chromatography. The products contained C_{17} and C_{18} hydrocarbons in the highest amount (85–92%) furthermore other compounds with lower (C_{17-}) and higher (C_{18+}) boiling point in minor amount.

In the C_{18} fraction by increasing the temperature the quantity of isoparaffins increased significantly above 340 °C. This effect was intensified by decreasing the liquid space velocity (*Fig. 3*). This figure also shows that the quantity of C_{18} hydrocarbons in the product decreased by increasing the temperature, which was caused by the hydrocracking reactions as it was mentioned earlier.

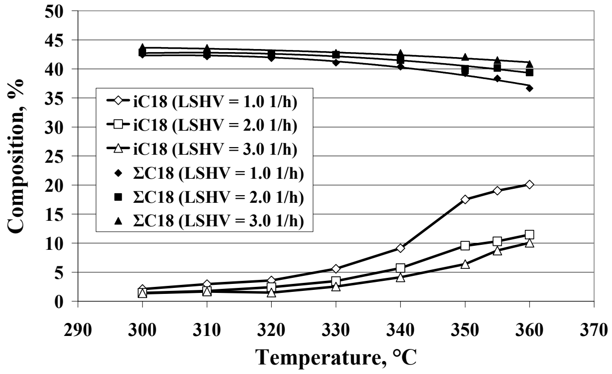


Figure 3: Composition of the C_{18} fraction as a function of the temperature and the LHSV (p = 40 bar)

In this fraction the quantity of isoparaffins increased by reducing the pressure, as well. The reason of why the decreasing pressure increased the rate of the formation of isomers and of lower components in the product is that the lower partial pressure of hydrogen the higher partial pressure of hydrocarbons, accordingly the rate of reactions increased, so the cracking reactions could become conspicuous, consequently the quantity of n-paraffins decreased.

In the C_{17} fraction (like in the C_{18} fraction) by increasing the temperature the quantity of isoparaffins increased significantly above 340 °C, which effect was intensified by decreasing the liquid space velocity (*Fig. 4*). This figure also illustrates that the quantity of C_{17} hydrocarbons in the product decreased by increasing the temperature.

In the C_{17} fraction the quantity of isoparaffins increased by reducing the pressure. By lowering the liquid space velocity the degree of the conversion increased in this case, as well. According to these effects the total isomer content increased by increasing the temperature and by reducing the pressure and the liquid space velocity (*Fig. 5*).

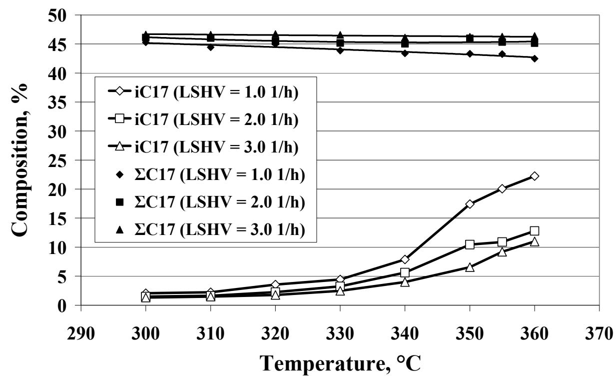


Figure 4: Composition of the C_{17} fraction as a function of the temperature and the LHSV (p = 40 bar)

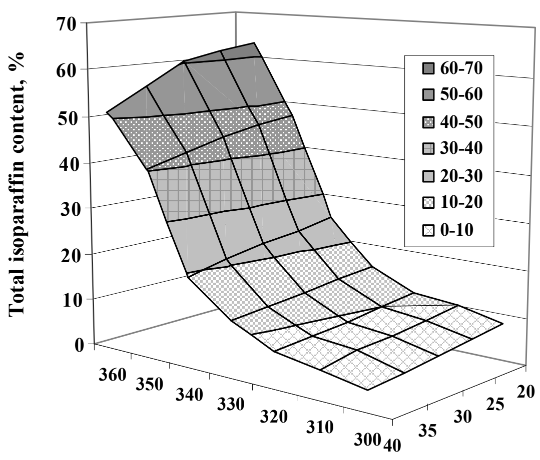


Figure 5: Total isoparaffin content of the products as a function of the temperature and the pressure (LHSV = 1.0 1/h)

The cold filter plugging point

The cold filter plugging point (CFPP) is an important performance parameter during the application of diesel fuels, namely the precipitation of paraffin crystals caused by decreasing the temperature leads to derangements or could cause unserviceability in the fuel supply system.

We found that the CFPP values of the products decreased by increasing the temperature and by decreasing the pressure and the liquid space velocity (*Fig. 6*). The reason of this fact was the increase of the isoparaffin content, namely the isoparaffins have a lower freezing point than n-paraffins do. In *Fig. 7* the correlation between the quantity of isoparaffins and the CFPP values can be seen. The CFPP values were also improved by the formation of lighter hydrocarbons generated in the hydrocracking reactions beside the isomerisation of paraffins.

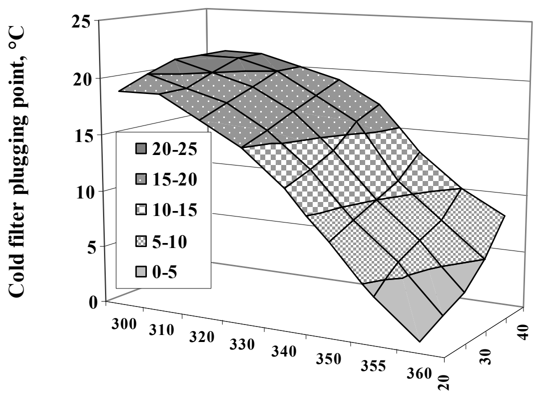


Figure 6: CFFP values of the products as a function of the temperature and the pressure (LHSV = 1.0 1/h)

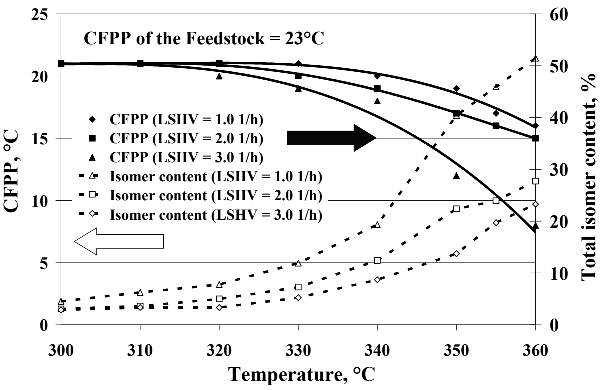


Figure 7: Total isoparaffin content and the CFFP value of the products as a function of the temperature and the LHSV (p = 40 bar)

Other product parameters

The removal of sulphur and nitrogen content from the fuels has numerous advantages. The most significant ones are that the storage stability of the products increase, the risk of corrosion decreases, the oil change interval is undiminished and the poisoning of the three-way catalyst is avoidable. Besides, the removal of heteroatoms is important from environmental and human biological considerations, because by this way the quantity of the harmful materials (sulphur-dioxide, nitrogen-oxides, etc.) generated during the combustion in the engine could be reduced, furthermore the medical risk caused by the carcinogenic heterocyclic nitrogen compounds could be decreased.

The sulphur content of the feedstock and consequently that of the products was lower than 10 mg/kg in all cases, which satisfied the requirements of the valid standard. All products had lower than 3 mg/kg sulphur content and lower than 2.5 mg/kg nitrogen content, and these values were several times close to the lower limit of the detection (it is about 0.5 mg/kg).

The values of the flash point were 35–45 °C in every case, because the flash point of the hydrogenated vegetable oil used as feedstock was also low, in addition the light component generated during the hydrocracking reactions had low flash point as well. This quality parameter could be easily set by a simple product distillation to the specified value of 55 °C of the standard.

During the investigation of the kinematical viscosity of the product at 40 °C, we found that the viscosity of the products decreased by increasing the reaction temperature and by decreasing the pressure and the space velocity, but these values satisfied the requirements of the standard in all cases.

Summary

During the experiments the production possibilities of bio gas oil with good flow properties from high n-paraffin containing mixture produced from sunflower oil by catalytic hydrogenation on SAPO-11 catalyst were investigated.

It was concluded that in the investigated process parameter range the higher temperature, the lower pressure and the lower space velocity are favourable for the isomerisation of the n-paraffins and for the decrease of CFPP values.

At 360 °C temperature, 30–40 bar pressure and 1.0 h^{-1} liquid space velocity the products had high yield (86–89 %) and high isoparaffin content (50–58 %). At these operational parameters the CFPP values of the products were favourable (between +8 °C and +3 °C). These values satisfy without addition the summer grade requirements of the standard and with some addition the further grade could be fulfilled as well. By the stabilisation of the product the flashpoint values agree with the regulation of the standard. The viscosity and the sulphur content of the products meet the specifications of the standard.

Summarizing, an excellent quality diesel gas oil blending component with high i-paraffin content was produced which was practically free of heteroatom content which satisfied with some addition all the requirements of the European diesel fuel standard.

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