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EXPANDING FEEDSTOCK SUPPLIES OF THE SECOND GENERATION BIO-FUELS OF DIESEL-ENGINES

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Nowadays the first generation bio-fuels are already introduced in the European Union and amongst them the one used in Diesel-engines is the triglyceride containing feedstock derived product, the so-called biodiesel. However these fatty-acid-methyl-esters have multiple disadvantages (e.g.: poor oxidation and heat stability, lower energy content than the fossil derived diesel fuels, etc.) because of their chemical structure. Therefore it has become necessary to develop new bio-derived fuels on triglyceride supply, with other chemical structure. These bio-derived fuels are the second generation bio-fuels and amongst them the most promising product is the bio gas oil. The bio gas oil is a mixture of n- and i-paraffins (these are the primal components of the fossil diesel fuels also) in the gas oil boiling point range made from triglyceride containing feedstock. To ensure the eligible quantity and quality of bio gas oils, it is necessary to examine the utilization of other feedstocks with high triglyceride content. The European Union also urges the expanding of the feedstock supplies of the bio-derived motor fuels [COM(2006)34]. During our experimental work we examined the possibilities of the catalytic hydrogenation of mixtures of gas oil and lard or vegetable oil respectively, on $NiMo/Al_2O_3$ catalyst. Besides the examination of the reaction parameters (temperature: 360 °C, pressure: 80 bar, LHSV: 1.0 h^{-1} , H_2/feedstock ratio: 600 Nm^3/m^3) which were found to be congenial for the catalytic conversion of vegetable oils for the conversion of the different, respectively lard or vegetable oil containing (0–10–20–30–50–100%) gas oil feedstocks we investigated the convertibility of the triglyceride part and the effect of the feedstock on the quality and the quantity of the product, furthermore the effect of the triglyceride in the feedstock on the desulphurisation, denitrification and dearomatisation. We determined that in the case of respectively 10% vegetable oil or lard containing feedstocks, the product was already an excellent bio-constituent containing diesel fuel blending component.

Keywords:, bio gas oil, lard, sunflower oil, bio-derived blending component, catalytic co-processing

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 (>97%) 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) [1, 2, 3].

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 [4, 5, 6].

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 [4]. 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 it becomes achievable to increase the share of bio motor fuels to 10% till 2020 [6].

In the 2009/28/EC 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 [6].

To suit the valid 2009/28/EC directive, the valid diesel fuel standard also changed. 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. The tendency of the automotive fuel market in the European Union – before the worldwide economic crisis – showed a probable increase in the demand [7] for diesel fuels. 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* and *2).* 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 [1, 2, 3, 8]. 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 biodiesel from the first generation biofuels. This is made by the catalytic esterification of vegetable oils and other fats (Fig. 1) [1, 2, 3, 9].

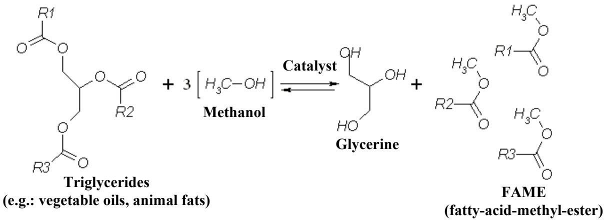

Figure 1: The reaction pathway of the esterification of an average triglyceride molecule (vegetable oil)
(R_1, R_2, R_3: carbon chains with C_{11}-C_{23} carbon number)

However the technologies producing biodiesel and the product itself also have numerous disadvantages [1, 2, 3, 9]:

- 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).

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. [1, 2, 3, 10, 11, 12, 13, 14], 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. 2).

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 [3, 10, 11, 12, 13, 14].

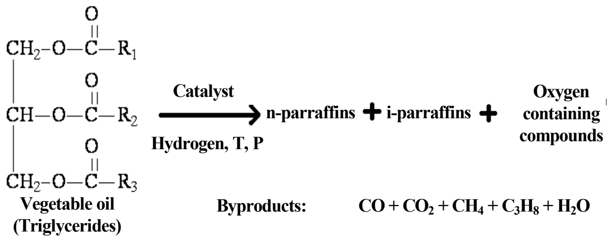

Figure 2: The reaction pathway of the bio gas oil production
(R_1,R_2,R_3: carbon chains with C_{11}-C_{23} carbon number)

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 [3, 12, 13]. 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, fats, used frying oils, 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 but besides it, the product needs to be isomerized after the separation to improve its poor cold flow properties. 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 [11, 12, 13, 14, 15].

Experimental

During our experimental work our aim was to expand the feedstock supplies of the bio gas oils. In the course of it, the possibility of processing the lard as an agriculture-derived, renewable feedstock 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 0%, 10%, 20%, 30%, 50%, 100% lard or sunflower oil containing gas oil feedstock, respectively, on NiMo/Al_2O_3 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. The experimental work was carried out in continuous mode. The equipment contains all of the main apparatus of a heterogeneous catalytic hydrogenation plant [15].

Applied feedstocks and catalyst

As the base stock of the heterogeneous catalytic hydrogenating experiments we used lard and sunflower oil (fatty acid composition is in *Table 1*) of Hungarian origin and straight run gas oil stream – derived by MOL Plc. – obtained from Russian crude. As feedstocks we used 0%, 10%, 20%, 30%, 50%, 100% mixtures of gas oil and lard or sunflower oil, respectively.

Table 1: The typical fatty acid composition of the applied lard and sunflower oil

Fatty acid	Lard (L)	Sunflower oil (SO)
C12:0	1.70	0.00
C16:0	26.00	0.09
C16:1	2.30	6.33
C18:0	16.50	3.45
C18:1	36.60	21.64
C18:2	11.30	67.28
C18:3	0.70	0.09
C20:0	0.20	0.23
C20:1	0.80	0.13
C22:0	0.20	0.72
other	3.60	0.04

*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}

In the case of pure sunflower oil and lard, the sulphur content of the feedstock was adjusted to 1000 mg/kg with the use of sulphur containing chemical (dimethyl-disulphide) in the interest of preserving the sulphide state of the catalyst, otherwise, the sulphur content was covered by the gas oil part.

Table 2: The heteroatom and aromatic content of the feedstocks

Properties	Gas oil	L	SO
Sulphur content, mg/kg	10370	20	3
Nitrogen content, mg/kg	228	61	9
Aromatic content, %	33.0	0.0	0.0
Poliaromatic content, %	12.7		

As catalyst we applied in-situ sulphided NiMo/Al_2O_3 catalyst which was chosen on the basis of our previous experimental results.

Process parameters

The series of experiments were carried out at process parameters based on previous experimental results: T: 360 °C, P: 80 bar, LHSV: 1.0 h^{-1}, H_2/feedstock ratio: 600 Nm^3/m^3. By applying these process parameters high triglyceride conversion with high selectivity can be achieved [16], the dearomatization efficiency of the catalyst reaches its maximum at 350–360 °C [17], the desulphurization and denitrification activity of the catalyst is high too, while its hydrocracking activity is very low [17].

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

The fractionating of the product mixture was carried out as it can be seen in *Fig. 3.* 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. Their amount was negligible in each case (less than 0.1% compared to the feedstock). 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.

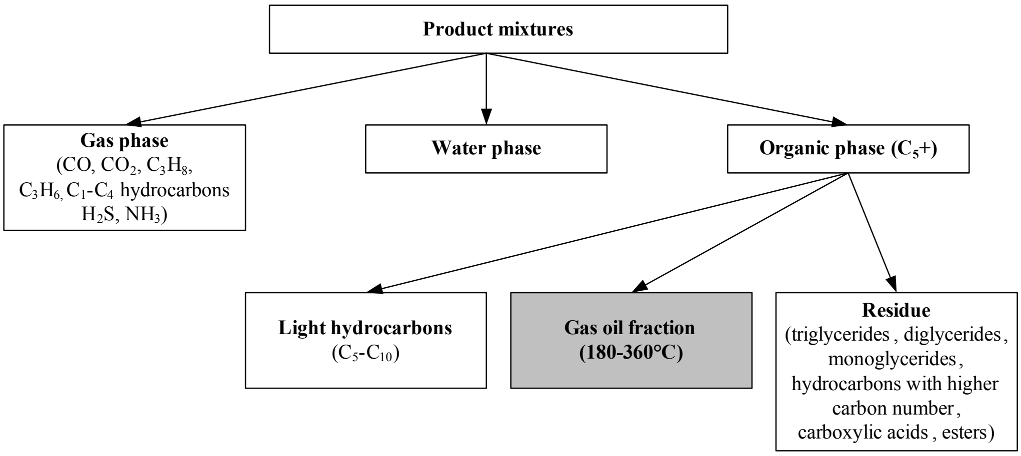

Figure 3: The method of the product fractionating

Results and discussion

The gaseous phase 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 latter one shows the low hydrocracking activity of the applied catalyst.

As it can be seen in *Fig. 4*, the yield of the gas oil boiling point range main product fraction decreased with increasing the triglyceride content of the feedstock, because in the course of the catalytic hydrogenating of the triglycerides, a large amount of propane and water forms too. In the case of lard containing feedstocks the yield of the main fraction decreased with the increasing lard content of the feedstock compared to the feedstocks containing sunflower oil. The cause of this was partially the higher oxygen content of the lard, which is the consequence of the lower carbon number fatty acids in the lard. Besides this, the lard contains fatty acids with higher carbon number than C_{22} which are not in the boiling point range to 360 °C (boiling point of n-C_{24}: 391 °C).

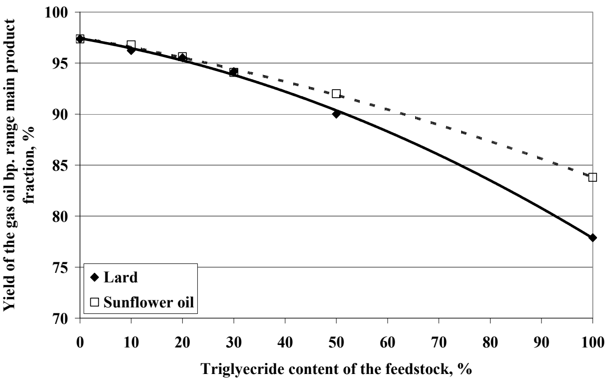

Figure 4: The yield of the gas oil boiling point range main product as the function of the triglyceride content of the feedstock

The yield of the residual fraction *(Fig. 5)* shows that to 50% sunflower oil content of the feedstock, the sunflower oil part was converted entirely, while in the case of lard, above 30% lard content of the feedstock the conversion was not complete. That is also due to the fatty acid chains with higher than C_{22} carbon number of the lard, since they are not in the boiling point range of the main product fraction.

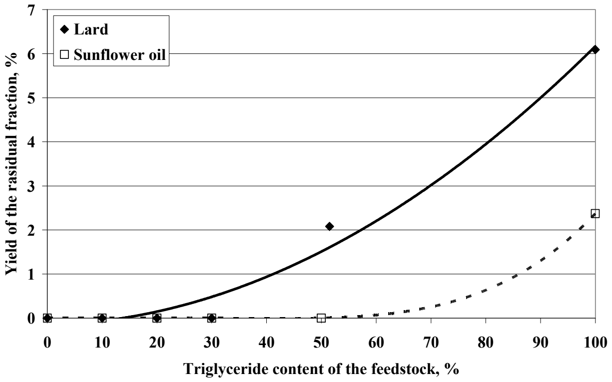

Figure 5: The yield of the residual fraction as a function of the triglyceride content of the feedstock

The differences between the products originated from the different fatty-acid composition of the sunflower oil and the lard are shown in *Fig. 6* and *7*. While the sunflower oil contains mainly C_{18} fatty-acids, and thus mainly C_{18} and C_{17} paraffins form during the catalytic hydrogenation, in the case of lard the amount of C_{18} fatty-acids is lower in it and in the feedstock, so that means less C_{18} and C_{17} paraffins in the product mixture.

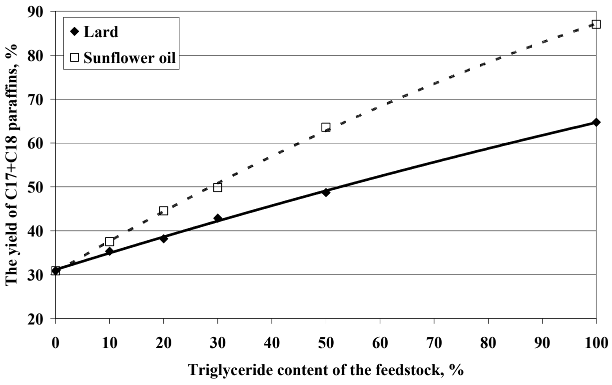

Figure 6: The yield of C_{17} and C_{18} paraffins as a function of the triglyceride content of the feedstock

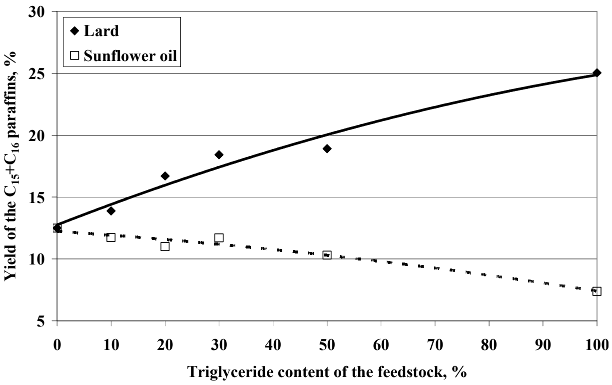

Figure 7: The yield of C_{15} and C_{16} paraffins as a function of the triglyceride content of the feedstock

The lard contains C_{16} fatty-acids in high concentration, so the amount of C_{15} and C_{16} paraffins increased the yield of the gas oil boiling point range main fraction with increasing the lard content of the feedstock.

On the other hand, the triglycerides forming the sunflower oil contain only a small amount of C_{16} fatty-acids (Table 1), and so the yield of the C_{15} and C_{16} paraffins *(Fig. 8)* decreased with the increasing sunflower oil content of the feedstock.

In the case of pure gas oil (22 mg/kg), sunflower oil (28–49 mg/kg) and as regards feedstocks up to 20% lard content (35–47 mg/kg), the sulphur content of the gas oil boiling point range main products was below 50 mg/kg, however we were not able to reach sulphur content below 10 mg/kg specified by the valid diesel fuel standard in either case. For the main products obtained in the case of feedstocks with lard content higher than 20%, the sulphur contents were 75 and 148 mg/kg, respectively. We did not find any significant difference between the sulphur contents (25 and 27 mg/kg) of the main product fractions obtained from pure sunflower oil or lard. This was caused by the process temperature, which entailed that the desulphurisation efficiency was not high enough.

The polyaromatic content of the products fulfilled the specification of maximum 8% of the valid diesel gas oil standard in every case.

As it can be seen in *Fig. 8, 9* and *10*, the desulphurization, denitrification and dearomatization efficiency decreased with the increasing triglyceride content of the feedstock, because these reactions occur on the same active sites of the catalyst as the deoxygenating of the triglycerides.

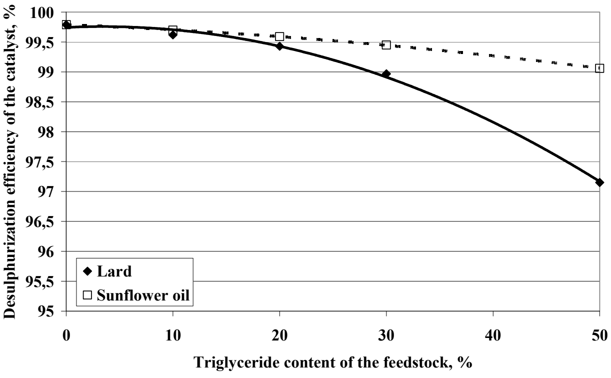

Figure 8: The desulphurization efficiency of the catalyst as a function of the triglyceride content of the feedstock

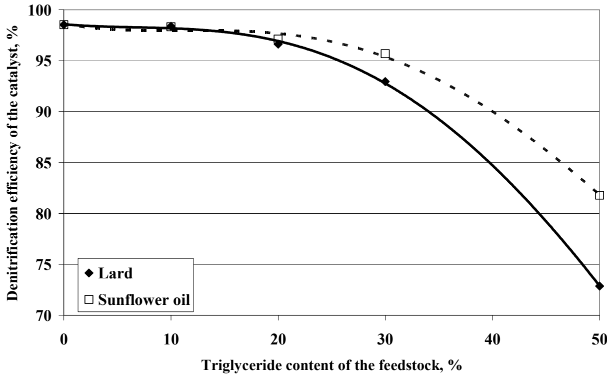

Figure 9: The denitrification efficiency of the catalyst as a function of the triglyceride content of the feedstock

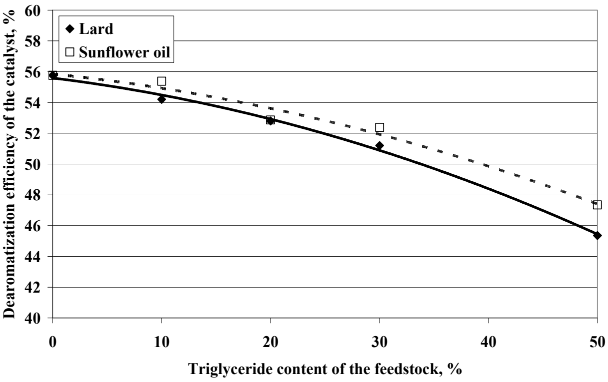

Figure 10: The dearomatization efficiency of the catalyst as a function of the triglyceride content of the feedstock

In the case of lard containing feedstocks the efficiency of desulphurization, denitrification, dearomatization fell behind compared to the feedstocks with sunflower oil content. The lard's higher heteroatom content *(Table 2)* compared to the sunflower oil's causes higher heteroatom concentration at the active sites which means the inhibition of the reactions.

The cold filter plugging points (CFPP) of the gas oil boiling point range main products obtained from lard containing feedstocks were more favourable (with 2–3 °C) compared to the sunflower oil containing feedstocks *(Fig. 11).* This effect was due to the high concentration of the forming C_{15} and C_{16} paraffins from the lard part of the feedstock. The CFPP values of these are more favourable than the CFPP values of the C_{17} and C_{18} paraffins.

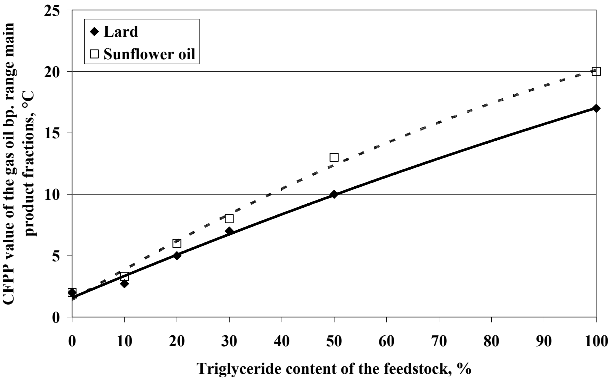

Figure 11: The CFPP value of the gas oil boiling point range main product fractions as a function of the triglyceride content of the feedstock

In spite of this, we obtained products that meet the maximum +5 °C CFPP value specified by the valid diesel fuel standard only in the case of pure gas oil and feedstock containing 10% triglyceride because mostly n-paraffins form during the conversion of triglycerides, of which cold flow properties are unfavourable (+15(-)+25 °C).

Summary and conclusions

On the basis of our experimental results we determined that in the case of lard the triglyceride conversion is lower (more residual fractions) compared to sunflower oil, because of the higher heteroatom concentration of the lard, and in consequence of the higher than C_{22} carbon number fatty-acid content (3.6%) of the lard, of which boiling point is above 360 °C.

The yield of the C_{17} and C_{18} paraffins was essentially higher (50% NO – 63.57% and 50% SZS – 48.72% respectively) in the case of sunflower oil containing feedstocks, because the sunflower oil builds up with mainly C_{18} fatty-acids. The yield of the C_{15} and C_{16} paraffins was higher (50% NO – 10.30% and 50% SZS – 18.9% respectively) in the event of lard containing feedstocks since the lard contains C_{16} fatty-acids in high concentrations. This surplus C_{16} in the case of lard containing feedstocks supplements the amount of C_{15} and C_{16} dropped out by the blending of the bio-component sunflower oil as a consequence of the lower gas oil (in the case of pure gas oil the C_{15} and C_{16} content is 12.49%) content of the feedstock and it even means a surplus in the yield.

Because of the effect of the higher heteroatom concentration of the lard, the dearomatization (50% SZS – 45.3% and 50% NO – 47.3% respectively), the desulphurization (50% SZS – 97.1% and 50% NO – 99.0% respectively) and the denitrification (50% SZS – 72.9% and 50% NO – 81.8% respectively) efficiency was higher in the case of feedstocks containing sunflower oil.

The obtained main product fractions – except for their CFPP values and sulphur contents – met the valid MSZ EN 590:2009+A1:2010 diesel gas oil standard. The obtained products can be excellent diesel gas oil blending components because of their low aromatic content and beside it their high cetane numbers (65–90) provided by the n-paraffins formed during the conversion of the triglycerides.

The CFPP values of the products obtained in the case of lard containing feedstocks were more favourable (with 2-3 °C) compared to the sunflower oil containing feedstocks, however it is necessary to improve these values (e.g.: by the catalytic isomerization of the n-paraffins).

On the whole, we found that the lard is suitable for the production of high quality agricultural-derived Diesel gas oil blending component through catalytic hydrogenation.

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