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INVESTIGATION OF THE HYDROCONVERSION OF LARD AND LARD-GAS OIL MIXTURE ON PtPd/USY CATALYST

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The necessity to maintain mobility and the increasing energy- and environmentally sound demands necessitated the research, development and utilization of engine fuels from renewable resources. Because of the negative features of the already and generally applied bio-derived Diesel fuel, the biodiesel, it was necessary to research and develop other chemical processes that convert triglycerides through different reaction ways. These second generation bio-fuels are the bio gas oils, which are mixtures of n- and i-paraffins. Otherwise these hydrocarbons are the choice components of the fossil derived Diesel fuels. During the experimental work our aim was to investigate the heterogeneous catalytic hydrogenation of waste lard – as a renewable agro-derived feedstock – and by mixing it to deep desulphurized gas oil stream, respectively on PtPd/USY catalyst. In the course of it, we studied the effects of the process parameters (temperature: 300–380 °C, pressure 40-60-80 bar, LHSV: 0.75–1.25 h^{-1}, H_2/feedstock rate: 600 Nm^3/m^3) on the quality and quantity of the products. We determined that during the co-processing of lard and desulphurized gas oil, the saturation of the aromatic content and the deoxygenation of the triglyceride part of the feedstock -isoparaffins formed - took place, respectively and at process temperatures (360–380 °C) found to be favourable by us, excellent, bio-component containing and significantly dearomatized diesel fuel blending components could be obtained. These products meet the valid diesel gas oil standard EN 590:2009+A1:2010, except for their cold flow properties.

Keywords: lard, hydrogenation, PtPd/USY, zeolite, coprocessing, renewable.

Introduction

Mobility is a keystone of great importance in the modern human society. It is essential for maintaining and developing the economy and thus the standard of living, and for meeting the social demands. The material equipment of mobility is the vehicles, nowadays almost every one of them (>95%) operates with fossil derived fuels. The limited amount and the unequal distribution of the available oil reserves is a source of international tensions, therewith to ensure the life standard of their citizens, most countries rely on import. Besides, there are more and more vehicles, so to ensure the mobility means more and more intense environmental pollution. For this reason, on the whole world research has started for the development and utilization of cleaner and more available energy sources. Among these alternative fuels, there are the renewable, agricultural-derived fuels from biomass and amongst them the bio-derived motor fuels (agro-motor fuels).

Bio-derived motor fuels in the European Union

Because of environmental consideration and its intense rely on import energy sources (>55%) the European Union treats the research of agriculture-derived, renewable energy sources with great attention and urges their utilization in greater volumes [1–3], besides attending the agricultural production too.

The 2003/30/EC directive is the first where the European Union literally declared the necessity of the production of bio motor fuels and their extensive utilization [1]. As an effect of this, the diesel fuel standards validated from 2004 allow the blending of bio-components (biodiesel - maximum 5 v/v%, then 7 v/v% from 2009).

The European Council in the COM(2006) 34 strategy of the Union announced seven political keystones and one of them is the effort to expand the feedstock supplies of bio motor fuels [5]. Besides this, the European Union in the COM(2006)845 report specified those steps which must be taken in the interest to increase the 1% share of bio-derived automotive fuels to 10% till 2020. In this report it was determined that the research and development of the second generation bio motor fuels could help to boost the innovation and to preserve the competitiveness of the European Union in the renewable energy sector, and also, with the partial utilization of the second generation bio motor fuels the goal becomes achievable [3].

In the 2009/28/EC (REN – Renewable Energy Directive) directive of the European Union, the European Council confirmed the content of the COM(2006)845 report, namely that the average share of the renewable energy sources must be raised to 20% until 2020, and in it the average content of renewable fuels must be raised to 10% in all automotive fuels in the European market until 2020. Besides, it affirms that the suggested blending amount of bio fuels must be set at minimum 5.75% until 2010 calculated on the basis of the energy content [3].

The valid 2009/30/EC (FQD – Fuel Quality Directive) directive specifies to decrease the GHG emission of the transportation sector with 6%, and to suit it, the valid diesel fuel standard got the supplement A1 [4]. Therefore in the currently valid EN 590:2009+A1:2010 diesel gas oil standard the blendable amount of biodiesel was increased from 5 v/v% to 7 v/v%. Thus the suggested blending amount – 5.75% until 2010 – urged by the European Committee became achievable.

Among the motor fuels, the use of Diesel-fuels decreased at present as a consequence of the worldwide economic crisis, but the long-distance tendency shows increase such as the total use of motor fuels increases and within it the share of the middle distillates increases. Before the worldwide economic crisis, the tendency of the automotive fuel market in the European Union showed a probable increase in the demand [8] for diesel fuels and this tendency will restore in contempt of the feasible spread of hybrid vehicles. Therefore the research and development of the agriculture-derived bio motor fuels is coming to the front.

Triglycerides and their derivatives

The main constituents of the vegetable oils and animal fats are the triglycerides, which are esters of a polyvalent alcohol, the glycerine, and fatty acids with different carbon number *(Fig. 1)*. Since they are natural triglycerides, their carbon number of the chain is always paired and they contain unsaturated bonds in different measure.

For the sake of satisfying the continuously increasing gas oil demand, vegetable oils and their different percentage mixtures with gas oil are attempted to be utilized. However the differences between the physical and utilization properties of the vegetable oils and the conventional diesel fuels do not permit to simply replace the conventional gas oils with vegetable oils [6]. Therefore it is necessary to convert them with different conversion pathways. These conversion pathways can be:

- thermal and
- catalytic pathway.

In practice, the more important is the latter one. From these types of conversions the most important ones are the esterification (specifically esterification with alcohols) and the hydrogenating with motor fuel purpose.

Biodiesel

Nowadays, the agriculture-derived bio motor fuel and bio blending component that is produced and utilized in the greatest volume is the FAME (fatty-acid-methyl-ester) or biodiesel from the first generation biofuels. This is made by the catalytic esterification of vegetable oils and other fats.

However the technologies producing biodiesel and the product itself also have numerous disadvantages [7]:

- high unsaturated content (causing bad thermal-, oxidation-, and thus storage stability),
- high water content (corrosion problems)
- sensitivity to hydrolysis (poor storage stability),
- methanol content (toxic),
- reactive OH-group (corrosion of coloured metals),
- low energy content that results in greater fuel consumption (~10–15%),
- unfavourable cold properties (cold-start and pulverizing, CFPP).
- high production costs compared to the applicational value, etc.

Bio gas oil

The most suitable for the utilization in Diesel engines and the most valuable compounds of the fossil derived gas oils are the normal- and iso-paraffins with high cetane number and with good cold flow properties. [7–11], therefore intense research has started to produce products with similar chemical structure on triglyceride (as a renewable agriculture-derived feedstock) base.

One of the alternatives to produce such a product rich in iso-paraffins on triglyceride base is the catalytic hydrogenation and if necessary, their isomerization. Then the conversion of triglycerides to a product rich in iso-paraffins is recommended by multistage catalytic process (Fig. 1).

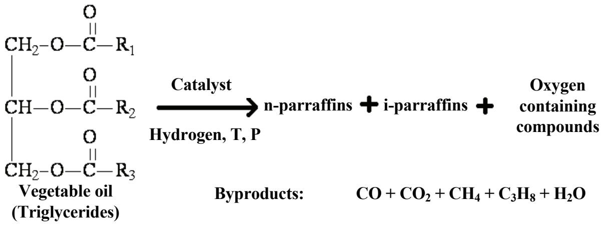

Figure 1: The reaction pathway of the bio gas oil production
(R_1,R_2,R_3: carbon chains with C_{11}-C_{23} carbon number)

Through the reaction pathway, in the first step the hydrogenating of the unsaturated bonds of the triglycerides takes place. Then deoxygenating reaction occurs. In this reaction, monoglycerides and carboxylic acids form and then these intermediates are converted to paraffins by three different pathways: decarboxylation, decarbonylation and hydrodeoxigenation (reduction, HDO). As the next possible step in the process isomerization reactions can occur, of which measure depends on the applied catalyst and process parameters. Cracking reactions may occur in the course of the whole process [8–12].

The product of the reaction is the so called bio gas oil, of which concept was introduced by the MOL Department of Hydrocarbon and Coal Processing of the University of Pannonia [13–14]. According to its definition, the bio gas oil is a mixture of n- and i-paraffins in the gas oil boiling point range, made with specific catalytic hydrogenating process of raw materials with high triglyceride content (vegetable oils, animal fats, used frying oils, brown greases of sewage works etc.).

To produce bio gas oil and products containing it, there are different technological methods according to our experiments and the literature data. It is possible to pre-treat the triglyceride containing feedstock in a pre-treater reactor and then hydrodeoxygenate it, in other words convert it in a second HDO reactor. The obtained product in this technology is rich in normal-paraffins, has very high cetane number (90–105) but besides it, the product needs to be isomerized after the separation to improve its poor cold flow properties (18–26 °C). The bio gas oil obtained with such technology can be blended to deeply desulphurized gas oil stream and thus gas oil with bio-component content can be made. Beyond that, through blending the pre-treated triglyceride containing feedstock to a straight run gas oil stream and process this feedstock mixture in an existing (or slightly modified) desulphurization plant, bio-component containing gas oil can be obtained *(Fig. 2)* [9–13].

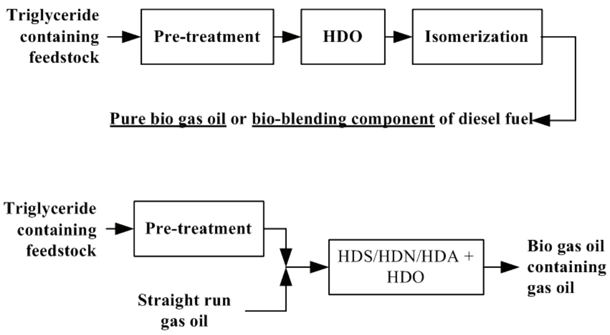

Figure 2: Possible technological solutions to produce bio gas oil

As we aforementioned, a wide range of publications engage in the examination of the conversion of triglycerides per se, or the so called co-processing. However these articles deal mostly with the applicability of desulphurization catalysts (NiMo/Al_2O_3, CoMo/Al_2O_3). The applicability of PtPd/USY catalyst examined in this paper, as we know, have never been published so far. Because of its strongly acidic support, this catalyst may be favourable of the skeletal isomerization of the forming n-paraffins, namely for the oxygen removal in one step and for the CFPP improvement via isomerization, too.

Experimental

During our experimental work our aim was to investigate the possibility of converting properly prepared lard as an agriculture-derived, triglyceride containing renewable feedstock, to bio gas oil on PtPd/USY catalyst. In the course of it, the possibility of processing lard was investigated to make a product which can be utilized in Diesel-engines by itself or as a bio-blending component to conventional gas oils.

Therefore we investigated the possibilities of heterogeneous catalytic conversion of pure (100%) lard and 50% lard containing deep desulphurized gas oil feedstocks, respectively, on PtPd/USY catalyst. The process parameters were chosen on the basis of our previous experimental results considering the physical and chemical properties of the feedstocks

Experimental equipment

The experiments were carried out on experimental equipment with a tubular reactor of 100 cm^3 active volume capacity *(Fig. 3)*. The experimental work was carried out in continuous mode. The equipment contains all of the main apparatus of a heterogeneous catalytic hydrogenation plant [12].

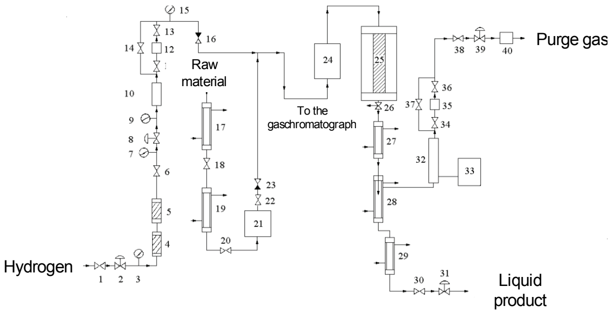

Figure 3: Experimental equipment

Applied feedstocks and catalyst

As the base stock of the heterogeneous catalytic hydrogenating experiments we used lard (fatty acid composition is in *Table 1*) of Hungarian origin and a deep desulphurized gas oil stream (properties in *Table 2*) – derived by MOL Plc. – obtained from Russian crude. As feedstocks we used pure lard, pure gas oil and their mixtures of 50%.

As catalyst we applied PtPd/USY catalyst. This catalyst sensible for sulphur containing compounds, that is why we used already deep desulphurized gas oil fraction as our gas oil feedstock.

Table 1: The typical fatty acid composition of the applied lard feedstock

Fatty Acid	Lard
C14:0	1.19
C16:0	21.35
C16:1	2.04
C18:0	11.54
C18:1	45.40
C18:2	12.50
C18:3	0.78
C20:1	1.06
C22:2	0.67

*CX:Y, where

X: carbon number of the fatty acid,

Y: number of the unsaturated bonds in the fatty acids.

**other – fatty acids with higher carbon number than C_{22}

Table 2: The heteroatom and aromatic content of the feedstocks

Properties	Gas oil	Lard
Sulphur content, mg/kg	5	20
Nitrogen content, mg/kg	<1	61
Aromatic content, %	22.5	0.0
Polyaromatic content, %	2.4	

Process parameters

The series of experiments were carried out at process parameters based on previous experimental results: T: 300–380 °C, P: 40-60-80 bar, LHSV: 0.75-1.25-2.0 h^{-1}, H_2/feedstock ratio: 600 Nm^3/m^3.

Analytical methods

The properties of the feedstocks and the products were specified according to the specifications of the valid EN 590:2009+A1:2010 diesel fuel standard, and with standardised calculation methods. The obtained liquid organic product's composition was identified by gas chromatography.

Obtaining the main product fraction

The fractionating of the product mixture was carried out as it can be seen in *Fig. 4*. In the course of the experiments, the product mixture was separated into gaseous and liquid phase in the separator unit of the experimental equipment. After separating the water from the obtained liquid product mixture, we separated the light, C_5-C_9 hydrocarbon products by distillation up to 180 °C from the organic liquid phase.

The fraction above the boiling point of 180 °C was separated to gas oil boiling point range main product (C_{10}-C_{22} hydrocarbons up to the boiling point of 360 °C) and to residual fraction by vacuum-distillation. All product yields are based on the amount of the feedstock.

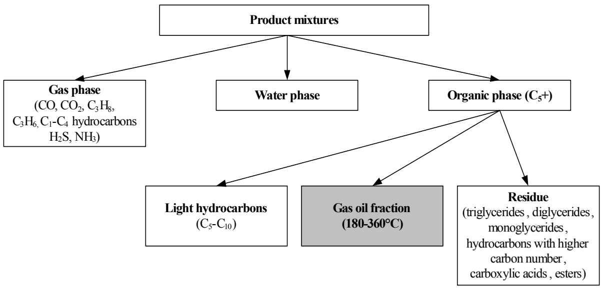

Figure 4: The method of the product fractionating

Results and discussion

The gaseous phase besides hydrogen, contained carbon-oxides formed during the deoxygenation, propane originated from the triglyceride molecule, hydrogen sulphide and ammonia formed in the course of heteroatom removal and a very small amount of lighter hydrocarbons (C_{4-}) originated from the hydrocracking reactions. The increasing amount of the lighter hydrocarbons (C_{4-}) in the gaseous phase and mainly the amount of the fraction below boiling point of 180 °C (C_5-C_{10}) shows *(Fig. 5)* that the hydrocracking activity of the applied catalyst increased with the temperature.

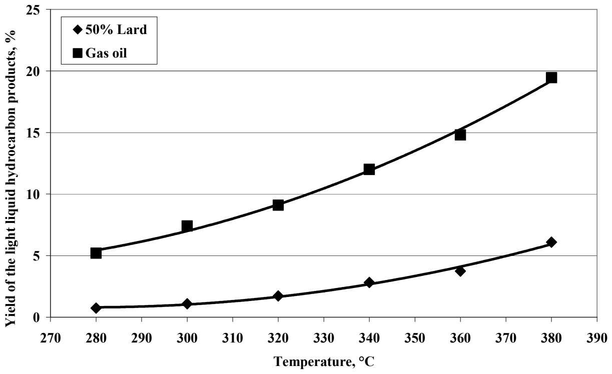

Figure 5: Yield of the light liquid hydrocarbons (boiling point <180 °C) as function of the temperature (40 bar, 1.25 h^{-1})

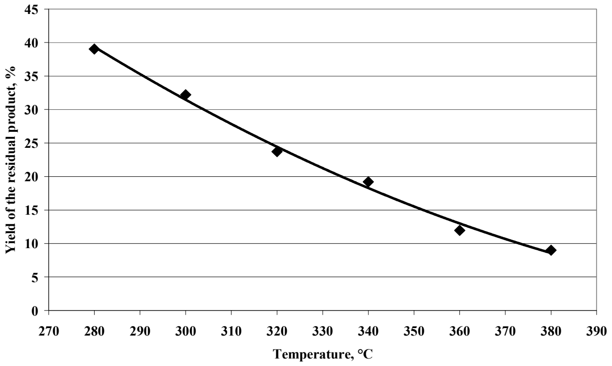

Figure 6: Yield of the residual fraction as a function of the temperature (40 bar, 1.25 h^{-1}, 50% Lard)

The decreasing yield of the residual fraction with increasing the temperature *(Fig. 6)* as well as the increasing yield of the main product fraction with increasing the temperature *(Fig. 7)* inform us about the increasing conversion of the triglyceride part of the feedstock.

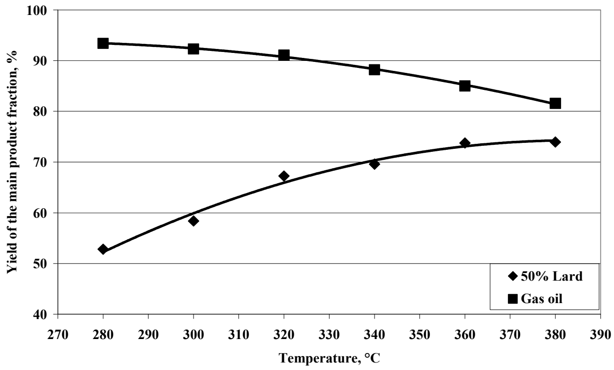

Figure 7: The yield of the gas oil boiling point range (180–360 °C) main product as a function of the temperature
(40 bar, 1.25 h^{-1})

Fig. 8 provides information about how the different deoxygenating reactions take place and about the relationship between them. In the course of the deoxygenation of the natural – and so its is containing fatty acids with conjugated carbon numbers in their carbon chains – triglycerides, during the hydrodeoxygenation (HDO) reaction pathway paraffins with the same carbon numbers as the fatty acids are forming next to water, while in the course of decarboxylation-decarbonylation (DCX) reaction pathways, paraffins with one less carbon numbers as the fatty acids are forming next to carbon oxides.. As it can be seen on Fig. 8, the DCX reaction pathway come to the front with increasing the temperature, at the expense of the HDO reaction pathway.

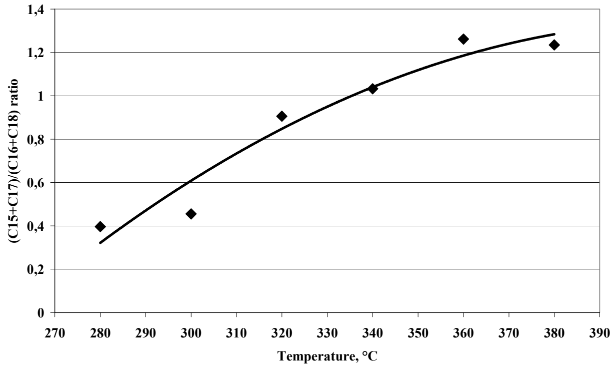

Figure 8: The ratio of DCX/HDO reaction pathways as a fiunction of the temperature
(40 bar, 1.25 h^{-1}, 50% Lard)

By increasing the pressure as a process parameter, it can be seen that the yield of the main product fraction decreased in the case of each feedstock *(Fig. 9)*. Fig. 9 suggests that in the case of pure lard feedstock the conversion is lower than 50% and in the case of the most favourable process parameters only a maximum conversion of about 60% has been achieved nevertheless that the maximum theoretical conversion is about 80.7–85.5%, in the case of DCX-HDO reaction pathway, respectively. Based on this, it can be stated, that the applied catalyst is not suitable for the hydrodeoxygenation of pure triglyceride feedstock or at least not at the examined process parameters. However, in the case, of 50% triglyceride containing feedstock, higher conversion of the triglyceride part can be achieved and at process parameters of 380 °C, 40–60 bar and 0.75 h^{-1} full conversion of the triglyceride part occurs. On *Fig. 10*, it can be seen, that with increasing the pressure, the HDO reaction pathway come to the front, while the DCX reaction pathway declined.

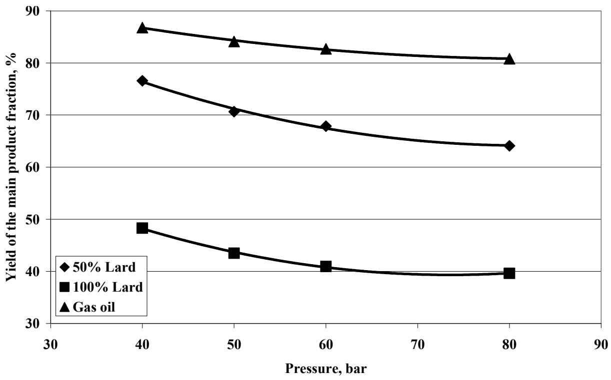

Figure 9: Yield of the main product fraction as a function of the pressure
(360 °C, 1.25 h^{-1})

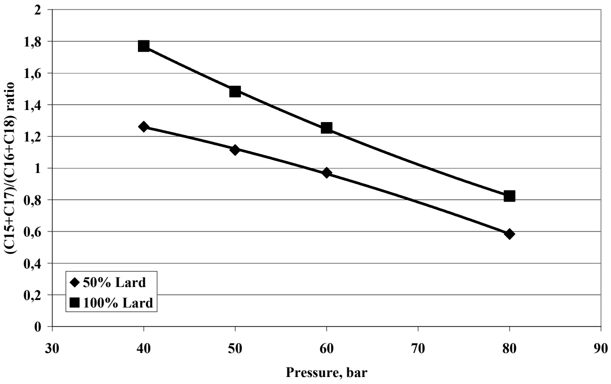

Figure 10: The ratio of DCX/HDO reaction pathways as a function of the pressure
(360 °C, 1.25 h^{-1})

On *Fig. 11*, the yield of the gas oil boiling point range main product fraction can be seen as a function of the liquid hourly space velocity. It can be seen, that with increasing liquid hourly space velocity, the yield of the main product fraction increases in the case of pure gas oil feedstock, while it is decreases in the case of triglyceride or triglyceride containing feedstock, because of the lowering retention time with the increasing liquid hourly space velocity. In the first place, crack reactions decline, and in the case of triglyceride containing feedstocks, the triglyceride conversion decreases. By increasing the liquid hourly space velocity, in the case of pure lard feedstock, the DCX reaction pathway come to the front *(Fig. 12)*, while in the case of 50% lard containing feedstock, opposing trend can be seen, namely, the HDO reaction pathway come to the front while the DCX reaction pathway declined. This occurs, because of the different heteroatom content of the feedstocks, as in the case of pure lard, the oxygen content of the feedstock is about 11.6% without detectable aromatic content, while in the case of 50% lard containing feedstock means 5.8% oxygen heteroatom with nearly 12.5% aromatic content from the gas oil part of the feedstock. So, with increasing pressure, different reaction pathways come to the front in the case of different feedstocks.

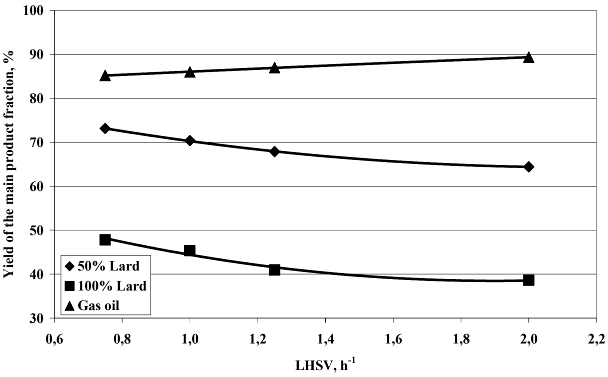

Figure 11: Yield of the main product fraction as a function of the liquid hourly space velocity (360 °C, 60 bar)

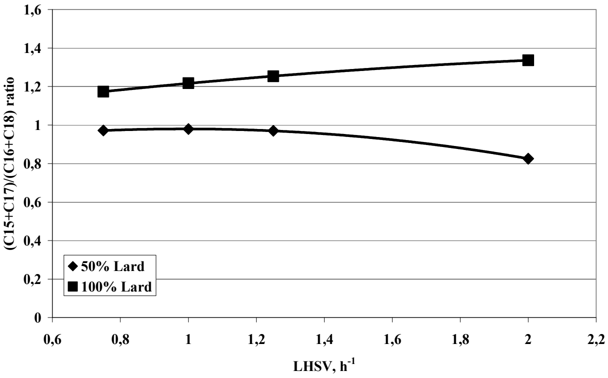

Figure 12: The ration of DCX/HDO reaction pathways as a function of the liquid hourly space velocity (360 °C, 60 bar)

To produce up to date Diesel gas oils the dearomatization of the feedstocks is necessary too. The decrease of the aromatic content of the gas oils are essential not only because the regulations of the valid standards. With decreasing the aromatic content the cetane number of the gas oil increasing and thus the emission. In the case of a two step desulphurizating and dearomatizating process, the PtPd/USY catalyst examined in this paper can be applied for the second, dearomatizing step.

On *Fig. 13* it can be seen, that at the temperature of 320 °C and above the quantity of the aromatic compounds decreased significantly (Fig. 7). This effect shows the increasing hydrogenating activity of the catalyst with increasing temperature. As an affect of the increasing temperature, above 330–340 °C the dearomatization efficiency – on account of the thermodynamical inhibition caused by the exothermal dearomatization reactions – decreased.

By applying the most favourable process parameters for dearomatization (340 °C, 40 bar, 0.75–1.25 h^{-1}) a dearomatization efficiency of about 70% is achieved. On Fig. 13, it can be seen that in the case of 50% triglyceride containing feedstock, compared with what can be experienced in the case of pure gas oil feedstock, it is turned up, that the most favourable process temperature for achieve the maximum dearomatizing efficiency slightly higher, thanks to the high heteroatom content of the feedstock originated from its triglyceride part.

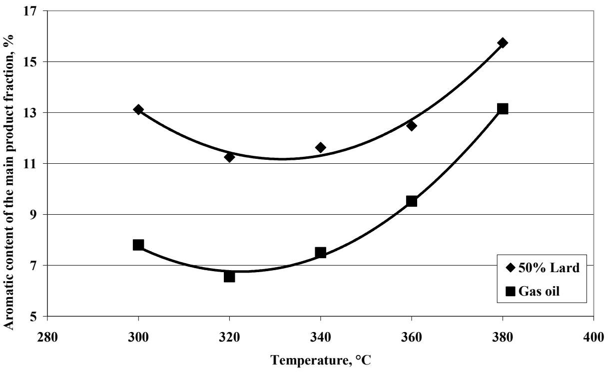

Figure 13: The aromatic content of the main product fractions as a function of the temperature (40 bar, 1.25 h^{-1}, 50% Lard)

Conclusions

In this paper we shortly introduced the necessity for the research and development of the bio-derived motor-fuels, the already known bio-derived fuels of Diesel-engines and the bio gas oil or bio gas oil containing gas oil producing technologies, respectively.

During our experimental work we investigated the heterogenous catalytic hydrogenation of lard, as a renewable agriculture-derived feedstock, deep desulphurized gas oil fraction and their 50% mixture on PtPd/USY catalyst. The properties of the feedstocks and the products were specified according to the specifications of the valid EN 590:2009+A1:2010 diesel fuel standard, and with standardised calculation methods.

We found that with the applied catalyst, in the case of pure lard feedstock even at the most favourable process parameters (380 °C, 40 bar, 0.75 h^{-1}) only about a conversion of 60% can be achieved. In the case of 50% lard containing feedstock, by applying these favourable process parameters (380 °C, 40 bar, 0.75 h^{-1}) full conversion of the triglyceride part can be achieved, however in the case of this process temperature, the dearomatization efficiency (38.7%) of the gas oil part declined because of thermodynamical inhibition and because of the high oxygen content (5.8%) originated from the triglyceride part of the feedstock. In the case of these process parameters, the cracking activity of the applied catalyst significantly increased too, since the yield of the light liquid hydrocarbons (C_5-C_{10}) was about 20%. Meanwhile, the yield of the gaseous product did not increase significantly. The cold filter plugging point of the obtained main product fractions at the most favourable process parameters did not decrease below +15°C in the case of 50% lard containing feedstock, because of the high amount of n-paraffins formed during the conversion of the triglyceride part. In the case of 50% lard containing feedstock, at process parameters of 340–360 °C, 40–60 bar and 0.75–1.25 h^{-1} a main product yield of about 85% can be achieved on the basis of the feedstock and in addition, the aromatic content of the products also decreased significantly. The properties of the main product fractions obtained at these process parameter combinations and in the case of 50% lard containing feedstock meet the valid diesel gas oil standard EN 590:2009+A1:2010, besides their cold flow properties (15–17 °C).

However these products could be excellent diesel gas oil blending components because their low sulphur-, nitrogen-, and aromatic content, and because their high cetane number (about 75 unit) ensured by the n-paraffins forming during the triglyceride conversion.

The cold flow properties of the products are improvable by catalytic hydroisomerization of the n-paraffins then with additives. Hereby high quality bio-motor fuel or bio-derived blending component containing Diesel motor fuel could have been obtained which meet the valid diesel gas oil standard EN 590:2009+A1:2010.

In short, we determined, that by the application of PtPd/USY catalyst in the case of pure lard feedstock, full hydrodeoxygenating conversion of the triglyceride is not achievable, however in the case of mixture feedstock of 50% lard and 50% deep desulphurized gas oil fraction, by applying the favourable process parameters (340–360 °C, 40–60 bar), nearly full conversion of the triglyceride part can be achieved, while the dearomatizing of the gas oil part occurs substantially also.

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