

## INVESTIGATION OF HYDROGENATION OF CONVENTIONAL AND HIGH OLEIC ACID CONTENT RAPESEED OR SUNFLOWER OILS

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The European Union created the 2003/30/EC and later the 2009/28/EC directives to encourage the blending of bio components in the motor fuels. Nowadays the second generation or new generation bio fuels researching, improving and market introduction are facilitated. The main reason of this is the demand for better quality and wide raw material basis. All this above-mentioned things make it reasonable to investigate lower cost feedstock or researching of more efficiently processable or raw material basis. For example these special modified hybrids can be rapeseed oil with high euric acid content (*Bassica Napus*), rapeseed oil with high oleic acid (Pioneer Hi-Berd 45A37), or sunflower oil with high oleic acid (*Saaten Union Capella*). These raw materials can be converted to motor fuels by heterogenic catalytic hydrogenation, thus we can produce outstanding gasoil blending components. Further advantages are that the motor fuel purpose crop products can not meet the human health aspects hence genetically modified breeds can be applicable, therefore these raw materials do not endanger the security of food supplement. Hence the aim of our research activities was to produce bio gas oil from properly prepared oil with various fatty acid composition vegetable oil. We made the experiment on commercial available aluminium-oxide supported Co/Mo. The applied process parameters were based on our earlier research: temperature: 300–380 °C, pressure: 20–80 bar, liquid hourly space velocity: 0.5–3.0 h<sup>-1</sup>, H<sub>2</sub>/triglycerides ratio: 600 Nm<sup>3</sup>/m<sup>3</sup>. During the conversion of high oleic acid vegetable oils while applying the favourable process parameter combination the yield was higher and the hydrogen consumption was unequivocally lower.

**Keywords:** bio-gasoil, hydrodeoxygenation, sunflower oil, rapeseed oil

### Introduction

In the European Union the main reason of the consumption of biofuels within the alternative fuels is the insufficient quantities and availability of energy carriers (primarily the crude oil and natural gas) and the effort in the passenger and freight transport to reduce the dependence on fossil fuels which are produced from import crude oil. To achieve these goals, the European Union created the 2003/30/EC and 2009/28/EC directives. The main purpose of the directives is to promote the use of biofuels in the engine fuels specifying the recommended or required quantity of biofuels in engine fuels. Nowadays the research, development and market introduction of second or next generation biofuels is going on. This is mainly due to the disadvantages of conventional biofuels (biodiesel, bioethanol), the demand for better quality of motor fuels (blending components), the wider base of raw materials (climate, topography, soil conditions) and the support by the European Union for the second generation biofuel research and development [COM(2006) 34].

From among the biocomponents used as blending components in diesel fuels in short and medium term the bio gas oils will be highlighted. The bio gas oil is a

mixture of normal and isoparaffins having a boiling point range similar to diesel fraction which can be produced by one- or more-step catalytic hydrotreating of different natural triglycerides (fatty acid esters, fatty acids, etc.) [2, 3]. Regarding the performance properties they contain the best utilization technical components of the crude oil derived gas oils which have improved and “cleaner” ignition, and it results in lower emissions. To reach all these goals we must define all of these cultivated species which can accomplish the industrial usage specific demands as a consequence of their specific composition. The cost of bio motor fuel production is defined by the applied oilseeds yield and the fatty acid composition from the biological side. In southern regions the sunflower, in the northern regions the rapeseed means the potential source of bio gas oil production. In the Hungarian region the sunflower was grown in the biggest volume in 2010, of this area was 501 thousand hectares and the average yield was 2.2 t/ha. The rapeseed was grown on 259 hectares and the average yield was 2 t/ha. We investigated the effect of the operation parameters on the product quality, including the type of hydrogenation reactions during processing various fatty acid composition feedstocks.

During the conversion of triglyceride molecule to biogasoil the following reactions take place [8-12, 16]:

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

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

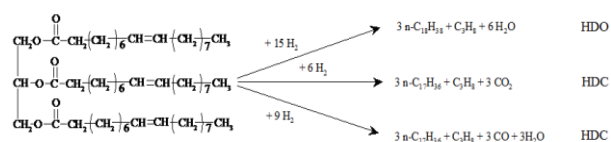


Figure 1: Possible pathways of vegetable oil oxygen removal (fatty acid component: oleic acid)

As Fig. 1 shows the yield of the organic products depends on the carbon number of the hydrocarbon chains, the feedstock and the reaction pathways [4, 5]. The reaction pathways were investigated in full details.[e.g. 14, 15]

## Experimental

On the basis of the above-mentioned reasons the aim of our experimental work was the investigation of heterogenic catalytic hydrothreating oxygen removal of sunflower and rapeseed oil pressed from expediently grown high oleic acid sunflower and rapeseed of Hungarian origin on a commercial available CoMo/Al<sub>2</sub>O<sub>3</sub> (Mo: 13,5 %, Co: 2,9 %, F<sub>BET</sub>: 193 m<sup>2</sup>/g) catalyst. In this context we studied the processing options (with this end the conversion and hydrogen consumption) of the conversion of triglycerides, the yield of the organic products and the yield of the target fraction. Furthermore the effect of the operation parameters (temperature, pressure, LHSV, H<sub>2</sub>/CH ratio), the effect of the degree and the type of the deoxygenation reaction were also investigated.

## Feedstocks

The feedstock of the hydrotreating experiments was conventional and high oleic acid sunflower and rapeseed oil pressed form Hungarian sunflower and rape seed and it was properly pre-treated (filtered). Its important properties are summarized in Table 1. The catalyst was a commercial available supported bimetallic CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst. The catalyst was pre-treated in hydrogen stream.

Table 1: The main properties and fatty acid composition of the applied sunflower oils

| Properties                                      | Conventional Sunflower | High oleic acid Sunflower | Conventional Rapeseed | High oleic acid Rapeseed |
|---|------------------------|---------------------------|-----------------------|--------------------------|
| Kinematic viscosity, (40 °C) mm <sup>2</sup> /s | 37.04                  | 39.6                      | 34.4                  | 39.9                     |
| Density (15.6 °C), g/cm <sup>3</sup>            | 0.9153                 | 0.9132                    | 0.915                 | 0.917                    |
| Cloud point, °C                                 | -1                     | 2                         | -2                    | 3                        |
| Iodine number, g I <sub>2</sub> /100g           | 134                    | 84                        | 114                   | 90                       |
| Cetane number                                   | 38                     | 37                        | 37                    | 36                       |
| Fatty acid composition (CX:Y*), %               |                        |                           |                       |                          |
| C16:0   | 6.0                    | 2.1                       | 4.5                   | 3.2                      |
| C16:1   | 0                      | 0                         | 0                     | 0.3                      |
| C18:0   | 4.0                    | 1.6                       | 1.9                   | 1.9                      |
| C18:1   | 20.0                   | 91.6                      | 61.5                  | 74.4                     |
| C18:2   | 68.0                   | 1.2                       | 20.8                  | 9.3                      |
| C18:3   | 0                      | 0.1                       | 9.7                   | 7.9                      |
| C20:0   | 0                      | 0.1                       | 0.3                   | 0.7                      |
| C20:1   | 0                      | 0                         | 1.3                   | 1.1                      |
| C22:0   | 0                      | 0                         | 0                     | 0.1                      |
| C22:1   | 0                      | 0                         | 0                     | 1.4                      |
| Other   | 2.0                    | 3.2                       | 2.5                   | 0.8                      |

\*X: means the fatty acid carbon number; Y: means the number of olefinic double bonds

## 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 cm<sup>3</sup>). The reactor system contained all the equipment and devices applied in the reactor system of a hydrotreating plant [13].

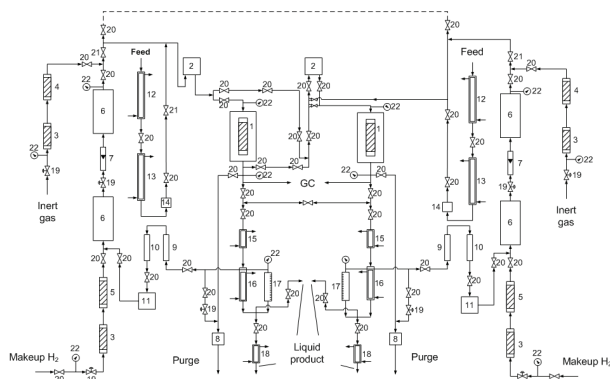


Figure 2: Simplified schema of the reactor system

The product mixtures obtained from the hydrotreating of sunflower 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 sunflower oil, furthermore the lighter hydrocarbons (C<sub>1</sub>-C<sub>4</sub> 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 (C<sub>5</sub>-C<sub>9</sub>) 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 C<sub>11</sub>-C<sub>19</sub> 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.

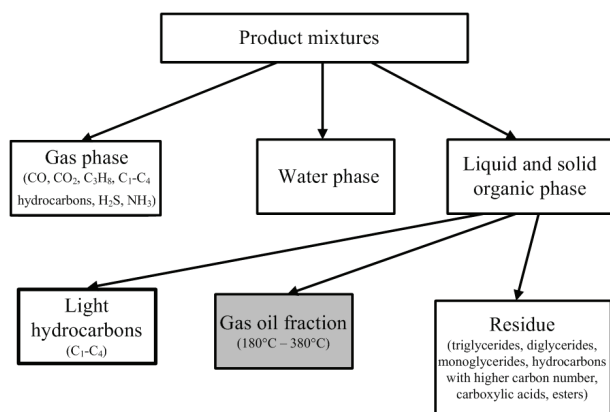


Figure 3: The separation of product fraction

## Process parametrs

The range of the applied process parameters based on our pre-experimental results were the following: temperature 300–380 °C, total pressure 20–80 bar, liquid hourly space velocity (LHSV): 1.0 h<sup>-1</sup> and H<sub>2</sub>/rapeseed oil volume ratio: 600 Nm<sup>3</sup>/m<sup>3</sup>.

## Analytical methods

The properties of the sunflower oil feedstock were measured according to standard methods (Table 2).

Table 3: Standard methods used for characterization of feedstocks

| Properties             | Standard methods                  |
|------------------------|-----------------------------------|
| 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<br>EN 14103:2004 |

The composition of the total organic products obtained from the catalytic conversion of the triglycerides was determined by high temperature gas chromatograph (Shimadzu 2010 GC [column: Phenomenex Zebron Inferno DB - 1HT]). The composition of the gas products was determined by gas chromatograph (Trace GC - Thermo Finnigan) with thermal conductivity detector (TCD) [column: Supelco Carboxen 1006 Plot (30 m x 0.32 mm)]

## Results and discussions

The aim of our experimental work was the investigation and comparison of conventional and high oleic acid sunflower and rapeseed oil hydrotreating option for motor fuels. In this context we investigated the yield of gasoil boiling point range products and the effects of the operation parameters on the yield and quality of the target products by various fatty acid composition vegetable oil feedstocks.

On the basis of our experimental results we obtained that during the processing of sunflower and rapeseed oil the conversion was higher in the case of high oleic acid hybrid feedstocks. Its possible cause is that the high oleic acid content vegetable oil has a lower olefinic double bond content (it is shown by the iodine number of the used vegetable oil, the difference of 50 units between the conventional and high oleic acid vegetable oil). Furthermore, while using both the conventional and high oleic acid content vegetable oil the conversion increased with the increase of the pressure and temperature (with the increasing severity). It is shown in Fig. 4/A, B.

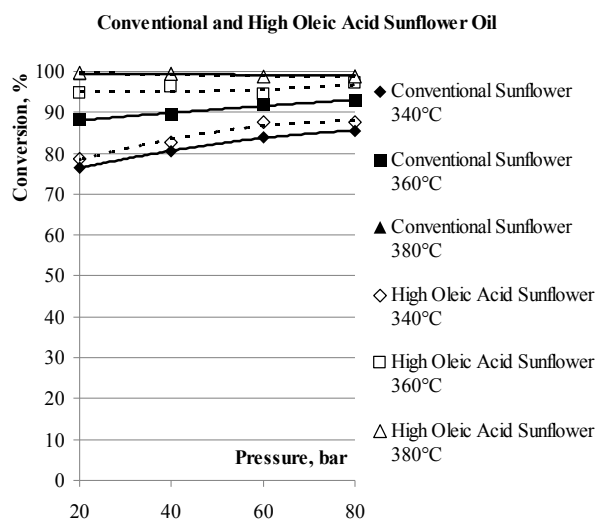


Figure 4/A. The conversion of conventional and high oleic acid content sunflower oil as the function of the pressure (LHSV:  $1.0 \text{ h}^{-1}$ ;  $\text{H}_2/\text{vegetable oil ratio}$ :  $600 \text{ Nm}^3/\text{m}^3$ )

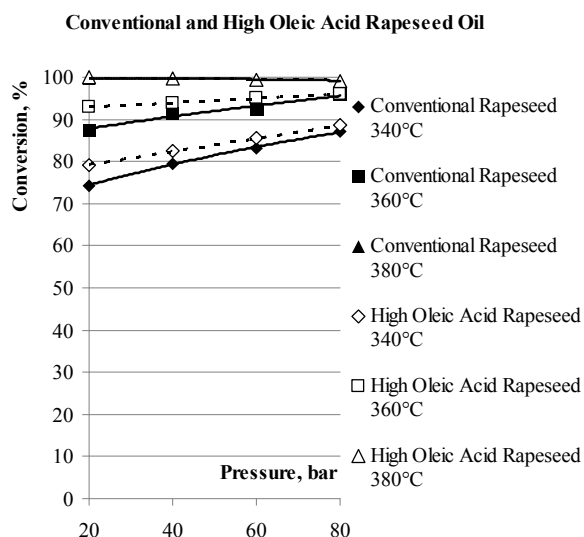


Figure 4/B. The bio gasoil yield of conventional and high oleic acid content rapeseed oil as the function of the temperature (LHSV:  $1.0 \text{ h}^{-1}$ ;  $\text{H}_2/\text{vegetable oil ratio}$ :  $600 \text{ Nm}^3/\text{m}^3$ )

On the basis of our experimental results we obtained that the yield of the target fraction increased with increasing the temperature. At lower temperatures the yield of the main fraction increased significantly with increasing the pressure, but at a higher temperature the yield of the main fraction drew a maximum curve (Fig. 5). It can be explained by that that at a higher temperature the HDC reactions took place in a higher degree (due to the formation of  $\text{CO}_2$  the generated products were shorter by one  $\text{CH}_2$ - group) and the crack reactions took place in a higher degree and it decreased the yield of the target fraction.

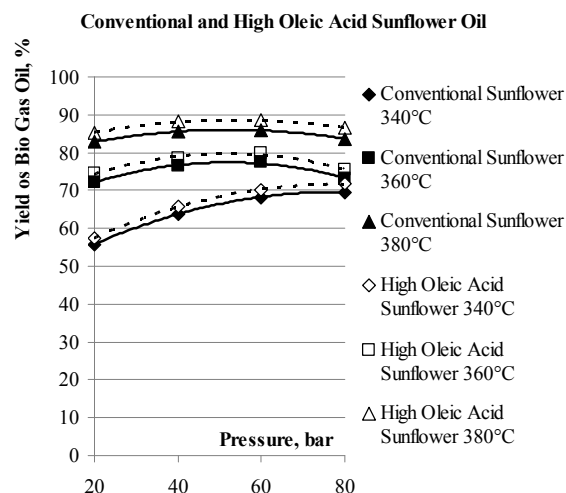


Figure 5/A. The bio gasoil yield of conventional and high oleic acid content sunflower oil as the function of the pressure (LHSV:  $1.0 \text{ h}^{-1}$ ;  $\text{H}_2/\text{vegetable oil ratio}$ :  $600 \text{ Nm}^3/\text{m}^3$ )

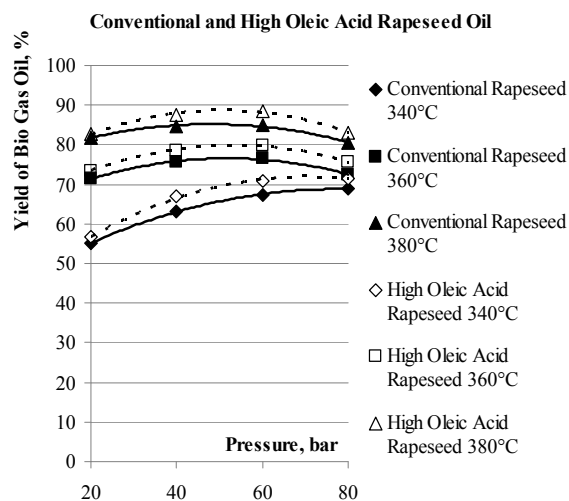


Figure 5/B. The bio gasoil yield of conventional and high oleic acid content rapeseed oil as the function of the temperature (LHSV:  $1.0 \text{ h}^{-1}$ ;  $\text{H}_2/\text{vegetable oil ratio}$ :  $600 \text{ Nm}^3/\text{m}^3$ )

The fatty acids as one acid value even carbon number carboxylic acids have more than 200 known variables. The synthesis of fatty acids starts from acetyl-CoA and in consecutive steps it gets longer with 2 carbon number in every step. This is main reason why the various fatty acids only have an even carbon number chain [17]. Thus uneven carbon number paraffins in the product fraction only came from HDC (decarboxilation, decarbinilation) and crack reactions. In the case of the mainly  $\text{C}_{18}$  carbon number fatty acid containing vegetable oils the  $\text{C}_{17}/\text{C}_{18}$  paraffin ratio in the main fraction is the outstanding marker to follow the HDO/HDC reaction ratio. We concluded that the  $\text{C}_{18}/\text{C}_{17}$  ratio in the main fraction decreased with the increasing temperature and it increased with the increasing pressure. Consequently at higher pressure the HDC reactions resulting in mole number increase took place in a lower degree, while at a higher temperature the oxygen removal occurred mainly by HDC reactions (Fig. 1) On the basis of our experimental

results we obtained that in case of hydrogenation of high oleic acid sunflower and rapeseed oil the oxygen removal mainly took place in the HDC reactions resulting lower hydrogen consumption.

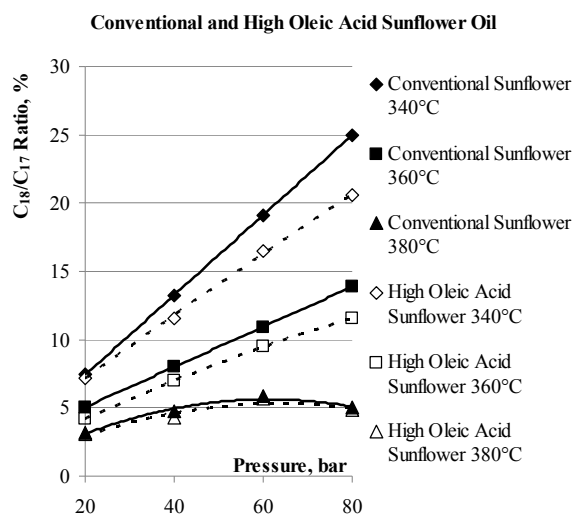


Figure 6/A. The  $C_{18}/C_{17}$  ratio of conventional and high oleic acid content sunflower oil as the function of the pressure (LHSV:  $1.0 \text{ h}^{-1}$ ;  $\text{H}_2/\text{vegetable oil ratio}$ :  $600 \text{ Nm}^3/\text{m}^3$ )

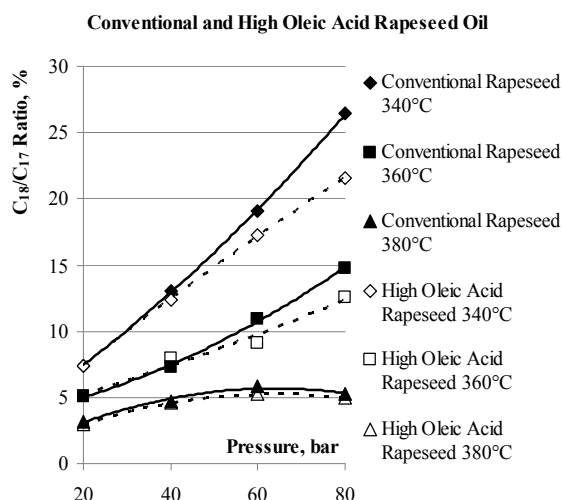


Figure 6/B. The  $C_{18}/C_{17}$  ratio of conventional and high oleic acid content rapeseed oil as the function of the pressure (LHSV:  $1.0 \text{ h}^{-1}$ ;  $\text{H}_2/\text{vegetable oil ratio}$ :  $600 \text{ Nm}^3/\text{m}^3$ )

Furthermore our experiments covered the effect of the fatty acid composition on the hydrogen consumption. On the basis of the gas phase analysis we concluded that during the hydrogenation of high oleic acid vegetable oils the hydrogen consumption was significantly lower than during the processing of conventional vegetable oils. It can be explained by the high oleic acid hybrids' lower olefinic double bond content.

On the basis of experimental results we obtained that at a higher temperature and pressure the oxygen removal took place by HDO reactions resulting higher hydrogen consumption.

Conventional and High Oleic Acid Sunflower Oil

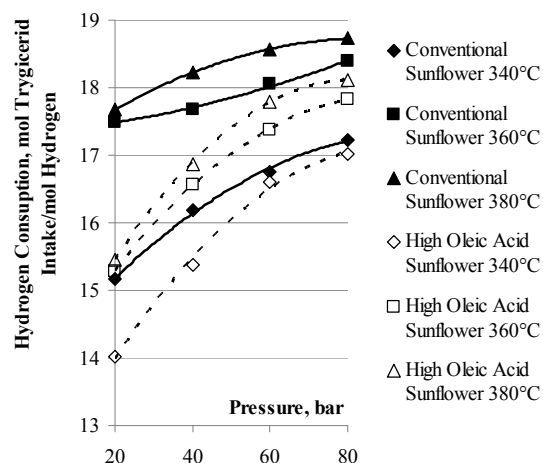


Figure 7/A. The hydrogen consumption of conventional and high oleic acid content sunflower oil as the function of the pressure (LHSV:  $1.0 \text{ h}^{-1}$ ;  $\text{H}_2/\text{vegetable oil ratio}$ :  $600 \text{ Nm}^3/\text{m}^3$ )

Conventional and High Oleic Acid Rapeseed Oil

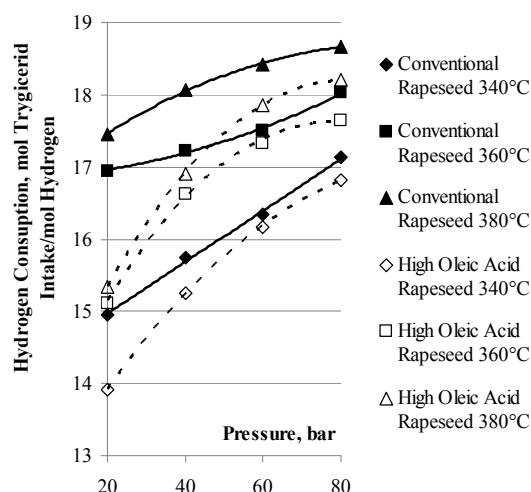


Figure 7/B. The hydrogen consumption of conventional and high oleic acid content rapeseed oil as the function of the pressure (LHSV:  $1.0 \text{ h}^{-1}$ ;  $\text{H}_2/\text{vegetable oil ratio}$ :  $600 \text{ Nm}^3/\text{m}^3$ )

## Summary

We investigated the motor fuel purpose hydrogenation of conventional and high oleic acid content sunflower and rapeseed oil on a  $\text{CoMo}/\text{Al}_2\text{O}_3$  catalyst while applying various operation parameters. We concluded that the triglyceride conversion was close to 100 %, the bio gas oil yield was near 80 % in case of both conventional and high oleic acid content sunflower and rapeseed while applying a  $\text{CoMo}/\text{Al}_2\text{O}_3$  catalyst in the favourable operation parameter range,  $380 \text{ }^\circ\text{C}$ ,  $40\text{--}60 \text{ bar}$ ,  $600 \text{ Nm}^3/\text{m}^3$   $\text{H}_2/\text{vegetable oil ratio}$ , LHSV:  $1.0 \text{ h}^{-1}$ . During processing high oleic acid sunflower and rapeseed oil the hydrogen consumption was 5–12 relative percent lower than in case of the conventional sunflower or rapeseed oil.

## ACKNOWLEDGEMENT

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