

Research Article

Bio Gas Oil Production from Waste Lard

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Besides the second generations bio fuels, one of the most promising products is the bio gas oil, which is a high iso-paraffin containing fuel, which could be produced by the catalytic hydrogenation of different triglycerides. To broaden the feedstock of the bio gas oil the catalytic hydrogenation of waste lard over sulphided NiMo/Al₂O₃ catalyst, and as the second step, the isomerization of the produced normal paraffin rich mixture (intermediate product) over Pt/SAPO-11 catalyst was investigated. It was found that both the hydrogenation and the decarboxylation/decarbonylation oxygen removing reactions took place but their ratio depended on the process parameters ($T = 280\text{--}380^\circ\text{C}$, $P = 20\text{--}80$ bar, LHSV = 0.75–3.0 h⁻¹ and H₂/lard ratio: 600 Nm³/m³). In case of the isomerization at the favourable process parameters ($T = 360\text{--}370^\circ\text{C}$, $P = 40\text{--}50$ bar, LHSV = 1.0 h⁻¹ and H₂/hydrocarbon ratio: 400 Nm³/m³) mainly mono-branching isoparaffins were obtained. The obtained products are excellent Diesel fuel blending components, which are practically free of heteroatoms.

1. Introduction

Nowadays the production and utilisation of agricultural origin fuels have come to the front because of environmental protection, political and economical reasons. In the increase of the utilisation of these bio-fuels the energy policy of the European Union has a dominant role, of which the aim is the decrease of the energy and the crude oil dependency. In consequence, the EU implemented the 2003/30/EC and the 2009/28/EC directives to inspire the utilisation of bio-fuels by determining the suggested and specified ratio of bio-fuels in the transportation fuels. In order to attain these objectives, the fuel blending components produced from different natural triglyceride containing feedstocks (like vegetable oils, used frying oils, animal fats, algae oils, trap grease of sewage works) could have an important role.

Currently only the biodiesels (fatty acid methyl esters) belonging to the first generation bio-fuels are used as bio-origin fuel or a blending component for Diesel engines. But the production and utilisation of these have numerous disadvantages (formation of hazardous wastes, difficulties of glycerol sales, high content of olefinic double bond → poor heat and oxidation stability → poor storage stability; ester bonds and high water content → hydrolysis sensitivity →

corrosion; phosphor content → poisonous effect on the three-way catalyst, etc.) [1–3].

Because of these disadvantages and the demand for better quality, the production possibilities of biofuels for diesel engines which have different chemical structure, consequently dissimilar service properties are keenly researched. The research, production and utilization of this kind of second generation biofuels are supported with high priority by the European Union. Besides these the so-called bio gas oils could come to the front in the short and middle-term. The bio gas oils are the mixtures of gas oil boiling point range hydrocarbons (mainly >99% normal and isoparaffins) produced from mainly triglyceride containing feedstocks (vegetable oils, used frying oils, animal fats, etc.) by heterogenic catalytic hydrogenation in one or more stages. The bio gas oils eliminate every disadvantage of the biodiesels (fatty acid esters), accordingly their economical production with high yield could have high importance in the future [4, 5].

The mixtures of the gas oil boiling point range hydrocarbons produced by the catalytic hydrogenation of triglycerides contain mainly normal paraffins. They have outstanding cetane number (>85), but their cold flow properties (e.g., cold filter plugging point) are unfavourable (e.g., the freezing points of the C₁₆–C₁₈ normal paraffins are between +18°C

and +28°C). For this reason, the chemical structure of the *n*-paraffins has to be modified to be excellent gas oil blending components. For this purpose, the most suitable technical solution is the catalytic hydroisomerisation. During the isomerization the normal paraffins having high freezing point and outstanding cetane number could be converted to isoparaffins having by far lower freezing points and still high cetane number [4, 5].

Accordingly, the mentioned two-stage catalytic conversion of the triglycerides of different vegetable oils to bio gas oil is discussed in several publications. But there is only a little information about the utilisation of waste fats. Because of these, and to broaden the range of the feedstock of the bio gas oils, we investigated the two-stage catalytic transformation of lard produced from slaughterhouse waste.

The aim of our experimental work was the investigation of the fuel purpose convertibility (to good quality gasoil boiling range product with high isomer content) of properly pretreated Hungarian lard produced from slaughter house waste over an expediently chosen NiMo/Al₂O₃ then on a Pt/SAPO-11 catalyst. The experiments were carried out in a laboratory scale reactor system in continuous operation, while the activity of the catalyst, the yield and composition of the products, the possible reaction routes of the deoxygenation and the quantity of isomers, as well as the applicability of the products were investigated in function of the process parameters (temperature, pressure, liquid hourly space velocity, H₂/hydrocarbon volume ratio).

2. Experimental Part

2.1. Feedstocks. The feedstock of the hydrogenation experiments was properly pretreated (filtered, purified by bleaching earth) lard which was produced from slaughter house wastes. Its important properties are summarized in Table 1. For the catalytic hydrogenation of the feedstock, the applied catalyst was a conventional hydrotreating NiMo/Al₂O₃ catalyst. The Ni-content of the catalyst was 3.23% and the Mo-content was 13.4%; the BET surface area was 214 m²/g and the acidity was 0.489 mmol NH₃/g. The catalyst was presulphided before the experiments with previously deep desulphurized gas oil having enhanced (2.5% with dimethyl-disulphide) sulphur content. To maintain the sulphided form of the catalyst, the sulphur content of the feedstock was adjusted to 1000 mg/kg with dimethyl-disulphide. This compound easily dissociates in the applied temperature range. For the isomerization of the intermediate paraffin rich mixture the catalyst was a 0.5% Pt/SAPO-11 catalyst. The dispersion of the platinum was 91%, the BET surface area was 100.1 m²/g, and the acidity of the catalyst was 0.66 mmol NH₃/g. Prior to the activity measurements, the catalysts were pre-treated in situ, as described in our earlier publication [5].

2.2. Experimental Apparatus and Product Separation. The experimental tests were carried out in a high pressure reactor system containing two tubular reactors with effective catalyst volume of 100 cm³ [5]. The reactor system contained all the equipment and devices applied in the reactor system of

a hydrogenation and isomerization plant. The apparatus was suitable to keep the major process parameters with at least such precision as used in the industry.

The intermediate product mixtures obtained from the hydrogenation of the waste lard were separated to gas phase, water phase and liquid organic phase (hereafter organic phase) (Figure 1). The gas phase obtained from the separator of the reactor system contained mainly hydrogen, carbon-monoxide, carbon-dioxide, propane, hydrogen-sulphide, ammonia which evolved during the heteroatom removal of the triglyceride molecules, furthermore the lighter hydrocarbons (C₁–C₄ as valuable by-products) which formed during the hydrocracking reactions. The liquid product mixtures obtained from the separator of the reactor system contained water, hydrocarbons and oxygen containing compounds. After the separation of water, we obtained the light (C₅–C₉) hydrocarbons (gasoline boiling range) from the organic fraction by distillation up to 180°C.

The residue of atmospheric distillation was separated by vacuum distillation into the intermediate product (gas oil boiling range fraction, mainly C₁₁–C₁₉ hydrocarbons) and the residue. The residue contained the unconverted triglycerides, the evolved and unconverted diglycerides and monoglycerides, furthermore fatty acids and esters, which evolved as intermediate products or were originally in the feedstock. After the isomerization of the normal paraffin rich intermediate product the bio gas oil and some light hydrocarbons were obtained.

2.3. Analytical Methods and Calculation Methods. The properties of the lard feedstock, the hydrogenated intermediate products and the target products were measured according to standard methods (see Table 1).

The composition of the organic product mixtures, obtained from the catalytic conversion of triglycerides was determined by high temperature gas chromatograph (Shimadzu 2010 GC) at the following measurement parameters:

- (i) Zebron DB-1HT (30 m × 0.32 mm × 0.1 μm) column,
- (ii) PTV (Programmed Temperature Vaporization) injector (temperature program: 100°C → 400°C, 30°C/min heating rate, then 18 min at 400°C),
- (iii) oven temperature program: 40°C (4 min) → 240°C, 15°C/min heating rate → 400°C 8°C/min heating rate, then 11 min at 400°C,
- (iv) FID (flame ionization) detector (400°C),
- (v) carrier gas: H₂ (5.0), pressure 58.0 kPa, column flow 4.00 cm³/min.

The nickel and molybdenum content of the hydrogenation catalyst was measured with ICP-OES method. The SAPO-11 catalysts were prepared as described and characterized according to HU 225 912 patent [6]. The platinum content of the isomerization catalyst was determined according to UOP-274 standard. The dispersity of the platinum was determined by H₂ chemisorption [7]. The surface properties of the catalyst were investigated

TABLE 1: The main properties and fatty acid composition of the applied waste lard.

Properties	Value	Standard methods
Kinematic viscosity, 40°C, mm ² /s	39.53	EN ISO 3104:1996
Density (40°C), g/cm ³	0.9385	EN ISO 3675: 2000
Sulphur content, mg/kg	6	EN ISO 20846:2004
Acid number, mg KOH/g	0.63	EN 14104:2004
Iodine number, g I ₂ /100 g	78	EN 14111:2004
Carbon residue, %	0.11	EN ISO 10370:1997
Flash point, °C	>250	EN ISO 2719:2003
Cold filter plugging point, °C	37	EN 116:1999
Fatty acid composition*, %		
C14:0	1.04	
C16:0	20.47	
C16:1	7.65	
C18:0	12.83	EN ISO 5509:2000;
C18:1	32.99	EN 14103:2004
C18:2	17.32	
C18:3	6.70	
C20:x	0.86	
Other	0.14	
Calculated oxygen content, %	11.2	

* The first number represents the number of carbon atoms and the second means the number of double bonds in the molecule.

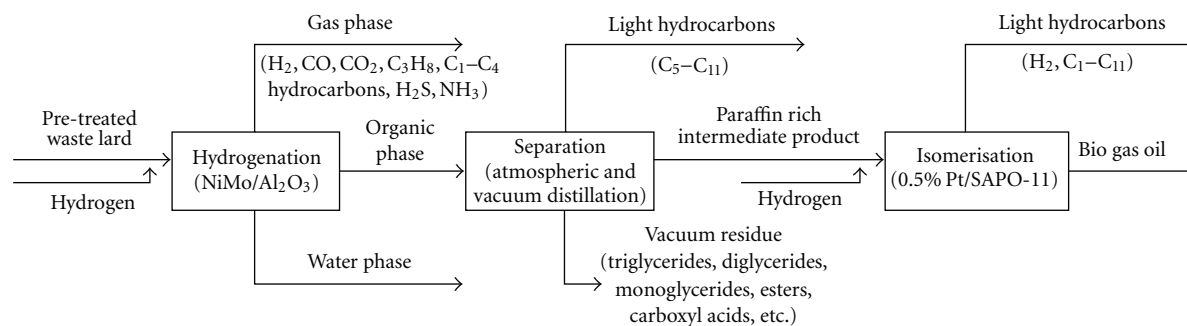


FIGURE 1: The scheme of the laboratory scale production of the bio gas oil.

by ASAP 2000 (Micromeritics) equipment (pore diameter in the range of 1.7–300 nm) and by mercury penetration method with CARLO-ERBA equipment (pore diameter in the range of 7.5–15000 nm). The surface area of the catalysts was calculated by using BET-plots. The acidity of the catalysts was determined with temperature programmed desorption of ammonia (TPD-NH₃).

We calculated the conversion of triglycerides by the following equation:

$$\text{Conversion} = \frac{X_{\text{feedstock}} - X_{\text{products}}}{X_{\text{feedstock}}} * 100, \quad (1)$$

where $X_{\text{feedstock}}$: triglyceride content of the feedstock and X_{products} : triglyceride content of the products.

3. Results and Discussion

3.1. The Catalytic Hydrogenation of the Waste Lard. The range of the applied process parameters—based on our pre-experimental results—was the following: temperature 280–380°C, total pressure 20–80 bar, liquid hourly space velocity (LHSV) = 0.75–3.0 h⁻¹ and H₂/waste lard volume ratio = 600 Nm³/m³.

3.1.1. Conversions and Product Yields. The conversion of triglycerides increased significantly by increasing the severity of the process parameters, namely by increasing the temperature and the pressure furthermore by decreasing the LHSV (Figures 2 and 3). At every investigated value of pressure, at least 1.5 h⁻¹ and lower LHSV and at least 320°C or higher temperature was necessary to reach at least 95% conversion of the triglycerides at the 600 Nm³/m³ H₂/lard volume ratio,

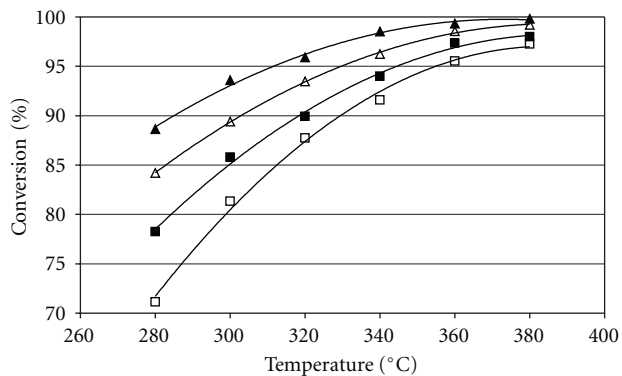


FIGURE 2: Conversion of triglycerides as a function of the temperature and the pressure; where: \square -20 bar, \blacksquare -40 bar, \triangle -60 bar and \blacktriangle -80 bar pressure (LHSV = 1.0 h^{-1} , $\text{H}_2/\text{waste lard volume ratio} = 600 \text{ Nm}^3/\text{m}^3$).

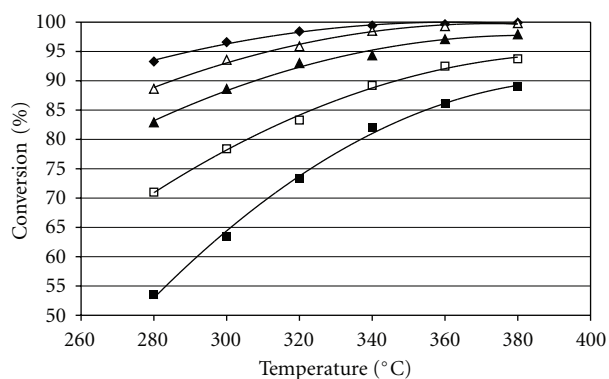


FIGURE 3: Conversion of triglycerides as a function of the temperature and the LHSV; where: \blacklozenge - 0.75 h^{-1} , \triangle - 1.0 h^{-1} , \blacktriangle - 1.5 h^{-1} , \square - 2.0 h^{-1} and \blacksquare - 3.0 h^{-1} of LHSV ($P = 80 \text{ bar}$, $\text{H}_2/\text{waste lard volume ratio} = 600 \text{ Nm}^3/\text{m}^3$).

which was found to be favourable according to our pre-experiments.

The yield of the intermediate normal paraffin-rich product (INPRP) in the gas oil boiling range was significantly influenced by the temperature, the pressure and the LHSV (Figures 4 and 5). At every value of pressure and LHSV, up to 320°C , the yield of the intermediate product increased by increasing the temperature in accordance with the increasing rate of triglyceride conversion. But when the rate of conversion exceeded 95%–98%, then the further increase of temperature caused lower amount of plus paraffins than the amount of hydrocarbon which was decomposed by cracking; consequently, the yield started to decrease. So the yield of INPRP changed according to a maximum curve as a function of the temperature at LHSV of 0.75 and 1.0 h^{-1} , because in these cases the contact time of the hydrocarbons and oxygenic compounds generated from the triglycerides was too long; consequently, by increasing the temperature above 320°C (LHSV = 0.75 h^{-1}) and 360°C (LHSV = 1.0 h^{-1}), the yield decreased because of the increasing rate of cracking. The low yield of INPRP at LHSV of 1.5 – 3.0 h^{-1} was caused

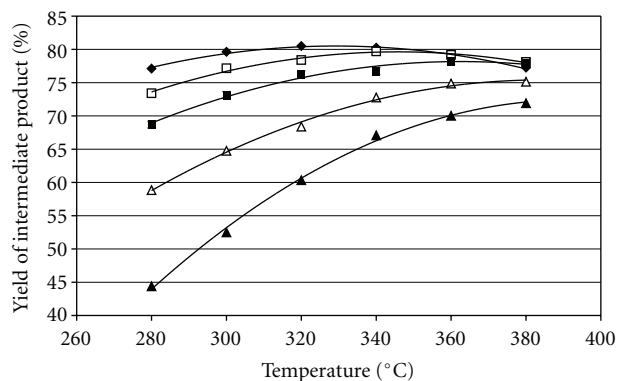


FIGURE 4: Yield of the INPRP as a function of the temperature and the LHSV; where: \blacklozenge - 0.75 h^{-1} , \triangle - 1.0 h^{-1} , \blacktriangle - 1.5 h^{-1} , \square - 2.0 h^{-1} and \blacksquare - 3.0 h^{-1} of LHSV ($P = 80 \text{ bar}$, $\text{H}_2/\text{waste lard volume ratio} = 600 \text{ Nm}^3/\text{m}^3$).

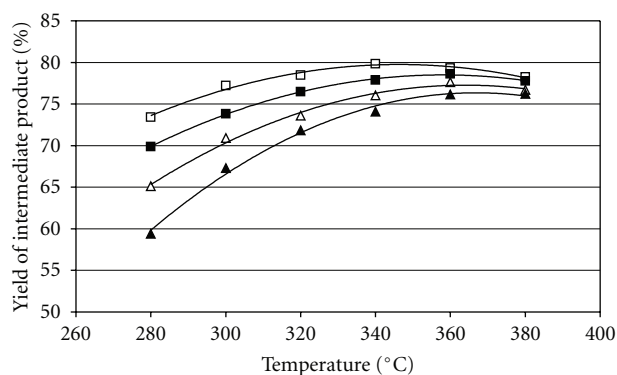


FIGURE 5: Yield of the INPRP as a function of the temperature and the pressure; where: \blacktriangle -20 bar, \triangle -40 bar, \blacksquare -60 bar and \square -80 bar pressure (LHSV = 1.0 h^{-1} , $\text{H}_2/\text{waste lard volume ratio} = 600 \text{ Nm}^3/\text{m}^3$).

unequivocally by the low conversion of the triglycerides, as these molecules could not contact long enough with the active sites of the catalyst. In the investigated parameter range at constant temperature, the higher the pressure was the higher yield of INPRP was reached in accordance with the increasing rate of triglyceride conversion (in spite of the fact that the higher the pressure was, the higher the rate of hydrocracking reactions was, as well). (It should be highlighted that in case of the investigated waste lard having the mentioned composition (Table 1), the maximum yield of the gas oil boiling range intermediate product (mainly C_{11} – C_{19} paraffins) could be 85.7% supposing only HDO reaction, and 80.8% supposing only decarboxylation/decarbonylation.) As at the favourable conversion (>95%), the ratio of the hydrocracking of the hydrocarbons was significant (>3%); so at the most favourable yield of INPRP was 80.5%. This approaches well the theoretical values. By increasing the temperature and the INPRP increasing effect of the pressure was lower and lower.

To sum it up, we concluded that favourable yields of intermediate product were obtained at the following process

TABLE 2: Composition of the gas product ($T = 360^\circ\text{C}$, $P = 80\text{ bar}$, $\text{LHSV} = 1.0\text{ h}^{-1}$, $\text{H}_2/\text{feedstock ratio} = 600\text{ Nm}^3/\text{m}^3$).

Component	Value	
	Mass %	Volume %
Hydrogen	23.94	85.86
Hydrogen-sulphide	0.45	0.09
Carbon-dioxide	28.39	4.66
Carbon-monoxide	7.18	1.85
Methane	1.30	0.59
Ethane	0.39	0.09
Propane	26.82	4.39
Iso-butane	0.11	0.01
Butane	0.17	0.02
Others	11.24	2.43

parameters: $T = 320\text{--}360^\circ\text{C}$, $P = 40\text{--}80\text{ bar}$, $\text{LHSV} = 1.0\text{--}1.5\text{ h}^{-1}$, $\text{H}_2/\text{feedstock ratio} = 600\text{ Nm}^3/\text{m}^3$. Application of the LHSV of 0.75 h^{-1} is not only unadvised by the univocal decrease of the yield, but by the loss of plant capacity by 25% and 50% regarding the same reactor capacity.

The INPRP contained olefins in a low concentration (iodine number between 1.0 and 10.0) at low temperature ($\leq 320^\circ\text{C}$), low hydrogen pressure ($\leq 40\text{ bar}$) and high LHSV ($\geq 1.5\text{ h}^{-1}$), where the saturation of the olefinic double bonds was insufficient, but at the favourable process parameters, it was almost complete (iodine number < 1.0).

3.1.2. Oxygen Removing Reaction Paths and Their Ratio. During the conversion of triglycerides to the paraffin rich mixture, the saturation of double bonds, heteroatom removing (oxygen and other heteroatoms), isomerization and different side-reactions took place [8–11]. The oxygen removal could happen by different reactions. In case of the hydrodeoxygenation (HDO) beside the normal paraffins having the same carbon number than that of the carboxyl acids composing the triglycerides only propane and water generate, while during the decarboxylation and decarbonylation the carbon number of the paraffins shortens by one and carbon-dioxide and carbon-monoxide also generate, respectively, beside the propane and water [12–15]. For example, Table 2 contains the composition of the gas products at 360°C , 80 bar , $\text{LHSV} = 1.0\text{ h}^{-1}$ and $\text{H}_2/\text{feedstock ratio} = 600\text{ Nm}^3/\text{m}^3$.

According to the composition of the INPRP, the ratio of the HDO to decarboxylation/decarbonylation reactions could be determined. But to determine the ratio of decarboxylation to decarbonylation the exact quantity of the CO , CO_2 and water has to be known, but that is not possible in the applied catalytic system, because of other side reactions (e.g., water-gas shift reaction, cracking of the hydrocarbons). The main part ($>99.5\%$) of the carbon number of the fatty acids of the triglycerids of the used lard (feedstock) was an even number—similar to most of the natural triglycerides—wherein 98.0% was C_{16} and C_{18} carboxyl acids (Table 1), so from the ratio of the generated C_{15} and C_{16} furthermore the C_{17} and C_{18} paraffins, the ratio of the hydrodeoxygenation

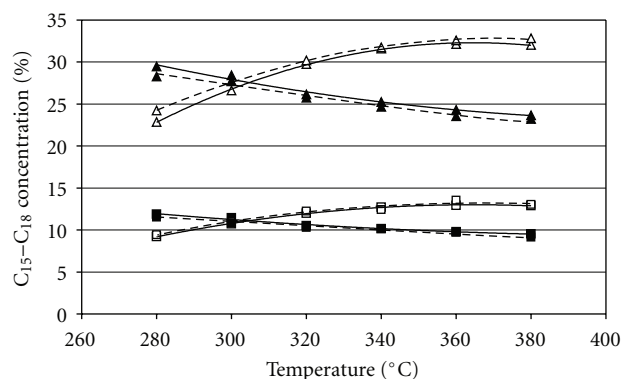


FIGURE 6: The concentration of the $\text{C}_{15}\text{--C}_{18}$ paraffins of the intermediate product; where: \square - C_{15} , \blacksquare - C_{16} , \triangle - C_{17} and \blacktriangle - C_{18} fraction (broken line: $P = 20\text{ bar}$, continuous line: $P = 80\text{ bar}$) ($\text{LHSV} = 1.0\text{ h}^{-1}$, $\text{H}_2/\text{feedstock volume ratio} = 600\text{ Nm}^3/\text{m}^3$).

(HDO) and the decarboxylation/decarbonylation reactions was determined. At $600\text{ Nm}^3/\text{m}^3$ $\text{H}_2/\text{waste lard}$ ratio and LHSV of 1.0 h^{-1} which were found to be favourable furthermore in the whole investigated pressure range (see the corner points in Figure 6), the degree of the HDO and the other two reactions was almost the same (as C_{15} and C_{16} furthermore C_{17} and C_{18} paraffins were generated in similar quantity) at around 300°C . By increasing the temperature ($320\text{--}360^\circ\text{C}$), the decarboxylation/decarbonylation reactions became dominant (the concentration of the odd carbon number paraffins was higher than that of the even carbon number paraffins).

The ratio of the hydrodeoxygenation (HDO) and decarboxylation/decarbonylation is presented as a function of the C_{18} and C_{17} paraffins (Figure 7). The ratio of the $\text{C}_{18}/\text{C}_{17}$ paraffins decreased significantly by increasing the temperature and a little by decreasing the pressure over the applied catalyst in the investigated parameter range. This means that the ratio of decarboxylation/decarbonylation increased compared to the hydrodeoxygenation. Similar tendencies were found in case of the change of the ratio of the C_{15} and C_{16} paraffins.

To determine the stability of the used catalyst and to produce a sufficient quantity of intermediate normal paraffin-rich product (INPRP) as the feedstock of the second stage of the bio gas oil production (isomerization) a 400-hour-long test was carried out at the favourable, expediently chosen parameter combination ($T = 360^\circ\text{C}$, $P = 60\text{ bar}$; $\text{LHSV} = 1.0\text{ h}^{-1}$, $\text{H}_2/\text{waste lard volume ratio} = 600\text{ Nm}^3/\text{m}^3$). According to the results (Figure 8) the activity and the selectivity of the catalyst—after the initial decrease of activity—were unchanged during the experiment.

3.1.3. The Service Properties of the Intermediate Product. The cetane number of the INPRP produced from waste lard over sulphided $\text{NiMo}/\text{Al}_2\text{O}_3$ catalyst was outstanding (101 unit) as it contained $\text{C}_{15}\text{--C}_{18}$ paraffins in the highest degree ($>95\%$) which have very high cetane number (100–105). Regarding the cold flow properties, the favourable

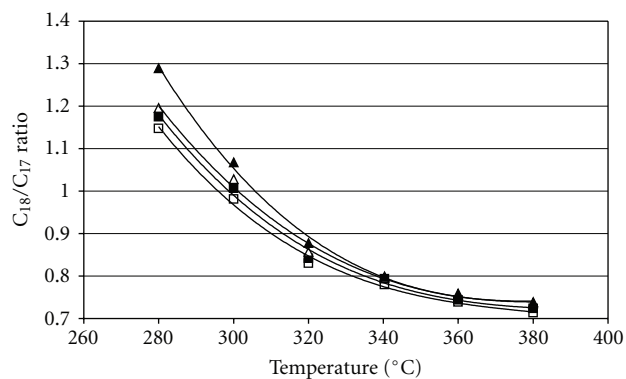


FIGURE 7: The ratio of C_{18}/C_{17} paraffins as a function of the temperature and the pressure; where: \square -20 bar, \blacksquare -40 bar, \triangle -60 bar and \blacktriangle -80 bar pressure (LHSV = 1.0 h^{-1} , $\text{H}_2/\text{waste lard volume ratio} = 600 \text{ Nm}^3/\text{m}^3$).

fatty acid composition of this waste lard has to be highlighted. While the earlier investigated vegetable oils [13–15] contain mainly C_{18} or longer fatty acids (90%–95%), our lard contained 28.12% C_{16} fatty acids. Consequently, our products containing about 28% of C_{15} and C_{16} paraffins (of which freezing points are $+10^\circ\text{C}$ and $+15^\circ\text{C}$, resp.) having more favourable CFPP ($+19^\circ\text{C}$) than that of the product mixture ($+23^\circ\text{C}$) [16] containing mainly (>90%) C_{17} and C_{18} paraffins (freezing point $+22^\circ\text{C}$ and $+28^\circ\text{C}$) produced over the same catalyst and at the same process parameters. Furthermore, as the isomers of the shorter carbon number paraffins have a lower freezing point than that of the longer ones, so by the isomerization of C_{15} and C_{16} paraffins a more favourable product could be obtained.

3.2. The Isomerization of the Normal Paraffin-Rich Intermediate Product. The catalytic isomerisation of the crude oil origin mixture having relatively high normal paraffin content (the other is cyclo and aromatic hydrocarbons) for improving the cold flow properties was carried out over noble metal containing catalysts [17–21]. Such catalysts with high isomerization activity are for example the different noble metal containing zeolites (ZSM-5, ZSM-22, ZSM-23), silica-alumina-phosphates (SAPO-11, SAPO-31, SAPO-41) and different mesoporous structures (MCM-41, Al-MCM-41) [17, 22]. But there are only a few articles dealing with the isomerisation of paraffin mixes of alternative source with different composition (e.g., containing oxygenic components) [4, 5, 16, 22].

During the isomerization experiment over Pt/SAPO-11, we used a mixture with high normal paraffin content produced from waste lard (Table 3). The composition of this feedstock and the products were investigated by GC-FID method using standard hydrocarbons. The feedstock was produced during the mentioned 400-hour-long experiment at process parameters ($T = 360^\circ\text{C}$, $P = 60 \text{ bar}$, LHSV = 1.0 h^{-1} , $\text{H}_2/\text{lard ratio} = 600 \text{ Nm}^3/\text{m}^3$) that were found to be favourable for the hydro-deoxygenation of waste lard,

TABLE 3: Main properties of the high n -paraffin containing feedstock.

Properties	Value	
Density at 40°C , g/cm^3	0.7689	
Cold filter plugging point, $^\circ\text{C}$	21	
Cetane number	101	
Sulphur content, mg/kg	3.2	
Nitrogen content, mg/kg	2.1	
	$i\text{-C}_{15}$	0.13
	$n\text{-C}_{15}$	15.59
	$i\text{-C}_{16}$	0.10
	$n\text{-C}_{16}$	11.83
Paraffin content, %	$i\text{-C}_{17}$	0.37
	$n\text{-C}_{17}$	39.61
	$i\text{-C}_{18}$	0.28
	$n\text{-C}_{18}$	29.97
Total isoparaffin concentration %	0.92	
Concentration of the oxygen containing compounds, %	0.43	
Aromatic and cycloparaffin content, %	0.3	

because the n -paraffin yield was high and the amount of the partially converted oxygen containing components (carboxylic-acids, esters, etc.) was very low in the product mixture. That was because the chosen Pt/SAPO-11 catalyst was found to be highly selective [5, 18–21] with great thermal stability [23]; however, it is highly sensitive for hydrolysis [16, 24]. According to the abovementioned, the investigation of the applicability of that is necessary in case of the feedstock produced from waste lard different from the already investigated ones.

3.2.1. Yields of the Products. During our isomerisation experiment, we applied an $\text{H}_2/\text{intermediate product volume ratio}$ found to be favourable during our previous experiments [16, 22], and we only examined the effects of the change of temperature, LHSV, and pressure which essentially affect the isomerization reactions. Consequently, the range of the applied process parameters was the following: temperature 320°C – 380°C , total pressure 30–60 bar, liquid hourly space velocity (LHSV) = 1.0 – 3.0 h^{-1} and $\text{H}_2/\text{hydrocarbon volume ratio} = 400 \text{ Nm}^3/\text{m}^3$.

The yield of the product mixtures decreased with increasing the temperature and with decreasing the pressure and the LHSV (Figures 9 and 10). The reason of this effect was that during the isomerization, the carbenium ions which have lower stability than the saturated hydrocarbons forming on the surface of the catalyst were cracked more easily at higher temperatures and at lower partial pressure caused by decreasing the hydrogen pressure, furthermore because of the lower LHSV and the longer contact time of the molecules on the surface of the catalyst. At the applied experimental process parameters, the yield of the products—except for one case—exceeded 90%.

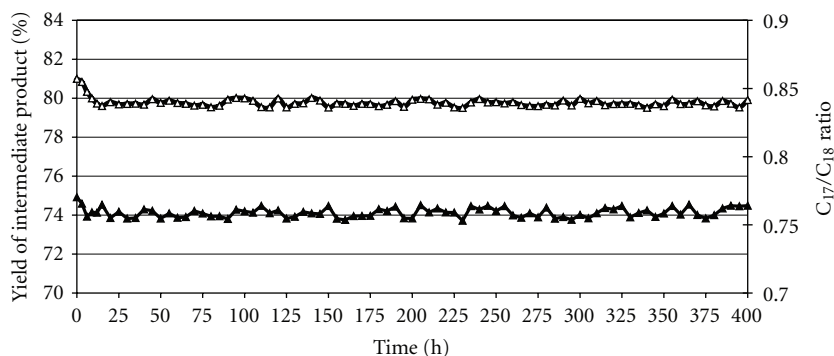


FIGURE 8: The change of the yield of the INPRP and the C_{17}/C_{18} ratio as a function of time; where: Δ -yield of intermediate product and \blacktriangle - C_{17}/C_{18} ratio ($T = 360^\circ\text{C}$, $P = 60$ bar, $\text{LHSV} = 1.0\text{ h}^{-1}$, $\text{H}_2/\text{waste lard volume ratio} = 600\text{ Nm}^3/\text{m}^3$).

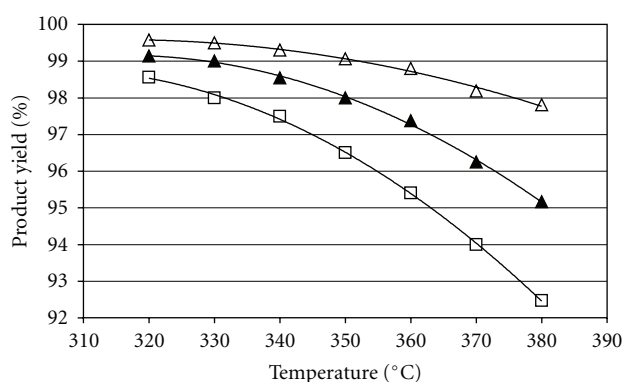


FIGURE 9: Product yields as a function of temperature and LHSV; where: \square - 1.0 h^{-1} , \blacktriangle - 2.0 h^{-1} and \blacklozenge - 3.0 h^{-1} of LHSV ($P = 40$ bar, $\text{H}_2/\text{hydrocarbon volume ratio} = 400\text{ Nm}^3/\text{m}^3$).

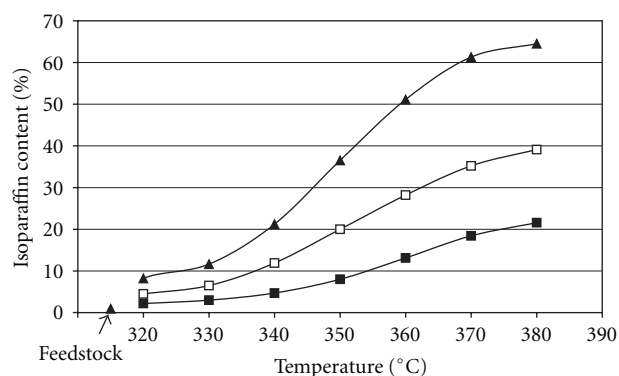


FIGURE 11: The isoparaffin content of the products as a function of temperature and LHSV; where: \blacktriangle - 1.0 h^{-1} , \square - 2.0 h^{-1} and \blacksquare - 3.0 h^{-1} of LHSV ($P = 40$ bar, $\text{H}_2/\text{hydrocarbon volume ratio} = 400\text{ Nm}^3/\text{m}^3$).

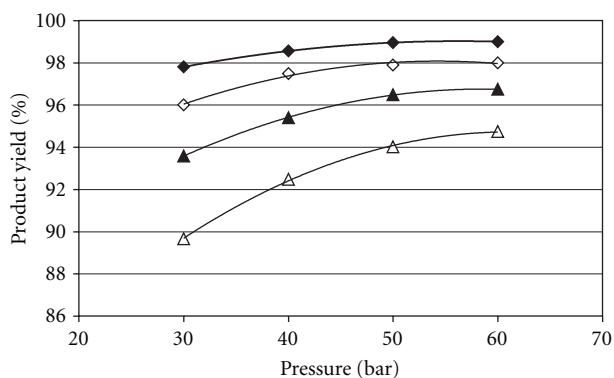


FIGURE 10: Product yields as a function of temperature and pressure; where \blacklozenge - 320°C , \diamond - 340°C , \blacktriangle - 360°C and Δ - 380°C ($\text{LHSV} = 1.0\text{ h}^{-1}$, $\text{H}_2/\text{hydrocarbon volume ratio} = 400\text{ Nm}^3/\text{m}^3$).

3.2.2. The Composition of the Products. The isoparaffin content of the products significantly increased above 330°C with the increasing temperature, namely, the rate of isomerization increased. The degree of the increase in the isoparaffin yield at 360°C – 370°C started to decrease, partly because of the closer approaching to the thermodynamic equilibrium, and partly because of the closer approach of the equilibrium

concentrations and thermodynamic inhibition (the isomerization reactions are exothermic reactions) furthermore partly because of the intensifying cracking reactions. This tendency rose with decreasing the LHSV (Figure 11) as the contact time increased which called for a higher rate of the cracking reactions.

Out of the obtained isomers, up to 360°C , the product contained mainly (85%–90%) monobranched (monomethyl) isomers of which freezing point is substantially lower (e.g., *n*-octadecane: $+28^\circ\text{C}$; 2-methyl-heptadecane: $+5.5^\circ\text{C}$, 5-methyl-tetradecane: -34.4°C) than that of the *n*-paraffins of the same carbon number and their cetane number is lower by only 20–25 unit than that of equivalent *n*-paraffins [25]. These latter values are at least 15–35 units above the 51 unit required by the European standard (EN 590:2009). However, above this process temperature multibranched isomers were also produced with increasing rate (15%–35%) of which cold flow properties are more favourable, but their cetane number is significantly lower [25]. So it is practical to determine a favourable compromise between the cold flow properties and the cetane number.

In the investigated range of process parameters, the decreasing pressure increased the rate of isomerization till 340°C . This occurred because by decreasing the partial

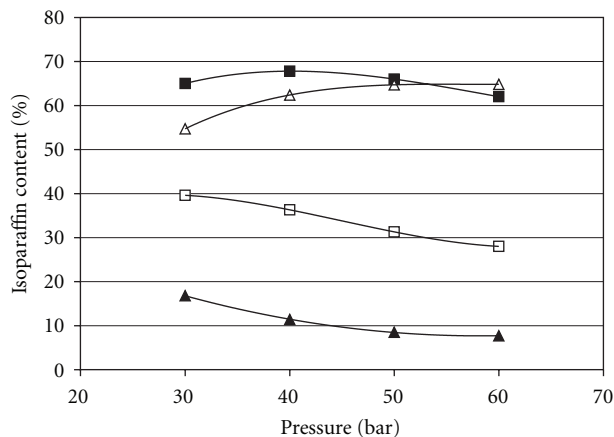


FIGURE 12: Total isoparaffin content of the products as a function of pressure, and temperature; where: \blacktriangle -320°C, \square -340°C, \blacksquare -360°C and \blacktriangledown -380°C (LHSV = 1.0 h⁻¹, H₂/ hydrocarbon volume ratio = 400 Nm³/m³).

pressure of the hydrogen, the first step of isomerization, namely, the dehydrogenation of hydrocarbons to olefins took place more easily on the active sites of the platinum catalyst. However, at 360°C the isoparaffin content reached a maximum as a function of the pressure, while at 380°C the decrease in the pressure caused a decrease in the isomer content (Figure 12). The reason of that was that the isoparaffin content was lowered by the intensive hydrocracking reactions at high temperatures, which rate was confined by the increase of the partial pressure of the hydrogen, namely, the rate of the hydrogenation of the labile carbenium ions generating on the surface of the catalyst increased.

3.2.3. The Main Properties of the Products. The cold filter plugging point (CFPP) is a very important property for diesel gas oils, because the paraffin crystals settled out with the decreasing temperature could cause plugging in the fuel filter and this could cause unserviceability in the fuel supply system. The CFPP values of the products decreased by increasing the temperature and by decreasing the pressure and the LHSV (Figure 13). The cause of this effect was mainly the increase in the isoparaffin content of the product, because their freezing-point is significantly lower than that of the *n*-paraffins. Besides the abovementioned, the lower freezing-point light hydrocarbons forming in the hydrocracking reactions also helped to improve the CFPP values of the products.

The increasing temperature (in the investigated range) positively affected the CFPP values (unequivocally lowering it). The reason of this was that besides the mono-branched isomers, the concentration of the multi-branched isomers also increased, because at higher temperatures not only the reaction rate of the forming of the mono-branched isomers increased, but in consecutive reactions there is a potential of the forming of multi-branched isomers, as well. These components have a positive effect on the cold flow properties; however, their other important property, the cetane number,

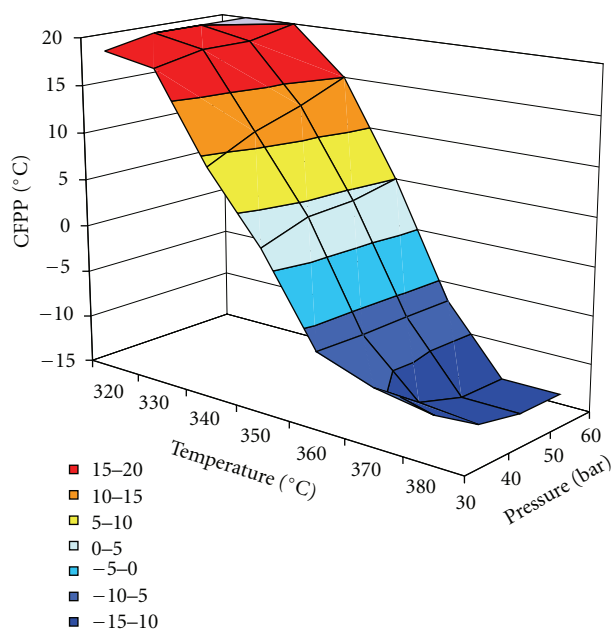


FIGURE 13: CFPP values of the products as a function of temperature, pressure and LHSV.

is by far more unfavourable. Therefore the cetane number of these products decreased compared to the normal paraffin mixture (101 unit), because of the increasingly produced multi-branched isomers. However, the products obtained at the favourable process parameters ($T = 360\text{--}370^\circ\text{C}$, $P = 50$ bar, LHSV = 1.0 h⁻¹, H₂/intermediate product volume ratio = 400 Nm³/m³) determined by compromises (yield of organic liquid phase, ratio of multi-branched *i*-paraffins, location of the branches) had cetane number between 76–88, which greatly exceeds the 51 specified in the valid standard, while their CFPP values were between –5 and –15°C.

4. Conclusions

Based on our experimental results it was concluded that on the expediently chosen sulphided NiMo/Al₂O₃ catalyst and at the favourable process parameters ($T = 320\text{--}360^\circ\text{C}$, $P = 40\text{--}80$ bar, LHSV = 0.75–1.5 h⁻¹, H₂/waste lard volume ratio = 600 Nm³/m³) the INPRP having gas oil boiling range contained merely paraffins (>99.5%) which were mainly C₁₅, C₁₆, C₁₇ and C₁₈ paraffins, namely on the applied catalyst both the HDO and the decarboxylation/decarbonylation reactions took place, as well. The yields of the intermediate product were high (73.9%–79.7%), which approaches well the theoretical values that could be reached in case of the HDO and decarboxylation/decarbonylation reactions; 80.8 and 85.7, resp.). At 300°C, the two main reaction pathways took place at a nearly equivalent degree; by increasing the temperature (320–360°C) the decarboxylation/decarbonylation reactions came to the front. The cold flow properties (e.g., cold filter plugging point) of the intermediate products were unfavourable with 19°C, which was decreased to between –5 and –15 by

the isomerisation over 0.5% Pt/SAPO-11 ($T = 360\text{--}370^\circ\text{C}$, $P = 50$ bar, $\text{LHSV} = 1.0\text{ h}^{-1}$, $\text{H}_2/\text{intermediate product volume ratio} = 400\text{ Nm}^3/\text{m}^3$). The obtained products are excellent waste-origin blending components for diesel gas oils as their cetane number is high (76–88), and because these products are also aromatic-free, burn cleanly, and are environmentally friendly.

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