Synthesis and Characterization of Some Ester-type Biolubricants of Soiabean Fatty Acids

SORINA BORAN, SABINA NITU*
Politehnica UniversityTimisoara, Faculty of Industrial Chemistry and Environmental Engineering, 6 V. Parvan Blvd., 300223, Timisoara, România

Growing demands from industry for the use of eco-friendly lubricants led research towards finding environmentally friendly products with superior lubricating characteristics. Vegetable oils and synthetic ester oils are competitive base oils used to obtain lubricants with good physico-chemical, rheological and tribotechnical properties, biodegradable lubricants without negative environmental impacts. In this study we aimed the synthesis and characterization of bioesters with lubricant properties, using as acid component the soybean oil fatty acids in conjunction with the following hydroxyl compounds n-buthanol (P1) and 1,2-propilenglycole (P2), respectively. These complex esters were synthesized in a microwave reactor in a single stage in the presence of the catalyst at the reflux temperature. Characterization was carried out in the respective of structural point of view and as a lubricant.

Keywords: biolubricants, vegetable oils, fatty acid esters, microwave reactor

Due to biodegradability, low toxicity and low price, the vegetable oils can be used as an alternative source of lubricant, replacing with very good results esters, synthetic lubricants, particularly in sensitive areas in terms of ecological, such as forestry, agriculture or mining [1-4].

Evaluating biodegradability of mineral oils synthesized with bio lubricants based on vegetable oils, the biolubricants are found to be less harmful to the environment [5] and show better thermal stability compared to synthetic esters [6].

The purpose of modern technologies is to find energetic efficient processes and ecological ones that can replace the classical technologies. As examples are polymerization, which is a process with wide application [7-10], and esterification processes in bubble column reactors. As presented by Popa et all [11-14] polymers synthesized in a bubble gas column reactor are ecological ones, because they do not contain residual monomer. The energetic efficiency calculation of such a reactor is presented for some esterification processes in [15]. Because intensification of heat transfer of all thermal processes is an important technological issue, calculation of boiling heat transfer coefficients may be of high value [16-19].

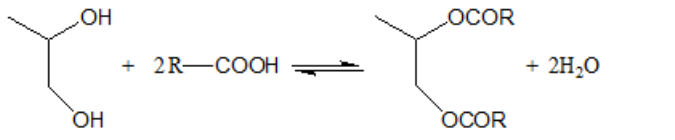
To reduce the negative effects of industrial activities on the environment can be used the following solutions: reducing wastes by recycling some of these materials [20-23], reusing wastes to obtain other useful products [24-25] or to immobilize other hazardous waste [26-27] and replacing of raw materials with new products.

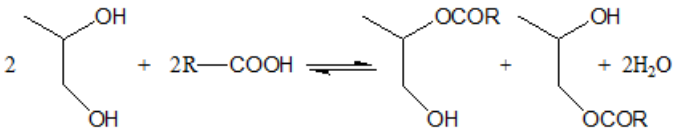
Experimental part

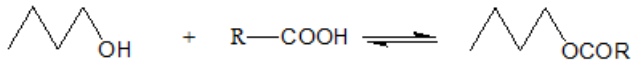
Materials and methods

The fatty acids esters were obtained in a microwave reactor, using as the acid component the soybean oil fatty acids, in conjunction with hydroxyl compounds, namely n-butanol to give compound P1 and 1,2-propyleneglycol to give compound P2, respectively. The reactions were developed in a single stage in the presence of the catalyst: p-toluenesulphonic acid, in the 0.4% proportion towards the acids from soybean oil fatty acids, at reflux temperature.

The possible reactions in these syntheses are the following:







where R-COOH = soybean oil fatty acids.

Synthetic variants thereof are shown in table 1.

The physico-chemical properties of fatty acids from soybean oil: appearance: viscous liquid without mechanical impurities; color: yellow; molecular weight, g / mole: 280; density at 20°C, g/cm^3: 0.89; melting point, °C: 14-16; acid number, mg KOH/ g: 193.4; refraction index, la 20°C: 1.458. The alcohols used are from Fluka. The characteristics of the chemical reactor with microwave heating are: model: DB-001; microwave power: 0 ~ 800W; microwave frequency: 50MHz 2450+; Shaking: magnetic stirrer.

The variation of the acid number of the reaction mass according to the reaction time was the tracking reaction parameter.

For compound P1, synthesis parameters are drawn in table 2.

For compound P2, synthesis parameters are drawn in table 3.

From tables 1 and 2 it can be seen that the use of a chemical reactor with microwave heating, both reactions

* *email: sabina.nitu@upt.ro*

Raw materials	MU	Synthesis variant abbreviations	
		P1	P2
soybean oil fatty acids	mols	1	1
n-butanol	mols	1.2	-
1,2-propilenglycol	mols	-	0.55
p-toluenesulphonic acid	%	0.4	0.4
Reaction conditions			
Time of reaction	min.	180	215
Temperature of reaction	^{0}C	118	180

Table 1
THE SYNTHESIS VARIANTS OF ESTERS FROM SOYBEAN OIL FATTY ACIDS

Table 2
REACTION PARAMETERS FOR THE ESTER P1

Temperature, °C	Time, min	Acid number, mg KOH/g
70	0	132.26
118	30	41.12
118	60	34.26
118	90	33.86
118	120	27.16
118	150	18.85
118	180	5.92

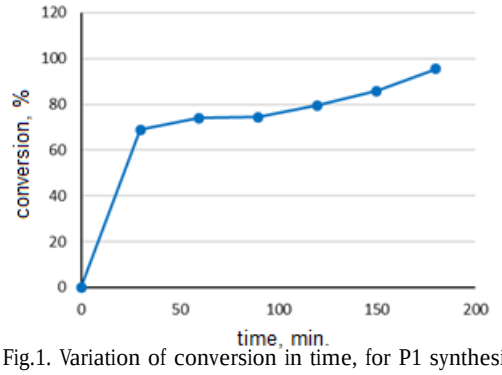


Fig.1. Variation of conversion in time, for P1 synthesis

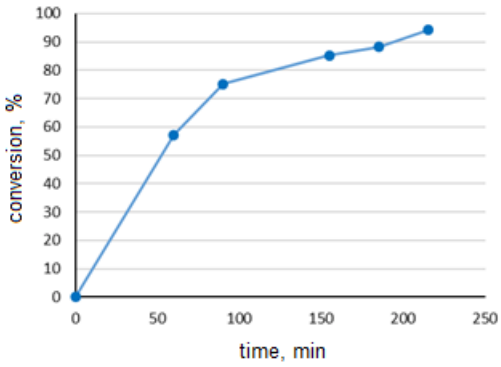


Fig. 2. Variation of conversion in time, for P2 synthesis

are held in a much shorter time as compared with conventional esterification processes [28-29].

The graph in figure 1 shows the variation of conversion in time, and it can be observed a sharp increase in the conversion in the first 30 min followed by a slow rise, so

Table 3
REACTION PARAMETERS FOR THE ESTER P2

Temperature, °C	Time, min	Acid number, mg KOH/g
160	0	173.42
180	60	74.25
180	90	43.21
180	155	25.72
180	185	20.5
180	215	9.89

that ultimately a high conversion yield of about 96% is obtained.

As in the case of P1 synthesis, the reaction to obtain the product P2 follows similar variation in the acid number and of the conversion in time (fig. 2).

Finally, the obtained results are very good, with a low acid number and a very good conversion.

Structural characterization of P1 and P2 esters synthesized: the dynamic viscosity - the viscometer type RV-Rheotest (EBV Prüfgeräte-Werk Medingen / Dresden); refractive index - Abbe refractometer at 200C; density - the pycnometer at 20°C; the acid number – according to SR ISO 3682; saponification index - ISO 3657: 2013 iodine index - according to SR EN ISO 3961: 2013 A;

Evaluation of P1 and P2 synthesized esters as lubricant: flashpoint - according to SR 5489: 2008; the kinematic viscositythe, viscosity index respectively - with the viscometer Ubbelohde ASTM 445; scar diameter - ASTM D-4172; thermogravimetric analysis (TG) / (DTG) and differential scanning calorimetry (DSC) were performed with NETZSCH STA apparatus STA449F1A 449F1-0220-M. A quantity of between 3 ÷ 7 mg sample was heated in a crucible of Al_2O_3, with the rate of 5°C / min., under a nitrogen atmosphere in the temperature range of 20 ÷ 600 ° C.

Results and discussions

Physico-chemical properties of the synthesized esters (P1 and P2) are shown in table 4.

Both P1 and P2 products have the values of density, viscosity and refractive index comparable to those of soybean oil (standard). In comparison to the soybean oil, the iodine values corresponding to the synthesized compounds are smaller, which indicates a lower degree of unsaturation. In all cases, the acid number is below unity.

Property	P1	P2	Soybean oil
Density, ρ^{20} / kg m^{-3}	883.5	1142.3	919-925
Refractive index, n_D^{20}	1.4598	1.4678	1.466-1.470
Viscosity, η^{20} / mPa s	80.91	84.58	83.22
Saponification index, mg KOH g^{-1}	220	124.1	189-195
Acid number, mg KOH g^{-1}	< 1	< 1	< 1
Iodine index, g I_2 100 g^{-1}	110	80.2	120-140

Table 4
PHYSICO-CHEMICAL PROPERTIES OF THE SYNTHESIZED ESTERS P1 AND P2

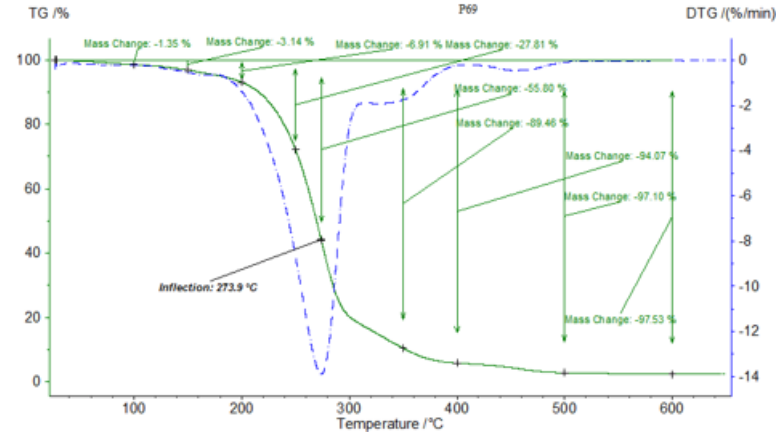


Fig.3. TG/DTG curves for P1 ester in nitrogen atmosphere

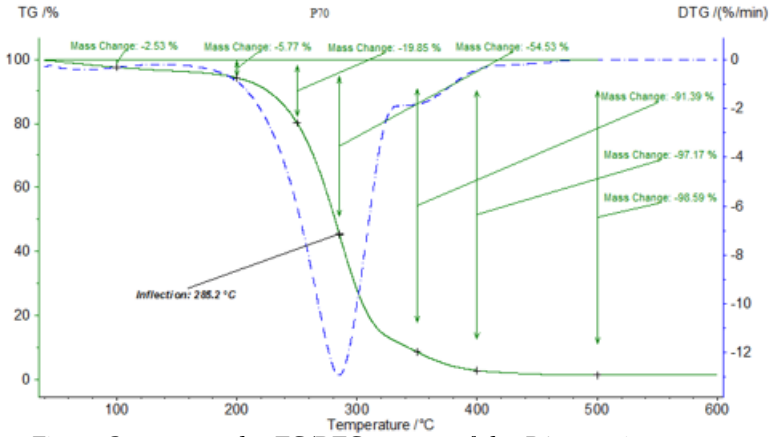


Fig.4. TG/DTG curves for P2 ester in nitrogen atmosphere

Figure 3 presents the TG/DTG curves of the P1 ester in nitrogen atmosphere, and figure 4 presents the TG/DTG curves of the P2 ester in nitrogen atmosphere.

Figures 3 and 4 show that in both cases we have a good thermal behavior until about 200°C, the temperature to which the weight loss is not significant. Over 250°C starts the rapidly losing of mass as the temperature increases. In the case of compound P1 the highest mass loss occurs at 273.9°C, while in the case of compound P2 at the temperature of 285.2°C. For both compounds P1 and P2, the total mass loss occurs in the range of 500-600°C.

After characterization from physico-chemical point of view of an organic substance, esters synthesized were analyzed as lubricants.

In table 5 the rheological characteristics of soybean oil and the synthesized compounds P1 and P2 are presented.

From table 5 it is noted that the inflammation temperature and viscosity index show high values, that increase with increasing molecular weight and with decreasing capacity of evaporation respectively.

To determine the lubricating ability of these synthetic oils, the test with four balls was carried out, whose results are shown in table 6.

The results show that the species without additives and to a level test of 60 daN for 60 min, scar diameters are generally very good, placing it in the range of 0.47-0.61 mm. Adding additive to oils result in a slight improvement in behavior in all cases. The compounds show a good compatibility with such synthetic anti-wear additives.

Characteristics		Base oil		
		Soybean oil	P1	P2
Kinematic viscosity, mm^2/s	40°C	32.5	7.3	7.7
	100°C	7.85	2.22	2.3
Viscosity index, IV		226.7	117.2	121.3
Temperature of inflammation, °C		228	186	201

Table 5
RHEOLOGICAL CHARACTERISTICS OF VEGETABLE OILS AND OF SYNTHESIZED ESTERS

Compound	Without additives	The addition of 1.5% Zn dithiophosphate		The addition 1,5% Zn ditiocarbonat	
	Scar diameter, mm	Scar diameter, mm		Scar diameter, mm	
	60 daN 60 min	40 daN 60 min	150 daN 1 min	40 daN 60 min	150 daN 1 min
P1	0.52	0.44	1.60	0.48	1.61
P2	0.47	0.42	1.65	0.47	1.74
Soybean oil	0.61	0.46	1.77	0.56	1.90

Table 6
SCAR DIAMETER AND FOUR-BALL TEST

Conclusions

The aim of this work was the synthesis and characterization of some bioesters using as the acid component fatty acids of soya bean oil in conjunction with various hydroxy compounds, namely n-butanol to give the compound P1, and 1,2-propylene glycol to give the compound P2. The reactions developed in a single stage, in the presence of the catalyst, p-toluenesulfonic acid (0.4% to the acids from soybean oil fatty acids) at reflux temperature.

By the use of a chemical reactor with microwave heating, both synthesis are held in a much shorter time as compared with the conventional esterification.

The esters thus synthesized have been characterized as lubricants, in this sense determining their flash point, kinematic viscosity and viscosity index, scar length for the species with or without additives. Thermogravimetry (TG)/(DTG) analyzes and calorimetric differential scanning (DSC) were also performed.

The obtained results have certified the possibility of using these compounds as lubricants, which are of outstanding quality in tribological fluids domain, having characteristic features of lubricating oils.

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