

Application of waste glycerol from biodiesel production for obtaining of modifiers for reduced friction of different motor oils

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Glycerol mono oleate (GMO) was made from waste glycerol (WG) from biodiesel productions by condensation with oleic acid in presence of titanium alcoholate as catalyst. The total acid number was obtained with titration of the samples of GMO with alcohol solution of potassium hydroxide (ASKON). The neutralization of extra oleic acid was made by alcohol solution of methyl amine or 25% ammonia. The prepared sample from the obtained modifier was analysed by standard method with four-ball method and the reduced friction was assessed.

Key words: waste glycerol, glycerol monooleate, titanium catalysts, friction modifiers

INTRODUCTION

In a number of publications was described the obtaining of GMO started from 30th years of the last century. It was known that this compound can be obtain from:

- Glycerolize
- Hydrolyses of triglycerides
- Direct esterification of glycerol with oleic acid

The third method was possible to be made with or without catalysts. The first possibility was made usually at high temperature or pressure. The applied catalysts were acids [1,2] or basis [3,4]. Usually the application of catalysts decreases the temperature and the time. The application of solid catalysts (oxides, zeolites and others) widely investigated and it will not be described in this paper. The reaction between oleic acid (OA) and ammonia or amines was well known, because $-\text{COOH}$ was acidic, but amines were bases. In [6] was described the obtaining of amides from fatty acids and methylamine. The same authors have another article, published in 2013 year. The application of enzymes was described in a lot of articles [7]. We investigated the possibility for making of glycerol mono oleate from waste glycerol obtained in biodiesel production. The reaction was made in the presence of a new titan tetra alcoholic containing catalysts (TiAl) applied in syntheses of synthetic oils [8]. Because they have some excess of oleic acid, we decided to combine it with methyl

amine. The reaction between glycerol $-\text{OH}$ groups and oleic acid in the presence of TiAl was investigated at two temperatures and the activation energy ($E_{\text{act.}}$) was determined.

EXPERIMENTAL

The compound WG was investigated by elemental analysis (EA) with apparatus Euro EA 3000 (Euro Vector Sp A, Italy). The carbon, nitrogen and hydrogen content were measured in the analyzed samples by burning of the material with weight 0.5 – 1.5 mg at 980°C in oxygen atmosphere. The obtained gas mixture passed through chemical/absorption zone. Then CO_2 , N_2 and H_2O were separated by gas chromatography. It was known, that glycerol have no nitrogen in his molecule, but in WG it was possible to have some small amount of nitrogen from protein of the raw oils applied in biodiesel production. The standard curve was made through analyses of acetone (C₃H₆O) with computer product Calligus. From the obtained results, the content of glycerol (G) was calculated. The results from EA were compared by data obtained with UV-VIS analyses, made by apparatus Cary 100 Scan UV-VIS spectrophotometer (Varian, Germany) by obtaining the spectra of WG and pharmacopeius G, 99% product of Chemapol Ltd, Dimitrovgrad, Bulgaria and of G, p.a., product of Valerus Ltd, Sofia, Bulgaria. From the obtained spectra of the second company, the dependence concentration of G – C, / absorption A was made and there were calculated the equations of several maxima in the specter of G with different values of accuracy of the obtained

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equations and experimental values (correlation coefficient R^2). With the equations at 222 nm and A from spectrum of WG it was calculated the glycerol content in the WG. The obtained value was 62%. The syntheses of GMO were made in 150°C for 3 h in the presence of 0.43 ml TiAl, 0.5 mol. standard OK, p.a., product of Valerus Ltd. and 0.6 mol. WG. The same synthesis was made with standard OK and G, p.a. The obtained products were investigated by ^1H NMR (by apparatus Bruker Avance DRX250), UV-VIS and FTIR spectroscopies (by apparatus Cary 100 Scan UV-VIS and Varian FTIR). The investigation with UV-VIS were made in 10 mm cuvettes. The investigation with FTIR were made in thin layers of the obtained materials. The friction properties of GMO obtained from WG and from pure raw materials were investigated by standard method like additive of engine oil with four ball machine [9].

RESULTS AND DISCUSSION

The characteristics of WG were investigated with elemental analyses, UV-VIS and FTIR spectroscopies. The spectra of G, product of Chemapol Ltd, Dimitrovgrad, Bulgaria were made with UV-VIS spectroscopy but they have not maxima in the area 200 – 400 nm (fig. 1).

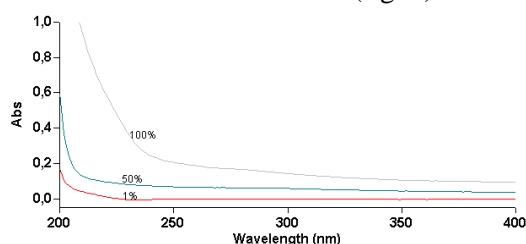


Fig. 1. UV-VIS spectra of G, product of Chemapol Ltd, Dimitrovgrad

The spectra of glycerol published in the literature have several maxima in this area. This is the reason to make the same investigations with G, p.a., product of Valerus Ltd, Sofia, Bulgaria. The obtained spectra are presented in fig. 2

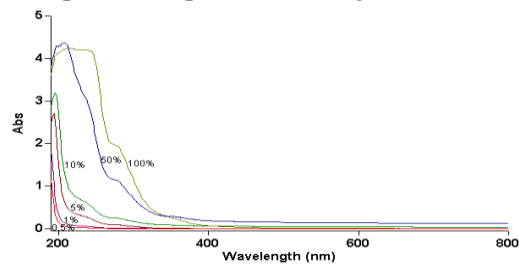


Fig. 2. UV-VIS spectra of G, product of Valerus Ltd, Sofia, Bulgaria

From the obtained spectra were made equations concentration C, % / absorption A for maxima at

285, 225, 222 and 218 nm. It was known, that the equations are true if $R^2 > 0.99$. This is the reason to make calculations only with equation at 222 nm. From this equation and from the data for WG given in fig. 3 the concentration of G in WG was calculated, namely 62%.

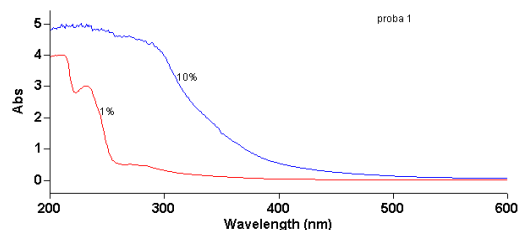


Fig. 3. UV-VIS spectra of water solutions of WG

In ^1H NMR spectrum of WG have maxima for protons in $-\text{CH}-$, $-\text{CH}$ и $-\text{OH}$ groups. These groups were with bands, shown in FTIR spectrum of WG. For example $-\text{OH}$ was with band at 3354.45 cm^{-1} . Because WG was very reactive, was made spectrum in thin layer on the plate from CaF_2 with apparatus ThermoScientific Nicolet 6700

GMO, obtained from WG and standard OA, like product, made only from standard G and OA were investigated with ^1H NMR, UV-VIS and FTIR spectroscopies. Data for ^1H NMR of GMO, made from WG was analogical of data for this compound, published in [10]. In fig. 4 was given UV-VIS spectrum of GMO from WG and standard OA. The place of two maxima for 1% -en alcohol solution of GMO was under of 300 nm

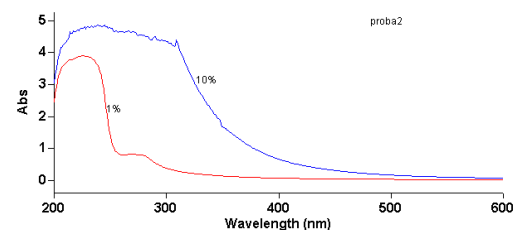


Fig. 4. UV-VIS spectra of alcohol solutions of GMO, made from WG with TiA.

FTIR spectrum of GMO, obtained with the same catalyst from WG and standard OA was shown in fig. 5. The bands for $-\text{OH}$ group was at 3382.660 cm^{-1} , for $-\text{CH}-$ and CH_2 groups were at 2926.058 , 2853.929 , 1463.020 , 1410.009 and 723.009 cm^{-1} and for $-\text{CO}$ was at 1711.729 cm^{-1} . The values of some bands were at the same position, like in row glycerol, but in some bands were in a new places, because were for a new compound. In FTIR spectrum of GMO, obtained at the same catalyst from standard raw materials, shown in fig. 7 had the same bands. The differences in the values of some bands were so small, that were after decimal point.

In the spectra of GMO after neutralization of the remained acids with alcohol solution of methylamine ore with 25% water solution of ammonia, shown in figures 7 and 8 had analogical bands.

The activation energy E_{act} of the esterification of $-OH$ groups in GMO with OA was obtained in the investigation of the reaction in two temperatures –

room at $80^{\circ}C$. From the values of the velocities $W_1 = 0.052$ mg KOH/g.h. and $W_2 = 0.7515$ mg.

KOH/g.h. was obtained the value of activation energy $E_{act} = 9.15$ kJ/mol. The values of acid numbers (AN) were obtained with alcohol solution of KOH by standard method, described in [11]. The obtained values were in table 1.

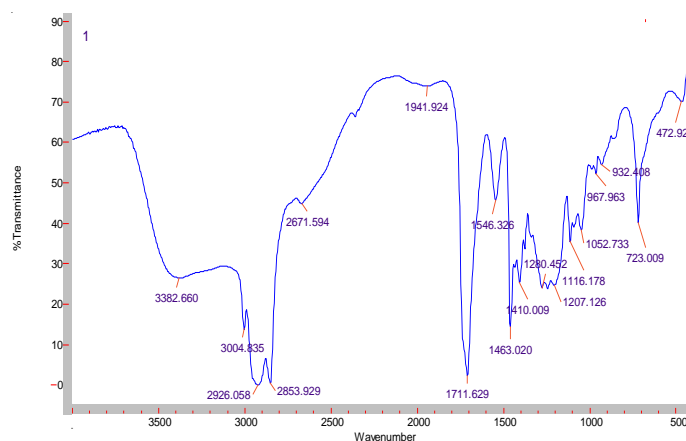


Fig 5 FTIR spectrum of GMO, obtained from WG and standard OA with TiAl

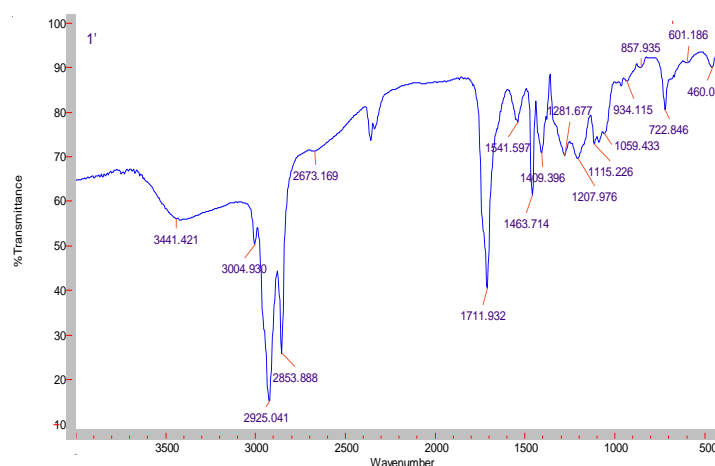


Fig. 6. FTIR spectrum of GMO, obtained from standards G and OA with TiAl.



Fig. 7. FTIR spectrum of GMO, obtained from WG with catalyst TiAl and after neutralization of the remained acids with alcohol solution of methylamine.

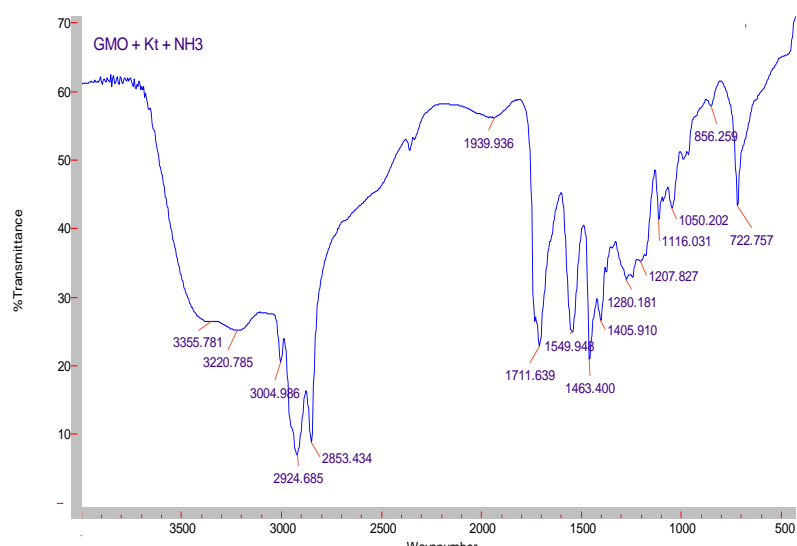


Fig. 8. FTIR spectrum of GMO obtained from WG with catalyst TiAl and after neutralization of the remained acids with water solution of 25% ammonia

Table 1. Data for A.N. of GMO and its mixtures with methylamine (MA)(1 -11.02, 2 – 19.02, 3 – 02.04)in room temperature

N	Probe (ml/ml)	A.N.1,mg KOH*/ g	A.N. 2,mg KOH*/ g	A.N..3,mg KOH*/ g
1	GMO from WG	101.15	80.53	79.68
2	GMO: MA= 5 : 1	71.34	51.78	51.55
3	GMO: MA = 5 : 3	61.97	alkaline	alkaline
4	GMO: MA = 5 : 5	42.28	alkaline	alkaline

Table 2. Dependences between average diameter of wearing of the balls (d_{eva}) and of anti wearing index (AWI),from the quantity, % and the kind of investigated modifiersin mineral motor oil M10D₂/E₁

N ^o	Quantity,% and the kind of modifier ,	d_{eva} Of wearing,mm	AWI, N
1	0	0.60	243
2	2, Zn succinide	0.36	346
3	0.5, Zn succinide	0.39	329
4	0.5, Cu oleate	0.45	-
5	GMO obtained from WG	0.43	302
6	GMO obtained from standard materials	0.42	324

Table3. Dependences between average diameter of wearing of the balls (d_{av}), %, Δ from the quantity, % and the kind of investigated modifiersin motor oilSN 500

N ^o	Quantity,% and the kind of modifier ,	d_{av} of wearing, mm., %, Δ
1	0 , Mineral motor oil SN 500,	0.70, 100, 0
2	1, anilidoleate	0.57, 81.43, 18.57
3	0.5, anilidoleate	0.62, 88.57, 11,43
4	1, Cu oleate	0.65, 92.86, 7.14
5	0.5, Cu oleate	0.60, 85.71, 14.29
6	2, Complex polyester	0.63, 90, 10
7	1, Complex polyester	0.63, 90, 10
8	2, GO obtained from WG	0.60, 85,71, 14.29
9	1, GO obtained from WG	0,56, 80, 20
10	0,5, GO obtained from WG	0,56, 80, 20
11	2, GO obtained from standard materials	0.60, 85.71, 14.29
12	1, GO obtained from standard materials	0,55, 78.57, 21.13
13	0,5, GO obtained from standard materials	0,55, 78.57, 21.13

Table 4. Dependences between average diameter of wearing of the balls (d_{av}), %, Δ from the quantity, % and the kind of investigated modifiers in synthetic motor oil 5W40 according SAESL/CF по API

№	Quantity, % and the kind of modifier ,	d_{av} of wearing, mm., %, Δ
1	0, syntetic motor oil 5W40	0.59, 100, 0
2	1, anilidoleate	0.53, 89.83, 10.17
3	0.5, anilidoleate	0.54, 91.53, 8.47
4	1, Cu oleate	0.50, 84.75, 15.24
5	0.5, Cu oleate	0.55, 93.22, 6.78
6	2, Complex polyester	0.47, 79.66, 20.34
7	1, Complex polyester	0.50, 84.75, 15.24
8	0,5, Complex polyester	0.55, 93.22, 6.78
8	2, GO obtained from WG	0.55, 93.22, 6.78
9	1, GO obtained from WG	0.55, 93.22, 6.78
10	0,5, GO obtained from WG	0.54, 91.53, 8.47
11	2, GO obtained from standard materials	0.52, 88.14, 11.86
12	1, GO obtained from standard materials	0.52, 88.14, 11.86
13	0,5, GO obtained from standard materials	0.54, 91.53, 8.47
14	1, Zn oleate	0.55, 93.22, 6.78
15	0,5, Zn oleate	0.55, 93.22, 6.78
16	1, Titanium oleate	0.52, 88.14, 11.86
17	0,5, Titanium oleate	0.55, 93.22, 6.78

Data for AN of GMO, obtained at 80°C were analogical. MA was 33% solution of the gaze CH_3NH_2 in pure ethanol. If the sample was alkaline was no possible the determination of AN. Maybe the esterification of GMO and OA prolonged, because in the molecule of G have 3 OH groups, capable to react with – COOH groups of OA. In the presence of MA this possibility increased (probes NN 3 and 4).

The properties of the obtained compounds like friction modifier of different motor oils were determined with four ball machine by standard method. For comparison were made investigations with standard friction modifiers. The investigations were made in acidities laboratory for oil products of "Prista Oil" Ltd. In 120°C for 1h – table 2 and in laboratories of university of Russe "Angel Kanchev", given in tables 3, and 4.

From the results, shown in table 2 was evident, that anti wearing properties of the oil with frictions modifiers (d_{eva} mm and AWI) increased with friction modifier Zn succinidewith 30%. With the decreasing of the concentration of the modifier those % was decreased from $d_{eva} = 0,36$ mm for 2% to 0,39 mm for 0,5%, but was enough for anti wearing properties of motor oil. With anti wearing modifier Cu oleate were obtained the best results, compared with results of friction modifier GMO, obtained with catalyst TiAl. From the data in table 2 was evident, that the modifier GMO, made from WG and OA were similar with the anti wearing properties of GMO, obtained from standard materials. The increasing was about 25%. From the results, shown in tables 3 and 4 were evident, that

the obtaining materials were the good frictions modifiers

CONCLUSION

The results for decreasing of the quantity of different friction modifiers, given in tables 2, 3 and 4 in mineral and synthetic motor oils were no every time in connection with theory of friction modifiers, but the results, obtained with investigated materials from WG were comparable or better with data, obtained with known friction modifiers.

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ПРИЛОЖЕНИЕ НА ОТПАДЪЧЕН ГЛИЦЕРОЛ ОТ ПРОИЗВОДСТВОТО НА БИОДИЗЕЛ ЗА ПОЛУЧАВАНЕ НА МОДИФИКАТОР НА ТРИЕНЕ НА РАЗЛИЧНИ МОТОРНИ МАСЛА

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(Резюме)

Глицерол моно олеат (ГМО) беше получен от отпадъчен глицерол (ОГ) от производството на биодизел при кондензация с олеинова киселина с катализатор титанов алкохолат. Общото киселинно число беше получено с титруване на проби от ГМО с алкохолен разтвор на калиева основа (АРКОН). Неутрализацията на излишната олеинова киселина беше направено с алкохолен разтвор на метиламин или 25% амоняк при стайна температура. Получените проби от модификатора на триене бяха изследвани със стандартен метод с четирисачмяна машина и промяната на триенето беше оценена.