

APPLICATION OF IMPROVED BIO-PARAFFINS IN DIESEL FUELS

T. KASZA¹, Cs. TÓTH², J. HANCSÓK²✉

¹MOL Hungarian Oil and Gas Plc., Százhalombatta, HUNGARY

²University of Pannonia, MOL Department of Hydrocarbon and Coal Processing, 10 Egyetem Str., Veszprém, HUNGARY

✉E-mail: hancsojk@almos.uni-pannon.hu

Bio-paraffin containing mixtures produced from different natural triglycerides (conventional and improved vegetable oils, used cooking oils and fats, etc.) have high cetane number (95–105 units), but their freezing points are high (between +15 and +32°C). This property can be improved by catalytic hydroisomerization. Products obtained over 0.5% Pt/SAPO-11 catalysts ($T = 280\text{--}380^\circ\text{C}$; $P = 20\text{--}80$ bar; $LHSV = 0.25\text{--}4.0$ h⁻¹; apparent contact time: between 1/3 and 4.0 h (at $LHSV = 3.0$ h⁻¹; $H_2/\text{feedstock} = 400$ Nm³/m³) had CFPP values of +5°C; -20°C and -32°C. At the same time, there was decreased cetane number of the isomerates (87, 70 and 65 unit, respectively) relative to the feedstock. These biogasols are suitable for bio-components of premium quality diesel fuel or for the improvement of cetane number. They can also reduce the density of low grade components providing some economic savings and some flexibility to refineries.

Keywords: biogasols, biofuels, cetane number, cold flow properties

Introduction

The energy demand of the world is continuously increasing because of the industrial development and the population growth. Because of these and the environmental advantages, the importance of different bio fuels is significant nowadays [1–3] through the energy policy of the European Union. Its aim is to decrease the energy and oil dependency. To inspire the utilization of bio fuels 2003/30/EC, and then 2009/28/EC directives were created specifying the recommended and compulsory share of bio-components in the transportation fuels.

Currently, mainly the biodiesels (mixtures of methyl esters) are used as Diesel fuel blending components, which have numerous performance disadvantages; for example, their oxidation and heat stability is poor because of the great number of olefinic bonds [3–10]. Water content and the hydrolysis of ester bonds brings about corrosion problems [3, 7, 8] resulting in poor storage stability [3–6]. In addition, because of the good conductivity, corrosion may damage the metallic parts. Furthermore, the solving nature may cause compatibility problems with plastic construction materials [7–12]. Due to these disadvantages, the maintenance costs are higher, and the lifetime of the engine is shorter [10]. Because of the lower energy content the fuel consumption is higher [9–13]. The combustion characteristics differ from those of diesel fuels (ignition delay, adiabatic flame temperature, radiation heat loss, etc.), the NO_x emission is higher [9, 13–16], and the aldehyde emission is also higher [13]. In addition, the cold filter plugging point is higher [10, 15]. They have inadequate compatibility with

lubricating oils [10]. The after-treatment catalysts may be damaged by alkali and/or alkaline earth metals and phosphorus present in fatty oils [7]. The production costs are also higher than for diesel fuels [6, 17, 18]. For these reasons, car manufacturers recommend the blending concentration of the fatty acid methyl esters by 7.0 v/v% in the European Union in accordance with the EN 590:2009 standard. At the same time, up to 2020 the European Union prescribed to use 10% of bio origin components in fuels.

Accordingly, the production of fuels having a preferable chemical structure from different triglyceride containing feedstocks (e.g. oils of conventional and ennobled plants, used frying oils and animal fats, algae oils, fats from meat and leather industry, so called brown grease from the sewage farms, etc.) has an important role in reaching the purposes of the mentioned directives [19].

A promising solution is the fuel purpose catalytic hydrogenation of these triglycerides. The utilization of these products is already supported by the CWA 15940:2009 standard. For this mainly sulfided transition metal(s) (Ni, Co, Mo, W) containing catalysts having high heteroatom removal activity are suggested [19–24].

During the catalytic hydrogenation of triglycerides, mainly normal paraffins and some iso-paraffins generate beside the formation of propane, carbon oxides (CO₂, CO), water, and oxygenic compounds according to *Figure 1* [19].

There are two main approaches to the hydrogenation of triglycerides: co-processing or stand-alone catalytic conversion. The co-processing systems require only slight changes in the existing HDS units, which cost only a few percent of refinery installation costs.

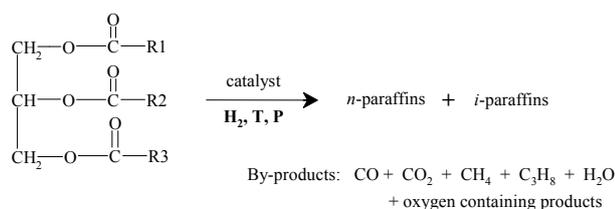


Figure 1: General reaction scheme of the hydrogenation of triglycerides

During the co-processing of gasoil – triglyceride mixtures in a two-step process biogasol containing gasoils can be produced with improved cetane number and suitable cold flow properties [20]. In the case of stand-alone systems the investment costs are higher compared to co-processing systems, but there is higher control on the process and higher product quality can be realized [21]. In this study biogasols produced in such a stand-alone system are considered. The stand-alone produced, stabilized biogasols have good heat and storage stability and outstanding cetane number (95-105). But their freezing points are high (between +15 and +32°C); accordingly to their cold filter plugging points (CFPP), they cannot satisfy either the summer grade specification of the temperate zone (at most +5°C) or the winter grade specifications (at most – 20°C). Therefore their molecular structure has to be modified in order to that the CFPP value fulfill the standard specification.

For this purpose, the most suitable technology is the isomerization as the freezing point of the branching paraffins is lower by 20–40°C than that of the normal paraffins having the same carbon number. To reach favourable yields, high activity and selectivity catalysts should be used. These kinds of catalysts can be the 10-member-ring zeolites (e.g. ZSM-22, ZSM-23) and zeolite analogues (SAPO-11, SAPO-31, SAPO-41) containing different noble metals (Pt, Pd) [25–27].

During the hydroisomerization, the convenient selection of the operational parameters is very important because of the favourable yield and composition, as well as because of the disadvantageous effects on the catalyst activity. Accordingly, the goal of our experiments was the investigation of the effects of the process parameters (temperature: 280–400°C, pressure: 5–80 bar, liquid hourly space velocity (LHSV): 0.5–4.0 h⁻¹, H₂/hydrocarbon ratio: 200–800 Nm³/m³) on the yield and product quality during the isomerization of normal paraffin mixture produced from sunflower oil. Furthermore, we compared the performance properties of the produced biogasols with those of fossil gasoils.

Experimental Section

Apparatus

The experiments were carried out in an apparatus containing a tubular down-flow reactor of 100 cm³ effective volume. It contains all the equipment and

devices applied in the reactor system of an industrial heterogeneous catalytic plant [3]. The experiments were carried out in continuous operation with steady-state activity catalyst.

Materials

During our heterogenic catalytic experiments, a normal paraffin mixture (CFPP = 23°C; hydrocarbons: C₁₇: 6.3%, i-C₁₇: 0.3%, n-C₁₇: 46.7%, i-C₁₈: 0.4%, n-C₁₈: 43.3%, C₁₉₊: 2.0%, content of oxygenic compounds: 0.06%, oxygen content : 68 mg/kg) produced with high yield (84.8%; which is relatively high regarding the theoretically highest yield, which is about 86.2% in the case of sunflower oil, which could change as a function of the oleic acid composition of the used triglyceride) from Hungarian sunflower oil over commercial hydrotreating NiMo/Al₂O₃ catalysts was used as a base feedstock. The 0.5% Pt/SAPO-11 catalyst was prepared as described and characterized according to HU 225 912 patent.

Methods

The properties of the feedstock and the products were analyzed according to EU and ASTM standards and GC (Shimadzu 2010 GC) and GC-MS (HP 6980A). The oxygen content of the feedstock and products was determined by CHNS/O analysis.

The crystal structure of the catalyst and its change during the experiments were determined by X-ray diffraction (XRD). XRD data were collected by Siemens D500 equipment, Philips PW 1730/10 (PW 1050/70 goniometer) diffractometer, CuKα (40 kV, 35 mA) ray were applied. The XRD characterization of the obtained powder confirmed that it was SAPO-11. The synthesized SAPO-11 microporous molecular sieve was impregnated with Pt(NH₃)₄Cl₂ solution. The platinum content was determined according to the UOP-274 standard. The platinum dispersion was determined by H₂ chemisorption [29], which was 91%. The surface properties of the catalyst were determined by ASAP 2000 equipment (Micromeritics) (pore range of 1.7–300 nm) and mercury penetration method using CARLO-ERBA equipment (pore range 7.5–15000 nm). The specific surface area of the catalyst was 100.1 m²/g. The acidity was determined by ammonium adsorption, which was 0.66 mmol NH₃/g. Prior to the activity measurements the catalysts were pre-treated in situ, as described in our earlier publication [3].

Results and Discussion

The experiments were carried out in a wide range of process parameters ($T = 280\text{--}380^\circ\text{C}$; $P = 20\text{--}80$ bar; $\text{LHSV} = 0.25\text{--}4.0$ h⁻¹; apparent contact time: between $\frac{1}{3}$ and 4.0 h (at $\text{LHSV} = 3.0$ h⁻¹). Our aim was to find a combination where the liquid yield is at least 90% similarly to the industrially required yield. It is

necessary to avoid the fast deactivation because of the significant cracking and industrially at least 90–95% liquid yield is required. According to our pre-experiments using practically heteroatom free (lower than 10 mgS/kg) feedstocks, it was concluded that the increase of the platinum content increased the isoparaffin content of the products significantly up to 0.5%. It was because the increase of the number of the hydrogenation-dehydrogenation active sites promoted the isomerization reactions and the prompt hydrogenation of the intermediate carbenium ions as a consequence inhibited their cracking. The further increase of the platinum content had only insignificant effects [30, 31]. Consequently, the platinum content of the applied Pt/SAPO-11 was 0.5%.

Product yield and composition

During the systematic isomerization of the practically heteroatom-free normal paraffin mixture, the products were separated to gas and liquid phases. The gas products taken from the top of the separator contained mainly hydrogen and light hydrocarbons generated in the hydrocracking reactions. These hydrocarbons were mainly normal and isobutane (higher than 40% of the light hydrocarbons) which could be used in the oil industry for several purposes (e.g. LPG production, alkylation of $i\text{-C}_4$ with olefins, dehydrogenation of $i\text{-C}_4$ to isobutylene, etc.) [32]. The target product contained the C_{11} and heavier hydrocarbons beside which $\text{C}_5\text{-C}_{10}$ valuable side products were also generated in a small quantity.

The yield of the target products decreased by increasing the temperature; this effect was intensified by decreasing the LHSV (Figure 2). The reason of this was that the chain breaking of the unstable carbenium ions could happen easily at higher temperature on the catalyst surface; furthermore, the lower the flow rate of the molecule was the higher the contact time was and the higher the possibility of the cracking was.

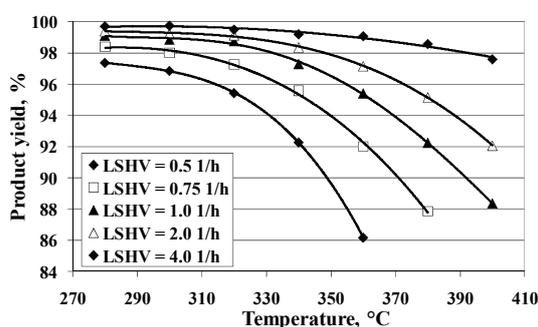


Figure 2: Product yields as a function of the temperature and the LHSV ($P = 40$ bar, $\text{H}_2/\text{feedstock}$ ratio = $400 \text{ Nm}^3/\text{m}^3$)

The yield of the products decreased by decreasing the pressure in the investigated pressure range (20–80 bar) because the partial pressure of the hydrocarbons increased resulting in a lower degree of hydrogenation of the instable carbenium ions, thus

increasing the possibility of the cracking. The product yield also decreased by decreasing the hydrogen/hydrocarbon ratio similarly to the decrease of the total pressure, because of the rising cracking. It was especially dominant below $400 \text{ Nm}^3/\text{m}^3$.

Increasing the contact time by reacting again and again the paraffin rich mixture at 360°C , 40 bar, and LHSV of 3.0 h^{-1} , (where the cracking selectivity is relatively low) the yield continuously decreased, since more and more polybranched paraffins were generated (see Figure 6), which are more susceptible to cracking than normal and monobranched paraffins.

The isoparaffin content of the product increased significantly above 300°C by increasing the temperature, but it started to decrease at about 360°C partly because of the thermodynamic inhibition (as the isomerization reactions are exothermic), partly because of the better approach of the thermodynamic equilibrium, and partly because of the cracking reactions (Figure 3).

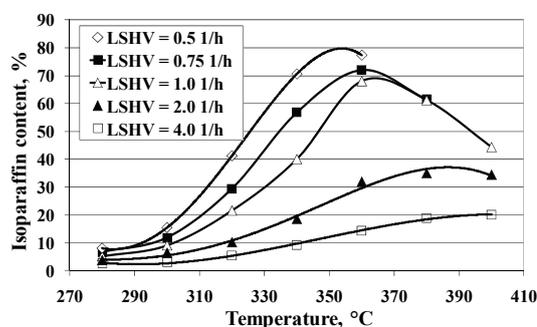


Figure 3: The isoparaffin content of the products as a function of the temperature and LHSV ($P = 40$ bars, $\text{H}_2/\text{feedstock}$ ratio = $400 \text{ Nm}^3/\text{m}^3$)

Up to about 360°C , mainly (>85%) mono branched paraffins were generated, whose significant part (>98%) was mono-methyl-paraffins. It was because, in the case of the 10-member ring zeolites, only a small amount of isoparaffins having alkyl chain of more than one carbon number can form due to the steric inhibition [33]. Their freezing points are more favourable than those of the normal paraffins, and their cetane number is high enough (Figure 4).

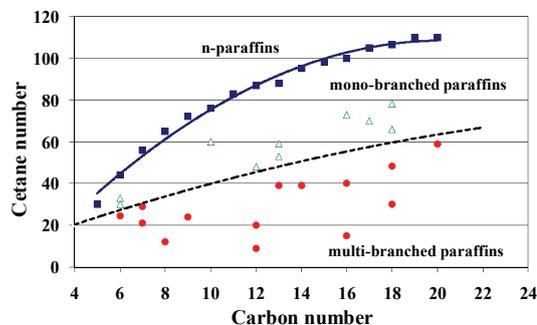


Figure 4: Cetane number of the paraffins as a function of the carbon number [34]

However, above 360°C a significant amount (15–35%) of multi-branched paraffins formed, which also have favourable cold flow properties, but their cetane number

is low (e.g. 2,2,4,4,6,8,8-heptamethylnonane: freezing point: 0°C, cetane number: 15 unit). This effect was increased by decreasing the LHSV (*Fig. 3*).

Up to 340°C, the concentration of isoparaffins increased by decreasing the pressure to 20 bar, because by decreasing the hydrogen pressure the conversion of hydrocarbons could be increased. But above 360°C the increase of the pressure to 50 bar was favourable, because the partial pressure of the hydrogen could roll back the cracking reactions (*Figure 5*).

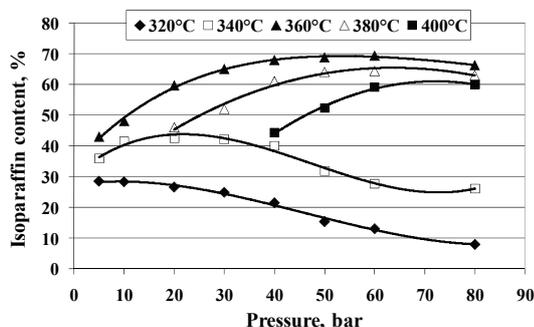


Figure 5: The isoparaffin content of the products as a function of the pressure and the temperature (LHSV = 1.0 h⁻¹, H₂/feedstock ratio = 400 Nm³/m³)

At 360°C, which was favourable regarding both the yield and the isoparaffins content, at least 400 Nm³/m³ H₂/feedstock volume ratio was necessary to reach a high isoparaffin content. In the case of lower values, the concentration of the isoparaffins was decreased by the hydrocracking reactions.

Increasing the apparent contact time (number of runs multiplied by 1/LHSV), the isoparaffin content of the product continuously increased by reacting again and again the paraffin rich mixture in the reactor (at 360°C, 40 bar and LHSV of 3.0 h⁻¹). At the apparent contact time of 2.0 h [= 6 x 1/(3.0 h⁻¹)] the isoparaffin content exceeded 90%. Further increase of the conversion increased only the concentration of polybranched paraffins (*Fig. 6*).

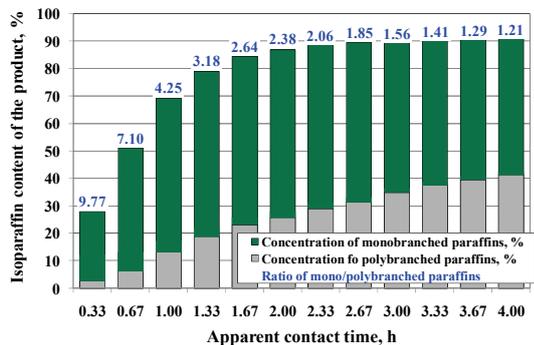


Figure 6: The mono- and polybranched isoparaffin in the products as a function of the apparent contact time

Performance properties

The cold filter plugging point (CFPP) of the products having gasoil boiling range decreased by increasing the

concentration of the isoparaffins. At relatively low conversion of *n*-paraffins (<30%), the CFPP decreased only some units (*Figure 7*). It was because the resolvent effect of isoparaffins could not inhibit the formation and growing of *n*-paraffin crystals. At higher conversion, not only the higher isoparaffin concentration improved the value of CFPP, but the formation of lower carbon number molecules generating mainly at higher than 70% of conversion by the cracking of polybranched paraffins. Accordingly, the CFPP value of the products can satisfy not only the winter specification of the temperature zone, but the specification valid in the arctic zone (-20°C; -26°C; -32°C and -38°C) as well.

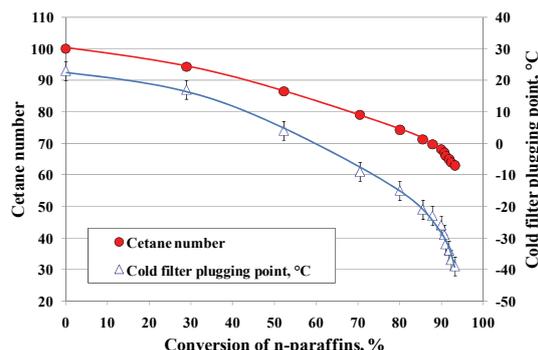


Figure 7: The cold filter plugging point and the cetane number of the products as a function of the *n*-paraffin conversion

(T = 360°C; P = 40 bar; H₂/feedstock ratio = 400 Nm³/m³)

The cetane number of the products decreased as a function of the conversion (*Fig. 7*) relative to that of the feedstock (101 unit), as the mono-methyl paraffins and polybranched paraffins have lower cetane numbers (60–75 and 40–65 unit, respectively) than those of the normal paraffins (90–110 unit) [34]. The cetane numbers of the products having improved cold flow properties (satisfying at least the summer grade specification) were between 65–86 unit, which is significantly higher than the specified value (51 unit) of the current Diesel fuel standard (EN 590:2009 + A1:2010).

While the viscosity of the obtained biogasols was in the range of 2.5–3.5 mm²/s meeting the specification, the density could not provide direct blending as it was in the range of 0.772–0.782 g/cm³ underachieving the expected 0.820 g/cm³ (*Figure 8*).

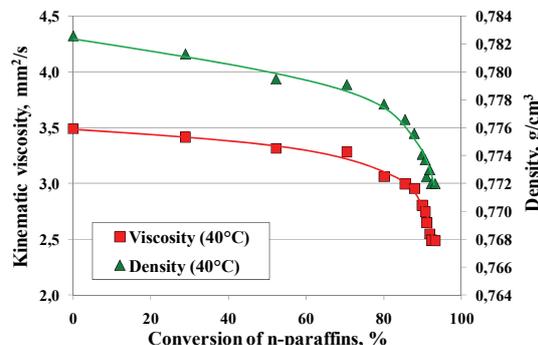


Figure 8: The viscosity and density of the products as a function of the *n*-paraffin conversion

(T = 360°C; P = 40 bar; H₂/feedstock ratio = 400 Nm³/m³)

Utilization possibilities of biogasols

Since biogasols consist of purely normal and isoparaffins, they have more preferable chemical structures than biodiesels. Accordingly, they can eliminate the above disadvantages having an important role in reaching the purposes of the mentioned directives.

Furthermore, these products are excellent Diesel fuel blending components, as they are practically free of sulfur and aromatic compounds, and burn exceptionally clearly. Accordingly, biogasols can be used for premium quality diesel fuels or using these low density products could provide some economic savings and some flexibility for crude refineries in case of blending of gasoils having high aromatic content and low cetane number.

We note that during the production of these improved products the yield decreases. Furthermore, the usability of isoparaffin rich Jet and gasoline fractions has to be considered as well.

Biogasols as blending components of premium quality diesel fuels

Regarding the production costs, the feedstock price (Figure 9) of biogasols, which is the most significant cost of bio-fuels, can be lower than that of biodiesels since (as it was mentioned) they can be produced from a broader base of feedstock. On the other hand, the installation cost of a biogasol plant can be higher than that of a biodiesel plant because of the relatively high price of the hydrogenation catalysts and the pressurized equipment. Regarding the operational costs, the hydrogen consumption represents one of the highest items in the case of biogasols. However, because of the high exothermic nature of the hydrogenation reactions, biogasol production has a net steam production capability, which can be utilized effectively in a refinery. To sum it up, biogasols can be competitive with biodiesels regarding only the costs, while they excel those performance properties.

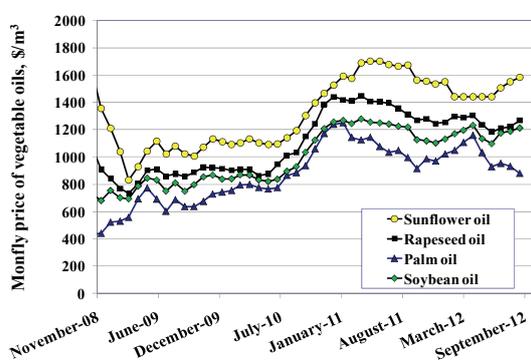


Figure 9: The monthly price of vegetable oils [35]

Comparing only the current product price of biogasols with that of low sulphur diesel gasoils (950-1050 \$/t), biogasols can hardly compete because of

the high feedstock price ($800\text{--}1400\text{ } \$/\text{m}^3 \approx 850\text{--}1450\text{ } \$/\text{t}$). Considering the performance properties as well, the competitiveness of biogasols seems to be more favorable, since the production of gasoils with CFPP value of -20°C or lower can be realized with some yield loss and significant extra costs. In addition to the production of gasoils with biodiesel content, the CFPP value can be a further challenge (CFPP of biodiesels is in the range of -5°C and $+5^\circ\text{C}$ depending on the feedstock) [6]. Consequently, a high amount of additives has to be used. On the other hand, biogasols having low density and excellent cold flow properties may have a positive effect on the cold flow properties of gasoils, therefore, they might improve the economy of premium gasoil production.

Biogasols used for quality improvement of gasoils having low cetane number and high density

In order to increase the profitability refineries try to increase the distillate yield, especially the diesel yield. Some of the easier options are that the refineries can consider crude selection, cut points, operating modes, and catalysts. For further distillate yield improvement, such technologies should be used that break or crack larger, higher boiling point components into smaller, lower boiling point components. These options require capital investment and higher operating costs [36, 37].

As an alternative option, many European refineries try to change the FCC unit for increased distillate production using new catalyst formulations with better cracking capabilities [37]. However, the blending of light cycle oil (LCO) having gasoil boiling range into diesel pool requires further processing as it generally has a high aromatic content (65–75%), low cetane number (15–25), and a relatively high sulfur content (100–1000 mg/kg). During the processing of relatively low value (650–700 \$/t) LCO, the hydrogen consumption is significant (20–25 kg/t); the cetane number can be improved reasonably up to about 30–35 unit. In the case of biogasol production, hydrogen consumption is similar, approximately 20–25 kg/t as a function of the feedstock composition, but the cetane number is in the range of 65–86 unit.

Experiments showed that during the blending of biogasols into gasoils the physical-chemical properties and the cetane number change almost linearly as a function of the biogasol content in the gasoil [38]. These data correlated well with our results. We used an obtained biogasol product (CFPP = -12°C ; cetane number: 74.3) and a conventional light cyclic oil. The main properties of the blended mixture are summarized in Table 1.

As the data of Table 1 show different blends obtained by the admixture of a low density, high cetane number biogasol and a high density, low cetane number light cyclic oil meets the specification of the diesel standard.

Table 1. Main properties and the estimated production cost of mixtures of a biogasoil and a light cyclic oil

Property	Biogasoil	Biogasoil and light cyclic oil mixtures					Hydrotreated LCO
		80:20	60:40	50:50	40:60	20:80	
Density, g/cm ³	0.777	0.808	0.838	0.854	0.869	0.899	0.930
Cetane number	74.3	65.8	57.3	53.1	48.9	40.4	32.0
CFPP, °C	-12	-9	-6	-4	-3	0	3
Production cost, \$/t	1500	1350	1200	1125	1050	900	750

The CFPP value of the obtained mixture was more favourable than that of the LCO. Accordingly, the quality of the LCO improved with biogasoil can be a suitable gasoil blending component. Mixtures containing 40-60% biogasoil as a blending component have a production cost – depending on the price of the feedstock – competitive with the production cost of diesel fuels.

Conclusion

The 0.5%Pt/SAPO-11 catalyst is suitable for the isomerization of normal paraffin-rich mixtures produced from natural triglycerides in order to improve the cold flow properties. The products have outstanding cetane number and are excellent Diesel fuel blending components, as they are practically free of sulphur and aromatic compounds, and burn exceptionally clearly.

Accordingly, they are suitable for bio-components of premium quality diesel fuel. Using these biogasoils for the improvement of cetane number and the reductions in density could provide some economic savings and some flexibility to refineries (e.g. economical application of light cyclic oil of FCC units).

Acknowledgement

This work was supported by the European Union and co-financed by the European Social Fund in the frame of the TÁMOP-4.2.1/B-09/1/KONV-2010-0003 and TÁMOP-4.2.2/B-10/1-2010-0025 projects.

REFERENCES

1. A. DEMIRBAS: Political, economic and environmental impacts of biofuels: A review, *Applied energy*, 86 (2009) pp. 108–117
2. A. P. C. FAAIJ: Bio-energy in Europe: changing technology choices, *Energy Policy*, 34 (2006) pp. 322–342
3. J. HANCSÓK, M. KRÁR, SZ. MAGYAR, L. BODA, A. HOLLÓ, D. KALLÓ: Investigation of the production of high cetane number bio gas oil from pre-hydrogenated vegetable oils over Pt/HZSM-22/Al₂O₃, *Microporous and Mesoporous Materials*, 101 (2007) pp. 148–152
4. M. MITTELBACH, C. REMSCHMIDT: *Biodiesel the comprehensive handbook*, Martin Mittelbach Publisher, Graz (2004)
5. G. KNOTHE, J. VAN GERPEN, J. KRAHL: *The Biodiesel Handbook*, The American Oil Chemists' Society Publishing, Champaign, USA (2005)
6. A. E. ATABANI, A. S. SILITONGA, I. S. BADRUDDIN, T. M. I. MAHLIA, H. H. MASJUKI, S. MEKHILEF: A comprehensive review on biodiesel as an alternative energy resource and its characteristics, *Renew. Sust. Energ. Rev.*, 16 (2012) pp. 2070–2093
7. M. CANAKCI, H. SANLI: Biodiesel production from various feedstocks and their effects on the fuel properties, *J. Ind. Microbiol. Biot.*, 35(5) (2008) pp. 431–441
8. I. M. ATADASHI, M. K. AROUA, A. R. ABDUL AZIZ, N. M. N. SULAIMAN: The effects of water on biodiesel production and refining technologies: A review, *Renew. Sust. Energ. Rev.*, 16 (2012) pp. 3456–3470
9. E. BAKEAS, G. KARAVALAKIS, S. STOURNAS: Biodiesel emissions profile in modern diesel vehicles, Part 1: Effect of biodiesel origin on the criteria emissions. *Sci. Total. Environ.*, 409 (2011) pp. 1670–1676
10. M. A. FAZAL, A. S. M. A. HASEEB, H. H. MASJUKI: Biodiesel feasibility study: An evaluation of material compatibility; performance; emission and engine durability. *Renew. Sust. Energ. Rev.*, 15 (2011) pp. 1314–1324
11. A. S. M. A. HASEEB, M. A. FAZAL, M. I. JAHIRUL, H. H. MASJUKI: Compatibility of automotive materials in biodiesel: A review, *Fuel*, 90 (2011) pp. 922–931
12. M. A. FAZAL, A. S. M. A. HASEEB, H. H. MASJUKI: Effect of different corrosion inhibitors on the corrosion of cast iron in palm biodiesel, *Fuel Process, Technol.*, 92 (2011) pp. 2154–2159
13. J. XUE, T. E. GRIFT, A. C. HANSEN: Effect of biodiesel on engine performances and emissions, *Renew. Sust. Energ. Rev.*, 15 (2011) pp. 1098–1116
14. M. LAPUERTA, O. ARMAS, J. RODRÍGUEZ-FERNÁNDEZ: Effect of biodiesel fuels on diesel engine emissions, *Prog. Energy. Combust.*, 34(2) (2008) pp. 198–223
15. C. C. ENWEREMADU, H. L. RUTTO: Combustion, emission and engine performance characteristics of used cooking oil biodiesel – A review. *Renew. Sust. Energ. Rev.*, 14 (2010) 2863–2873.

16. HOEKMAN, S. K., ROBBINS, C.: Review of the effects of biodiesel on NO_x emissions, *Fuel Process, Technol.*, 96 (2012) pp. 237–249
17. H. C. ONG, T. M. I. MAHLIA, H. H. MASJUKI, D. HONNERY: Life cycle cost and sensitivity analysis of palm biodiesel production, *Fuel*, 98 (2012) pp. 131–139
18. J. M. MARCHETTI: The effect of economic variables over a biodiesel production plant, *Energy Conversi. Manage.*, 52 (2011) pp. 3227–3233
19. M. KRÁR, A. THERNESZ, CS. TÓTH, T. KASZA, J. HANCSÓK: Investigation of catalytic conversion of vegetable oil/gas oil mixtures. Silica and Silicates in Modern Catalysis, *Transworld Research Network* (2010) pp. 435–455
20. CS. TÓTH, T. KASZA, J. HANCSÓK: Production of diesel fuel by hydroisomerization of co-processed vegetable oil – gas oil mixtures. 15th Nordic Symposium on Catalysis, Mariehamn, Åland, Finland, June 10–12, 2012
21. H. AATOLA, M. LARMI, T. SARJOVAARA, S. MIKKONEN: Hydrotreated Vegetable Oil (HVO) as a Renewable Diesel Fuel: Trade-off between NO_x, Particulate Emission, and Fuel Consumption of a Heavy Duty Engine, www.nesteoil.com, letöltés ideje: 2012. 10. 31.
22. G. W. HUBER, A. CORMA: Synergies between Bio- and oil refineries for the production of fuels from biomass, *Angewandte Chemie International Edition*, 46 (2007) pp. 7184–7201
23. D. KUBIČKA: Future refining catalysis – introduction of biomass feedstocks, *Collect. Czech. Chem. Commun.*, 73 (2008) pp. 1015–1044
24. J. HANCSÓK, T. KASZA, S. KOVÁCS, P. SOLYMOŠI, A. HOLLÓ: Production of bioparaffins by the catalytic hydrogenation of natural triglycerides, *Journal of Cleaner Production*, 34 (2012) pp. 76–81
25. H. DELDARI: Suitable catalysts for hydroisomerization of long-chain normal paraffins, *Applied Catalysis A: General*, 293 (2005) pp. 1–10
26. K. C. PARK, S. K. IHM: Comparison of Pt/zeolite catalysts for n-hexadecane hydroisomerization, *Applied Catalysis A: General*, 203 (2000) pp. 201–209
27. C. PEREGO: Micro- and mesoporous materials for sustainable energy, 16th International Zeolite Conference – 7th International Mesostructured Materials Symposium, KN-8, July 4-9 (2010) Italy, Sorrento
28. J. HANCSÓK, S. KOVÁCS, GY. PÖLCZMANN, T. KASZA: Investigation the effect of oxygenic compounds on the isomerisation of bioparaffins over Pt/SAPO-11, *Topics in Catalysis*, 54 (2011) pp. 1094–1101
29. J. HANCSÓK, G. GÁRDOS, M. BAUMANN: Hungarian Journal of Industrial Chemistry, 17 (1989) pp. 131–137
30. T. KASZA, A. HOLLÓ, A. THERNESZ, J. HANCSÓK: Production of bio gas oil from bioparaffins over Pt/SAPO-11. *Chemical Engineering Transactions*, 21 (2010) pp. 1225–1230
31. J. HANCSÓK, M. KRÁR, SZ. MAGYAR, L. BODA, A. HOLLÓ, D. KALLÓ: Investigation of the production of high quality biogasoil from prehydrogenated vegetable oils over Pt/SAPO-11/Al₂O₃, *Studies in Surface Science and Catalysis*, 170 (2007) pp. 1605–1610
32. T. KASZA, J. HANCSÓK: Investigation of fuel components produced by the isomerization of bioparaffin mixtures, *Hungarian Journal of Industrial Chemistry*, 39(1) (2011) pp. 121–126
33. J. A. MARTENS, M. TIELEN, P. A. JACOBS, J. WEITKAMP: Estimation of the void structure and pore dimensions of molecular sieve zeolites using the hydroconversion of n-decane, *Zeolites*, 4 (1984) pp. 98–107
34. M. J. MURPHY, J. D. TAYLOR, R. L. MCCORMICK: Compendium of Experimental Cetane Number Data, Subcontractor report, National Renewable Energy Laboratory, NREL/SR-540-36805, 2004.
35. <http://www.indexmundi.com/>, October, 2012
36. D. GIBBONS: Naphtha to diesel via novel routes – An unconventional, synthetic approach to converting LPG and naphtha components could boost diesel production, *Petroleum Technology Quarterly* (2011) Q3, pp. 27–33
37. R. KARLIN, A. MACRIS, R. ADARME, K. WU: Flexible solution for increased diesel production, *Petroleum Technology Quarterly* (2009) Q4, pp. 27–42
38. M. LAPUERTA, M. VILLAJOS, J. R. AGUDELO, A. L. BOEHMAN: Key properties and blending strategies of hydrotreated vegetable oil as biofuel for diesel engines, *Fuel Processing Technology*, 92 (2011) pp. 2406–2411