

FUEL PRODUCTION FROM TRIGLYCERIDES CONTAINING GAS OILS

CS. TÓTH[✉], P. BALADINCZ, J. HANCSÓK

University of Pannonia, Institute of Chemical and Process Engineering, Department of Hydrocarbon and Coal Processing
H-8201 Veszprém, P.O.Box.: 158, HUNGARY

[✉]E-mail: tothcs@almos.uni-pannon.hu

Lately the development and the use of energy sources which are of bio-origin are required. The engine fuels have special importance. Based on their origin they can be conventional, alternative or conventional + alternative. Biofuels which can be produced from biomass, thus from a renewable energy source, are alternative fuels.

The objective of our research work was to investigate the production of diesel fuel with excellent quality and/or of diesel fuel blending component by heterogeneous catalytic conversion of gas oil fraction containing 75% sunflower oil. Furthermore, our aim was to determine the advantageous process parameters (temperature, pressure, liquid hourly space velocity, hydrogen/hydrocarbon ratio) during application of the selected NiMo/Al₂O₃ catalyst. Based on the results obtained we determined that the main properties of these products were significantly better compared to the feed as diesel fuel components. The products which were made under desired combination of process parameters ($T = 350\text{--}380\text{ }^{\circ}\text{C}$; $p = 80\text{ bar}$; $\text{LHSV} = 1,0\text{--}1,5\text{ h}^{-1}$; $\text{H}_2/\text{feed ratio} = 600\text{ Nm}^3/\text{m}^3$) had lower than 10 mg/kg sulphur and nitrogen content, and the cetane numbers were significantly higher than it is specified in the MSZ EN 590:2009 standard (minimum 51).

Keywords: vegetable oil, gas oil, mixtures, sunflower oil, biogasoil, heterogenous catalytic hydrogenation

Introduction

For modern society, it is very important to maintain mobility, of which energy need is covered mostly with fossil derived energy sources.

The depletion of crude oil stocks, the dependence of crude oil and import energy sources, and the need to reduce the environmental pollution necessitates the development and application of alternative energy sources.

The energy sources include the paramount importance engine-fuels which, according to its origin, may be conventional, alternative, or conventional & alternative (Fig. 1) [1-4].

Bio-engine-fuels that belong to alternative engine-fuels are produced from a renewable energy source as e.g. biomass. Widely used alternative engine-fuels come into view, for example the derivatives of vegetable-oils (out of them esters) and furthermore nowadays products made with catalytic hydrogenation. The carbon-dioxide originating during the application of these fuels does not burden the environment, because it builds in again through the photosynthesis of the plants. As a result of the lower emission, the use of biofuels burdens the environment less than the use of fossil derived fuels [1-4].

In the directives and valid standards, the European Union supports and orders more application of bio-derived energy sources, among them bio engine-fuels.

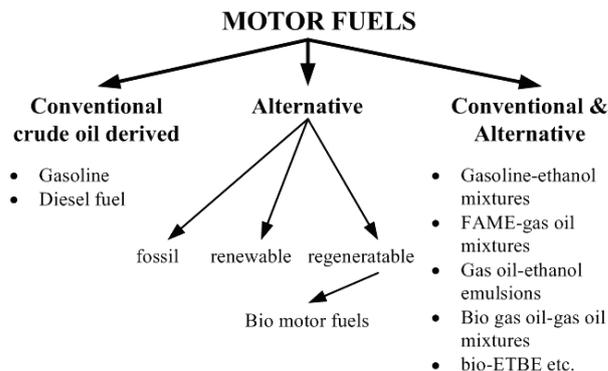


Figure 1: Classification of motor fuels

The diesel fuel standard valid since 2000 (MSZ EN 590:2000, then MSZ EN 590:2004 and MSZ EN 590:2009) permits the use of bio-derived blending components, but it specifies the composition (fatty-acid-methyl-esters) and sets limits to blended quantity (MSZ EN 590:2009: maximum 7 v/v%).

The European Union confirmed and extended Directive 2003/30/EC multiple times and fixed the ratio of bio engine-fuels in 10% till 2020 [5-8].

In Hungary, the development and application of bio-derived engine-fuels and blending components – among them mainly vegetable-oils and its derivatives – is very important, too. The engine-fuel consumption in the European Union swings to diesel-fuel and according to the prognosis, more increase is probable in the rate of diesel-fuel and gasoline [9]. The engine-fuel market in

Hungary exfoliates such as the European, but in our country, the usage of gasoline still increases, although more slightly than the use of diesel-fuel (*Figure 2*) [10].

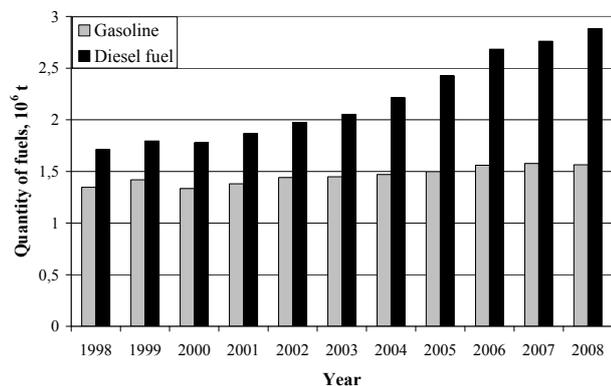


Figure 2: The change in the use of gasoline and diesel fuels in Hungary

Therefore increasing the quantity and improving the quality of the bio-derived diesel-fuel blending components has great importance. In Hungary, for this purpose nowadays the biodiesel (fatty-acid-methyl-ester), in the immediate future the bio gas oil (from the heterogeneous catalytic hydrogenation of triglycerides containing mainly normal- and isoparaffins having a similar boiling point range as the traditional gas oil; the denomination and the notion was introduced at Institute of Chemical and Process Engineering, Department of Hydrocarbon and Coal Processing, University of Pannonia at first [11-12]) and someday the synthetic bio gas oil (mainly a mixture of normal- and isoparaffins from biomass based synthesis gas) will be available.

The technologies produce biodiesels and the produced biodiesels also have a lot of problems and disadvantages (high unsaturated content causing bad thermal, oxidation, and thus storage stability; high water content causing corrosion problems; sensitivity to hydrolysis causing poor storage stability; unfavourable cold properties; low energy content; methanol) which damage the profit of the utilization and production [13-14].

To overcome these problems and to attain better quality, the alternative is the chemical conversion of triglyceride based feeds, mainly hydrocarbons rich in paraffins, which products can be utilized in Diesel-engines mixed with diesel gas oil or directly.

From the available sources of triglyceride containing materials the most advantageously used are the oils made from oil-bearing vegetables.

The heterogenous catalytic conversion of vegetable oil – gas oil mixtures can occur in two major ways. In the first way, shown in *Figure 3*, the vegetable oil is pre-treated in a reactor first then it is deoxygenated in the HDO reactor. The product - rich in n-paraffins, has a very high cetane number, but poor cold flow properties – is mixed with desulphurized gas oil stream after separation. In the second way, the vegetable oil is mixed in a gas oil stream in the refinery after pre-treatment. After it, the mixture is converted in a conventional (or slightly modified) desulphurization plant [15-17].

With further isomerisation or dewaxing, gas oil product can gain high cetane number and good cold flow properties. With these methods it is also possible to use the product as a blending component for quality boosting in gas oil streams with poor quality (low cetane number, high aromatic-, sulphur- and nitrogen content).

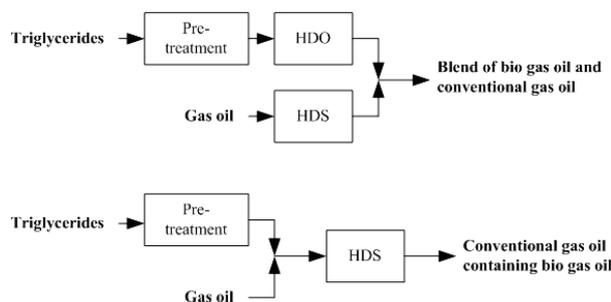


Figure 3: Options of the catalytic conversion of the vegetable oil-gas oil mixtures. (HDO: hydrodeoxygenation; HDS: hydrodesulphurization)

In the case of these methods, the pre-treatment of the vegetable oils is necessary, which step should be brought to effect by the building of a continuous, pre-treatment catalyst containing reactor. In the pre-treatment reactor the metal- (Ca, K, Mg), the phosphorus- and the solid impurities contents of the vegetable oil are removed [15-17].

For the time being, many leading corporations and departments of research examine the realization of these methods, respectively tailoring them for the regional capabilities [18-26].

The aim of the experimental work was the investigation of preparing high-quality products by the catalytic hydrogenation of mixtures of vegetable oil and crude gas oil distillate, which is useful in pure form as diesel fuel or as gas oil blending component as well. Within this, our goal was to specify the favourable operation parameters (temperature, pressure, LHSV, hydrogen/feedstock volume ratio) on a commercial NiMo/Al₂O₃ catalyst.

Experimental work

This paper presents experimental results obtained via the investigation of heterogeneous catalytic transformation of gas oil distillate containing sunflower oil in 75%, on NiMo/Al₂O₃ catalyst. Beside this, our goal was to determine the favourable operation parameters (temperature, pressure, LHSV, hydrogen/feedstock volume ratio) applying a commercial NiMo/Al₂O₃ catalyst. During the experimental work, the influence of the process parameters on the yield of the organic and gas products, and on the yield and main physical-chemical properties and application impact of the gas oil boiling point range fraction of the product was studied. The combinations of process parameters were selected on the basis of the results of our pre-experiments, taking into account the physical and chemical properties of gas oil distillate and the sunflower oil.

Experimental equipment

The experiments were carried out in experimental equipment (Figure 4) which contains all the main devices of a heterogeneous catalytic hydrogenation

plant. This process equipment has a tubular reactor of 100 cm³ active volume capacity [27]. The experimental work was carried out in continuous mode in a single reactor array catalytic system.

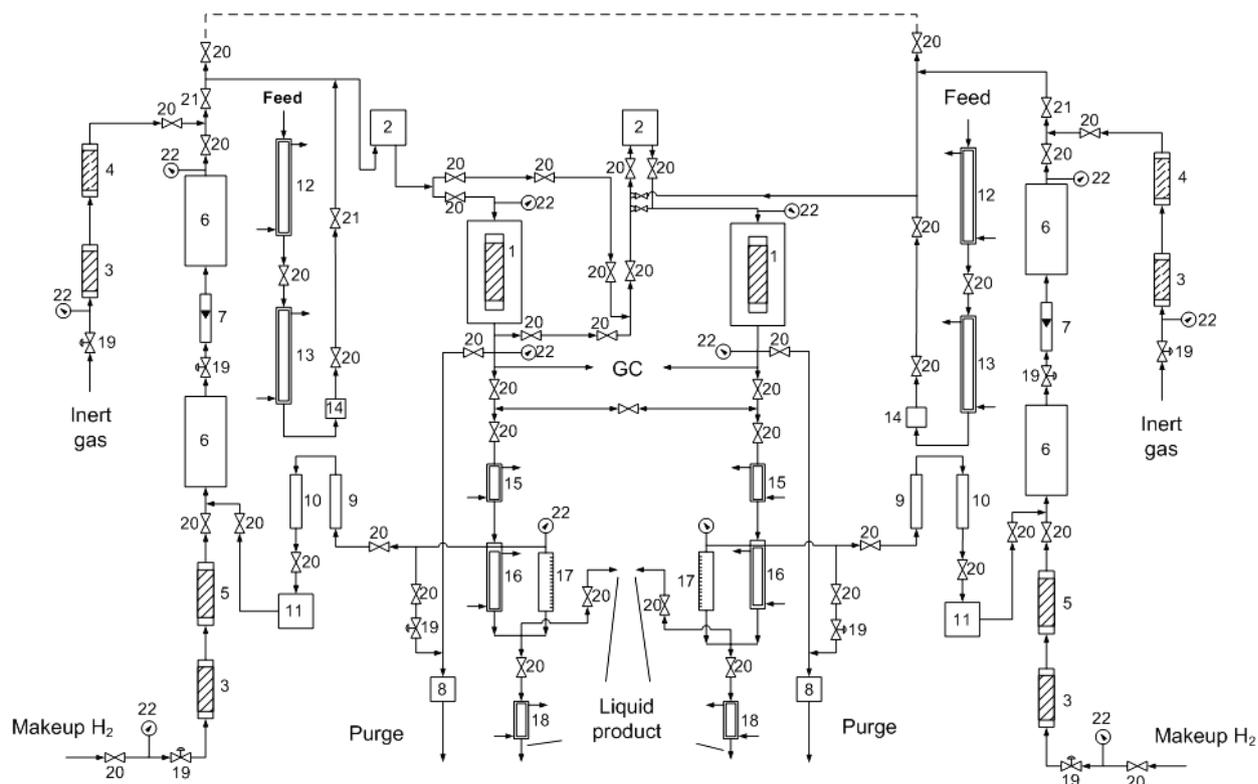


Figure 4: Simplified scheme of the test apparatus

(1 reactor; 2 pre-heater; 3 oxygen converter; 4, 5 gas dryer; 6, 10 gas filter; 7 gas flow meter; 8 gas flow meter; 9 demister; 11 compressor; 12, 13 burettes for liquid feed; 14 pump; 15, 18 cooler; 16 separator; 17 level meter; 19 closing valve; 20 control valve; 21 back valve; 22 manometer)

Feedstocks

The feedstock of the heterogeneous catalytic experiment was gas oil-vegetable oil mixture with 75% vegetable oil content of properly pre-treated sunflower oil originating from a supplier in Hungary. Important properties of these mixtures are summarized in Table 1.

The catalyst was NiMo/Al₂O₃, which was chosen on the basis of other experiments previously performed by the Department of Hydrocarbon and Coal Processing at the University of Pannonia.

Analytical and calculation methods

The properties of the feedstocks and the products were specified as the specifications of the MSZ EN 590:2009 standard, relevant for Diesel-fuels and with standardised calculation methods. The ensued cetane numbers were specified with IQT apparatus according to standard ASTM D6890-03a.

Process parameters

The experiments were carried out – on the basis of other experiments previously performed – on combinations of the following process parameters, T = 300–360 °C, p = 80 bar, LHSV: 1,0–3,0 h⁻¹, H₂/feedstock volume ratio: 600 Nm³/m³.

Table 1: Main properties of the feeds

Properties	Gas oil	Gas oil-vegetable oil mixture
Density (15.6 °C), g/cm ³	0,8513	0,8451
Kinematic viscosity, (40 °C), mm ² /s	5,36	24,73
Iodine number, g I ₂ /100 g	0,5	90
Sulphur content, mg/kg	10370	2594
Nitrogen content, mg/kg	228	58
Flash point, °C	79	79
Cold filter plugging point, °C	2	15
Aromatic content, %	37,6	9,4
Cetane number	49	43

Results and discussion

By the heterogeneous catalytic conversion of the gas oil containing vegetable oil, the product was separated to three main fractions as gas fraction, water fraction and organic fraction. In the gas phase, products besides the hydrogen are not used in the reactions, there is a high amount of gases formed through the hydrogenation reaction routes, such as carbon-oxides, propane arises from the triglyceride and lighter hydrocarbons originate from the cracking reactions (Figure 5). The yield of the gas fraction significantly increases with the temperature, which is at first caused by the conversion of the vegetable oil, then at higher temperatures (>340 °C) boosts so that the hydrocracking reactions become conspicuous.

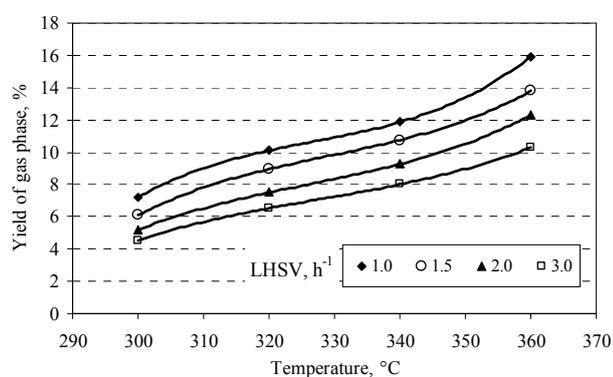


Figure 5: The change of the yield of gas phase as a function of temperature

The yield of the liquid organic product (C_{6+} fraction) decreased with increasing temperature and pressure as well as with decreasing LHSV (Figure 6). This was caused by the higher conversion of vegetable oil – while water, CO_2 , CO and lighter products formed, decreasing the yield of the liquid product – and also the hydrocracking of the hydrocarbons.

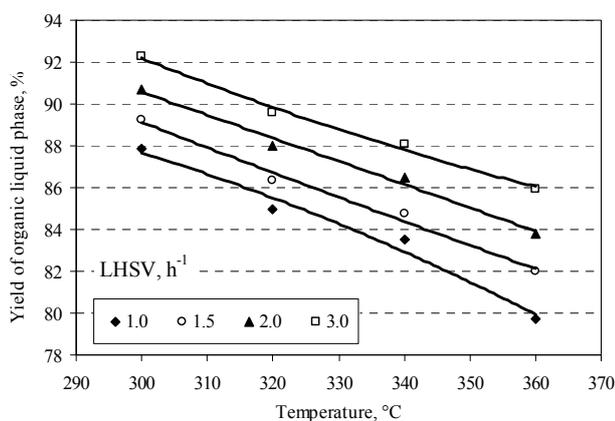


Figure 6: The change of the yield of organic products (C_{6+}) as a function of temperature.

One of the main goals of the experiment was to convert the triglyceride molecule to a product which is in the gas oil boiling point range. For that very reason, it

is important to know how the quantity of the products in boiling point range 180–360 °C – which was obtained via distillation – changed with the process parameters.

The yield of the gas oil boiling point range product changes as the maximum-curve of the temperature (Figure 7). Till 320–330 °C the yield increased with the rate of the conversion, which can be seen well on the decrease of the residual fraction (Figure 8), and with the further increase of the temperature the yield significantly decreases because of the hydrocracking reactions. With increasing LHSV, the yield of the main product increased because of the foreshortening of the contact time.

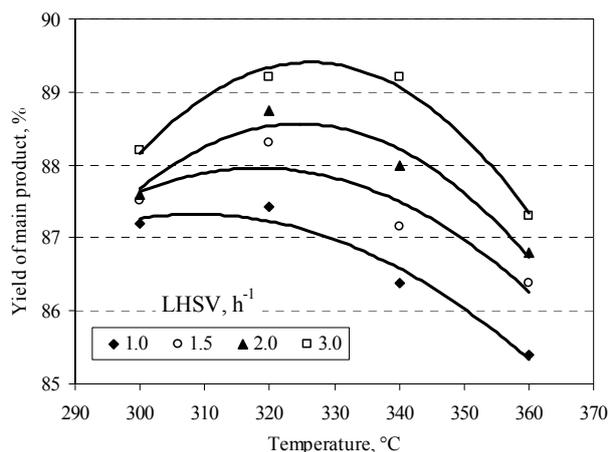


Figure 7: The change of the yield of the gas oil boiling point range product as a function of temperature ($p = 80$ bar)

While specifying the main product, the change in the sulphur and aromatic content was compared to the experiments with the gas oil used for the blending of the feedstock.

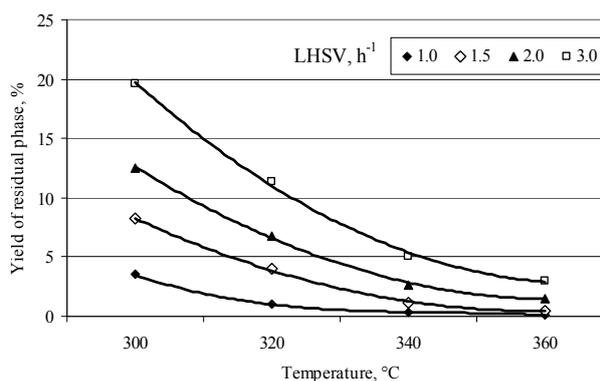


Figure 8: The change of the yield of residue as a function of temperature.

On the basis of the results, we determined that the desulphurization efficiency increased with increasing the temperature (Figure 9), namely the sulphur content of the main product decreased. At the most severe process parameters ($T = 360$ °C, $LHSV = 1.0$ h^{-1}) a product, eligible for the valid diesel gas oil standard (MSZ EN 590:2009) (<10 mg/kg) was produced. As it can be seen in the figure, the sulphur content of the gas

oil decreased more than in the case of the products made from mixtures, because the parallel reactions via the hydrogenation – saturation of double bonds, deoxygenation, dearomatization – the desulphurization confining as these reactions take place on the same catalytic places.

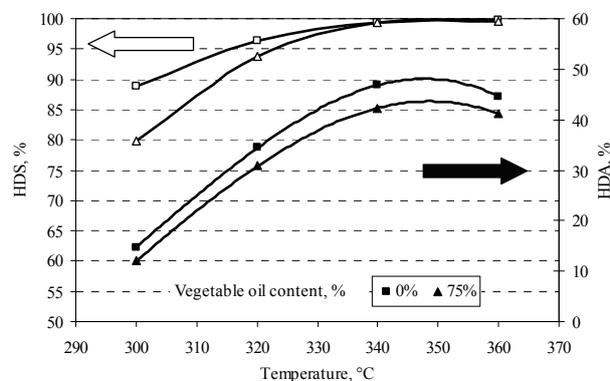


Figure 9: The changes in desulphurisation(HDS)- and dearomatization(HDA) efficiency as a function of temperature ($p = 80$ bar, $LSHV = 1,0$ h⁻¹)

Dearomatization efficiency changes as the maximum-curve in the case of both feedstocks. This is because with the increasing of the temperature, above 350 °C – the thermodynamic inhibition made by the exothermic reactions – the dearomatization is confined.

One of the important attributes of diesel-fuels is the cold filter plugging point, which as we determined, decreases with the increasing temperature (Figure 10), because on account of the hydrocracking reaction, more lighter hydrocarbon products formed and their CFPP is more favourable.

Via isomerisation and/or with additives, a product can be made of which CFPP satisfies the valid diesel-fuel standards (summer grade: +5 °C, winter grade: -20 °C).

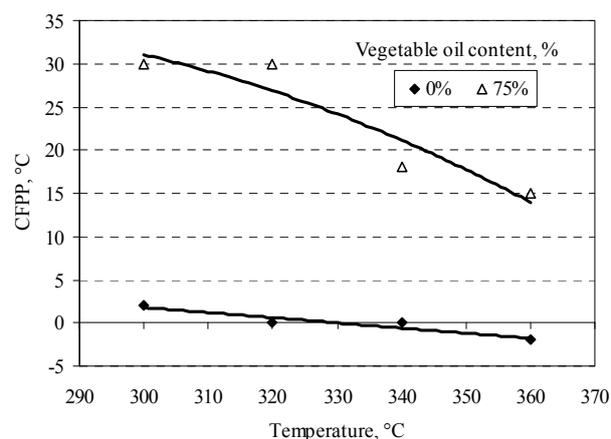


Figure 10: The changes in CFPP value of the main fraction as a function of temperature.

One of the most important quality properties for the gas oil boiling point range products is its cetane number. The cetane number of these products improves 24-29 points in the case of the preferential process parameters,

which is significantly higher than the valid standards minimum specification, 51.

Summary and conclusion

It was found that during the catalytic conversion, the properties of the products (first of all, the cetane number) were improved significantly comparing that to the properties of the feedstock. Applying the desired combinations of process parameters ($T = 350\text{--}380$ °C; $p = 80$ bar; $LHSV = 1,0\text{--}1,5$ h⁻¹; $H_2/\text{feedstock}$ ratio: 600 Nm³/m³), the sulphur content of the products were less than 10 mg/kg and their cetane number were significantly higher than that in the valid diesel gas oil standards (MSZ EN 590:2009). Increase of the cetane number is caused by the high n-paraffin content of the products, which is produced mainly in the catalytic conversion of the vegetable oil portion of the feedstock. Products were made which, with further isomerization and/or addition, meet the property values of the diesel gas oil standard in every respect.

REFERENCES

- HANCSÓK J., BALADINCZ J.: Issue of Műszaki Kémiai Napok'04, (2004), 1–16.
- HANCSÓK J., KRÁR M., HOLLÓ A., THERNESZ A.: Magyar Kémikusok Lapja, (2006) 61(8), 260–264.
- MAGYAR J., HANCSÓK J., KRÁR M., PÖLCZMANN GY.: Magyar Kémikusok Lapja, (2006) 61(9-10), 309–314.
- MAGYAR SZ., MOLNÁR ZS., JUHÁSZ K., HANCSÓK J.: Magyar Kémikusok Lapja, (2006) 61(11), 361–366.
- Official Journal of the European Union, 142, (2003), 42–46
- Commission of the European Communities, COM(2006) 34 final, (2006)
- Commission of the European Communities, COM(2006) 845 final, (2007)
- Commission of the European Communities, COM(2006) 848 final, (2006)
- DASTILLUNG M.: Concawe Report, (2009) No. 03/09
- Hungarian Customs and Finance Guard; Excise Statistic, <http://vam.gov.hu/loadBinaryContent.do?binaryId=15223>
- HANCSÓK J., KRÁR M., MAGYAR SZ., BODA L., HOLLÓ A., KALLÓ D.: Microporous and Mesoporous Materials, (2007) 101(1-2), 148–152.
- HANCSÓK J., KRÁR M., MAGYAR SZ., BODA L., HOLLÓ A., KALLÓ D.: Studies in Surface Science and Catalysis 170 B, (2007) 170, 1605–1610.
- KRÁR M., HANCSÓK J.: Proceedings of 7th International Colloquium Fuels, Mineral Oil Based and Alternative Fuels, (2009) Stuttgart/Ostfildern, Germany, 507–514.
- BOZBAS K.: Renewable & Sustainable Energy Reviews, (2008) 12, 542–552.

15. HANCSÓK J., KOVÁCS F., KRÁR M.: 5th International Symposium on “Materials made from Renewable Resources”, (2005) Germany, Erfurt 112. Proceedings P-17
16. HANCSÓK J., KRÁR M., KASZA T., TÓTH CS.: 5th International Conference on Environmental Catalysis, (2008) Belfast, Proceedings 427.
17. KRÁR M., MAGYAR SZ., THERNESZ A., HOLLÓ A. BODA L., HANCSÓK J.: 15th European Biomass Conference & Exhibition. Biomass for Energy, Industry and Climate Protection, (2007) Germany, Berlin, Proceedings 1988–1992.
18. LEIVELD B.: Catalysts Courier, (2006) 65, 8–9.
19. COSTA P. R.: PTQ Biofuels, (2007), 32–33.
20. MELIS S., MAYO S., LELIVELD B.: Biofuels Technology, (2009) 1, 43–47.
21. CORMA A., HUBER G. W.: Angewandte Chemie International Edition, (2007) 46, 7184–7201.
22. HUBER G. W., O’CONNOR P., CORMA A.: Applied Catalysis A: General 329, (2007), 120–129.
23. BEZERGIANNI S., KALOGIANNI A., VASALOS I. A.: Bioresource Technology, (2009) 100, 3036–3042.
24. WALANDZIEWSKI J., STOLARSKI M., ŁUŻNY R., KLIMEK B.: Fuel Processing Technology, (2009) 90, 686–691.
25. KUBIČKOVÁ I., SNĀRE M., ERÄNEN K., MÄKI-ARVELA P., MURZIN D. Y.: Catalysis Today, (2005) 106, 197–200.
26. MÄKI-ARVELA P., KUBIČKOVÁ I., SNĀRE M., ERÄNEN K., MURZIN D. Y.: Energy and Fuel, (2007) 21(1), 30–41.
27. HANCSÓK J., MAGYAR SZ., SZOBOSZLAI ZS., KALLÓ D.: Fuel Processing Technology, (2007) 88(4), 393–399.