

Catalytic Hydrotreating of Triglycerides for the Production of Bioparaffin Mixture

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The aim of our experiments was to investigate the applicability of an expediently modified NiMoW/Al₂O₃ catalyst for the conversion of specially pretreated Hungarian sunflower oil with high oleic acid (>90%) content which was ennobled for our experiments to produce motor fuels. The changes of the specific hydrocracking activity of the applied catalyst, the pathways of hydrodeoxygenation reactions and the effect of the process parameters on the yield and on the quality of the products were also investigated.

It was concluded that on the investigated modified NiMoW/Al₂O₃ catalyst products with high (>70%) paraffin content (T = 340-360 °C, p = 20-40 bar, LHSV = 1.0-1.5 h⁻¹, H₂/sunflower oil volume ratio: 600 Nm³/m³) could be produced. In case of every investigated process parameter the C₁₇- and C₁₈- paraffins were formed, i.e. on the applied catalyst both the HDO and the decarboxylation/decarbonylation (DECARB) reactions took place as a function of the process parameters. The gas oil boiling range target products had significantly higher isoparaffin-content than other transition metal/support catalysts derived products. Therefore the best quality product mixtures had large cetane number (71-76) and favorable CFPP value.

1. Introduction

The production and application of biofuels (from agricultural products and the wastes of slaughterhouses and wastewater treatment) have emerged into focus in the last couple of years. A number of factors which are affecting the whole of humanity has confirmed and strengthened this process, they are of environmental, political and economic nature. The main reason of this tendency is the energy policy of the European Union, the aim of which is to reduce the dependence from import crude and energy. To achieve these objectives, the European Union has created the 2003/30/EC and 2009/28/EC directives which regulate the application of biomass derived fuels. According to 2003/30/EC and 2009/28/EC for Hungary as a Member state of the European Union the values are 5.75 % in 2010 and 10.0 % in 2020. This proposed value can be reached by the conversion of different triglyceride-containing biofeedstocks (e.g. vegetable oils, used frying oils, animal fats, algae oils) to different biofuels or blending components. Biodiesels, the first

generations biofuels, are the almost exclusively used bio blending components in diesel fuels nowadays; however, they have numerous disadvantages during the production and application (e.g. poor thermal, oxidation and storage stability, sensitivity for hydrolysis). Due to these disadvantages and to reach better quality, intensive research has begun to find out the possibility of the transformation of triglycerides to fuels which have a different chemical structure and better quality than the fatty acid methyl esters. The research, production and application of these second generation biofuels were intensively subsidized by the European Union (Demirbas, 2009; Hayes, 2009; Balat and Balat, 2008; Maher and Bressler, 2007; Twaiq et al., 2003; Chew and Bhatia, 2008). One of the solutions can be the hydrogenation of different triglyceride containing feedstocks (e.g. vegetable oils, used frying oils, animal fats, algae oils) and their conversion into "bio gas oil" with a heterogeneous catalyst. The bio gas oil is a mixture of hydrocarbons (especially normal and isoparaffins) having boiling points similar to diesel fraction, obtained from triglycerides (e.g. vegetable oils, used cooking oils, animal fat) (Hancsók et al., 2007). The bio gas oil eliminates the disadvantages of NOME-s. Therefore their economical production with high yield has high importance (Hancsók et al., 2007).

2. Experimental Work

According to the aforementioned, our aim was to investigate the applicability of an expediently modified NiMoW/Al₂O₃ catalyst for the conversion of specially pretreated Hungarian sunflower oil with high oleic acid (> 90%) content which was ennobled for our experiments to produce motor fuels (good quality, high paraffin containing gas oil boiling range product). The aim of the selection of a feed with high oleic acid (> 90%) content was to reduce the hydrogen consumption during the chemical reaction (olefinic double bond saturating) and this way to improve the economy of the process. The changes of the hydrocracking (olefinic double bond saturating, oxygen removing, isomerization) activity of the applied catalyst, the pathways of hydrodeoxygenation reactions and the effect of the process parameters (temperature, pressure, LHSV, H₂/sunflower oil ratio) on the yield and on the quality of the products were also investigated.

2.1 Experimental conditions

The experiments were carried out in an apparatus containing a tubular down-flow reactor of 100 cm³ effective volume and all the equipment and devices applied in the reactor system of an industrial heterogeneous catalytic plant (Nagy et al., 2007). The experiments were carried out in continuous operation. The product mixtures of the heterogeneous catalytic transformation of the sunflower oil were separated into three fractions: gaseous-, water-, and organic phases (Figure 1).

During our hydrotreating experiments we used specially pretreated Hungarian sunflower oil with high oleic acid (> 90 %) content as a feed (Table 1).

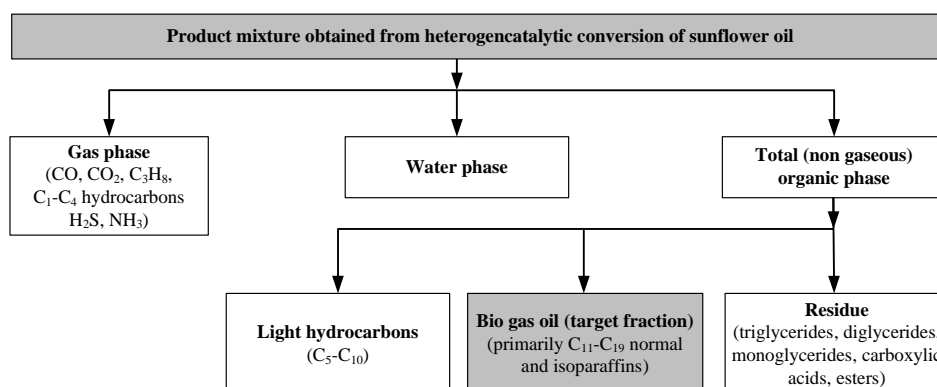


Figure 1: The separation scheme of product mixture.

Table 1 The main properties and the fatty acid composition of the feed.

Properties	Value	Fatty acid composition (*)	Value, %
Kinematic viscosity (40°C), mm ² /s	39.91	Palmitic acid (C16:0)	2.5
Density (15.6°C), g/cm ³	0.9133	Stearic acid (C18:0)	2.5
Acid number, mg KOH/g	2.6	Oleic acid (C18:1)	91.8
Iodine number, g I ₂ /100 g	95	Linoleic acid (C18:2)	1.2
CFPP, °C	35	Linolenic acid (C18:3)	0.6
Carbon residue, %	0.16	Arachidic acid (C20:0)	0.8
Sulphur content, mg/kg	5	Eicosenoic acid (C20:1)	0.5
Nitrogen content, mg/kg	8	Behenic acid (C22:0)	0.1

*The first number represents the number of carbon atoms and the second means the number of double bonds in the molecule

The properties of the feedstock and the products were measured and calculated according to the methods of the EN 590:2009+A1:2010 standard. The fatty acid composition of the sunflower oil was determined according to the methods EN ISO 5509:2000 and EN 14103:2003. The compositions of the organic product mixtures, obtained from the catalytic conversion of triglycerides were determined by high temperature gas chromatographic method (30m x 0.32mm x 0.1 μm, Zebron DB-1HT column).

2.2 Results and discussion

The primary objective of the fuel purpose hydrotreating of sunflower oil - in addition to the double bonds saturation - was the removal of the oxygen from the triglycerides, namely the production of a gas oil boiling range target fraction (mainly C₁₅-C₁₈ n-and isoparaffins) with the highest yield. During our systematic research work the range of the applied process parameters - based on our preliminary experiments - were the following: temperature: 300-380 °C, pressure: 20-80 bar, LHSV: 1.0-3.0 h⁻¹, H₂/sunflower oil volume ratio: 600 Nm³/m³.

As the main objective of our experimental work was the conversion of sunflower oil into products in the gas oil boiling point range, in this paper we present in detail only the effect of the process parameters on the yield and quality of these target products (target fractions).

Through the evaluation of the results of the changes in the yield of the target fractions we concluded that the yield of the gas oil boiling point range target fraction increased with increasing the temperature and decreasing the liquid hour space velocity (increasing the contact time), as it can be seen in Figures 2 and 3. So increasing the temperature enhanced the triglyceride conversion which means a higher yield of the target fraction. However, increasing the pressure did not have such a good effect, as because of the cracking products the yield of the target fraction decreased (Figure 2) the value changed between 73-81%.

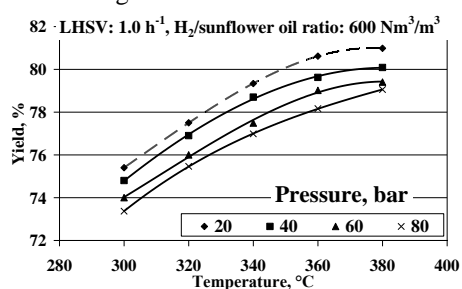


Figure 2: The yield of the target fraction as a function of temperature.

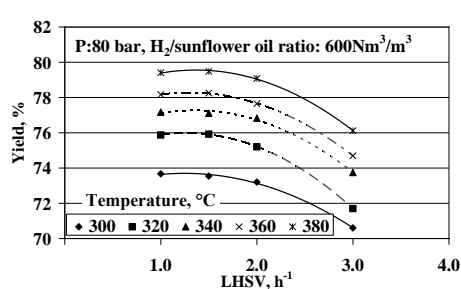


Figure 3: The yield of the target fraction as a function of LHSV.

The feedstock contained significant amount of C_{18} fatty acids, but did not contain C_{17} fatty acids. So the processes through the conversion can be followed well by investigating the amount of C_{17} and C_{18} paraffins in the product.

We concluded from the hydrocarbon compositions of the organic products that on the investigated catalyst at the applied process parameter combinations the concentrations of the C_{17} paraffins changed according to maximum curve (Figure 4). The reason was that with increasing temperature the ratio of decarboxylation/decarbonylation was higher than the HDO reaction, which increased the partial ratio of the C_{17} hydrocarbons. But with the further increase of the temperature the cracking hydrocarbon products force back the partial ratio of the C_{17} paraffins. In case of the investigated feedstock the highest C_{17} paraffin concentrations (51-52 %) were reached at 340-350 °C (Figure 4). In the investigated temperature range the amount of C_{18} paraffins decreased with increasing temperature because of the higher ratio of decarboxylation/decarbonylation and the cracking reactions. Furthermore we concluded that the increase of the pressure enhanced the amount of the produced C_{18} paraffins formed in the HDO reaction, because the higher partial pressure of the hydrogen facilitates the HDO reaction.

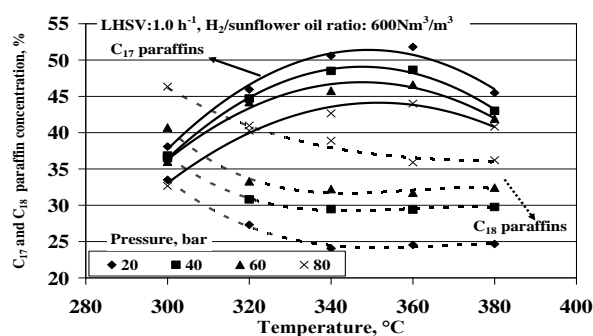


Figure 4. The concentration of C_{17} and C_{18} paraffins in total organic product as a function of temperature.

We concluded from the composition data of the organic fractions that they contained isoparaffins in significant amount among the n-paraffins. Increasing the temperature from 300 °C to 380 °C the amount of iso- C_{17} and iso- C_{18} paraffins in the total organic product mixture increased with 7 % (Figure 5). The explanation is that through the isomerization with the temperature increase the isoparaffins are formed in higher amount, but at higher temperatures the instable intermediates (isocarbenium ions) are cracked, so this value starts to decrease above 360 °C. The isoparaffin concentrations in the organic product mixture continuously increased with decreasing pressure. The cause is that the partial pressure of the hydrocarbons at lower pressures (with the same other parameters) is higher which is favorable for the enaction of the isomerisation reactions.

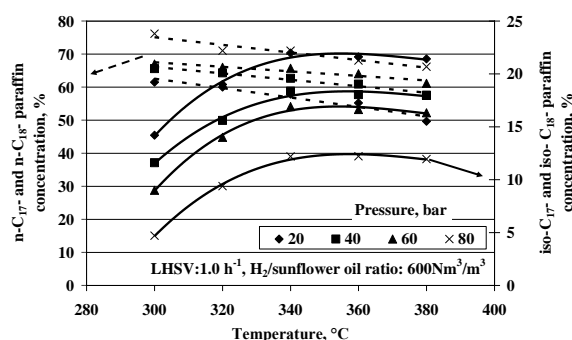


Figure 5: The concentration of n- / i- C_{17} and C_{18} paraffins in total organic product as a function of temperature.

We proved with our experimental results that through the special hydrocracking of sunflower oil with high oleic acid content the hydrogen consumption is definitely smaller than in case of using conventional sunflower oils. The cause of this is the lower average number of olefinic bonds in the feedstock. But this was a function of the ratio of the enacting HDO and decarboxylating/decarbonilation reactions. The decrease in hydrogen consumption can reach about 12-24 %.

3. Conclusions

Based on the experimental results of the catalytic conversion of the high oleic sunflower oil on the investigated NiMoW/Al₂O₃ catalyst it can be concluded that products with high (77-81%) paraffin content (T = 340-360 °C, p = 20-40 bar, LHSV = 1.0-1.5 h⁻¹, H₂/sunflower oil volume ratio: 600 Nm³/m³) could be produced. In case of every investigated process parameter the C₁₈- and C₁₇- paraffins were formed, i.e. on the applied catalyst both the HDO and the decarboxylation/decarbonylation (DECARB) reactions took place. We emphasize that the catalyst had a significant isomerization activity. Therefore we could produce products with higher isoparaffin content (23-29 %), advantageous cold flow properties (CFPP=9-13 °C) and high cetane number (71-76), than on the commonly used hydrotreating catalyst (e.g. NiMo/Al₂O₃) derived paraffin mixture. It was further concluded that in case of the special hydrocracking of the ennobled sunflower oil the hydrogen consumption was definitely smaller (12-14 abs.%), than in case of conventional sunflower oil, because of the lower average number of the olefinic double bonds.

Acknowledgment

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