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PRODUCTION OF DEPRESSED FREEZING POINT BIO GAS OIL FROM SLAUGHTER HOUSE WASTE LARD

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Besides the second generation bio fuels the bio gas oil, which is a high iso-paraffin containing fuel in the boiling range of the Diesel gasoil could be produced by the catalytic hydrogenation of different triglycerides. In this paper to improve the cold flow properties the isomerization of a normal paraffin rich mixture which was produced by the catalytic hydrogenation of slaughter house's wastes lard was investigated over a Pt/SAPO-11 catalyst at the temperature of 320–380 °C, pressure of 30–60 bar, space velocity of 1.0–3.0 h^{-1} and H_2/feedsock volume ratio of 400 Nm^3/m^3. At the favourable process parameters excellent Diesel fuel blending components (cetane number: 76–88; cold filter plugging point: between -7 and-13) were obtained, which were practically free of heteroatoms and had high isoparaffin content.

Keywords: biogasoil, waste fat, catalytic hydroisomerisation, SAPO-11 catalyst

Introduction

The importance of bio-fuels produced from agrarian products and wastes is higher and higher because of the forecast depletion of crude oil reserves, the increasing crude oil price, the efforts to reduce the dependence on crude oil import, the increasing demands of quantity, the environmental regulations, furthermore the expectations of the European Union, and this tendency will continue in the near future [1, 2, 3, 4, 5, 6].

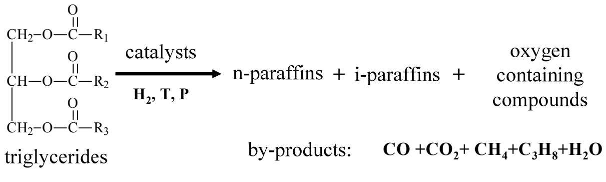
The different vegetable oils and their esters furthermore the products obtained from these by catalytic hydrogenation belong to the bio-fuels. As the utilisation of unconverted vegetable oils as Diesel fuel do not work properly, the chemical conversion of the vegetable oils to fuels or fuel blending components having proper quality is necessary [7, 8].

The biodiesels used currently in the highest degree are produced by the transesterification of vegetable oils. These have numerous disadvantage e.g. poor oxidation and heat stability, hydrolysis sensitivity (corrosion), low energy content, poor cold flow properties, high viscosity, etc. [7, 8]. Because of these disadvantages the quantity of fatty acid methyl esters which could be blended to the Diesel fuels was limited to 7.0 v/v% in the EN 590:2009 standard according to the suggestion of the car manufacturers.

To satisfy the bio component demand in the near future the so called bio gas oil could be a good solution, which could be produced by the catalytic hydrogenation of different triglycedes and which have high isoparaffin content and are in the diesel boiling range [8, 9, 10, 11, 12].

The feedstock of the bio gas oil could be conventional and ennobled vegetable oils (e.g. rape, sunflower, soy and coconut oils) grown in high quantity for biodiesel production, furthermore fats from the alimentary industry (used cooking oils and fats) and meat and leather industry, furthermore from trap fats of sewage farms, etc. having a lower price. Such kinds of feedstocks could be used as well which could be grown in invaluable lands (like jathropa oils) or could be extracted from algaes.

In the reactions taking place during the catalytic hydrogenation of triglycerides mainly normal paraffins, propane, carbon dioxide and monoxide, water and oxygenic compounds generate according the following reaction scheme [8, 9, 10, 11, 12, 13, 14, 15]:



The regulations of Diesel fuels could be satisfied in the highest degree by that gasoil which has high n- and i-paraffin content and is practically free of sulphur and nitrogen and has low aromatic content. But the high content of normal paraffins having high carbon number is unfavourable in the arctic zone and in winter in the temperate zone regarding the cold flow properties. These affect unfavourably the freezing point, pour point and cold filter plugging point (CFPP) [12, 13, 14, 15].

The products obtained from triglycerides by catalytic hydrogenation contain mainly C_{15}-C_{18} normal paraffins. Accordingly the catalytic conversion of the paraffins has high importance, as their cold flow properties do not satisfy the specified values (e.g. cold filter plugging point) of the standard. Formerly the isomerisation of smaller carbon number paraffins (C_8-C_{12}) was investigated; industrially just the isomerisation of C_5-C_7 hydrocarbons is practised now.

The reason of this is that the catalytic transformation of these paraffins could be realised over a high isomerisation activity catalyst to reach favourable yield and high isomer content contrary to the earlier used mainly hydrocracking catalysts. Such highly selective catalysts are the different noblemetal containing zeolites (ZSM-5, ZSM-22, ZSM-23), silica-alumina-phosphates (SAPO-11, SAPO-31, SAPO-41) and mesoporous materials (MCM-41, Al-MCM-41) [5].

The freezing points of the isoparaffins are significantly better than that of the normal paraffins. It decreases by decreasing the carbon number and by shifting of the branch toward the centre of the molecule. *(Fig. 1)*. Furthermore the increase of the number of the branching improves the cold flow properties as well.

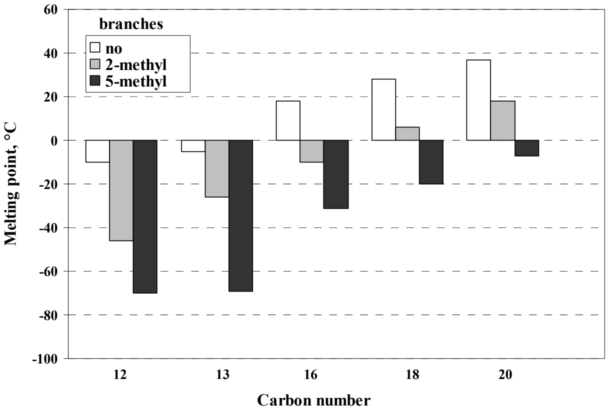


Figure 1: Freezing points of the paraffins as a function of the carbon number

Because of the abovementioned, the aim of our research work was the production of fuel blending components having favourable cold flow properties over a SAPO-11 catalyst found to have high isomerisation activity [12]. The feedstock was a high normal paraffin containing mixture produced from slaughter house waste fat, which has lower value than that of the vegetable oils. Besides our aim was the investigation of the effects of the process parameters (temperature, pressure, liquid hourly space velocity, hydrogen/ hydrocarbon volume ratio) on the product yield and quality and based on these the determination of the favourable process parameters.

Experimental

During our experiments the ranges of the process parameters were the following: temperature: 300–360 °C; pressure: 20–40 bar; liquid space hourly velocity 1.0–3.0 h^{-1}. The H_2/feedstock volume ratio was constant 400 Nm^3/m^3, as during our pre-experiments it was found that the utilisation 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 utilisation of higher amount of hydrogen to feedstock ratio – higher than 400 Nm^3/m^3 – is unfavourable regarding economical aspects; moreover it could roll back the degree of the isomerization.

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

Materials and methods

Table 1 contains the main properties of the feedstock of the isomerization. The applied catalyst was a Pt/SAPO-11 [10]. The properties of the feedstock and the products were determined according to the test methods specified in the EN 590:2009 standard and were calculated by other methods *(Table 2)*.

Table 1: The main properties of the feedstock having high normal paraffin content

Property		Value
Density at 40°C, g/cm^3		0.7689
Cold filter plugging point, °C		23
Cetane number		101
Sulphur content, mg/kg		6.4
Nitrogen content, mg/kg		5.2
Paraffin content, %	i-C_{15}	0.06
	n-C_{15}	11.94
	i-C_{16}	0.06
	n-C_{16}	13.23
	i-C_{17}	0.31
	n-C_{17}	35.47
	i-C_{18}	0.43
	n-C_{18}	33.35
Total isoparaffin content, %		0.89
Aromatic and cycloparaffon content, %		0.3

Table 2: Applied test methods

Property	Method
Density	EN ISO 12185:1998
Cold filter plugging point	MSZ EN 116:1999
Sulphur content	EN ISO 20846:2004
Nitrogen content	ASTM-D 6366-99
Hydrocarbon composition	gas chromatography (Trace GC 2000)
Distillation characteristics	EN ISO 3405:2000

Results and discussion

During our experiments the catalytic conversion of a high paraffin containing mixture produced from slaughter house waste (lard) by catalytic hydrogenation was investigated over a Pt/SAPO-11 catalyst at the temperature of 300–360 °C, pressure of 20–40 bar, liquid hourly space velocity of 1.0–3.0 h^{-1} and H_2/feedstock ratio of 400 Nm^3/m^3. In this paper the most important results of this experiment are presented.

The yields of products

The yield of the product mixtures decreased by increasing the temperature and by decreasing the pressure and the LHSV (*Fig. 2* and *3*). The reason of this was that the carbeniumions 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 and at lower pressure. In the investigated process parameter range, the yield of the product exceeded 90% in every case.

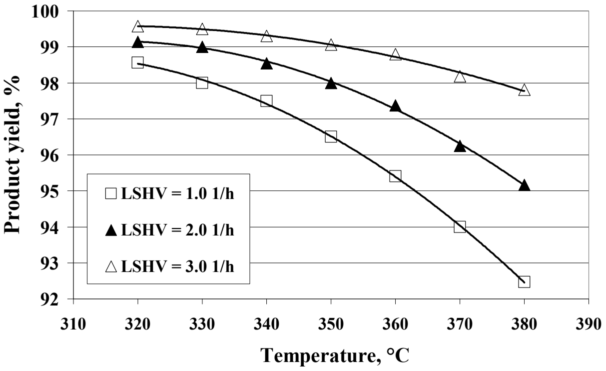


Figure 2: Product yields as a function of temperature and LHSV (p = 40 bar)

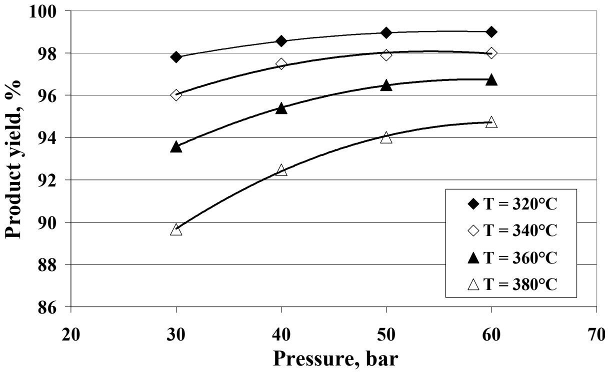


Figure 3: Product yields as a function of temperature and pressure (LHSV = 1,0 h^{-1})

Product composition

The isoparaffin concentration of the products increased significantly by increasing the temperature above 340 °C, namely the degree of isomerization become greater. The degree of increase started to decrease at 360–370 °C partially because of by the thermodynamic inhibition (namely the isomerization reactions are exothermic) and partially because of the increase of the cracking. This tendency rose with decreasing the LHSV *(Fig. 4)*, because of this the contact time increased, so the reaction could take place in higher degree.

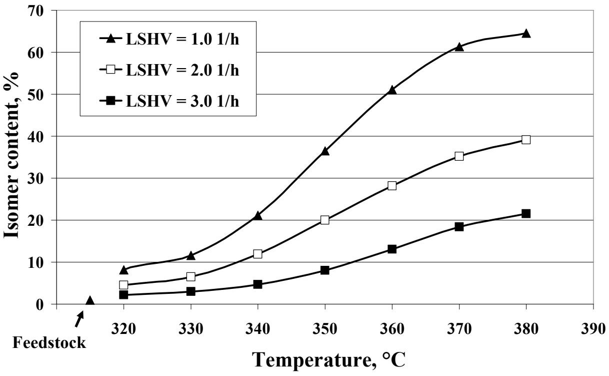


Figure 4: The paraffin content of the products as a function of temperature and LHSV (P = 40 bar, H_2/hydrocarbon ratio: 400 Nm^3/m^3)

Besides the obtained isomers mainly (85–90%) mono branching isomers were generated up to 360°C. The freezing point of these is significantly lower than that of the normal paraffins (e.g. 2-methyl-heptadecane: +5.5 °C; 5-methyl-tetradecane: -34.4 °C) and their cetane number is moderately lower than that of the corresponding normal paraffin (e.g. 9-methyl-heptadecane: 66) [16]. But higher amount of multi branched paraffins (15–35%) was generated above this temperature, which have better cold flow properties, however their cetane number is significantly lower (e.g. 2,2,4,4,6,8,8-heptamethyl-nonane: 15; 5,6-dibutyldecane: 30) [16].

The decrease of the pressure unequivocally increased the degree of isomerization up to 340 °C, as the first step of the isomerization, namely the dehydrogenation of the saturated paraffins to olefins could take place more easily on the active sites of the catalyst by decreasing the partial pressure of the hydrogen. At 360 °C the concentration of isoparaffins had maxima as a function of the pressure, while at 380 °C the decrease of the pressure caused the decrease of the isomer content *(Fig. 5)*. The reason of this was that the hydrocracking reactions taking place at higher degree at higher temperature decreased the concentration of the isoparaffins. These reactions were rolled back by the increase of the partial pressure of the hydrogen, because the rate of hydrogenation of the instable carbenium ions generating on the surface of the catalyst increased.

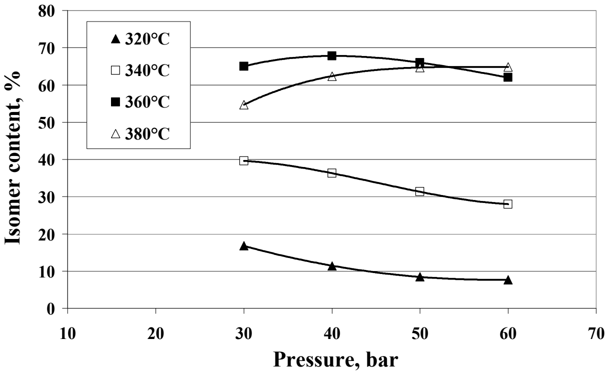


Figure 5: Total iso-paraffin content of the products as a function of pressure and temperature

Performance properties

The cold filter plugging point (CFPP) is an important performance property during the utilisation of the Diesel fuels, as the paraffin crystals precipitated by the decrease of the temperature could cause operational disorder or unserviceability of the fuel supply system. The CFPP values of the products decreased by increasing the temperature, decreasing the pressure and the LHSV *(Fig. 6)*. The reason of this was the increase of the concentration of the isoparaffins, while the freezing point of the isoparaffins is lower than that of the n-paraffins (see Fig. 1). The lighter hydrocarbons having low freezing point could decrease the CFPP values as well, which were generated in the hydrocracking reactions.

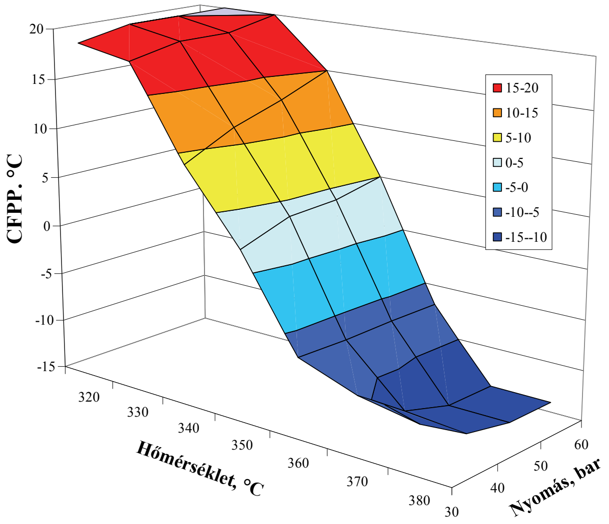


Figure 6: CFFP values of the products as a function of temperature, pressure and LHSV

The concentration of the multi-branched paraffins increased by increasing the temperature. The reason of this was that at higher temperature the structural transformation of the mono-branched paraffins increased, so in consecutive reactions the possibility of the formation of multi-branching was higher. These compounds affect favourably the cold flow properties, but another important performance property, their cetane number is low. Consequently the cetane number of the products decreased by increasing the rate of conversion relative to that of the normal paraffin rich feedstock (101 unit). The cetane numbers of the product were 76–88 unit at the favourable process parameters (determined by a compromise as a function of the yield and the ratio of the mono and multi-branched isoparaffins), which were higher than the specified value of the Diesel fuel standard (51 unit).

Summary

The production possibility of bio gas oil having good cold flow properties was investigated over a Pt/SAPO-11 catalyst. The feedstock was a mixture of mainly normal paraffins which were produced from slaughter house waste lard to broaden the feedstock of the bio gas oil.

It was concluded that in the investigated parameter range higher temperature, lower pressure and LSH are favourable for the conversion of isoparaffins. Regarding the values of the yield, CFPP and cetane number, the most favourable process parameter combinations were the following: temperature of 360–370 °C, pressure of 40–50 bar and LHSV of 1.0 h^{-1}.

At these parameters the products had high yield (95–96 %) and high isomer content (60–62 %). The CFPP values of the products were between -7 °C and -13 °C, which could satisfy the requirement of the summer grade fuel without addition, and the winter grade specification could be fulfilled with some addition as well. These excellent gas oil blending components are practically free of sulphur and have cetane number of 76–88 unit, which is significantly higher than that is specified in the EN 590:2009 standard (51 unit).

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