

Motor Fuel Purpose Hydrogenation of Used Cooking Oils

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The liquid motorfuels are the main power source both of the commercial and public transportation. Renewable fuels can play significant role to achieve the EU's plan, to reach the 10 % energy ratio of total fuel consumption until 2020. To achieve all this goals the European Union created the 2003/30/EC and further the 2009/28/EC directives. Unconventional feedstocks were investigated, for example non edible hybrids of oilseed plants such as rapeseed oils with high euric acid content or sunflower oils with high oleic acid content, used cooking oil. Beside the sustainability and the technical compatibility of these compounds with the current engine and vehicle constructions should be ensure, thus this bio components can be blend in the motor fuels unlimited quantity. The maximum amount of bio-component can be applied in motor fuels is 10 % bio-ethanol in gasoline and 7 % fatty acid-methyl-ester in diesel fuel. In this context heterogen catalytic hydrogenation of used cooking oil was studied on aluminium-oxide supported transition metal catalyst. The applied operation parameters were the following: temperature; 320 - 380 °C, pressure: 20 - 80 bar, LHSV: 1.0 h⁻¹, H₂/hydrocarbon ratio: 600 Nm³/m³. The yield of products in gas oil boiling range at the favourable operation parameters was close to the theoretical value (80–90%). Quality parameters of these products were the following; the cetane number was higher than 75, the aromatic content was lower than 0.1 % and the sulphur content was lower than 5 mg/kg. The actual EN 590:2009 +A1 2010 standard does not limit the blending ratio of these bio-components, the blending of biodiesel is limited (max 7 v/v%). Consequently these products can be blended in gasoil up to 10 %, and this way we can meet the requirements of the EU which prescribe at least 10-80 % bio component blending in motor fuels by 2020.

1. Introductions

The interest on alternative fuels is on the rise due to the unequal presence of the fossil energy carriers, the periodic rise of the price of fossil fuels, decreasing the dependence of crude oil and the regulations of European Union. The liquid fuels (included the alternative fuels) as the main power source both of the commercial and public transportation. The alternative fuels can play significant role to achieve of the EU's plan, to reach the 10 % energy ratio of total fuel consumption until 2020. Basis of these reasons the application of the bio-fuels can increase in large degree in long and middle term, for example: in some countries of the domestic demand on bio-fuels can be increased to 20 % until 2020, along with the decreasing motor fuels demand it can be up to 70 % until 2030, the world's biomass based energy production can reach 5 % until 2050 (Shell report, 2012) and also (Schollnberger, 2012). Sustainable and environmental friendly production of these compounds, are very important. Accordingly to ensure the availability of this feedstock can decrease the production costs. To achieve all this goals the European Union created several directives (1998/70/EC, 2001/77/EC, 2003/17/EC, 2003/30/EC, 2003/87/EC, 2009/28/CE, 2009/30/CE). Natural triglycerides like vegetable oils and animal fats (edible or non-edible/waste) can be feed stocks bio-fuels as alternative energy sources. Motor fuel purpose hydrogenation of sunflower oil was investigated on CoMo/Al₂O₃ non sulphided catalyst (Krár et al, 2010), NiMo/Al₂O₃, CoMo/Al₂O₃ sulphided catalysts (Krár et al, 2011) and NiMoW/Al₂O₃ sulphided catalyst (Kovács et al 2010). Oils obtained from special breeding non edible hybrids like rapeseed oil with high euric acid content on non sulphided CoMo/Al₂O₃ catalyst (Solymosi et al, 2011a) and sunflower and rapeseed oil with high oleic acid content on CoMo/Al₂O₃ catalyst (Solymosi et al, 2011b). Motor fuel purpose hydrogenation of animal fats or waste triglycerides were investigated on NiMo/Al₂O₃ (Baladincz et

al, 2010), CoMo/Al₂O₃ sulphided catalysts and Pt/Pd/USY (Baladincz et al, 2011,). Bezergianni et al (2010a) investigated the hydroconversion of used cooking oil including the product yields and reaction routes (Bezergianni et al, 2010b). Consequently, production of second generation bio fuels from alternative sources (mainly hydrotreated vegetable oils) is widely investigated. Using of these raw materials can decrease the CO₂ emission and dependence of crude oil. Beside the sustainability and the technical compatibility of these compounds with the current engine and vehicle constructions should be ensured, thus this bio-components can be blend in the motor fuels with unlimited quantity. Due to the low utilization properties of the present applied first generation bio-fuels these compounds are limited in the fuels. The maximum amount of bio-component can be applied in motor fuels is 10% bio-ethanol in gasoline and 7 % fatty acid-methyl-ester in diesel fuel. Disadvantages of the first generation bio-fuels are:

- limited in motor fuels
- storage problems (FAME)
- endangering the safety of food supply

The second generation of bio-fuels can be hydrogenated vegetable oils or hydrogenated triglycerides from other source, bio-ethanol from lignocelluloses. These compounds can be blend into motor fuels higher quantity due to their better utilization properties, which are:

- good quality
- blending into fuels with unlimited quantity
- fit to the available refining structure (in case of hydrogenation of vegetable oils)

The actual EN 590:2009 +A1 2010 standard does not limit the blending ratio of second generation bio-components, the blending of biodiesel is limited (max 7 v/v%). Consequently these products can be blended in gasoil up to 10%, and this way we can meet the requirements of the EU which prescribe at least 10-80% bio component blending in motor fuels by 2020. All of these above mentioned reasons explain the investigation of unconventional feedstocks which do not endanger the safety of food supplement and/or can be processed with lower operation costs. For example these feedstocks can be rapeseed oils with high erucic acid content obtained from special hybrids of rape (e.g. Brassica Napus) or high oleic acid containing oil of rapeseeds (Pioneer Hi-Bred 45A37) or sunflowers (Saaten Union Capella) waste triglycerides (slaughter-house waste lard, used cooking oil) or oil seeds that grow on long term unused agricultural area (waste land). Motor fuels purpose application of waste origin raw materials is important because the waste origin raw materials is recognized in double weight.

The basis of above mentioned facts it is necessary to investigation hydrogenation of other origin no edible (used cooking oil) triglyceride sources. It is because the aim of our experimental work was investigate the effect of the operation parameters of the product quality and the reaction pathways.

Conversion of natural triglycerides to bio gas oil via catalytic hydrogenation the first step is the saturation of double bonds, in the following step the oxygen removal is take place on two possible route HDO and HDC (Simacek et al, 2010). Da Rocha Filho et al (1993) observed the possible side reactions can be produced cyclic and aromatic molecules.

- full saturation of double bonds (hydrogenation),
- heteroatom removal
 - oxygen removal
 - hydrodeoxygenation (HDO reaction, reduction)
 - decarboxylation,
 - decarbonylation
 - removing of other heteroatoms (sulphur, nitrogen, phosphorus, metals),
- isomerisation of normal-paraffins which are formed during the oxygen removing
- different side reactions
 - hydrocracking of fatty acid chain of triglyceride molecule,
 - water-gas-shift reaction
 - methanization,
 - cyclization, aromatization, etc.

During the reduction reaction (HDO) normal paraffins form which carbon number are equal with the triglycerides builder fatty acids. In the case of decarboxylation and decarbonylation reactions (HDC) normal alkanes are produced which carbon number is lower by one the carbon number of fatty acids in the original vegetable. (Figure 1)

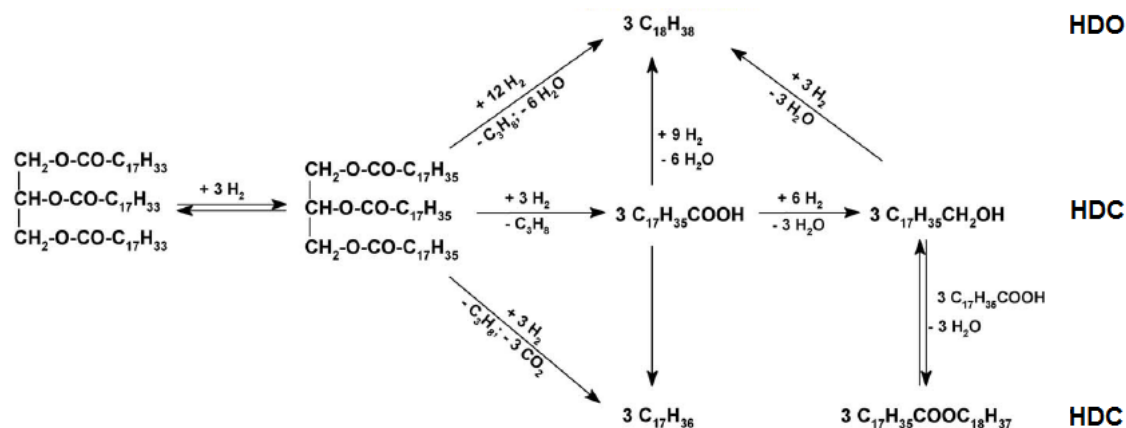


Figure 1: Possible pathways of vegetable oils oxygen removal

2. Experimental

2.1 Catalytic test

During our experimental work was investigated of heterogenic catalytic hydrotreating oxygen removal of used cooking oil on different catalyst. In this context the effect of operation parameters (temperature, pressure) was studied of the conversion of triglycerides and the yield of target fraction. Furthermore the degree and type of the deoxygenation reactions were also investigated.

2.2 Feedstocks

The feedstock of the hydrotreating experiments was used cooking oil which was collected in Hungary and it was properly pre-treated (filtered). The catalysts were commercial available supported bimetallic CoMo/Al₂O₃, NiMo/Al₂O₃, NiW/Al₂O₃, catalysts. The catalysts were in sulphide form.

2.3 Experimental apparatus and products separation

The experimental tests were carried out in one of the measure sections of a high pressure reactor system containing two flow reactors (isothermal catalyst volume: 100 cm³) The reactor system contained all the equipment and devices applied in the reactor system of a hydrotreating plant. The apparatus is suitable for keeping the main process parameters with such precision at least as used in the industry (Nagy et al, 2007).

The product mixtures obtained from the hydrotreating of used cooking oil were separated to gas phase, water and organic phase. The gas phase obtained from the separator of the reactor system contained carbon-monoxide, carbon-dioxide, propane, the hydrogen-sulphide and ammonia which evolved during the heteroatom removal of used cooking oil, furthermore the lighter hydrocarbons (C₁-C₄ as valuable by-products) which evolved during the hydrocracking reactions. The liquid product mixtures obtained from the separator of the reactor system contained water, hydrocarbons and oxygen containing compounds. After the separation of the water we obtained the light (C₅-C₉) hydrocarbons (gasoline boiling range) from the organic fraction by distillation up to 180 °C. The residue of the atmospheric distillation was separated by vacuum distillation into the target product (gas oil boiling range fraction, mainly C₁₁-C₁₉ hydrocarbons) and the residue. The residue contained the unconverted triglycerides, the evolved and unconverted diglycerides and monoglycerides, fatty acids, esters, which evolved as intermediate products or were originally in the feedstock.

2.4 Process parameters

The range of the applied process parameters – based on our earlier experimental results – were the following: temperature 320 – 380 °C, total pressure 20 – 80 bar, liquid hourly space velocity (LHSV): 1.0h⁻¹ and H₂/used cooking oil volume ratio: 600 Nm³/m³.

2.5 Analytical methods

The composition of the total organic products obtained from the catalytic conversion of the triglycerides were determined by high temperature gas chromatograph (Shimadzu 2010 GC [column: Phenomenex Zebron MXT]).

Table 1: List of analytical methods

Properties	Standard method
Kinematic viscosity	EN ISO 3104:1996
Density	EN ISO 3675:2000
Acid number	EN 14104:2004
Iodine number	EN 14111:2004
CFPP	EN 116:1999
Fatty acid composition	EN ISO 5509:2000; EN 14103:2004

3. Results and discussions

The aim of our experimental work was, as stated above, motor fuel purpose hydrogenation of used cooking oil on different catalyst and comparing the obtained results. In this context it was investigated the yield of the gas oil boiling range products via hydrogenation of used cooking oil on different metal content catalyst and the effect of the operation parameters of the yield and quality of the target products, furthermore the reaction pathways of hydrogenation (HDO/HDC). Based on our experimental results it was found that the highest rate of hydrogenation of used cooking oil take place on NiMo/Al₂O₃ catalyst (Figure 2), near total conversion was observed above 340 °C. In case of CoMo/Al₂O₃ the best achievable conversion was 88 %. In case of NiW/Al₂O₃ catalyst the conversion was near to 100 % because on more severity of operation parameters.

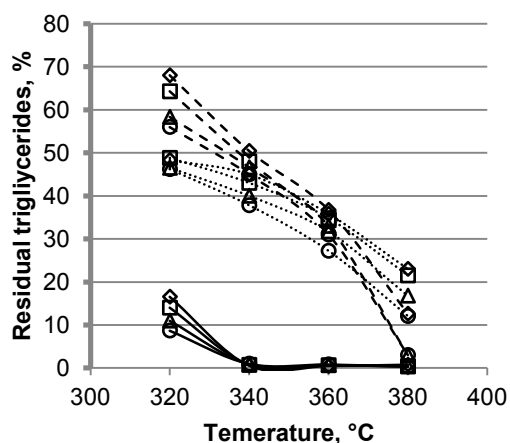


Figure 2: The yield of the unconverted used cooking oils as the function of operation parameters (stipple CoMo/Al₂O₃, continuous line NiMo/Al₂O₃, broken line NiW/Al₂O₃, ◇ 20 bar, □ 40 bar, △ 60 bar, ○ 80 bar)

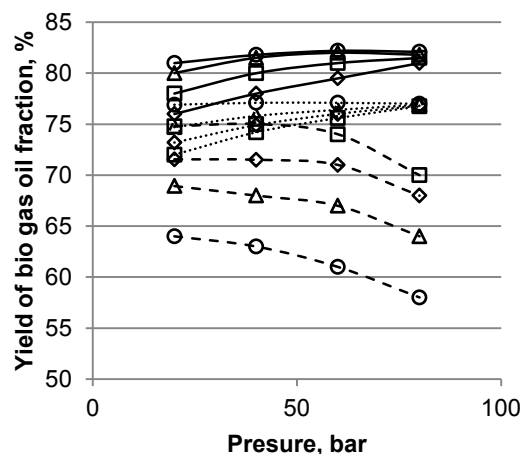


Figure 3: Yield of the bio gas oil fraction (target product) as a function of operation parameters (stipple CoMo/Al₂O₃, continuous line NiMo/Al₂O₃, broken line NiW/Al₂O₃, ◇ 20 bar, □ 40 bar, △ 60 bar, ○ 80 bar)

The yield of the target fraction increased with the severity of operation parameters on the NiMo/Al₂O₃ and CoMo/Al₂O₃. Lowest yield of target product was observed on NiW/Al₂O₃ catalyst (Figure 3). Due to the low activity of the catalyst on low temperature, and the high rate of cracking reaction on high temperature (on 380 °C and 80 bar the light fraction was 24 %). In case of NiW/Al₂O₃ catalyst on more severe operation parameters the yield of the light fraction (C₁₀-) was higher than other two catalyst. This fraction can be outstanding bio blending component of gasoline (high octane number) or JET (low crystallization point) due to it is high iso-paraffin content.

The fatty acids like one acid value even carbon number carboxylic acids, they have more than 200 known variables. The synthesis of fatty acids starts from acetyl-CoA (acetyl-coenzim A) and in consecutive steps it length every step by 2 carbon number. This is main reason to the various fatty acids only have an even carbon number chain (Hereszky et al, 2007). Thus uneven carbon number paraffins in the product fraction only came from HDC (decarboxylation, decarbonylation) and crack reactions. In the case of the mainly C₁₈ carbon number fatty acids contains vegetable oils the C₁₈/C₁₇ paraffin ratio in the main fraction is outstanding marker to follow the HDO/HDC reaction ratio. It was concluded that C₁₈/C₁₇ ratio in the main

fraction decreased with the increasing temperature and it increased with the increasing pressure (increasing partial pressure of hydrogen). Consequently at higher pressure the HDC reactions resulting mole number increase took place at lower degree, while at higher temperature the oxygen removal occurred by mainly HDC reactions (Figure 4) The basis of our experimental results it was obtained that the C_{18}/C_{17} ratio was significantly higher on $CoMo/Al_2O_3$ catalyst. Consequently the oxygen removal on $CoMo/Al_2O_3$ catalyst take place with the HDO way with higher hydrogen consumption. In case of $NiMo/Al_2O_3$ catalyst the HDC reactions take place at higher degree than $CoMo/Al_2O_3$ catalyst. More severe operation parameters on NiW/Al_2O_3 catalyst the C_{18}/C_{17} ratio did not show clearly the ratio of HDO/HDC reaction ways due to the high rate of cracking reactions. Lower pressure and temperature this catalyst showed the lowest C_{18}/C_{17} ratio. HDO/HDC. The ratio of the C_{18}/C_{17} increased in the order of $CoMo/Al_2O_3 < NiMo/Al_2O_3 < NiW/Al_2O_3$. Consequently it was found that on the high acidity catalyst the oxygen removal take place mainly with HDC reaction route.

The concentration of iso-paraffin content was given by refer to the total paraffin content ($\frac{i-C_x \text{ concentration}}{i-C_x+n-C_x} 100$). Based on experimental results it was found that on each catalyst the iso-paraffin content increased with increasing temperature, on the one temperature the isomerisation reactions take place higher degree on lower pressure (Figure 5). The highest yield of iso-paraffins was observed on NiW/Al_2O_3 catalyst, which was close to 45 % on 380 °C. In case of $CoMo/Al_2O_3$ catalyst the yield of iso-paraffins slightly increased with the increasing temperature, on the favourable operation parameters this was close to 20 %. On $NiMo/Al_2O_3$ catalyst the iso-paraffin content of the target fraction was lesser than on $CoMo/Al_2O_3$ catalyst and the yield of iso-paraffins slightly changed with the changing operation parameters. The products which were obtained on favourable operation parameters can be applied with other gas oil blending components. For example in mixture with middle distillate fractions which were obtained by chemical conversion of polyethylene, polypropylene waste. Hydrotreated vegetable oil can decrease the detrimental property of this last mentioned gas oil boiling range fraction due to it is high saturated paraffin content.

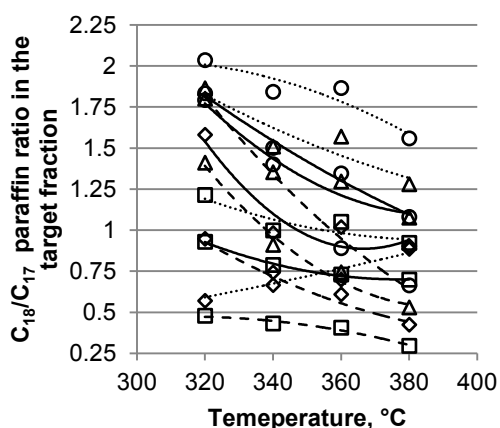


Figure 4: The C_{18}/C_{17} ratio as a function of operation parameters (stipple $CoMo/Al_2O_3$, continuous line $NiMo/Al_2O_3$, broken line NiW/Al_2O_3 , \diamond 20 bar, \square 40 bar, \triangle 60 bar, \circ 80 bar)

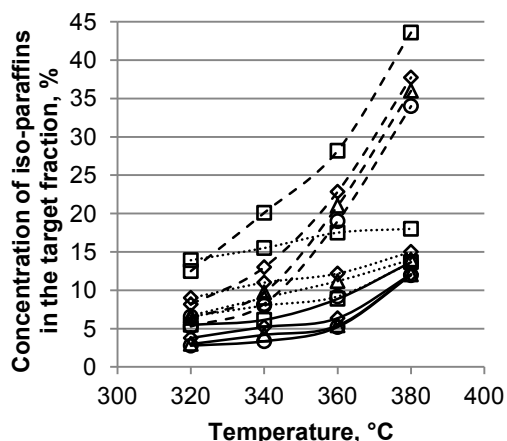


Figure 5: Concentration of iso-paraffins in the target fraction as the function of operation parameters (stipple $CoMo/Al_2O_3$, continuous line $NiMo/Al_2O_3$, broken line NiW/Al_2O_3 , \diamond 20 bar, \square 40 bar, \triangle 60 bar, \circ 80 bar)

4. Summary

Motor fuel purpose hydrogenation of used cooking oil was investigated on $CoMo/Al_2O_3$, $NiMo/Al_2O_3$, NiW/Al_2O_3 catalyst on several process parameters. It was obtained that the favourable operation parameters $NiMo/Al_2O_3$ catalyst was 340 °C, 20 - 40 bar. On the applied operation parameters the triglyceride conversion was close to 100 %, the yield of the bio gas oil was higher than 90 %, the iso-paraffin content was 5 % referring to the total paraffin content. In short on $NiMo/Al_2O_3$ catalyst used cooking oil can be processed used with high conversion. The obtained products can be blend into gas oil with unlimited quantity after isomerisation. In further works investigate a new mixed catalytic bed, that

ensure high conversion rate and high iso-paraffin content in the target fraction can be important. Consequently these products can be blended in gasoil up to 10 %, and with this we can meet the requirements of the EU which prescribe at least 10 - 80 % bio component blending in motor fuels by 2020.

5. Acknowledgement

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