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The Decreasing of the Organic Acidity of Technical Olein by Esterification with Glycol

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Abstract

The aim of this paper was to diminish the organic acidity of the residual fatty acid mixtures to make them able to be used as a component for emulsified fuels. For this reason, the residual fatty acid mixture, technical olein, was esterified directly with glycol, on different catalysts, at relatively high temperature. The proposed process conducts us to satisfactory results, limited by the presence of resins in technical olein.

Key words: *fatty, esterification, catalysis, glycerol*

Introduction

The natural fats are liquid or solid mixture of the esters of the fatty acids with glycol, consisting mainly in triglyceride. In small concentration, these content, always, other components as free fatty acids, phospholipids, sterols, hydrocarbons, pigments, waxes and vitamins. The natural fats approximate composition is: triglycerides near 97% wt. (triacylglycerides or trimesters of glycol with fatty acids), 2-3% wt. biglycerides (bi-acylglicerydes) and until 1%wt. monoglycerides (monoacylglycerides). Tri-, bi- and monoglycerides are formed particularly from aliphatic monocarboxylic fatty acids with linear chain with carbon atoms in range 4 to 24 [1].

The crude vegetable oils contain important quantities of free fatty acids, but also, besides above mentioned components, some metals traces, oxidation products and toxic compounds as polyaromatic hydrocarbons, mycotoxins, sulphur compounds and residual pesticides. The removal of these compounds is made by refining, the process arising usually with important glycerides loss.

The refining involves next steps:

- degumming for phosphatides removal;
- neutralizing by potassium hydroxide treatment or by distillation;
- blanching by adsorptive treatments;
- deodorizing or vacuum stripping.

A large quantity of the glycerides are lose in neutralization stage; mono- and bi-glycerides from the crude vegetable oil favor the emulsification of a part of triglycerides, entailing its in subproduct separated by centrifugation. So, the mainly source of residual fatty acids, free or esterifies, is the neutralization stage. Even (although) the concentration of free fatty acids in crude vegetable oils is 1-3% wt, in the refined oil this will be under 0,1%wt. When the free fatty acids are removed as soaps by treatment with lye, some other components as oxidation products of fatty acids, residual phosphatides, gums, phenols and aflatoxins are removed too [2, 3].

Practically, deacidifications are realized by lye treatment or by distillation. For industrial applications, deacidification by esterifying with glycol, by selective extraction with solvents or by adsorption is not important. The neutralization method by alkali treatment takes place at low concentration of the alkaline solution (1 N), to avoid the oil saponification. But even in these conditions a part of neutral oil is lost by entrapment in soap phase. The loss increases proportionally with the free fatty acids content in crude vegetable oil. The soap are usually converted in technical olein (a mixture of free fatty acids and neutral vegetable oil, natural gums and some others impurities separated from vegetable oil) by neutralization with am aqueous solution of suphuric acid 30% at 70°C [4].

Technical olein represents approximately 3% from refined vegetable oil production and has an acidity index in range of 110 – 170 mg KOH/g and a saponification index in range of 175 – 195 mg KOH/g. The difference between the two indexes is given by the presence of the mono-, bi- and triglycerides in mixture. The increasing quantities of technical olein on the market and the large costs for this subproduct processing make attractive the valorization by combustion. The high calorific content, the presence of oxygenated compounds which favor a clean combustion and the obtaining of the “green certificates”, represent the principals reasons for the valorization by preparation of emulsified fuels component of the technical olein separated at the vegetable oil refining. The mainly impediment is the high value of the free organic acidity, due to fatty acids presence.

Experimental

In this paper we propose a method to diminish the organic acidity of technical olein by esterifying free fatty acids with glycol obtained from biodiesel synthesis. Taking account of the relatively large costs of technical olein purification by distillation, we propose an esterification process in heterogeneous catalysis, in the presence of these impurities. The esterification process was realized at temperature in range of 130 - 180°C, in heterogeneous catalysis, in discontinuous system, in the presence of acid catalysts deposed on amorphous or crystalline supports.

Reaction vessel included a three-necked flask equipped with a Dean-Stark liquid – liquid separator and a refluxing condenser, a stirrer with mobile palettes and a thermometer. The temperature adjustment was achieved with an oil bath thermostat.

The quantities used in the experimental program of esterification were:

- technical olein	300 g;
- glycol	26 g;
- catalyst	4,89g.

The operating conditions were:

- temperature	145 - 180°C;
- reaction duration	14 h.

The textural characteristics of catalysts were measured on an Autosorb 1 Quantacrome apparatus and the thermal analysis were conducted on a DuPont Instruments ”Thermal Analyst 2000/2100” apparatus coupled with a ”912 Differential Scanning Calorimeter” module and a ”951 Thermogravimetric Analizer” module.

The starting materials used in this experimental program were the glycol p.a., technical olein and acid catalysts. Technical olein was taken from an industrial plant of sun flower oil refining, it mainly characteristics being:

- acidity index	133,6 mg KOH/g sample;
- saponification index	179,1 mg KOH/g sample.

For the catalysts preparation the starting materials were:

- two γ-Al_2O_3 supports:
    1. PURAL NG;
    2. PURAL KR-1.
- trifluoromethanesulfonic acid (TFA);
- phosphowolframic acid with chemical formula $H_3PW_{12}O_{40}$(HPW).

The powder hydrated alumina precursors characteristics (from SASOL) are shown in table 1.1.

Table 1. The characteristyics of SASOL hydrated alumina samples

Sample	Al_2O_3 (%)	Particle size distribution (%)		
		< 25μm	< 45 μm	<90 μm
PURAL NG	79.8	69.8	86.3	97.6
PURAL KR-1	73.1	22.8	44	100

To obtain γ-Al_2O_3, the hydrated alumina samples were calcinated at 500°C for 6 hours. The preparation of catalyst – support ensemble was carried out by applying dry pore volume impregnation method [5].

Table 2. The characteristics of acid catalysts on γ-Al_2O_3 support

Catalysts	*Precursor support*	Acid conc./ acid+support (%wt)
0_8 A_1	*γ-Al_2O_3: Pural NG*	5% TFA
0_8 A_3	*γ-Al_2O_3: Pural KR-1*	5% TFA
0_8 A_5	*γ-Al_2O_3: Pural KR-1*	10% TFA

The acid catalyst on mezoporous silica support MCM-41 O_8M_{27} was obtained by impregnation with HPW in conditions similar with those used at the preparation of the acid catalysts on alumina support, at a concentration of 30% HPW.

The catalysts used in this experimental program were:

1. Catalyst 0_8 A_1 containing triflic acid (trifluoromethanesulfonic acid, TFA) deposed on γ-alumina;
2. Catalyst 0_8 A_3 containing triflic acid deposed on γ-alumina;
3. Catalyst 0_8 A_5 containing triflic acid deposed on γ-alumina;
4. Catalyst 0_8 M_{27}, mezoporous zeolite MCM-41 type, impregnated with phosphowolframic acid, noted CAT 8;
5. Powder zeolite HZSM-5 modified with Zn during the crystallization process, noted CAT 10.

Results and Discussions

The acid components used on preparation of first three supported acid catalysts are sulphonic acid and heteropolyacids with Keggin structure, respectively. So, trifluoromethanesulfonic acid (TFA) with chemical formula F_3CSO_3H is considered one of the acids with the biggest strength of acidity (being 1000 times stronger than sulfuric acid), which is part of superacids group. The catalytic properties are dictated by it high thermal and chemical stability.

The trifluoromethanesulfonic acid with chemical formula $H_3PW_{12}O_{40}$ (HPW) has a Keggin type structure, consisting in a heteropolyanion, the charge compensatory cation being the H^+ proton. The HPA structure is accessible not only for water molecules, but also for polar organic molecules too (alcohols, amines, ethers). This fact has important consequences for heterogeneous catalysis on heteropolyacids.

The nitrogen adsorption – desorption isotherm at -196°C for alumina Pural KR-1 sample, calcinated at 500°C, is type IV, following IUPAC classification for mezoporous materials (figure 1). The histerezis loop is H3 type, characteristic to the aggregated particles in plaquettes shapes. The textural data were obtained by registration and automatic processing of nitrogen adsorption – desorption isotherms. The specific aria was calculated with BET equation from linear part of the adsorption isotherm. To evaluated the pore distribution it was used the desorption part of the isotherm and the BJH (Barret-Joyner-Halenda) method.

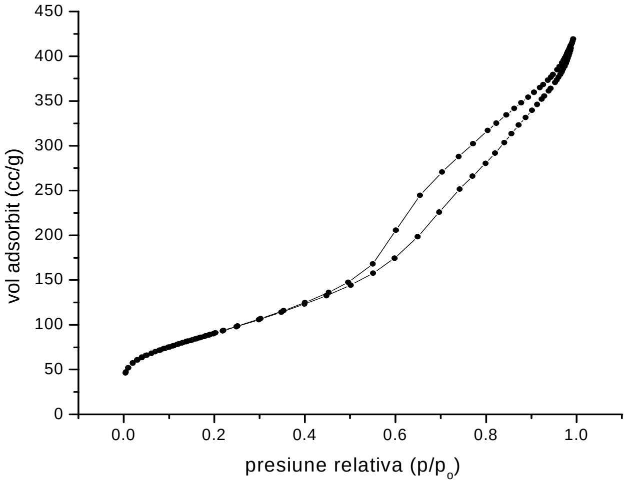

Fig. 1. The nitrogen adsorption – desorbtion isotherm for alumina obtained by calcination of hydrated alumina Pural KR-1 sample.

From figure 2 we can observe that mezeporous silica MCM-41 sample have a type IV adsorption isotherm, with a H_1 histerezis loop, which characterize MCM-41 structure, formed by cylindrical pores with dimension in "mezzo" domain.

On the adsorption curve appear clearly more zones. So, the low relative pressure zone p/p_o corresponds to physical adsorption of nitrogen in large quantities, usually associated with the adsorption of a nitrogen monolayer on the MCM-41 surface (on the external surface and into the mezopores).

The pressure increasing is associated in zone II by the multilayer adsorption. To this contribute the external surface and the mezopores. The obtained data in this zone are used for specific area calculation by BET method.

At a pressure $p/p_o \sim 0.38$, the adsorbed nitrogen quantities increase significantly (zone III) which means the capillary condensation of the nitrogen into the mezopores. The narrow field for p/p_o, in which take place the pore filling, can be associated with small dimension variations. The very small difference between desorption curve and an adsorption curves with a very narrow histerezis loop is another clue of the mezopores dimension homogeneity.

After the complete filling of the mezopores, the external surface of the material remains accessible for nitrogen adsorption (zone IV). The small curve panta in this area means that the external surface is small.

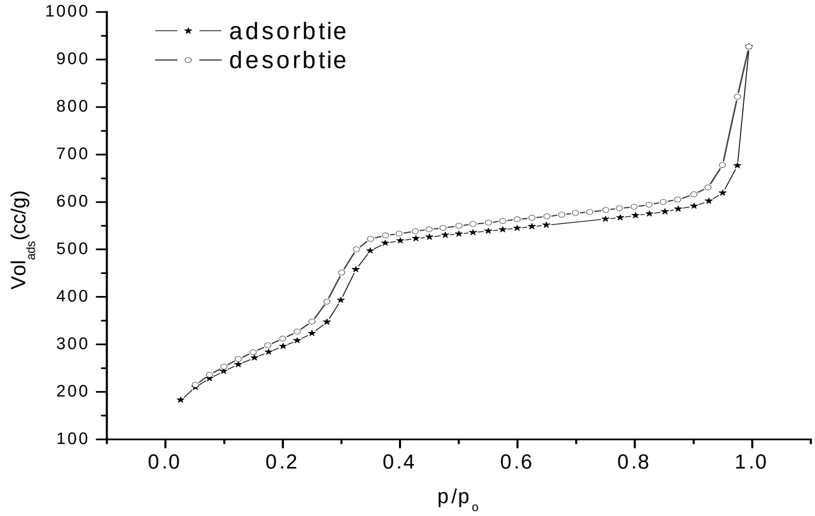

Fig. 2. The nitrogen adsorption – desorption curve on Si-MCM-41

Finally, at relative pressure near 1.0 we can observe an adsorbed volume increases and the presence of one small histerezis loop, this last one zone being associated with the nitrogen condensation in the spaces between the particles.

By desorption branch of the isotherm was calculated the pore size distribution by BRJ method, presented in figure 3.

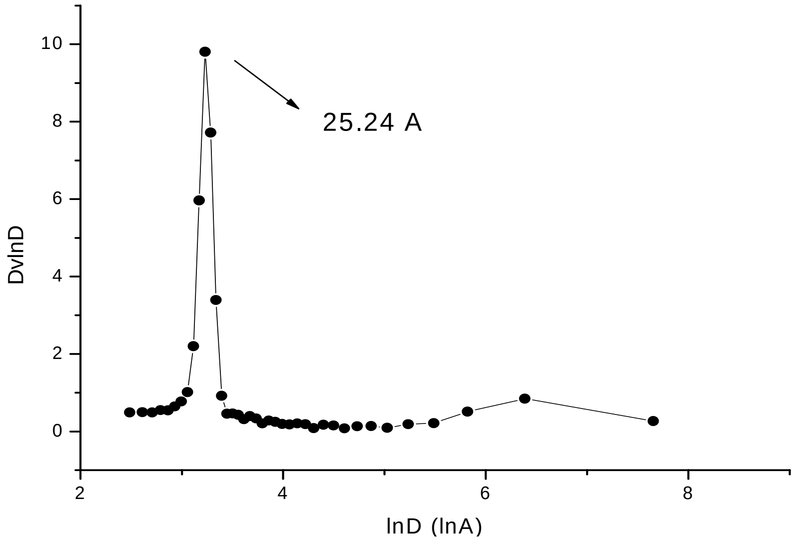

Fig. 3. The pore size ditribution in the mezoporous support Si-MCM-41

In table 3 are shown the textural data obtained for the catalysts prepared on alumina type Pural KR-1 type.

Table 3. The textural data of the acid catalysts on alumina support

Sample	Acid concentration on support	Textural data		
		S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore medium size (nm)
γ-Al_2O_3	-	328	0.925	5.82
0_8 A_3	5% TFA	326	0.91	5.4
0_8 A_5	5% TFA	286	0.79	5.4

In the table 4 are presented, comparatively, the textural data for MCM-41 support calcined and modified with HPW.

Table 4. The textural data of catalyst HPW on MCM-41 support

Sample	HPW concentration on support	Textural data		
		S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore medium size (nm)
MCM-41 support	-	1230	1.77	26.65
HPW/MCM-41 08 M_{27}	30%	1414	2.47	18.37

The increases of the total adsorbed volume after HPW modification reflect the macropores contribution, which was shown by the important increase of adsorbed nitrogen quantities, at relative pressure $p/p_0 > 0,9$.

The textural characteristics of the zeolite ZSM-5 type, in acid form, modified with zinc in the crystallization process are presented in table 5.

Table 5. The textural properties of Zn H-ZSM-5/Al_2O_3 zeolite

No.	Properties	Value	
1	Specific area (m^2 / g)	306.712	
2	Total pore volume (mm^3 / g)	523.75	
3	Medium pore radius (Å)	34.15	
4	Pore distribution. Pore radius (Å)	mm^3/g	%
	5 –10	175.28	33.48
	10 – 15	30.22	5.77
	15 –25	39.11	7.47
	25 –50	3.21	0.61
	50 –75	0.90	0.17
	75 – 100	14.94	2.85
	100 – 200	26.68	5.09
	200 – 300	18.23	3.48
	300 – 600	52.88	10.10
	600 –1000	37.94	7.24
	1000 – 5000	108.40	20.70
	5000 – 10000	9.08	1.73
	10000 –75000	3.88	0.74

The distribution of acid sites strength for the tested inorganic catalysts was determined by diethylamina desorption at temperature in range of 20 - 700°C. The thermal analysis were carried out on DuPont Instruments ”Thermal Analyst 2000/2100”apparatus, coupled with ”951 Thermogravimetric Analizer” module. The results are shown in figures 4 – 8.

The catalyst O_8A_1 has a narrow distribution of acid sites strength, with two maximum, at 100°C and 350° (see fig. 4).

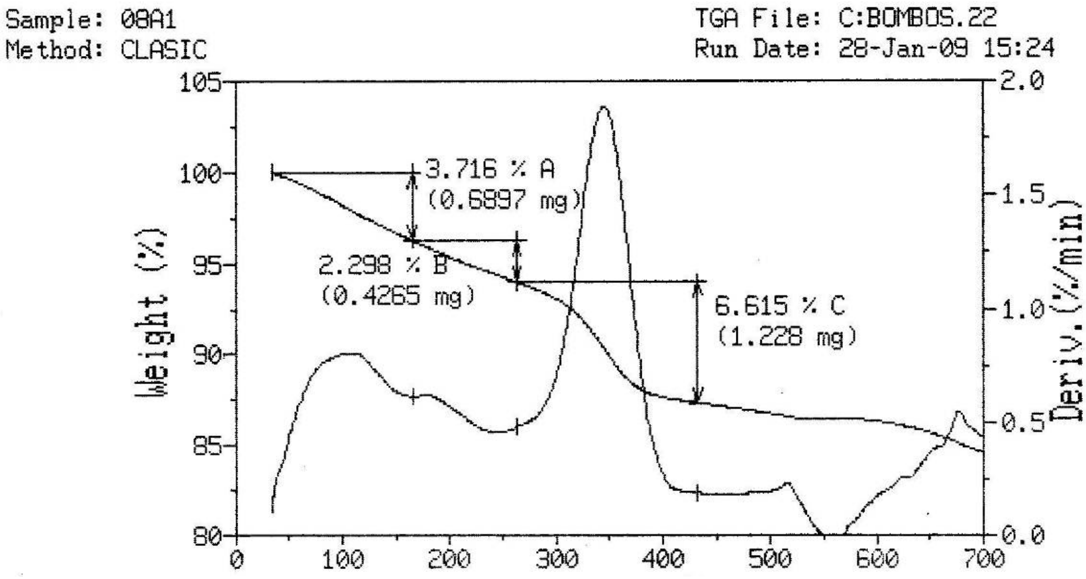

Fig. 4. The distribution of the acid sites strength for O_8A_1 catalyst

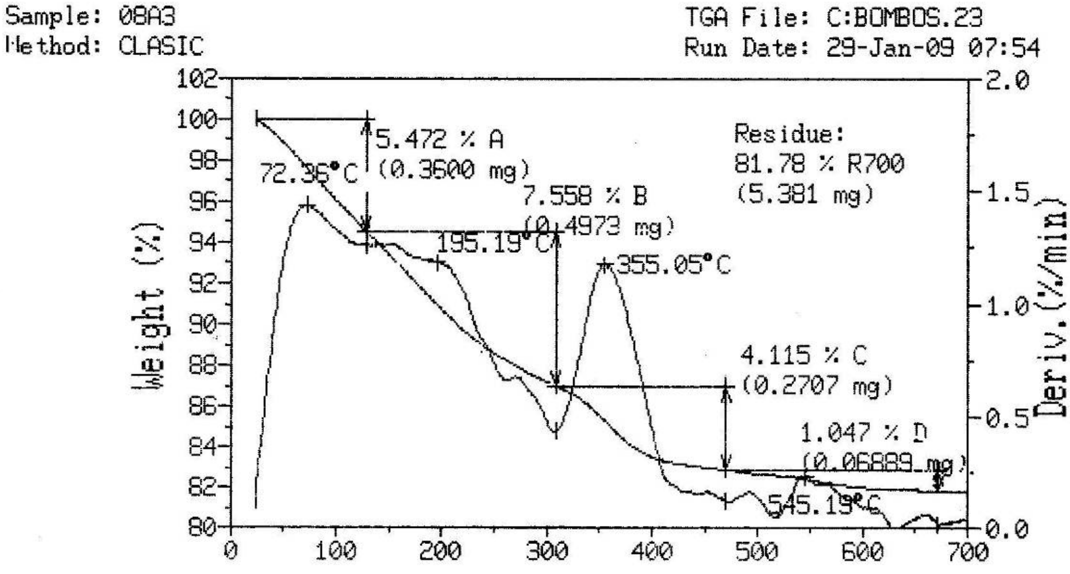

Fig. 5. The distribution of the acid sites strength for O_8A_3 catalyst

The catalyst O_8A_3 present a narrow distribution of acid sites strength with three maximum at 72,36; 195,19 and 355°C respectively (see fig. 5).

The catalyst O_8A_5 present a narrow distribution of acid sites strength, with two maximum, at 140 and 350^{0}C (see fig. 6).

The catalyst O_8M_{27} (sample CAT 8), containing mezoporous zeolite MCM-41, impregnated with phosphowolframic acid, has a narrow distribution of the acid sites strength with two maximum placed into the weak acid sites field, at 81,8 and 167,2^{0}C respectively, and one maximum into the strong acid site field, at 410°C, as is shown in figure 7.

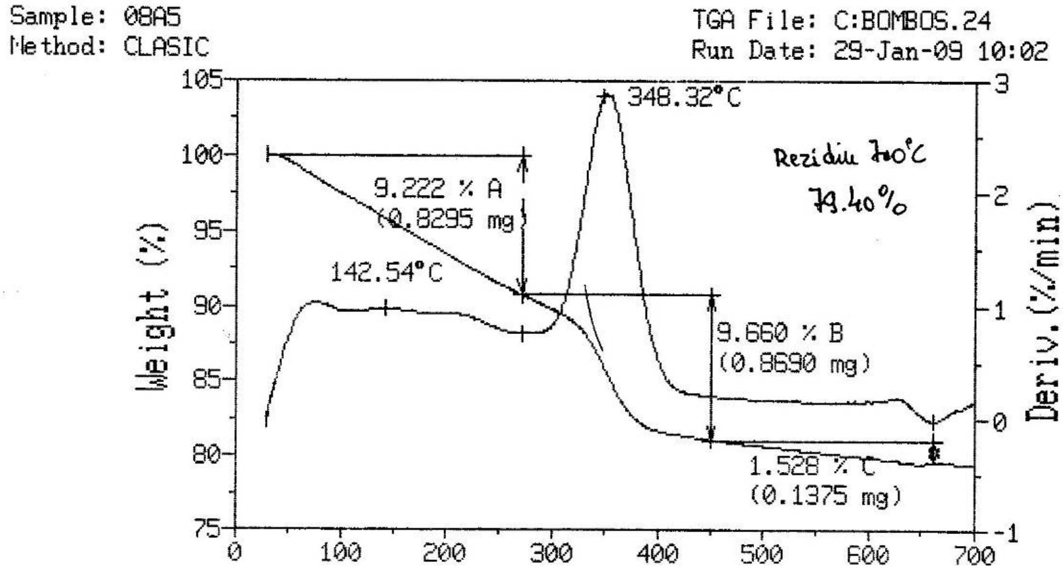

Fig. 6. The distribution of the acid sites strength for O_8A_5 catalyst

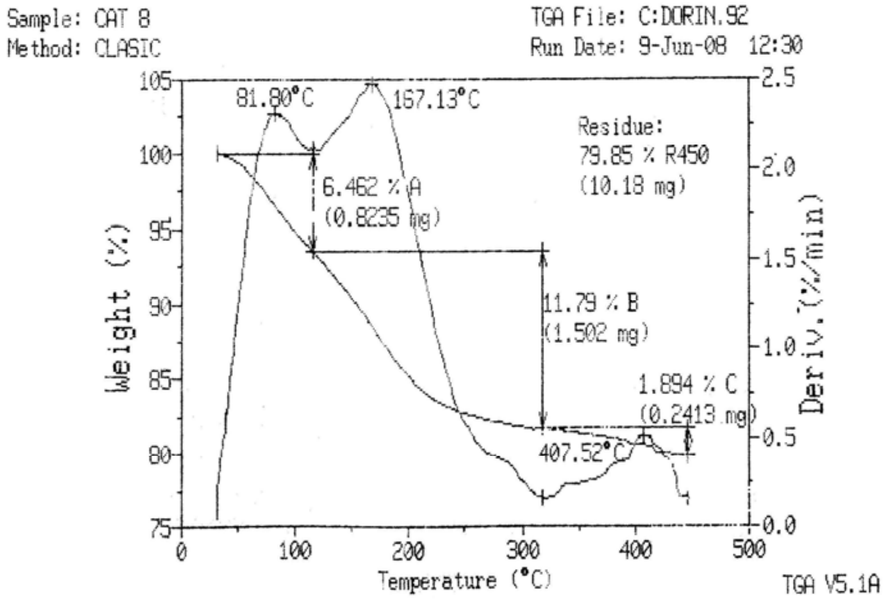

Fig. 7. The distribution of the acid sites strength for O_8M_{27} catalyst

The catalyst HZSM-5 modified with zinc in the crystallization process (CAT 10) present a large distribution of acid sites strength, the majority of maximum being placed into the weak acid sites field (70,67^{0}C and 134,62^{0}C) but are also present acid sites with medium strength (with a maximum at 286°C) and strong acid sites (at 424°C and 610°C).

The experimental program for technical olefin esterification with glycol was carried out using a 5% glycol excess to the stoechiometric ratio and at the same catalyst concentration (1,5% to the reaction mixture).

Evaluation of the tested catalysts performances was made by determination of eliminated water quantities in the esterification process, of the acidity index and the saponification index for the reaction products. Generally, all catalysts favor the esterification reaction, the performances being different due to the catalyst type (table 6).

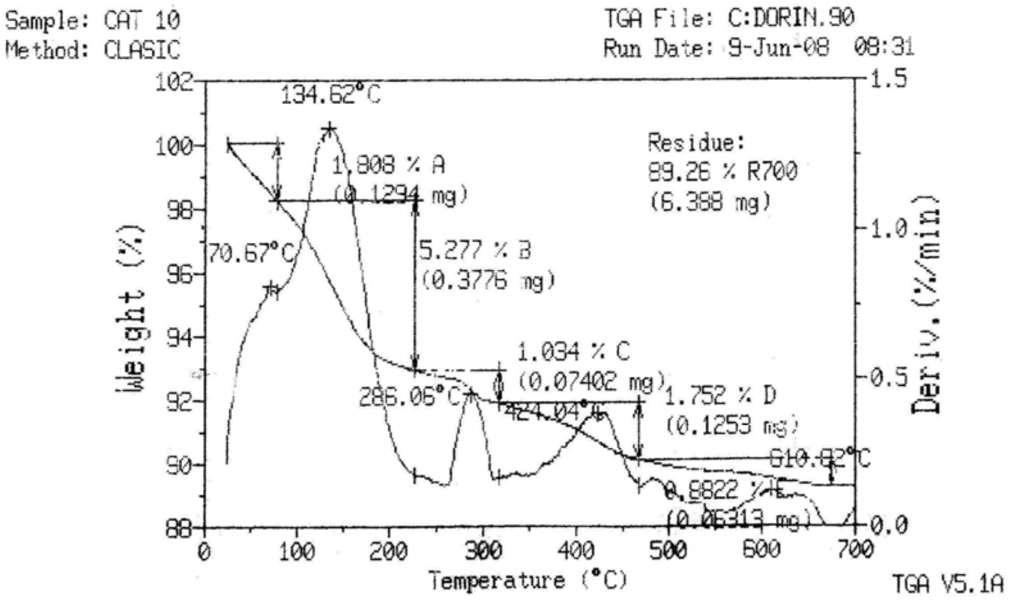

Fig. 8. The distribution of the acid sites strength for CAT 10 catalyst

Table 6. The experimental data of esterification process

Catalyst	Water quantities, g	A. I. mg.KOH/g	S. I. mg.KOH/g
O_8A_1	23	29.85	161.12
O_8A_3	24	32.13	162.32
O_8A_5	26	30.22	166.56
CAT 8	21	34.35	159.61
CAT 10	24	33.65	163.12

The zeolitic catalyst and the catalysts on triflic acid basis and phosphowolframic acid deposed on alumina or mezoporous MCM-41 support has shown satisfactory performances in the esterification process (decreasing of the acidity index is obvious), without a complete elimination of organic acidity of technical olein. The behavior may be due to catalytic pores clogged, because of the resinic compound present in technical olein.

Conclusions

The mixture of the residual fatty acid resulted from the vegetable oils refining (technical olein) has an acidity index in the range of 120-150 mg KOH/g, improper to combustion in burners;

The decreasing of the organic acidity of this olein was carried out by direct esterification with glycol, in acid catalysis;

The relative large costs for technical olein purification by distillation impose the realization of the esterification process in the presence of the impurities resulted from the vegetable oil refining process;

The process of the direct esterification of technical olein was carried out in discontinuous system, at high temperature (aprox. 160°C), without an entrapment;

The esterification process duration was evaluated by the rate of water vaporization and had values of up to 16 hours;

There were tested catalysts with high acidity, as triflic acid, and zeolitic catalysts, modified in acid form, eventually impregnated with compounds with acid character (phophowolframic acid);

The distribution of acid sites strength of the tested zeolitic catalysts was measured by diethylamina thermodesorption in the temperature range of 20 - 700°C;

The evaluation of tested catalysts performances was made by measuring the acidity and saponification index of reaction products. Generally, all catalysts favor esterification reaction, the performances being different depending on catalysts nature;

Zeolitic catalysts and the catalyst on triflic acid basis, supported, have shown satisfactory performances in the esterification process. This behavior may be due to catalytic pore blockages due to resins compound present in technical olein.

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Diminuarea acidității organice a oleinei tehnice prin esterificare cu glicol

Rezumat

În această lucrare s-a urmărit scăderea acidității organice a amestecurilor de acizi graşi reziduali în vederea folosiri acestora drept component pentru combustibilii de focare. În acest scop amestecul de acizi graşi reziduali, oleina tehnică, a fost supusă esterificării directe cu glicerină, pe diferiți catalizatori, la temperatură relativ ridicată. Procedeul propus a condus la rezultate satisfăcătoare, limitate totuşi de prezența compuşilor răşinoşi din oleina tehnică.