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INVESTIGATION OF THE HETEROGENEOUS CATALYTIC TRANSFORMATION OF VEGETABLE OIL/GAS OIL BLENDS

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The applicability of vegetable oils (tryglycerides) and their derivates is well-known for a long time. The main goal (to produce fuels from non-fossil based energy source) has been extended with the global aims of reducing the environmental pollution. Therefore the main objective now is to produce, store, transport and use fuels with lower emission levels. Until the last couple of years the vegetable oils were mostly transesterified catalytically to biodiesel to produce fuels. Because of the numerous disadvantages of biodiesel production and application the alternative chemical transformations of triglycerides were started to be studied intensively. One of the best alternative is to convert the vegetable oils (or other materials containing triglycerides) and/or their blends with gas oil to hydrocarbons rich in paraffins. These compounds can be applied in Diesel-engines directly or blended with petroleum-based gas oil. In our experimental work we examined the heterogeneous catalytic conversion of light gas oil fraction containing 10% sunflower oil on transition metal/Al_2O_3 catalyst. Our objective was to study the effect of the operating parameters to the yield of liquid organic products, to the yield of the fraction of gas oil boiling point range and to the product properties. Based on our results it can be concluded that with the catalytic hydrogenation of the feedstock containing 10% sunflower oil products with excellent properties can be produced with high yield. The product gas oil had <10 mg/kg sulphur and nitrogen content, lower than 10% total aromatic content and <-5°C cold filter plugging point. The cetane number of the products was significantly higher than the limit (51) of the EN 590:2004 standard.

Keywords: sunflower oil, vegetable oil-gas oil mixtures, biogasoil, heterogenous hydrogenation.

Introduction

The applicability of vegetable oils (tryglycerides) and their derivates is well-known for a long time. The main goal (to produce fuels from non-fossil based energy source) has been extended with the global aims of reducing the environmental pollution, thus to produce, store, transport and use fuels with lower emission levels (carbon-monoxide, hydrocarbons, sulphur- and nitrogen-oxides, particulates, carbon-dioxide). This could contribute to reduce the chances of acidic rains and the emergence of greenhouse effect. It is well-known that vegetable oils and their derivatives are biodegradable fuels.

The aim to use biofuels is significant mostly in the countries of European Union. The main reason for this is the deliberate energy policy of the European Union, which would like to decrease its dependence on import crude oil due to the unequal distribution of the world's crude oil reserves. To help this aim, the European Council and the European Parliament made the 2003/30/EC directive which commited the countries to raise their biofuel share to 2.0% (until 2005) and 5.75% (until 2010) according to the energy content of the transportation-use gasoline and gas oil [1]. As a result in the EU the share of biofuels was only 1.4% in 2005 [2]. According to the newest aims in the EU countries this value has to be raised to a minimum average of 10% until 2020 [3].

One of the solution could be the conversion of vegetable oils and other triglycerides to different fuels, primarily to gas oil boiling range products. Until the last couple of years the most commonly applied conversion of triglycerides containing vegetable oils was their catalytic transesterification to biodiesel fuel (vegetable oil fatty acid methyl esters) [4].

This technology and the biodiesel itself have numerous disadvantages which have adverse effect on the applicability and the economics. One main problem is the high amount of glycerol by-product, which caused overproduction in the world market and reduced the price of the glycerol *(Fig. 1).* The glycerol can be unmerchantable in the near future [5].

The alternative chemical transformations of triglycerides were started to be studied intensively due to the numerous disadvantages of biodiesel production and application [6-10] (e.g. high iodine value, high water content, higher CFPP (cold filter plugging point), higher viscosity, hydrolysis sensitivity, storage problems, phosphorous content, methanol content, lower energy content, lower heating value, higher cost).

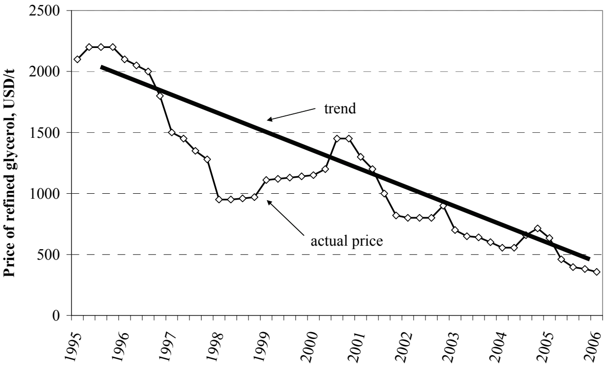
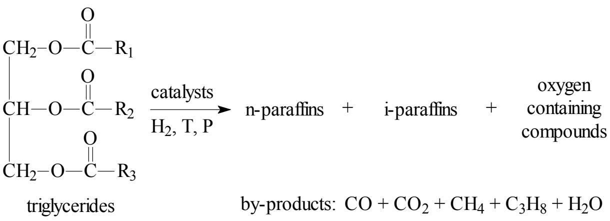


Figure 1: Changing of the price of refined glycerol

One of the best alternative is to convert the vegetable oils (or other materials containing triglycerides) and/or their blends with gas oil to hydrocarbons rich in paraffins. These compounds can be applied in Diesel-engines directly or blended with petroleum-based gas oil.

Through the reactions of catalytic hydrogenation of triglycerides primarily normal and isoparaffins, propane, carbon-oxides (CO_2, CO), water and oxygenate compounds are formed according to the next gross equation:

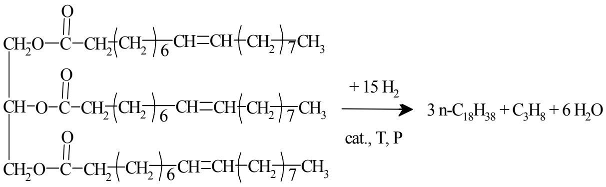


by-products: $CO + CO_2 + CH_4 + C_3H_8 + H_2O$

Through this process the adequately pretreated triglycerid molecules transform simultaneously or consecutively according to the following reactions [11,12]:

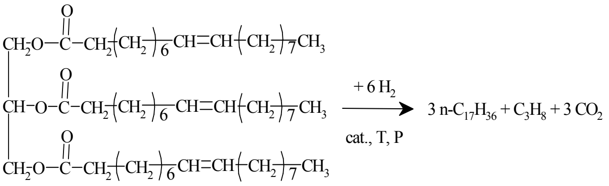
- saturation (hydrogenation) of double bonds,
- heteroatom removal,
  - hydrodeoxygenation (dehydration, HDO reaction),
  - decarboxylation,
  - decarbonization,
- (hydro)cracking of fatty acid chains.

Through the catalytic hydrodeoxygenation (dehydration, HDO reaction) 1 mol triglycerid molecule is converted to 3 mol n-paraffins having the same chain length as the fatty acid and furthermore, to propane and water (for example in the case of a triglycerid which contains three oleic acid chain) according to the followings:



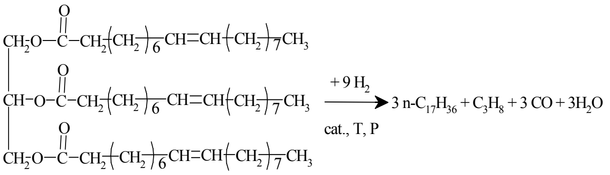
$$\xrightarrow[\text{cat., T, P}]{+15\,H_2} 3\ n\text{-}C_{18}H_{38} + C_3H_8 + 6\,H_2O$$

During decarboxylation reaction the deoxygenation produce CO_2 beside the saturation (hydrogenation) of the double bonds in the fatty acid chain. In this case carbon number of the emerging hydrocarbons is lower by one compared to the triglycerid chains. (for example in the case of a triglycerid which contains three oleic acid chain):



$$\xrightarrow[\text{cat., T, P}]{+6\,H_2} 3\ n\text{-}C_{17}H_{36} + C_3H_8 + 3\,CO_2$$

During decarbonization reaction 1 mol triglycerid is converted to 3 mol n-paraffins which have lower carbon number by one compared to the fatty acid chains. Propane, carbon-monoxide and water are also produced.



$$\xrightarrow[\text{cat., T, P}]{+9\,H_2} 3\ n\text{-}C_{17}H_{36} + C_3H_8 + 3\,CO + 3H_2O$$

The probability of these deoxygenation reactions depends on the catalyst, the temperature, the pressure and the liquid hourly space velocity. According to our experience, usually all three reactions take place simultaneously.

The heterogeneous catalytic transformation of vegetable oil triglycerides in the presence of hydrogen can be performed in different ways *(Fig. 2).* In the first alternative process the vegetable oil (or/and other triglycerid) is deoxygenated after adequate pretreatment, and the produced high n-paraffin containing mixture is isomerized (if necessary and after separation). The product, which has high cetane number and good cold flow properties, is called biogasoil [10, 13, 14]. In the second alternative process the vegetable oil are deoxygenated after the pretreatment and the produced high n-paraffin containing mixture (very high cetane number, but bad cold flow properties) is blended into ultra low sulphur gas oil [15].

In the third alternative process the pretreated vegetable oil is blended into a refinery gas oil stream and the mixture is converted in an existing (or slightly modified) desulphurization unit [16].

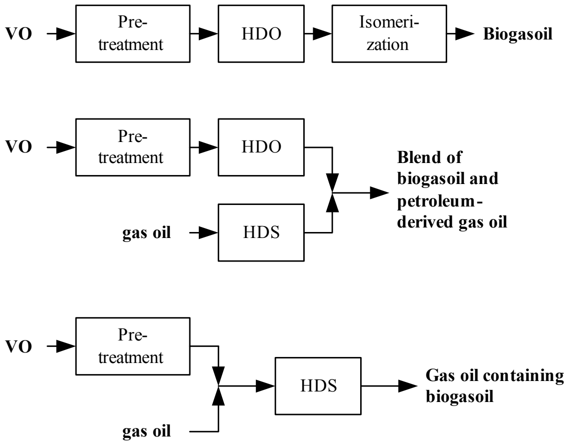


Figure 2: Alternatives for the production of biogasoil (VO: vegetable oil; HDO:hydrodeoxygenation; HDS: hydrodesulfurization)

In case of every technology pretreatment of vegetable oils is necessary with proper severity. This should be fitted to the other technology steps and should be made in a reactor containing protection catalyst and in continous operation. In the protection reactor the metal- (Ca, K, Mg), phosphorous and solid contaminant content of the vegetable oil (and/or other triglycerides) are eliminated with proper operating conditions and catalyst.

Currently a lot of companies and research institues are intensively studying the realization of the alternative processes and their setting to the local equipments. [10-17].

The goal of our experimental work was to examine a chemical conversion option to enhance the quality of gas oil fraction containing 10% sunflower oil to produce Diesel fuel and/or blending component with excellent properties. One of the major objectives was to find the advantageous process parameters (temperature, pressure, liquid hourly space velocity, hydrogen/hydrocarbon ratio) on the applied transition metal/Al_2O_3 catalyst for the conversion of this feedstock.

Experimental work

In the experimental work we examined the heterogeneous catalytic conversion of light gas oil fraction containing 10% sunflower oil on transition metal/Al_2O_3 catalyst. Our objective was to study the effect of the operating parameters on the yield of liquid organic products, on the yield of the gas oil boiling range fraction and on the product properties. The obtained results were compared to the results of the conversion of 100% gas oil and of 100% vegetable oil. The selection of the operating parameters was based on the results of our previous experiments and took into consideration the physical and chemical properties of the gas oil and the vegetable oil.

Apparatus

The experiments were carried out in an apparatus containing a tubular down-flow reactor of 100 cm^3 effective volume, and all the equipments and devices applied in the reactor system of an industrial heterogeneous catalytic plant. The experiments were carried out in continuous operation [18].

Materials

The feedstock was a gas oil – vegetable oil mixture which contained 10% properly pretreated Hungarian sunflower oil. The main properties of the feedstock are presented in *Table 1.*

The catalyst was an expediently chosen transition metal/Al_2O_3 catalyst.

Table 1: The main properties of the gas oil and the gas oil-vegetable oil mixture

Properties	Gas oil	Gas oil – vegetable oil mixture
Density at 15 °C, g/cm^3	0.7997	0.8091
Kinematic viscosity, 40°C, mm^2/s	1.66	2.06
Cetane number	51.0	50.7
Sulphur-/ nitrogen-content, mg/kg	540/11	499/9
Aromatic content, %		
mono	10.1	9.2
di	4.2	3.9
total	14.3	13.1

Analytical and calculation methods

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

Table 2: The applied analytical methods

Properties	Method/device
Density	EN ISO 12185:1996
Viscosity, 40°C	EN ISO 3104:1996
Cold Filter Plugging Point	EN 116:1997
Sulphur content	EN ISO 20846:2004 (Multi EA 3100 /Greenlab)
Nitrogen content	ASTM-D 6366-99 (Multi EA 3100 /Greenlab)
Hydrocarbon composition	gas chromatography (Trace GC 2000)
Distillation characteristic	EN ISO 3405:2000
Aromatic content	EN 12916:2000

Results and discussion

From the experiments carried out on multiple catalyst systems in wide range of parameters (T: 200–400°C; p: 20–100 bar; LHSV: 0.5–5.0 h^{-1}; H_2/feedstock volume ratio: 200–1000 Nm^3/m^3) in this paper the results of the heterogeneous catalytic experiments with gas oil of 10% sunflower oil content are presented between the following parameter range: 300–380°C; 80 bar; 1.0–3.0 h^{-1}; 600 Nm^3/m^3.

Product yields

The products were fractionated to three main fractions: gaseous-, water- and liquid organic fractions. The gaseous phase contained the carbon-monoxide, carbon-dioxide, the propane formed from the triglycerid molecule and other light hydrocarbons (from the cracking reactions). The main components of the liquid organic fraction (C_5-C_{20+} fraction) were the light liquid hydrocarbons (C_5-C_{10} paraffins), the gas oil boiling range hydrocarbons (C_{11}-C_{20} paraffins) and the residue (C_{20+}).

Based on our results it can be concluded that with increasing the pressure and the temperature and decreasing the LHSV the yield of total liquid organic product decreased. *(Fig. 3* and *4).* The reason of the previous is that the hydrocracking reactions became dominant higher vegetable oil conversion and causing gas oil component cracking. In the tested parameter range the liquid organic product yield was higher than 93% in every case related to the weight of the feedstock.

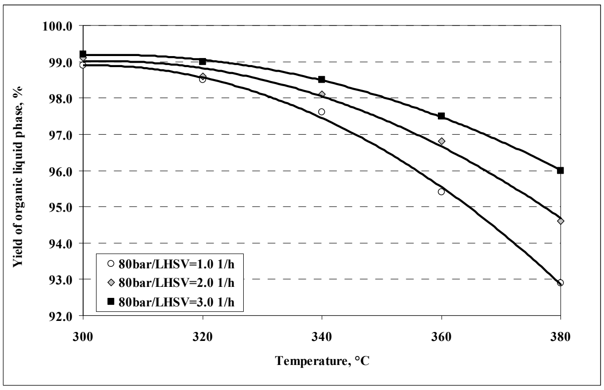


Figure 3: Organic liquid product yields as a function of temperature and LHSV

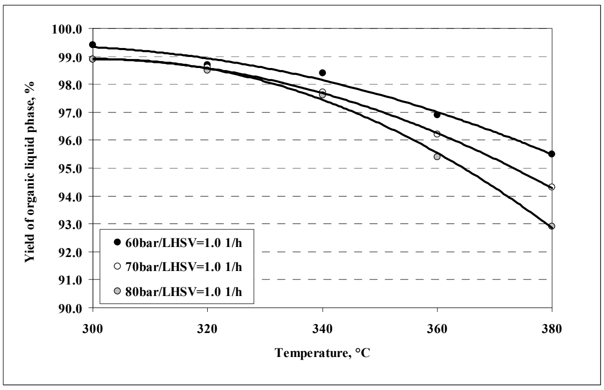


Figure 4: Organic liquid product yields as a function of temperature and pressure

The main objective of this experimental work was to convert the triglycerid molecules to gas oil boiling range product. So it is important to know how the amount of this target fraction (C_{11}-C_{20} hydrocarbons) changed as a function of different operating parameters. From the results it can be concluded that the amount of gas oil boiling range product increased with the decrease of temperature and increase of LHSV *(Fig. 5).* The reason is that the cracking reactions take place less frequently at lower temperatures and higher LHSV than at higher temperatures and lower LHSV. The amount of residues were in every case under 0.4%, which indicates the nearly total conversion of triglycerides.

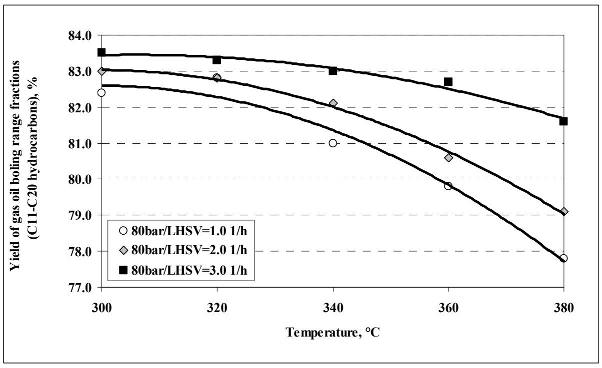


Figure 5. Yield of gas oil boling range fractions (C_{11}-C_{20} hydrocarbons) as a function of temperature and LHSV

We examined the effect of sunflower oil blending on the yield of the produced hydrocarbons at advantageous process parameters. The results are compared to the results of processing 100% sunflower oil.

On the examined catalyst and at the applied parameter combinations *(Fig. 6)* the yield of light hydrocarbons (C_5-C_{10}) decreased by 2–3%, however the gaseous product yield practically did not change (~ 6%) with the blending of 10% sunflower oil to the feedstock. During the experiments carried out with the 100% sunflower oil the yield of light hydrocarbons decreased significantly (12–17 absolut%).

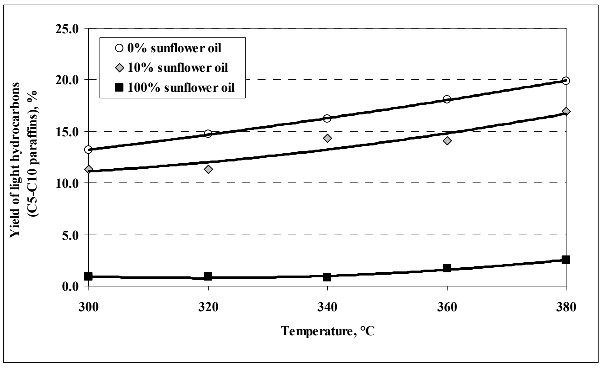


Figure 6: Yield of light hydrocarbons (C_5-C_{10} paraffins) as a function of the temperature and the sunflower oil content of the feedstock (80 bar, 1.0 h^{-1})

The yield of gas oil boiling range products (C_{11}-C_{20} hydrocarbons) decreased with increasing temperature because of the cracking reactions. The 10% sunflower oil content has good effect to the yield of this fraction *(Fig. 7).* That is because through the heterogeneous catalytic transformation mainly gas oil boiling range compounds (C_{11}-C_{20}) are produced from the triglycerides, as we presented in the introduction of this paper.

The yield of C_{15}-C_{18} paraffins increased with the sunflower oil blending (approximately 3%) of course *(Fig. 8),* but it was far from the thoretically available 8.1–8.6%. That is because at the examined severe operating conditions light hydrocarbons were produced in relatively high amount (12–17%) from the 10% sunflower oil content gas oil.

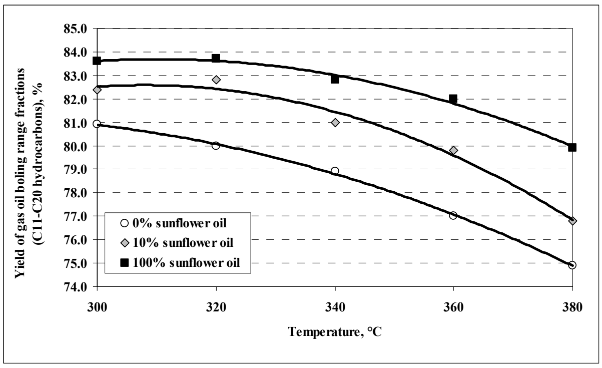


Figure 7: Yield of gas oil boling range fractions as a function of the temperature and the sunflower oil content of the feedstock (80 bar, 1.0 h^{-1})

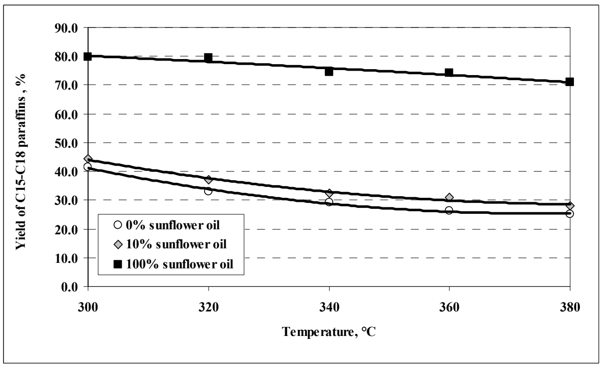


Figure 8: Yield of C_{15}-C_{18} paraffins as a function of the temperature and the sunflower oil content of the feedstock (80 bar, 1.0 h^{-1})

Main properties of gas oil boiling range fractions

Out of the properties of gas oil boiling range products (C_{11}-C_{20}) the changes in the sulphur- and aromatic content, the CFPP and the cetane number are presented in this paper.

The cold filter plugging points of gas oil boiling range fractions obtained from the 10% sunflower oil containing gas oil decreased with increasing temperature and decreasing LHSV *(Fig. 9)*. That is because through the cracking reactions lower carbon number products are formed with better CFPP. Increasing the sunflower oil content had an increasing effect to the CFPP of the products *(Fig. 10),* because the vegetable oil triglycerides were converted to mainly n-paraffins (C_{15}-C_{18}), which have disadvantageous cold flow properties (melting point: +10 – +28°C), but high cetane number (90–110). That is why the cetane number of gas oil boiling range products increased with 2,5–4,0 at these advantageous parameters and this value is higher than the value in the EN 590:2004 standard (51).

The sulphur contents of gas oil boiling point fractions made from the 10% sunflower oil content gas oil decreased with increasing temperature and decreasing LHSV *(Fig. 11)*. It can be concluded, that already at 340 °C, 60 bar and 3.0 h^{-1} we produced products with sulphur content lower than 10 mg/kg. Applying feedstock with higher sunflower oil content (with lower sulphur content) at same operating conditions the sulphur contents of the products were lower, of course.

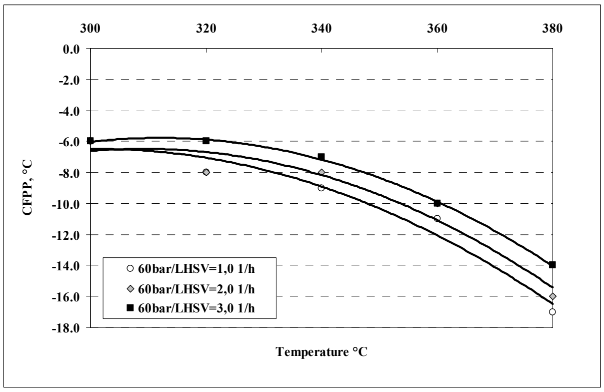


Figure 9: The CFPP of gas oil boiling range fractions (C_{11}-C_{20} paraffins) as a function of temperature and LHSV

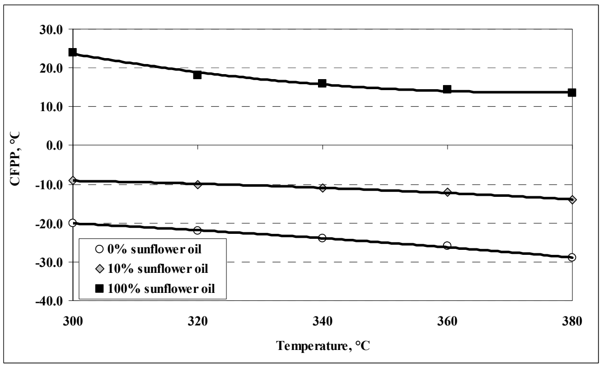


Figure 10: The CFPP of gas oil boiling range fractions (C_{11}-C_{20} paraffins) as a function of temperature and the sunflower oil content of the feedstock (80 bar, 1.0 h^{-1})

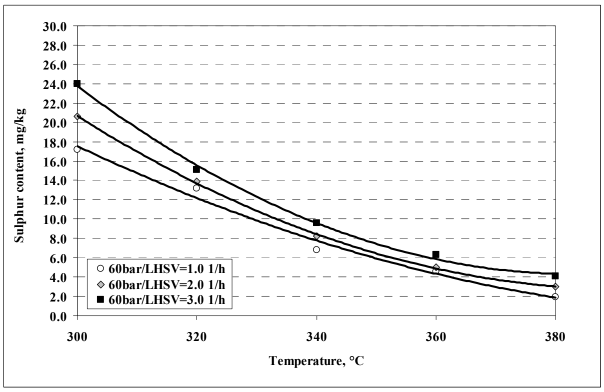


Figure 11: Sulphur content of gas oil boiling range fractions (C_{11}-C_{20} paraffins) as a function of temperature and LHSV

The aromatic contents of gas oil boiling range fractions obtained from the 10% sunflower oil containing gas oil changed according to minimum curve as a function of temperature *(Fig. 12)*. The reason is that below the advantageous temperature the kinetic inhibition, over the advantageous temperature the termodynamic inhibition suppresses the aromatic saturation. Since the sunflower oil do not contain aromatics, the higher blending ratio decreases the total aromatic content of the product, of course.

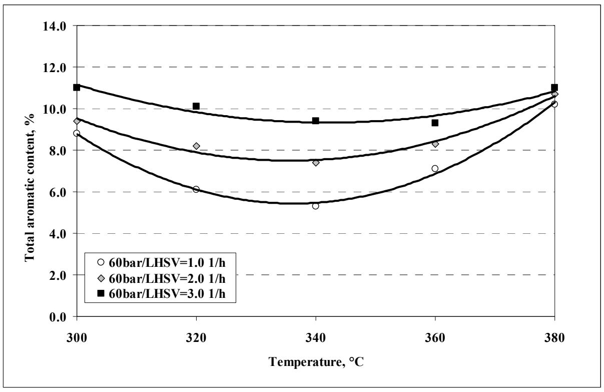


Figure 12. Total aromatic content of gas oil boiling range fractions (C_{11}-C_{20} paraffins) as a function of temperature and LHSV

Summary

Based on the results it can be concluded that with the hydrogenation of 10% sunflower oil containing gas oil products having excellent properties with high yield can be produced. We found the process parameters (T: 340–360 °C; p: 60-80 bar; LHSV: 1.0–3.0 h^{-1}; H_2/feed volume ratio: 600 Nm^3/m^3) where the produced gas oil boiling range products had sulphur- and nitrogen content lower than 10 mg/kg, total aromatic content lower than 10%, CFPP lower than -5°C and cetane number significantly higher than the value in the EN 590:2004 standard (≥51). This is due to the high paraffin content of the products which mainly derived from the conversion of the vegetable oil part of the feedstock.

REFERENCES

1. Official Journal of the European Union, 142, (2003) 42-46
2. Commission of the European Communities, COM(2006) 845 final, (2007)
3. Commission of the European Communities, COM(2006) 848 final, (2006)
4. ANON.: World Ethanol and Biofuels Report 4 (2006) 365.
5. GRAFF G.: Purchasing Magazine, 2006.06.15.
6. TYSON, K. S., MCCORMICK R. L.: NREL/TP-540-38836 Report (2006)
7. MITTELBACH, M., REMSCHMIDT, C.: Biodiesel: The Comprehensive Handbook, Martin Mittelbach, Graz, 332 pp (2004)
8. KNOTHE, G. VAN GERPEN, J. KRAHL, J.: The Biodiesel Handbook, The American Oil Chemists' Society, Champaign, IL USA, 303 pp (2005)
9. GRABOSKI, M. S. MCCORMICK R. L.: Prog. Energy and Comb. Science 24, (1998) 125-164
10. HANCSÓK J., KRÁR M., MAGYAR SZ., BODA L., HOLLÓ A., KALLÓ D.: Microporous and Mesoporous Materials, 101, (2007) 148-152
11. CORMA A., HUBER, G. W.: Angew. Chem. Int. Ed. 46, (2007) 7184-7201
12. KRÁR M., MAGYAR SZ., THERNESZ A., HOLLÓ, A. BODA L., HANCSÓK J.: In of 15th European Biomass Conference Proceedings (2007) 1988-1992
13. LEIVELD B.: Catalysts Courier, 65, (2006) 8-9
14. MARINANGELI R., MCCALL M., MARKER T., HOLMGREN J.: Alche Symp., Chicago, 11.10.06.
15. STUMBORG M., WONG A., HOGAN E.: Bioresource Technology 56, (1996) 13-18
16. COSTA P. R.: PTQ Biofuels (2007) 32-33
17. HANCSÓK J., KRÁR M., MAGYAR SZ. BODA L., HOLLÓ A., KALLÓ D.: Studies in Surface Science and Catalysis 170 B, (2007) 1605-1610
18. NAGY G. HANCSÓK J., VARGA Z., PÖLCZMANN GY., KALLÓ D.: Topics in Catalysis 45, (2007) 195-201