# Triglycerides Hydroconversion of Sunflower Oil on Ru / γ-Alumina Catalyst

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*Hydroconversion of sunflower oil to hydrocarbon fuel was performed on the Ru/γ-$Al_2O_3$ granular catalyst. Acid strength distribution of the catalyst where determined by termodesorption of diethyl amine in the temperature range 20-600°C. Experiments have been done at different reaction temperatures and pressures in order to establish their influence on the conversion and selectivity. The feed and products are analyzed by saponification value and gas chromatography (GC-MS Triple Quad Agilent Techologies). The activity of prepared catalyst was high, the conversion of sunflower oil having values higher of 80%. The major compounds identified were straight C≤17 hydrocarbons.*

*Keywords: hydroconversion, catalyst, ruthenium, sunflower oil, hydrocarbons*

Catalytic hydroprocessing of liquid biomass is a technology that offers great flexibility in biofuel market because it can convert a wide variety of liquid biomass (crude vegetable oils, animal fats or oils from algae) into biofuels with high conversion and yields. There are two options for producing diesel fuel from bio-oils: by catalyst transesterification of triglycerides to biodiesel and by catalytic hydroprocessing of triglycerides to get green diesel.

In recent years, has grown the interest in the optimal research and development to technologies that operate with the best catalyst in the most favorable reaction conditions. Main drawbacks of the wider application of technologies hydroconversion of vegetable oils and fats are availability of raw materials and high hydrogen consumption during the reaction that increase the process cost. Biofuels represent the energy most environmentally friendly source. Biofuels are a favorite choice due regenerability, biodegradability and acceptable quality of the gas emitted from combustion engines [1].

The main process in which hydrocarbons can be obtained from vegetable oils are [2-4]:

a) converting vegetable oil soaps (sodium salts) by basic hydrolysis, followed by dry distillation of the soap in the presence of sodium hydroxide;

b) hydrolysis of vegetable oil to fatty acids, followed by catalytic decarboxylation of the fatty acids;

c) thermal or catalytic pyrolysis;

d) hydroprocessing or hydroconversion of vegetable oils.

Hydroconversion process requires hydrogen to remove selectively the oxygen as water and to saturate the double bonds present in vegetable oils. Paraffins resulting from triglycerides hydroconversion has boiling point in diesel fuel field and are known as second generation biodiesel or green diesel. Unlike the biodiesel of the first generation, which is a mixture of fatty acids esters with methanol, the biodiesel in the new generation is a hydrocarbon mixture being more suitable to combustion in engines and compatible with the nowaday engine and without the need for mixing with the fosil diesel [5]

The study of global reaction for the triglycerides hydrogenation began in the 1980s. Researches carried out on the carboxylic acids or triglycerides showed that the reaction products are composed by linear alkanes having the same or less number of carbon atoms as the hydrocarbon chain of triglycerides, propane, water, $CO_2$, CO and $CH_4$. The distribution of these products is different depending on the reaction conditions the catalyst systems [6-13].

Triglycerides are converted to n-paraffins at temperatures of between 300-450°C and pressures greater than 3 MPa. The reaction scheme is very complex and consists of several consecutive steps:

- saturating double bonds >C=C<;
- hydrogenolysis of saturated triglycerides to form fatty acids and propane;
- decarboxylation;
- decarbonylation;
- hydrodeoxygenation.

Removing of oxygen from triglycerides is made by hydrodeoxygenation, decarboxylation and decarbonylation [14,15].

Unsaturated triglycerides requires a larger amount of hydrogen than saturated ones. Hydrocarbons with the same number of carbon atoms as the fatty acid components of the triglycerides, respectively hexadecane and octadecane, are reaction products of hydrodeoxigenation (by-product $H_2O$), while the hydrocarbons with one carbon atom less than the corresponding fatty acids, for example pentadecane and heptadecane, are products of decarbonylation and decarboxylation reactions (by-products CO, $CO_2$ and $H_2O$). To determine which of the two reaction paths prevails, have analyzed the distribution of hydrocarbons and, on that basis it calculate the ratio $C_{17}/C_{18}$ [16,17].

Unbearable molybdenum catalysts have hydroisomerizing activities of high alkanes. Porous support, for example alumina, decrease the activity and selectivity of isomerization due to strong interaction between metal and support. Isomerization mechanism is still unclear. It has been suggested that the active phase is molybdenum oxide or oxycarbides which binds to the active hydrogen [18].

Usually it works at medium temperatures and pressures and the unstable compounds, that can lead to the formation of gums and insoluble materials, are converted.

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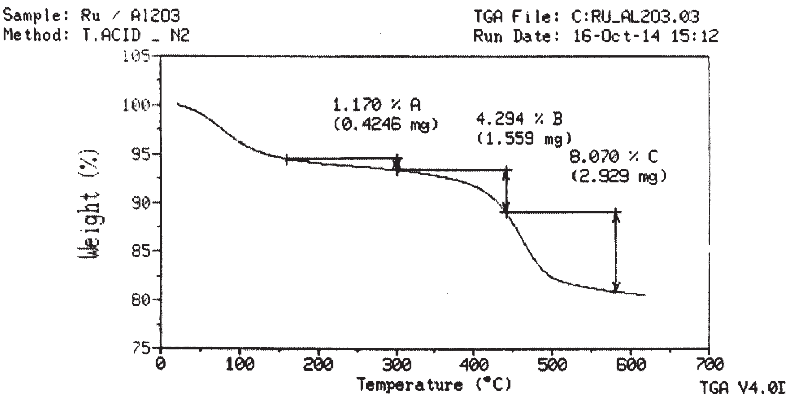

Fig.1. The distribution of the acid strength for active center of the Ru / γ-$Al_2O_3$ catalyst

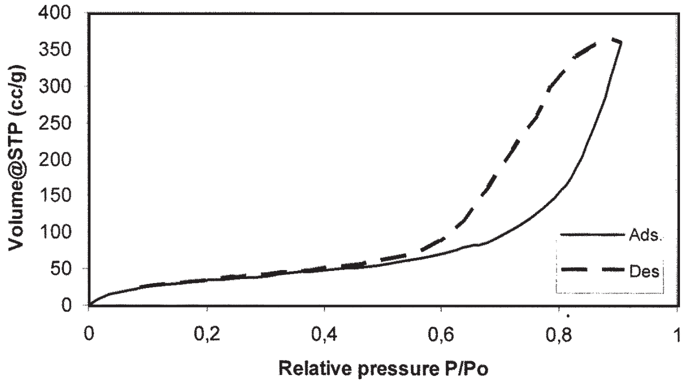

Fig.2. Isotherm of nitrogen adsorption / desorption on the Ru / γ-$Al_2O_3$ catalyst

The catalysts used are metals, for example NiMo or CoMo in a sulfur state deposited on γ-$Al_2O_3$ support [7, 19, 20]. Other catalysts used in hydrofining are of noble metal (Pt, Pd) deposited on the support [8] or NiMo / γ-$Al_2O_3$ whose acidity are improved by the addition of fluoride [8].

Raw materials commonly used in the manufacture of bio-diesel fuel is rapeseed oil, but strategic reserve state of sunflower oil, after the expiration of guarantee, can be an alternative feedstock for the production of biofuels. This paper addresses the study of hydroconversion of sunflower oil in ecological component for diesel fuel, over Ru/ γ-$Al_2O_3$ catalyst.

## Experimental part

The raw materials used in experiments were sunflower oil of technical grade, ruthenium (III) chloride hydrate (Sigma-Aldrich), γ-alumina granulated and electrolytic hydrogen purity from Linde Company. The fatty acid composition of sunflower oil have been reported earlier [19, 20].

The catalyst was synthesized by impregnating a γ-$Al_2O_3$ support granulated, with an aqueous solution of $RuCl_3$ by the method of pore filling. The concentration of Ru on catalyst support was 0.8%. The catalyst was dried 6 h at 120°C and calcined 4.5 h at 450°C in an oven. The catalyst activation was achieved in a stream of hydrogen at 450°C for 6 h.

Catalyst characterization was performed by determining the acid strength and textural characteristics. The acid strength distribution of the active center has been determined by the method of thermal desorption of diethyl-amine using as detector a thermogravimetric analyzer in the temperature range 20-700°C. Thermal analyzes were performed on a DuPont Instruments "Thermal Analyst 2000/2100" coupled with a module "951 Thermo-gravimetric Analizer".

Textural characteristics of the catalysts (surface area, pore volume, average pore diameter, pore-size-distribution) were determined on a Autosorb 1 Quantacrome. Texture data have been obtained by the automatic recording and processing of adsorption-desorption isotherms of nitrogen. The specific surface area was calculated using the equation in the linear part of the BET adsorption isotherm. In order to assess the distribution of pores and the pore size was used the desorption branch of isotherms with hysteresis, by applying the BJH method.

The experimental program was performed in a fixed bed catalytic reactor, in isothermal conditions. Reaction conditions for catalysts were:

- pressure: 20 – 40 atm;
- temperature: 375 - 425$^0$C ;
- volume hourly space velocities of sunflower oil (VHSV): 1.2 $h^{-1}$;
- molar ratio hydrogen/ sunflower oil (R): 10/1.

Vegetable oil and the hydrogenated products were analyzed by determination of the saponification value and by gas chromatography coupled with a mass spectrometer system, Triple Quad GC-MS Agilent Techologies. The conversion of triglycerides was determined based on the difference between the saponification number of raw materials and reaction products, and the selectivity in the reaction product was determined based on their composition determined by GC-MS.

## Results and discussions

Figure 1 shows the distribution of acidity center for catalyst Ru/γ-$Al_2O_3$ (A - concentration of centers with weak acidity, B - concentration of centers with medium acidity, C - concentration of centers with high acidity). On the basis of the weight loss was calculated the concentration of weak acid centers (0.160 meq./g), of acidic centers with medium acidity (0.588 meq./g) and of strong acidic centers (1.105 meq./g). It can be observed that the catalyst has a moderate total acidity, strong acids centers being dominant.

Figure 2 shown the nitrogen adsorption-desorption isotherm of Ru /γ-$Al_2O_3$ catalyst. The catalyst isotherm shows a hysteresis loop in the relative pressure range of p / $p_0$ from 0.6 to 0.92. According to the IUPAC isotherm

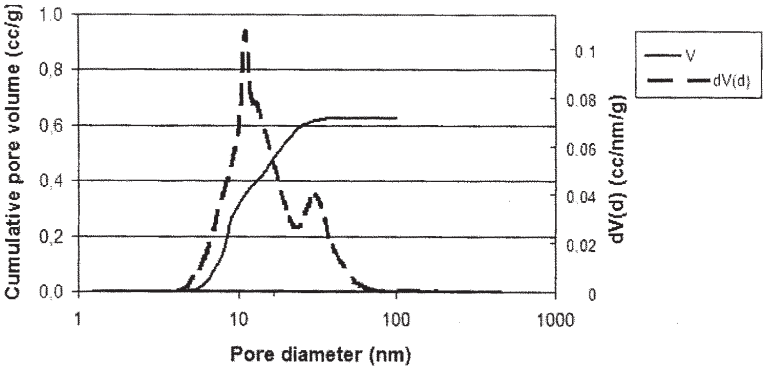

Fig.3. Pore volume and cumulative volume distribution, depending on pore diameter, for Ru / γ-$Al_2O_3$ catalyst

**Table 1**
TEXTURAL CHARACTERISTICS OF Ru / γ-$Al_2O_3$ CATALYST

| Catalyst | Specific surface area, $m^2/g$ | Pore volume, $cm^3/g$ | Pore diamete Å |
|---|---|---|---|
| Ru/ γ - $Al_2O_3$ | 255.297 | 0,628 | 72,25 |

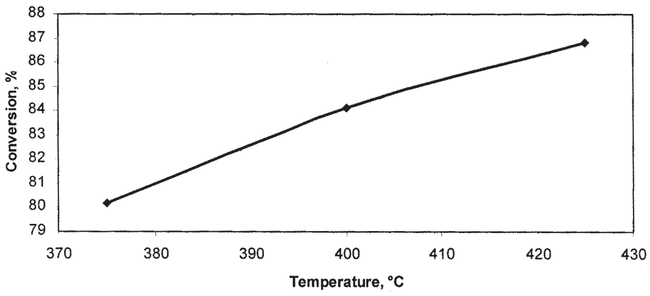

Fig. 4.The temperature influence on the sunflower oil conversion for the Ru / γ-$Al_2O_3$ catalyst

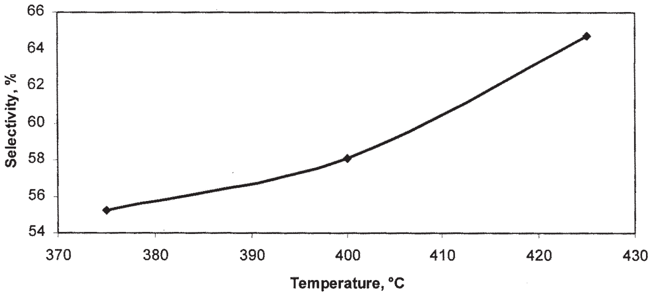

Fig. 5. Selectivity variation in C≤17 linear hydrocarbon with temperature, for Ru / γ-$Al_2O_3$ catalyst

classification, isotherm is the type V with hysteresis loop of $H_3$ type. This isotherm type is characteristic for mesoporous materials with low affinity for the adsorbent. Large area under the loop indicates a high volume of mesopores. At relative pressure $p/p_0$ lower 0.6, physical adsorption is carried out in monolayer. In figure 3 are represented the cumulative volume and specific volume according of pore size. The median pore diameter is in the mesopores field and has a value of 72.25 A°. The pores volume with a diameter below 60 A° (values under which triglycerides access in the pores is made it difficult) is 0.16 $cm^3/g$, the difference (0.468 $cm^3$ /g) is represented by mesopores with a size larger than 60 A°.

The main compounds identified in triglycerides from sunflower oil hydroconversion on the Ru / γ-$Al_2O_3$ catalyst were linear hydrocarbons with less than 17 carbon atoms (C ≤ 17 without C16) obtained by hydrocracking and decarboxylation-decarbonylation, linear hydrocarbons with 16 to 18 carbon atoms (C16 + C18) obtained by hydrogenolysis of triglycerides (hydrodeoxigenation-dehydration) and branched hydrocarbons obtained by isomerisation of straight hydrocarbons.

Variation of triglycerides conversion with temperature was studied on 375-450°C range, at constant values of the others parameters: 40 atm pressure, 1.2 $h^{-1}$ volume flow rate, molar ratio $H_2$/triglycerides equal to 10/1. Sunflower oil conversion on Ru / γ-$Al_2O_3$ catalyst increases with increasing temperature from 80.2% value at 375°C until 86.8 % at 425°C (fig. 4).

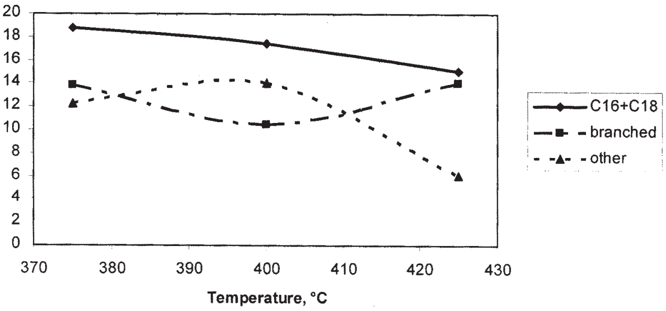

Fig.6. Selectivity variation in $C_{16}$ + $C_{18}$ linear hydrocarbons, branched hydrocarbons and other products with temperature, for Ru / γ-$Al_2O_3$ catalyst

Selectivity in main products are also influenced by temperature variation (figs.5 and 6). As a result of increasing of hydrocracking, decarboxylation and decarbonylation reactions, selectivity in C≤17 linear hydrocarbons increases with increasing temperature from 55.2% at 375°C to 64.8% at 425°C. Linear hydrocarbons $C_{16}$ + $C_{18}$ selectivity decreases from 18.9% at 375°C to 15% at 425°C; branched hydrocarbons selectivity decreases from 12.2% at 375°C to 10% at 400°C, then maintaining constant until at 425°C. Selectivity in other products maintained almost constantly from 13.8 to 14.2 % in the 375-400°C range.

The temperature increasing influences the proportion of decarboxylation/decarbonylation or hydrodeoxygenation/dehydration reactions. At 375°C and 425°C, nC16 /nC15 the ratio has values greater than 1 (i.e. 1,047; 1,113), which shows that reaction of hydrodeoxygenation is more likely than decarboxylation/decarbonylation. At 400°C this ratio is less than 1 (0.598), because decarbonylation and decarboxylation reactions become more important than hydrodeoxygenation. The ratio nC18/nC17 has lower values than the unit across the 375-425°C temperature range; consequently decarbonylation / decarboxylation reactions of carboxylic acids $C_{18}$ is more likely than hydrodeoxygenation (fig. 7).

The conversion of triglycerides increases with increasing pressure. Thus from 20 atm to 40 atm the conversion

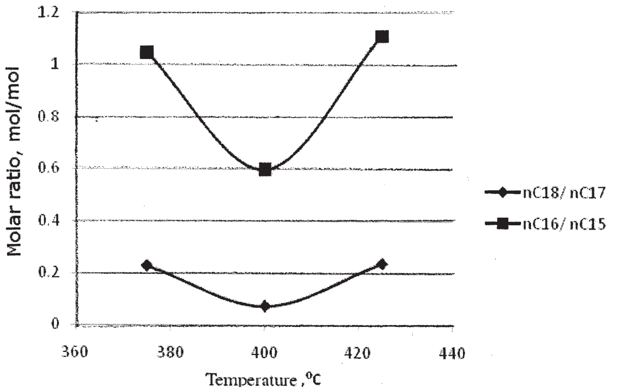

Fig.7. Molar ratios nC18 / nC17 and nC16 / nC15 variation with the temperature

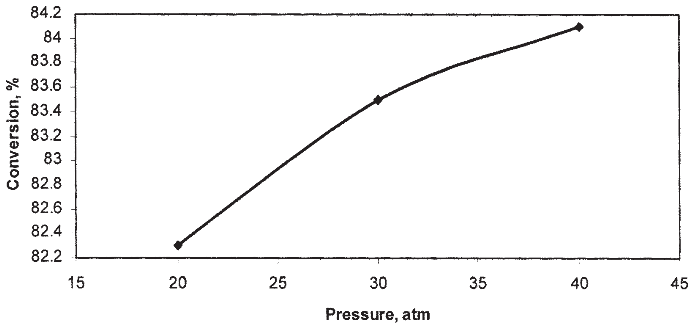

Fig.8. Conversion variation with pressure for Ru / γ-$Al_2O_3$ catalyst

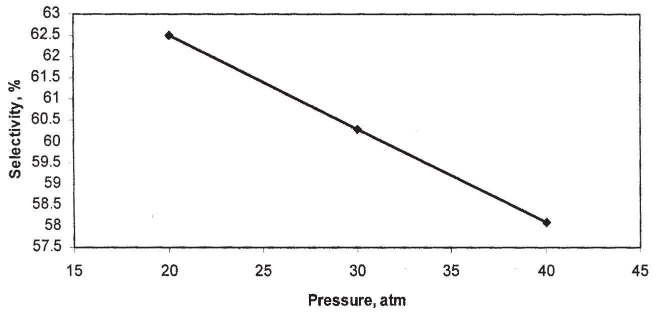

Fig.9. The pressure influence on C ≤ 17 selectivity for sunflower oil hydroconversion on Ru / γ-$Al_2O_3$ catalyst

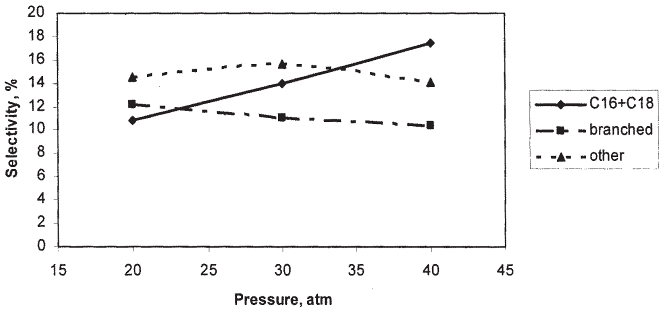

Fig.10. The pressure influence on the selectivity to reaction products for catalyst Ru /γ-$Al_2O_3$

increase from 82.3% until at least 84.1 % (fig. 9) under the conditions specified: 400°C, 1.2 $h^{-1}$ mole ratio of $H_2$/oil. The selectivity to C≤ 17 linear hydrocarbons decreases from 62.5% at 20 atm to 58.2 % at 40 atm (fig. 9). Selectivity in linear $C_{16}$ + $C_{18}$ hydrocarbons, resulting from fatty acids hydrodeoxygenation / dehydration, increases from 10.8% at 20 atm to 17.6% at 40 atm (fig. 10) .

Branched hydrocarbons selectivity decreases from 12% to 10.1% with the increase of the pressure from 20 to 40 atm. The selectivity for the other products remains approximately constant, about 14.5% accros the ranges of 20-40 atm. On the ranges of parameters studied the major compounds, identified at sunflower oil hydro-convesion, was straight hydrocarbons obtained by hydrocracking, with less than 17 carbon atoms (C ≤ 17).

## Conclusions

The Ru /γ-$Al_2O_3$ catalyst shows a middling acidity (1.853 meq. / g), surface area is relatively low (255.297 $m^2$/g), pore volume is small (0.628 $cm^3$/g) and mean pore diameter is relatively large (72.25A°).

The catalyst shows a middling activity in hydro-conversion of the sunflower oil, so the conversion varies in the range 80-87%, depending on the operating parameters.

Selectivity in C ≤ 17 linear hydrocarbons varies in the range 55-62% while the selectivity in $C_{16}$ + $C_{18}$ hydrocarbons and branched hydrocarbons is much lower (10-19% and 10-12%, respectively).

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