

Hydrodeoxygenation of Residual Fatty Acids Fraction over Ni-Mo / γ -Al₂O₃ Catalyst

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Abstract. The hydrodeoxygenation of the residual fraction of fatty acids from sunflower oil was performed on bimetallic Ni-Mo/ γ -Al₂O₃. Experiments were carried out on a in a continuous system at temperatures below 340 °C and pressures less than 70 bar. The catalyst shows a total acidity of 1.192 meq / g, from which 0.714 meq / g represents the concentration of weak acid centers, 0.438 meq / g represents the concentration of medium strength acid centers, while the concentration of strong centers is very small, only 0.041 meq / g. The analysis of the reaction products mainly highlighted the presence of linear hydrocarbons.

Keywords: residual fraction of fatty acids, hydrodeoxygenation, catalyst acidity, Ni, Mo, γ -Al₂O₃

1. Introduction

The fuel resulting from the direct hydroconversion of glycerides into fuels is commonly referred to as "renewable fuel or green diesel" to differentiate it from biodiesel. The general mechanism of its formation involves three reaction pathways: decarboxylation, decarbonylation and hydrodeoxygenation [1]. Unlike biodiesel, green diesel is fully compatible with petroleum fuel and presents a higher cetane numbers (80-90), a higher heating value (44Mj / kg), a low freezing points (between -5 and -30 °C) and a high oxidation stability [2,3]. In the case of biodiesel, where the properties of the fuels depend on the origin and the way of processing the raw materials, the properties of green diesel are independent of the origin of the raw material, and completely deoxygenated, it mixes very well with the conventional ones [4-6].

Deoxygenation of the natural carboxylic compounds proceeds either by decarboxylation or by decarbonylation or by hydrodeoxygenation. Decarboxylation consists of the removal of the carboxyl group in H₂ medium, the oxygen (O₂) being eliminated as carbon dioxide (CO₂). In the decarboxylation reaction, two types of reaction are involved: hydrogen transfer from the γ position and β -elimination. By β -elimination, the fatty acid and unsaturated compounds are formed, followed by its hydrogenation with the release of the fatty acid, resulting in hydrocarbons having a lower number of carbon atoms (C_{n-1}) [7]. The hydrogen transfer mechanism initiates the C-C bond breakage within the acyl group is formed a terminal olefin, which has two carbon atoms less than the fatty acid chain [8].

Decarbonylation involves the removal of triglyceride from the H₂ carbonyl group, with the formation of alkanes having one carbon atom less than the corresponding fatty acid and CO as a by-product [9]. If in decarboxylation, in most cases, fatty acids have been observed as intermediate products by β -elimination or hydrolysis of triglycerides, by decarbonylation of fatty acids, they release formic acid rather than CO₂ [10]. Subsequently, the breakdown of formic acid can take place through two parallel pathways: dehydration and dehydrogenation, or by dehydration with CO and H₂O being released, while H₂ and CO₂ are released by dehydrogenation with alkene formation [11].

Hydrodeoxygenation consist in removing of oxygen from the triglyceride molecule, by direct cleavage of the C-O bond, which is carried out in the presence of H₂, under certain conditions of pressure and temperature. During the process, the unsaturated bonds present, are transformed into saturated bonds and, consequently, the oxygen is removed in the form of water, resulting in n-alkanes

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with the same number of carbon atoms as the fatty acids they come from. During the hydrodeoxygenation, side reactions may take place, namely the gasification of carbon monoxide with water and the methanation reactions, which have as a result the increased consumption of hydrogen [12].

All these processes are accompanied by hydrocracking reactions. The main products obtained in the hydrocracking of triglycerides are linear and cyclic hydrocarbons, oxygenated compounds including aldehydes, ketones and carboxylic acids and olefins as a result of cracking, hydrolysis, isomerization, dehydrogenation and aromatization reactions. Triglyceride cracking has several disadvantages, most importantly being non-selective. Thus, the formation of too large an amount of oxygenated compounds limits the use as a fuel, due to the problems of storage and internal combustion of the engines.

In order to develop the reaction mechanisms of triglyceride deoxygenation processes, several research studies have been carried out using model compounds from vegetable oils, such as stearic acid [13,14], oleic acid [15], palmitic acid and linoleic acid [43], tristearin and tripalmitin [44] and other compounds or mixtures thereof.

Yenumala et al. [16] developed the mechanism for the hydroconversion of tristearine and tripalmitin, on Ni / γ -Al₂O₃ catalyst, at 30 bar and temperatures between 280 °C-390 °C. At these experimental conditions, tripalmitin and tristearin were converted to stearic acid and palmitic acid, as the main oxygenated intermediate products, and propane as a by-product. The fatty acids were reduced to octadecanal and hexadecanal, which subsequently turned into alkanes on two pathways: decarbonylation and hydrodeoxygenation. Through the decarbonylation reaction, heptadecane (C17) and pentadecane (C15) were formed, releasing one mole of carbon monoxide, which is the main reaction pathway. By hydrodeoxygenation, the octadecanal and hexadecanal were further reduced to octadecyl alcohol and hexadecyl alcohol, which were dehydrated to the corresponding olefins, after which the olefins were converted to paraffinic hydrocarbons with the same number of carbon atoms as those present in fatty acids. The transformation of the carbonyl compounds into alkane by the decarbonylation reaction is normally performed on the active metal centers of the catalyst. On the other hand, hydrodeoxygenation takes place on the acidic centers of the catalyst, in order to convert the alcohol into the alkene and on the metallic active centers for the reduction / hydrogenation reaction [17].

The hydroconversion process of the fatty acid methyl esters in castor oil was studied on Pd / C catalyst, at low hydrogen pressures under supercritical conditions. The main product identified, after 6 hours of reaction, at 340 °C and an pressure of 10 bar, was heptadecane. Heptadecane is obtained in 86%, and the CO: CO₂ ratio is 15: 1, indicating that decarbonylation is the dominant reaction mechanism when hydrotreating castor oil methyl esters on the Pd / C catalyst [18].

In the hydrotreatment reactions of biomass, to obtain the active phase, the metals are processed in different forms [19]. In general, hydrotreatment catalysts mainly contain two types of active metals: noble metals Pt or Pd [20], or transitional metals Ni, Ni (Co), Mo (W) as well as their sulphides [21, 22], deposited on a catalytic support such as γ - alumina. Catalysts based on Pd or Pt have excellent activity for de-oxygenation and give a high yield in paraffinic hydrocarbons, but their use is limited by the price of these metals, so the researches were aimed at improving the activity of Ni catalysts, by introducing promoters and choosing the appropriate support. The catalysts used in the hydrotreatment of triglycerides do not differ much from those used in the hydrotreatment of the oil fractions, in terms of the composition of the active elements, than in the introduction of promoters in some cases. Nickel monometallic catalysts have an increased activity for the hydroconversion of triglycerides from biomass, but they give hydrocracking reactions, with the formation of lower alkanes, which can lead to the formation of the coke, with its deposition on catalysts and deactivation of the catalyst. Ni-Cu catalysts have a lower activity on hydrogenolysis than Ni catalysts and are more selective for the hydrodeoxygenation reaction. Furthermore, the introduction of copper into Ni-based catalysts can improve the stability of the catalyst at sintering. The introduction of Mo into Ni catalysts can increase



the methanation activity and increase the sulfur poisoning resistance as well as the thermal resistance of the catalyst [23].

The use of catalysts in industrial processes is based on the following properties: activity, selectivity, lifetime and mechanical strength. The activity and selectivity of a hydrodeoxygenation catalyst are dependent on the characteristics of the active components, the ratio between the concentration of the acidic and metal centers, the total acidity, the distribution of the acid centers strength and the textural properties [24-29].

In this work, a Ni-Mo catalyst deposited on γ -Al₂O₃ was prepared for the study of the hydrodeoxygenation of a residual fraction of fatty acids, by-products from the refining of sunflower vegetable oil.

2. Materials and methods

The raw materials used in experiments were ammonium heptamolibdate (99.98%), nickel nitrate hexahydrate, (purum p.a.), γ -Al₂O₃ (Alfa Aesar) and hydrogen (Linde).

The catalysts were prepared by wet impregnation. After impregnation the catalytic precursor was dried and calcinated. The characterization of catalyst was done by determining the acid and textural characteristics. The distribution of the acidic center and the acid strength has been determined by thermal desorption of diethyl-amine on a DuPont Instruments Thermal Analyst. The temperature at which the desorption occurs is depending on the intensity of the interaction between the acid centers and the diethylamine [96], observed by the loss of mass, thus, the concentration of the acidic centers is determined from the mass losses in the temperature ranges:

- 160 - 300 °C, for weak acid centers;
- 300 - 450 °C, for acidic centers of medium strength;
- 450 - 600 °C, for strongly acidic centers;

The textural characteristics of the catalyst (pore-size-distribution, average pore diameter, pore volume and surface area) were determined on a Autosorb 1 Quantacrome.

Hydrodeoxygenation of the residual fraction of fatty acids, was carried out on a continuous reactor with electric heating and automatic adjustment of the temperature profile, in which the reactants are introduced through the upper part of the reactor. The catalyst was introduced into the isothermal zone of the reactor.

The characteristics of the residual fraction of sunflower fatty acids are mentioned in [30]. The main components are fatty acids and glycerides with a composition similar to that of sunflower oil.

The conditions under which the experiments were performed were:

- temperature (T): ranging from 300°C to 340°C,
- pressure (p) from 50 barr to 70 barr,
- liquid hourly space velocity (LHSV) from 0.2h⁻¹ to 0.4h⁻¹.

The composition of the reaction products was achieved by gas chromatography method (Varian 3800 chromatograph equipped with Agilent VF-5ms capillary column and coupled with Varian 4000 mass spectrometer).

The raw material conversion (C_x) was determined on the basis of the saponification value of the raw material and the reaction products:

$$C_x (\%) = [(C_{\text{Sap},\text{mp}} - C_{\text{Sap},i}) / C_{\text{Sap},\text{mp}}] \times 100, \quad (1)$$

- $C_{\text{Sap},\text{mp}}$, (mg KOH / g raw material), represents the saponification value of the raw material;

- $C_{\text{Sap},i}$, (mg KOH / g raw material), represents the saponification value of the reaction product;

Yield in (<n-C₁₅) linear hydrocarbons obtained by cracking: $\eta C_{<15}, \% = (\text{sum of moles linear hydrocarbons } C_{\leq 15} : \text{sum of moles components}) \times 100; (2)$

Yield in pentadecane and heptadecane (obtained by decarboxylation / decarbonylation): $\eta C_{15+17}, \% = (\text{sum of moles } n\text{-C}_{15+17} / \text{sum of moles components}) \times 100; (3)$

Yield in hexadecane and octadecane (obtained by hydrodeoxygenation): $\eta_{C_{16+18}}\% = (\text{sum of moles } n\text{-}C_{16+18} / \text{sum of moles components}) \times 100$;(4)

Yield in hydrocarbons $C_{>18}$ and oxygenated compounds):

$\eta_{\text{others}}\% = [\text{sum of moles (hydrocarbons } C_{>18}, \text{oxygenated compounds)} / \text{sum of moles components}] \times 100$;(5).

3. Results and discussions

In Figure 1 are shown diethylamine thermodesorption curves of the catalyst stand based on the loss of mass the acid strength distribution was determined.

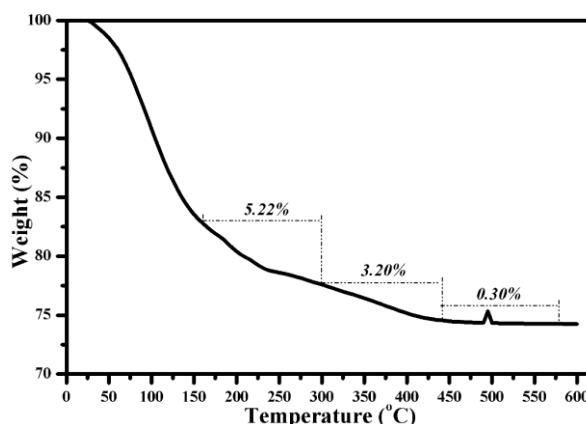


Figure 1. Thermodesorption of diethylamine from the catalyst $\text{Mo-Ni} / \gamma\text{-Al}_2\text{O}_3$

Table 1 shows the acid strength distribution of the $\text{Mo-Ni} / \gamma\text{-Al}_2\text{O}_3$ catalyst. The total acidity of this catalyst is 1.192 meq / g, of which 0.714 meq / g represents the concentration of low acidic centers. The concentration of medium-strength acidic centers is 0.438 meq / g, and the concentration of strongly acidic centers is very low, only 0.041 meq / g catalyst. The analysis of the acid strength distribution, indicates that this catalyst mainly presents the weak acidic centers.

Table 1. Acid strength of the $\text{mo-ni} / \gamma\text{-al}_2\text{o}_3$ catalyst

Acidic centers	Concentration (meq/g)
Weak acidic centers	0.714
Medium-strength acid centers	0.438
Strong acidic centers	0.041
Total acidity	1.192

The pore volume and the pore size distribution were calculated using the Barrett Joyner-Halenda (BJH) method, based on the volume adsorbed at the relative pressure of 0.99, on the desorption branch of the isotherms.

The $\text{Mo-Ni} / \gamma\text{-Al}_2\text{O}_3$ catalyst exhibits a type IV adsorption isotherm with a type E hysteresis loop (Figure 2), characteristic of the inkpot type pores, indicating that the deposition of the active phase and the treatment of the catalysts did not influence the pore shape, the specific surface area of the catalyst was $103.02 \text{ m}^2 / \text{g}$, and the total pore volume was $0.271 \text{ cm}^3 / \text{g}$. Figure 3 shows the pore volume distribution; a pore distribution with several maxima between 3-10 nm is observed.

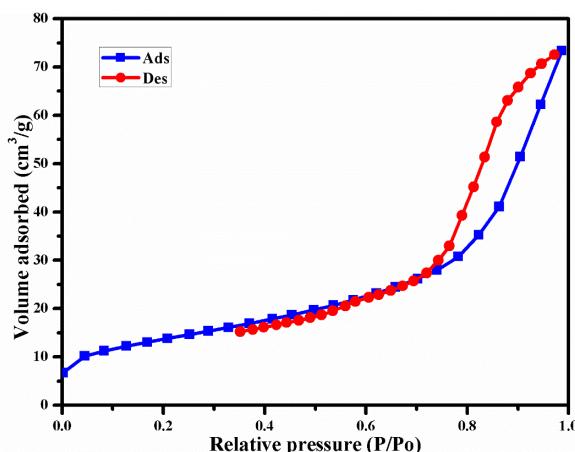


Figure 2. The isotherm of nitrogen adsorption - desorbtion

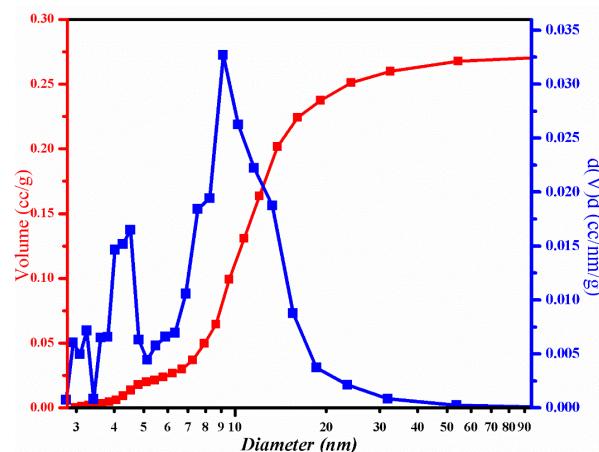


Figure 3. The distributions of the pore size

The distribution of the mesopore size is wide (Figure 3). The average pore diameter is 4.314 nm and the total pore volume is 0.312 cm³ /g (Table 2).

Table 2. Textural properties of the catalyst Mo-Ni / γ -Al₂O₃

Specific surface BET, (m ² /g)	Pore volume, (cm ³ /g)	Average pore diameter, (nm)
103.02	0.271	9.573

From Figure 4 it is observed that mainly shorter chain hydrocarbons (<C15) and linear hydrocarbons C15, C16, C17, C18 were identified. The alkenes or oxygenated products were not identified. Traces of iso-C17 were identified, but only under the experimental conditions of 300°C, 50 bar pressure and LHSV of 0.4 h⁻¹ (see chromatogram in).

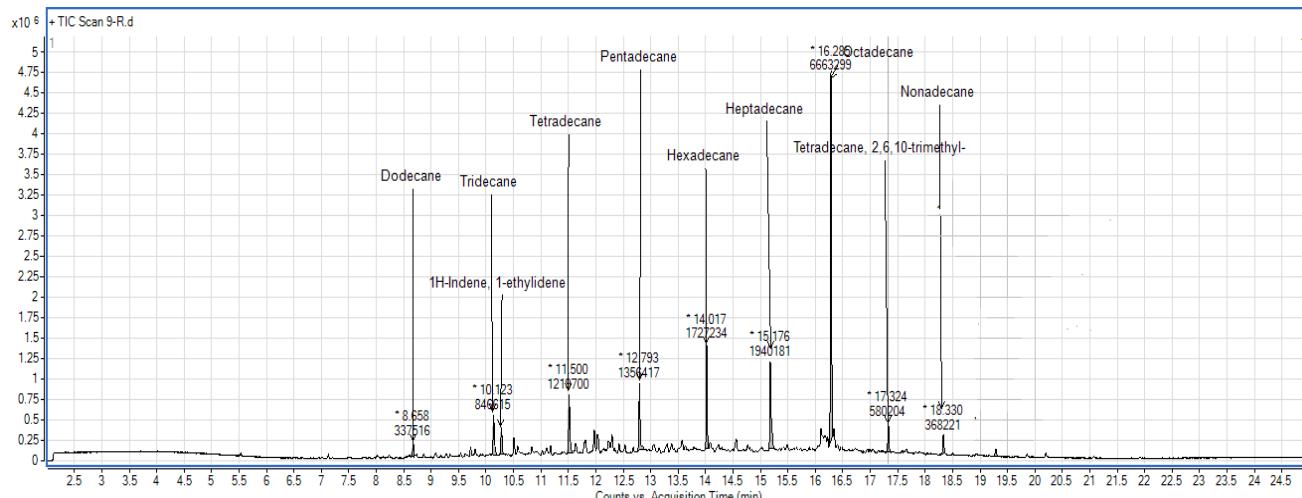


Figure 4. The chromatogram of reaction products

Figure 5 shows the performance of the Mo-Ni / γ -Al₂O₃ catalyst, over the temperature range 300-340°C, at constant volume pressure and LHSV (50 bar and 0.2 h⁻¹). It is observed that the catalytic activity is very high, the conversion of the raw material being almost total. The conversion increases from 96.8% and reaches 99.4% when the temperature rises from 300 to 340°C.

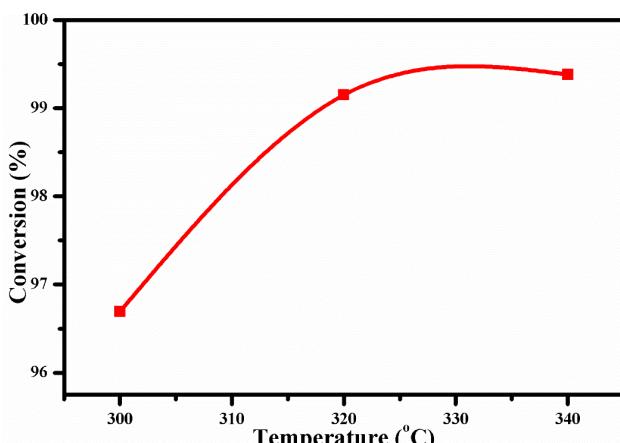


Figure 5. The variation of conversion with reaction temperature at 50 bar and LHSV 0.2 h⁻¹

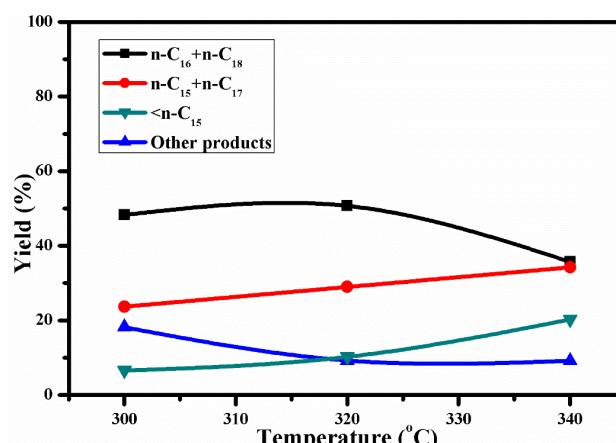


Figure 6. The variation of yield with temperature at 50 bar and 0.2 h⁻¹

The yield in C16 + C18 linear hydrocarbons increases from 50 to 52% when the temperature rises from 300 to 320°C, but at temperatures higher than 320°C, the yield in C16 + C18 linear hydrocarbons has begun to decline. The yield in paraffinic hydrocarbons C15 + C17 and the yield in paraffins with carbon numbers <C15, increases with increasing temperature throughout the studied temperature range, indicating that at temperatures higher than 320°C, cracking reactions begin (Figure 6).

Deoxygenation of the residual fraction of fatty acids from sunflower oil can occur through two reaction mechanisms: hydrodeoxygenation and decarboxylation / decarbonylation. To determine how the temperature influences the main reaction mechanism, the variation of the n-C18 / n-C17 hydrocarbons and n-C16 / n-C15 hydrocarbons ratios were evaluated, the results being presented in Figure 7. It is observed that the value of the n-C18 / n-C17 ratio is higher than the unit, in the temperature range 300-340°C, meaning that the hydrodeoxygenation process of the residual fraction of fatty acids C18, takes place after a mechanism of hydrodeoxygenation. In the case of C16 fatty acids, the C16 / C15 ratio is higher than the unit, only at temperatures below 320°C. Above 320°C, the ratio becomes subunit, with the process proceeding predominantly on the decarboxylation / decarbonylation mechanism (Figure 7).

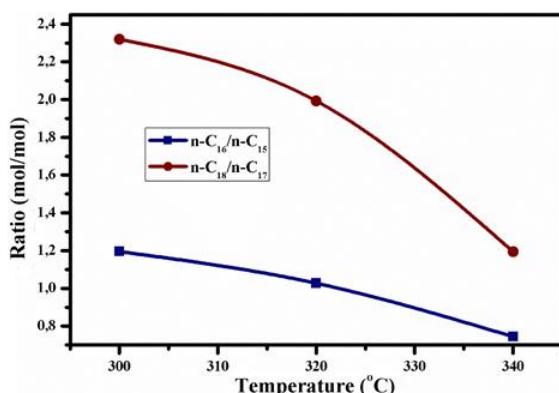


Figure 7. The variation of molar ratios nC₁₈/nC₁₇ and nC₁₆/nC₁₅ with temperature at 50 bar and 0.2 h⁻¹

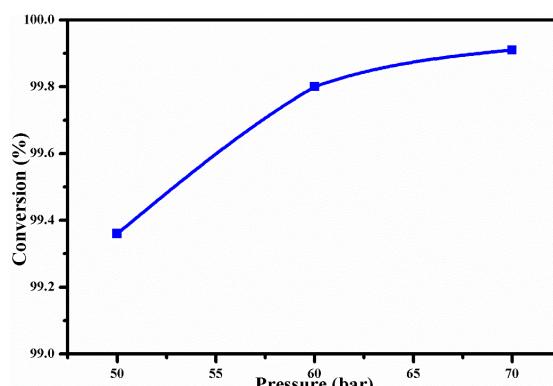


Figure 8. The variation of conversion with the pressure at 340°C and 0.2 h⁻¹

The influence of the pressure on the catalyst performance was studied between 50 bar and 70 bar, and the results are presented in Figures 8-9. At 340 °C and a volume speed of 0.2 h⁻¹, over the studied pressure range, the conversion is almost total, being greater than 99%. Thus, the increase of pressure

from 50 bar to 70 bar, determines an insignificant increase of the conversion (by 0.5%), already being almost total at 50 bar (Figure 9).

The growth of pressure significantly favored higher yields in C16 + C18 products. At 50 bar, 340 °C and LHSV of 0.2 h⁻¹, the yield in C16 + C18 is 35% and increased to almost 90% for the pressure of 70 bar, under the same conditions of temperature and LHSV. The yield in C15 + C17 products, on the other hand, decreased by about 25%, respectively from 35% to 10%, if the pressure increased from 50 to 70 bar (Figure 9). The decrease in yields in C15 + C17 hydrocarbons and <C15 hydrocarbons is due to the phenomenon of inhibition of cracking and decarboxylation / decarbonylation reactions, when pressure increases. Confirmation of inhibition of decarboxylation / decarbonylation reactions can also be seen from Figure 10, where the influence of the pressure at the molar ratios nC18 / nC17 and nC16 / nC15 is shown. In the case of nC18 / nC17, this ratio increases significantly with increasing pressure. If at 50 bar the ratio nC18 / nC17 has a value close to 1, at 70 bar the ratio nC18 / nC17 reaches 10, and the ratio nC16 / nC15 increased from 1 to 14. It can thus be stated that at the hydrodeoxygenation of the residual fraction of sunflower fatty acids, on the Mo-Ni /γ-Al₂O₃ catalyst, increasing the pressure favors the deoxygenation reaction.

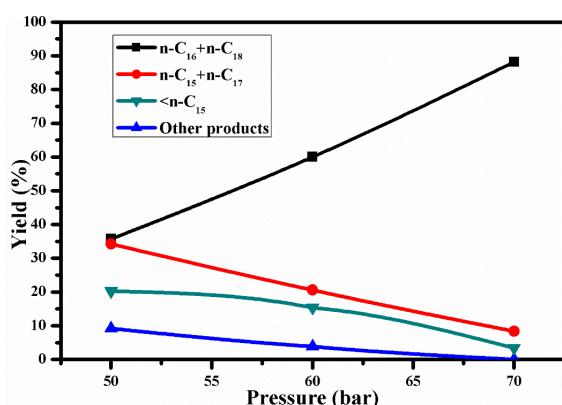


Figure 9. The variation of yield with pressure at 340°C and 0.2 h⁻¹

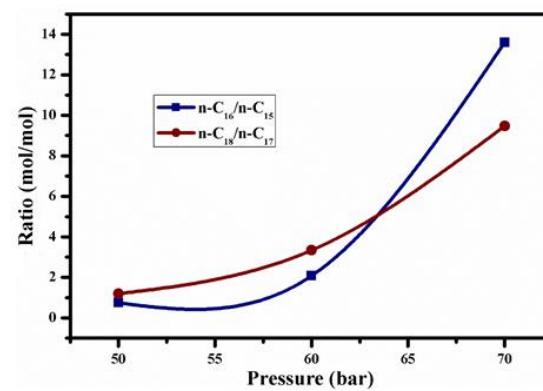


Figure 10. The variation of molar ratios nC₁₈/nC₁₇ and nC₁₆/nC₁₅ with pressure at 340°C and 0.2 h⁻¹

The variation of the conversion of the residual fraction of sunflower fatty acids with LHSV, at 340 °C and 70 bar, is shown in Figure 11. As expected, at higher LHSV, the conversion decreases. At a value of 0.2 h⁻¹, the conversion is almost total (99.9%) and reaches 97.4% at a volume speed of 0.4h⁻¹.

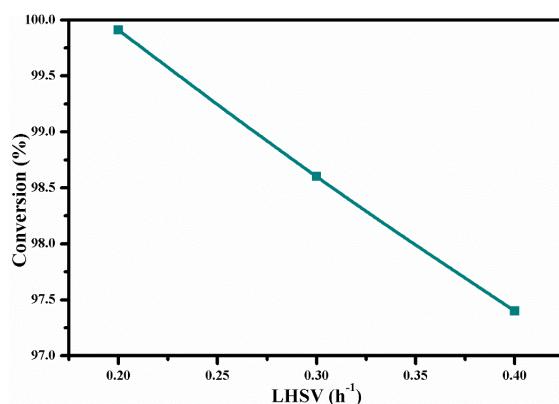


Figure 11. The variation of conversion with LHSV, at 340°C and 70 bar

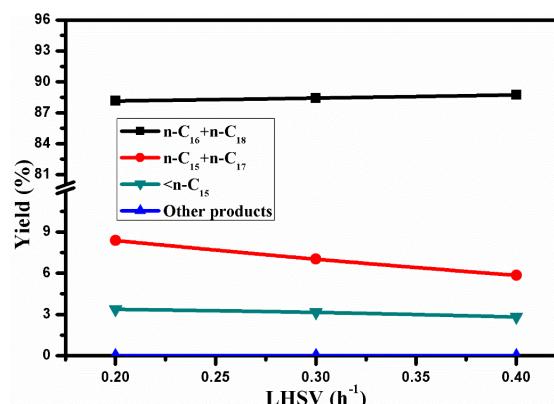


Figure 12. The variation of yield with the LHSV at 340°C and 70 bar

The variation of yields in reaction products with LHSV is shown in Figure 12. The yield in other products and in C <15 hydrocarbons varies slightly, while the yield in C16 + C18 hydrocarbons increases by approximately 2% with the increase in volume velocity in the studied area.

At 340°C, 50 bar pressure and LHSV between 0.2 h⁻¹ - 0.4 h⁻¹, the ratio between nC18 / nC17 hydrocarbons and nC16 / nC15 hydrocarbons have values greater than 1, the conversion of the residual fraction of sunflower fatty acids occurs predominantly by deoxygenation. The ratio between nC18 / nC17 hydrocarbons increased from 5 to 8, and the ratio between nC16 / nC15 increased from 13 to 21, with LHSV increasing from 0.2 h⁻¹ to 0.4 h⁻¹, indicating that under the studied reaction conditions, respectively the temperature 340°C and the pressure of 50 bar, a higher LHSV favors the hydrodeoxygenation reactions, to the detriment of the decarbonylation / decarboxylation reactions (Figure 13).

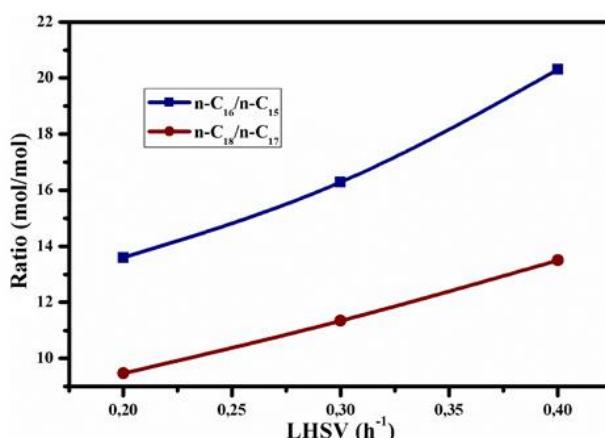


Figure 13. The variation of the molar ratios nC₁₈/nC₁₇ and nC₁₆/nC₁₅ with LHSV at 340°C and 70 bar

4. Conclusions

Hydrodeoxygenation of the residual fraction of fatty acids from sunflower oil, was carried out on bimetallic Ni-Mo/γ-Al₂O₃ catalyst in a fixed bed reactor. The catalyst presents a pore distribution with several maxima between 3-10 nm and a higher concentrations of the weak acid centers. Mainly linear C15, C16, C17 and C18 hydrocarbons and shorter chain hydrocarbons (<C15) were identified.

The conversion of the residual fraction of fatty acids increases with the temperature, on the studied temperature range.

The yield in C16 + C18 linear hydrocarbons increases when the temperature rises from 300°C to 320°C, but at temperatures higher than 320°C, the yield in C16 + C18 linear hydrocarbons has begun to decline; in contrast, the yield in paraffinic hydrocarbons C15 + C17 and the yield in paraffins C<15, increases with increasing temperature throughout the studied temperature range.

The value of the paraffins n-C18 / n-C17 ratio is higher than the unit, in the temperature range 300 -340°C, meaning that the hydrodeoxygenation process of the residual fraction of fatty acids C18, takes place predominantly after a mechanism of deoxygenation.

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