

Production of Bioparaffins from Natural Triglycerides

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The production possibilities of gasoil boiling range mixtures of paraffins were investigated over different catalysts as a function of the process parameters using different natural triglycerides. At the favourable operational parameters (T: 360-380°C; p: 60-80 bar; liquid hourly space velocity (LHSV): 1.0-2.0 m³ feedstock/ m³ catalyst · h; H₂/HC: 450 Nm³/m³) the yield of paraffin mixtures increased in the order of NiW/Al₂O₃ < NiMo/Al₂O₃ << CoMo/Al₂O₃. In the best cases the yields of paraffins reached 75-85% of the theoretical values. These compounds are excellent fuels of Diesel engines (cetane number: 89-92) using them as pure fuels or blending components.

1. Introduction

The bio-fuels which have high economical and environmental impacts play a more and more important role in the EU and all over the world (Huber, et al., 2006; Dembiras, 2009). The reasons of the utilisation of feedstock from renewable source are the possibility of significant decrease of greenhouse gas emission during the whole life cycle, and the possibility of better quality relative to the crude oil based compounds, etc. As bio-fuels of Diesel engines namely bio-components of Diesel fuels nowadays biodiesels (fatty acid methyl esters) are used in the highest degree all over the world which are produced from different vegetable oils and used frying oils by transesterification with generally methanol. But these have numerous disadvantages e.g. bad storage (oxidation and heat) stability because of the olefinic double bonds; aptitude to water intake; hydrolysis sensitivity of the ester bonds, which generates corrosive acids, unfavourable effect on the engine oils, etc. (Hancsók, et al., 2007a). Consequently in the EU the maximum blending quantity of the fatty acid methyl esters is limited to 7.0 V/V% in the EN 590:2009 standard by mainly the suggestion of the car manufacturers. At the same time the purpose in the EU is 10% bio component utilisation up to 2020.

Because of these disadvantages and so that the quantity of bio-origin fuels could be increased other kinds of fuel-purpose products have to be produced by other chemical processes from natural triglycerides (oils of conventional and improved vegetables, used cooking oils and fats, greases from meat and leather processing industry, “trap grease” from sewage farm, algae, etc.) of which molecular structure differs from that of the fatty acid methyl esters, consequently have better performance properties. Such kind of products could be the mixtures of normal and isoparaffins produced by special

hydrocracking of triglycerides, mono and diglycerides, fatty acids. The reason of this is that the mixtures of C_{12} - C_{18} iso and n-paraffins are the best components of the fuels of Diesel engines, consequently these are the best components of the conventional gas oils regarding both the performance properties and environmental aspects (free of sulphur, nitrogen, aromatic compounds and olefins, clear combustion, the most easily biodegradable compounds among the hydrocarbons) (Fig. 1 and 2) (Hancsók, et al., 2007b).

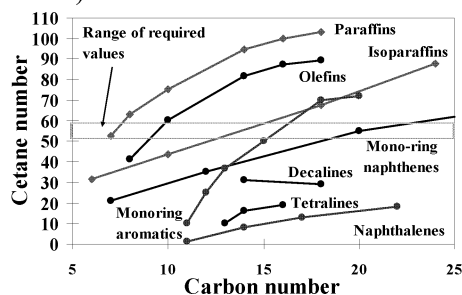


Fig. 1: Cetane numbers as a function of carbon number of hydrocarbons

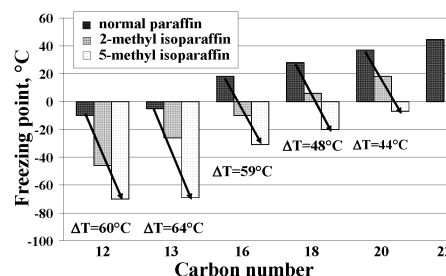


Fig. 2: Melting point of paraffins at various carbon numbers

The aim of the special hydrocracking is the removing of the oxygen atoms from the triglyceride molecules and the saturation of the olefinic double bonds of the hydrocarbon chains. During this the cleavage of the propane, generation of fatty acids and other oxygen containing compounds take place as well, consequently it is useful to call these reactions special hydrocracking as a collective noun instead of hydrogenating deoxygenation.

To catalyse the mentioned reactions different $CoMo/Al_2O_3$, $NiMo/Al_2O_3$ and NiW/Al_2O_3 , etc. catalysts are suggested. More contributions have already presented experimental results (e.g. Furimsky, 2000; Kovács, et al., 2010; Kubicka, et al., 2010) and the bio-plant in Finland. In case of different fatty acid composition feedstock the comparison of the performance (product yield, selectivity, etc.) of the catalysts are not complete. Consequently the aim of our research work was its investigation in detail. In this paper we present some relevant results of the systematic research series.

2. Experimental

2.1 Catalytic test

The catalytic reactions were carried out in a bench scale, high pressure reactor system containing a fix bed flow trough reactor with 100 cm^3 catalyst volume and free of back mixing (Hancsók, et al., 2007a). The reactor system contained all the equipment and devices applied in the reactor system of a hydrotreating plant. The reaction conditions – based on the results of the preliminary experiments – were varied in the following parameter ranges: temperature: $280\text{--}380^\circ\text{C}$, pressure: $20\text{--}100\text{ bar}$, LHSV: $0.75\text{--}3.0\text{ h}^{-1}$, H_2/feed ratio: $450\text{ Nm}^3/\text{m}^3$. The latter value was selected by considering the hydrogen consumption of the different reactions, and so that at least 1.3 times hydrogen excess

should be in the catalytic system. The product mixtures of the heterogeneous catalytic transformation of the sunflower oil were separated into three fractions: gaseous, water and organic phases. The products [mixtures of gasoil boiling range (180-360°C) normal and isoparaffins] were obtained by distillation of the organic fraction.

2.2 Catalysts and feeds

The non-confidential properties of the catalysts are the following: CoMo/ γ -Al₂O₃ - Mo: 13.2%, Co: 3.1%; NiMo/ γ -Al₂O₃ - Ni: 13.4; Mo: 3.2; NiW/ γ -Al₂O₃ - Ni: 8.1; W: 1.9; and the surface areas were 218, 230 and 226 m² respectively. Before the experiments the catalysts were reduced in hydrogen flow for 6 hours at 400°C. Table 1 presents the main properties of the feedstocks.

Table 1: Main properties and fatty acid composition of feeds

Properties	Value		Analytical methods
	Rapeseed oil	Sunflower oil	
Kinematic viscosity (40°C), mm ² /s	33.85	31.55	EN ISO 3104:1996
Density (15°C), g/cm ³	0.9195	0.9182	EN ISO 12185:1996
Acid number, mg KOH/g	1.2	1.8	EN 14104:2004
Iodine number, g I ₂ /100g	87.5	132	EN 14111:2004
Cold filter plugging point, °C	30	32	EN 116:1997
Cetane number	34	37	ASTM D 4737
Sulphur content, %	7	8	EN ISO 20846:2004
Fatty acid composition,%			
C14:0	-	0.09	
C16:0	2.1	6.33	
C18:0	0.6	3.45	EN ISO 5509: 2000
C18:1	93.7	21.64	EN 14103:2003
C18:2	3.3	67.78	
Others	0.3	0.71	
Average double bond number	3.1	4.5	

2.3 Analytical methods

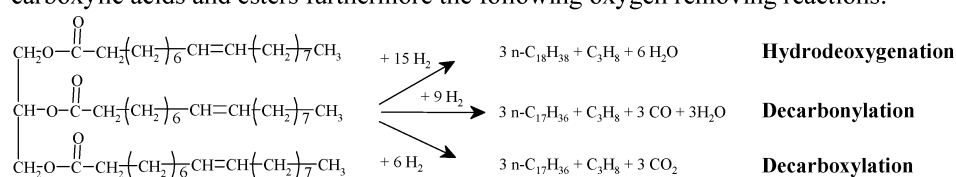
Table 1 shows a list of analyses employed and the EN and EN ISO standards describing them, as well. For gas chromatographic analysis of the composition of feedstocks and products a Thermo Scientific Trace GC was used. The analysis of the hydrocarbon composition and the i-/n-paraffin content was performed on a DB-1HT (Agilent) Capillary column (30 m x 0.32 mm x 0.1 µm). The olefin content of products was determined on a PONA type capillary column (50 m x 0.21 mm x 0.5 µm).

3. Results and Discussion

According to the experimental results it was found that the conversion of triglycerides increased by stricter the process parameters, namely by increasing the temperature and the pressure and by decreasing the liquid hourly space velocity (LHSV). Its degree changed not only as a function of the process parameters, but that of the catalyst

composition, but it was practically independent from the fatty acid composition of the feedstock, namely from the average double bond number (Fig. 4), which was significantly different (3.1 and 4.5). This refers to that that the saturation took place very quickly and practically in the same degree on the used catalysts at the applied process conditions, consequently it is a very fast reaction. We have to highlight that because of the extent limitation of this paper only the most important results and cogitations are presented as compact as possible. Consequently Figure 4 presents only that results which were constricted to a parameter combination (T: 340-380°C; P: 50-100 bar; LHSV: 0.75-3.0 h⁻¹; H₂/HC: 450 Nm³/m³) which were determined by the results of our pre-experiments.

The triglyceride conversion decreased in the order of CoMo/Al₂O₃ > NiMo/Al₂O₃ > NiW/Al₂O₃ at every investigated parameter combination, because of the different special hydrocracking activity of the catalysts in this complex catalytic system. The presented separation of the product mixture and their analytical tests showed that the main reactions are: saturation of olefinic double bonds, propane cleavage, generation of carboxylic acids and esters furthermore the following oxygen removing reactions:



As side reactions mainly water-gas shift, methanization and the hydrocracking of the generating paraffins took place beside the isomerisation of normal paraffins.

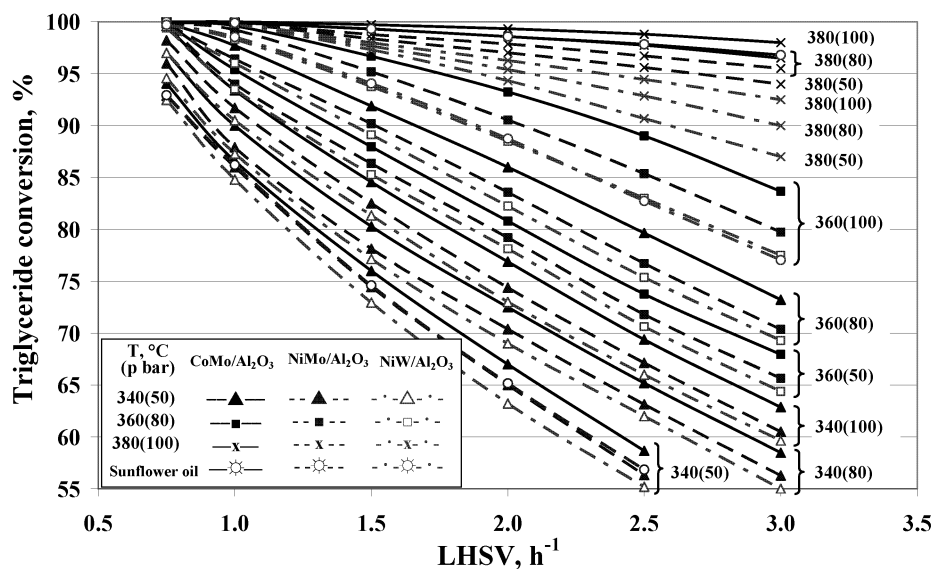


Fig. 4: The conversion of the triglycerides as a function of LHSV at different temperatures and pressures (feedstock rapeseed oil; H₂/HC: 450 Nm³/m³)

According to the results it was concluded that the favourable yield of LHSV is between 0.75 and 2.0 h⁻¹ regarding the triglyceride conversion. Regarding the yields of the products (gasoil boiling range normal and iso-paraffins) (Fig. 5) as well, this value comes to 1.0 h⁻¹. At a lower value of LHSV the yield decreased because of the hydrocracking of the paraffins, because of the longer contact time, but at higher values the yields were lower as well because of the lower conversion of the triglycerides, by reason of the insufficient contact time of the reactants on the active sites of the catalysts. In the view of the previously presented reactions the yields of the products cannot theoretically reach 100% relative to the feedstock. In case of the investigated feedstock the theoretically highest yield is 81.6 – 86.4% (rapeseed oil) and 81.2 – 86.0% (sunflower oil) as a function of the deoxygenation reactions. The significant difference of the fatty acid composition of the feedstock did not influence the yield of the products. Its reasons are the same as the ones given in case of the evaluation of the triglyceride conversion.

Based on the previously detailed evaluation the most favourable results (reaction conditions, product yield, main properties) are summarised in Table 2. According to Table 2 it was concluded that the gasoil boiling range product mixtures which contained practically only open-chain paraffins could be produced from the two feedstocks of different fatty acid composition over the applied catalysts at the favourable process parameters. The yields of the products increased in the order of NiW < NiMo << CoMo. In case of the latter catalyst the approaching of the theoretical yield was about 75-85% independently from the fatty acid composition of the feedstock. All of the products had excellent performance properties (cetane number: 89-92; EN 590:2010 > 51; CFPP satisfied the summer grade specifications without addition). They could be used as pure fuel and blending components, as well.

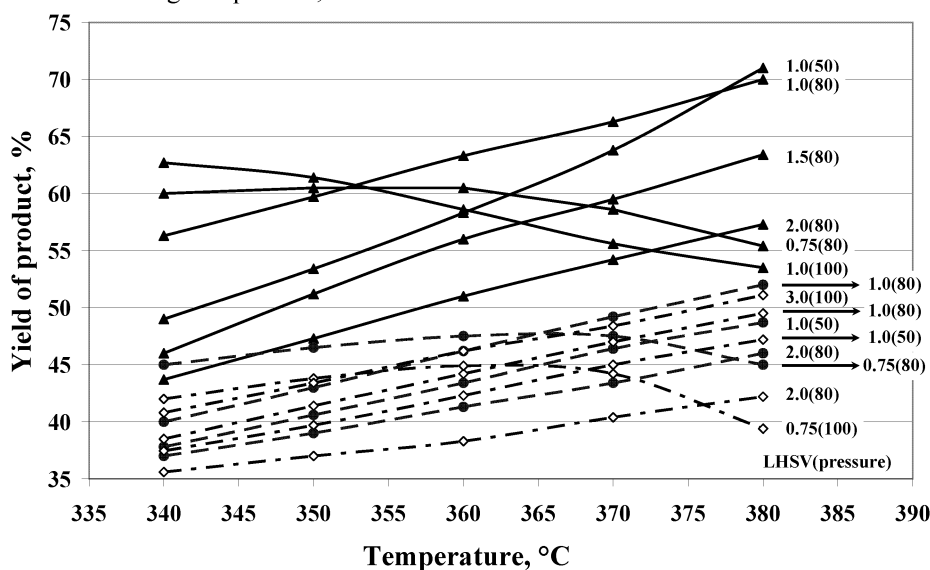


Fig. 5: The yields of the products as a function of the process parameters (CoMo/Al₂O₃: —▲—; NiMo/Al₂O₃: - -●- -; NiW/Al₂O₃: - -◇- -)

Table 2: The most favourable results (RO: rapeseed oil; SO: sunflower oil)

Property	CoMo/Al ₂ O ₃		NiMo/Al ₂ O ₃		NiW/Al ₂ O ₃	
	RO	SO	RO	SO	RO	SO
Triglyceride conversion, %	92.8-99.8	94.0-99.8	88.1-97.2	81.8-97.4	80.4-95.3	86.7-95.6
Main product	63.4-	63.1-	42.1-	42.0-	39.3-	39.4-
- yield, %	71.3	71.5	52.2	51.9	49.5	49.3
- approaching of theoretical value, %	75.5-84.9	75.5-85.5	50.1-62.1	50.2-62.1	46.8-58.9	47.1-59.0
- paraffin content, %	←————— < 99.95 —————→					
- density at 15,6°C, g/cm ³	0.775	0.776	0.777	0.776	0.777	0.776
- acid number, mg KOH/g	←————— < 0.1 —————→					
- sulphur content, mg/kg	←————— < 1 —————→					
- CFPP, °C	+ 1	+ 2	+ 5	+ 5	+ 3	+ 4
- cetane number	89	91	92	92	90	91
- iodine number, g I ₂ /100g	←————— < 1 —————→					

4. Conclusion

The reduced state CoMo/Al₂O₃, NiMo/Al₂O₃ and NiW/Al₂O₃ catalysts are suitable for the conversion of triglycerides of different fatty acid composition (different average double bond) to mixture of gasoil boiling range paraffins. At the favourable reaction conditions (T: 360-380°C; P: 60-80 bar; LHSV: 1.0-1.2 h⁻¹; H₂/HC: 450 Nm³/m³) the yields of paraffin mixtures reached 75-85% of the theoretical paraffin yield on the most active CoMo/Al₂O₃ (> NiMo > NiW) catalyst. The products are excellent fuels of Diesel engines as pure fuel and blending components (cetane number: 89-92; EN 590 specification: ≥ 51).

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