Biodiesel and Surfactants from Fats

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This paper describes the obtaining of biodiesel based on fatty acid methyl esters and simultaneously surfactants with a fatty acid monoglycerides structure, separation, purification and their physico-chemical characterization. The method is based on methanolysis of triglycerides from fats, in the presence of a catalyst mixture composed of guanidine carbonate with different amino compounds. Esteric fraction after separation of crude glycerol, was fractionated using a short path distillation plant, working at high vacuum (up to 1 x 10^{-6} bar). Fatty acid methyl esters (FAME) and monoglycerides (MG) results. FAME fraction could be used as biodiesel, eco-friendly solvent and raw materials for many surfactants. MG fraction is used as food emulsifier and raw materials for many surfactants. Intermediate and finished products were characterized analytically by GC and FTIR methods.

Keywords: biodiesel, fatty acid methyl esters, monoglycerides, transesterification, methanolysis, vegetable oils

Depletion of fossil energy resources, and excessive production of greenhouse gases, generated a general interest for alternative energy sources and non-petrochemical raw materials.

Biodiesel is an alternative fuel for diesel, is based on fatty acid methyl esters (FAME), and can be used for standard diesel vehicles. Almost all biodiesel is produced by transesterification of fatty acid triglycerides (TG) of vegetable oils or animal fats with methanol (M) in alkaline catalysis [1]. It is an economic process at atmospheric pressure and low temperatures, with yields greater than 96%.

The interest in biodiesel, related products based on fatty acids methyl esters and by products recovered from methanolysis, was in our research group and is reflected by some papers [2,3] and patents [4 - 7].

Methanolysis in alkaline catalysis takes place in competition with saponification and emulsification effect due to resulted soaps, complicates separation and purification of biodiesel and also of glycerine by-product.

Recently, fuel distribution stations, sells only blends of diesel fuel and biodiesel. Because biodiesel price is higher than that of diesel fuel, new solutions were searched for minimizing it. One way to reduce the biodiesel price is the recovery and purification of crude glycerol obtained as by-product [8].

Another alternative is to produce biodiesel together with fatty acid monoglycerides (MG), value-added surfactants, used as food emulsifiers or as raw materials for other classes of eco-friendly surfactants. Traditional manufacturing technologies for monoglycerides (MG) are based on glycerolysis of fatty acid triglycerides from fats. These processes require high temperatures (220-260°C), high reaction time (5-6 hours) and inorganic catalysts such as sodium, potassium or calcium hydroxides [9], [10]. An interesting method for obtaining monoglycerides, but with little chance of industrial-scale implementation, is focused on the condensation of fatty acids with glycerol carbonate in the presence of triethylamine as a catalyst at temperatures of 143-145°C. Monoglycerides are removed from the reaction mass and purified by recrystallization from petroleum ether [11]. By methanolysis of triglycerides in alkaline catalysis, monoglycerides are obtained only in low concentration (approx. 1 %)

This paper presents our results related to obtaining of biodiesel together with surfactants based on fatty acid monoglycerides, their separation, purification and physico-chemical characterization. The method has been focused on methanolysis of triglycerides, using as catalyst a mixture of guanidine carbonate with different amino derivatives. In the methanolysis process, a mixture of esters and glycerin (G) is formed which is separated by decantation. The esters mixture consisting of FAME, MG, DG, TG is fractionated by vacuum distillation in FAME and MG. Residue, consisting of DG and TG could be returned to the methanolysis stage.

The fraction with a major content of FAME and also the fraction with major content of MG have many uses.

Experimental part

Materials and methods

The following reagents and materials were used: methanol from SC Chimreactiv srl, ethylenediamine, N,N-diethylethanolamine, diethylamine, n-hexane, n-heptane from Merck Schuchardt, n-monobutylamine from Carlo Erba, N,N-dimethylethanolamine from Huntsman, pyridine, 1,3-dioleine from Sigma Aldrich, morpholine, monooleine, trioleine, tricaprine, methyl heptadecanoate, N-methyl-N-trimethylsilyltrifluoroacetamide (MSTFA), guanidine carbonate from Fluka, crude rapeseed oil degummed in our laboratory, with the following characteristics: saponification value: 186.8 mg KOH / g, acid value: 0.16 mg KOH / g, iodine value: 112.7 g iod/100 g, phosphorus content: 4.32 mg / kg.

Methanolysis of fatty acid triglycerides

500 g Soybean oil in 80.5 g methanol were mixed with a variable amount of amino derivative. After approx. 10 min of stirring, 0.5 g guanidine carbonate is added. The mixture was heated under stirring, maintaining the temperature at

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67-75°C, a variable time. After methanolysis is done, methanol and amino derivative are removed from the reaction mass by distillation at atmospheric pressure. Traces of methanol and the amino derivative are removed by vacuum distillation, without exceeding a temperature of 90°C. Crude glycerine (G) is separated by decantation from the ester fraction consisting of FAME, MG, DG, TG.

Separation, purification of MG and FAME

The separation and purification of FAME and also of MG from crude ester fraction resulted from methanolysis, was performed on Short Path Distillation Plant type KDL 5. The plant was bought from UIC GmbH, Alzenau-Horstein. The glass installation performs a downward film short path distillation which operate under advanced vacuum, up to 1 x 10^{-6} bar. This allows distillation of high boiling temperature and / or thermolabile products. The main parts of the plant are:

- a glass distillation unit, with oil double heating mantle, which heats evaporator surface and outlet connections for distillatate and residue; evaporator temperature: 50-350°C (thermostated). Wiper basket driver motor with variable speed (optimum speed: 375 min^{-1});
- a manual feed system, dropping funnel type with heating mantle, feed flow: 0.5 to 1.5 kg/h;
- a discharge system;
- a vacuum pump system consisting of a rotary vane pump and a diffusion pump; vacuum measuring device (according to Pirani measuring principle) with vacuum gauge (wear and tear part) and digital display, measuring range 0.001 mbar - 1000 mbar;
- a heating and cooling systems with programmed temperature.

Characterization of products

The composition of ester mixtures (FAME, MG, DG, TG) resulted from the methanolysis process was determined by gas chromatography. A GC Perkin-Elmer Clarus 500 was used, equipped with FID detector and a capillary column Elite 5HT with: 15m L, 0.320 mm ID and 0.10 μm film thickness in the following chromatographic conditions: Oven Temperature program: 50°C for 1 min, 15°C/min up to 180°C; 7°C up to 230°C; 10°C/min up to 370°C; 370°C for 5 min; Carrier Gas: H_2, 20 mL/min; Detector Temp.: 370° C; Injection Temp.: 350° C; Injection Mode: Splitless; Injection Volume: 1μL.

MG and DG have low volatility and can react with the stationary phase capillary column. In order to increase volatility the sample is derivatised by silylation method which imply transformation of -OH groups from MG and DG in-$OSi(CH_3)_3$ groups, by treatment with N-methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA). 1,2,3-tricaproylglycerol (tricaproin) was used as internal standard.

Determination of calibration functions for glycerides

Calibration functions for each type of glyceride (MG, DG, TG) were calculated with the following formulas:

$$M_m/M_{et} = a_m (A_m/A_{et}) + b_m$$
$$M_d/M_e = a_d (A_d/A_{et}) + b_d$$
$$M_t/M_{et} = a_t (A_t/A_{et}) + b_t$$

where:

M_m, M_d, M_t are the masses of mono-, di-, and trioleine in mg;

M_{et} is the mass of internal standard in mg;

A_m, A_d, A_t are mono-, di-, and trioleine peak areas;

A_{et} is the internal standard peak area;

a_m, b_m are constants derived from linear regression method for monooleine;

a_d, b_d are constants from linear regression method for dioleine;

a_t, b_t are constants derived from linear regression method for trioleine

Calculation of the percentage of the glycerides in sample

Mass percentage of glycerides in sample (MG, DG, TG) was calculated using the following equations:

$$M = [a_m(\sum A_{mi}/A_{et}) + b_m] (M_{et}/m) \times 100 \text{ for MG}$$
$$D = [a_d(\sum A_{di}/A_{et}) + b_d] (M_{et}/m) \times 100 \text{ for DG}$$
$$T = [a_t(\sum A_{ti}/A_{et}) + b_t] (M_{et}/m) \times 100 \text{ for TG}$$

where:

M, D, T are the mass percentages of mono-, di-, and triglycerides in sample

$\sum A_{mi}$, $\sum A_{di}$, $\sum A_{ti}$ are surface areas of mono-, di-, and triglycerides peaks

$\sum A_{et}$ is surface area of internal standard peak

M_{et} is mass of internal standard (mg)

M is sample mass (mg)

a_m, b_m are constants for monoglyceride resulted from linear regression method

a_d, b_d are constants for diglyceride resulted from linear regression method

a_t, b_t are constants for triglyceride resulted from linear regression method

FAME concentrations were determined in both esters mixtures resulted from methanolysis and FAME fraction purified by vacuum distillation, using internal calibration GC method and as internal standard methyl heptadecanoate. We used the same GC chromatograph Perkin-Elmer Clarus type 500, equipped with FID detector and a capillary column BP X70, 50 m L, 0.22 mm ID and 25 μm film thickness in the following chromatographic conditions: Oven Temp.: 210° C; Carrier Gas: H_2, 20 mL/min; Detector Temp.: 250° C; Injection Temp.: 250° C; Injection Mode: Split, 50:1; Injection Volume: 1μL.

Ester concentration, C, expressed as mass fraction, was calculated using the formula:

$$C = \{[(\sum A) - A_{St}]/A_{St} \times (C_{St} \times V_{St})/m\} \times 100\%$$

where:

$\sum A$ is the total peaks area of methyl esters;

A_{St} is the peak area corresponding to methyl heptadecanoate;

C_{St} is the concentration of methyl heptadecanoate used, in mg / mL solution;

V_{St} is the volume of methyl heptadecanoate solution used, in mL;

m is the mass of the sample, expressed in mg

MG purified fraction by high vacuum short path distillation, was characterized by IR spectroscopy. We used a Brucker Tensor 27 FTIR spectrometer equipped with diamond ATR crystal, covering the middle infrared with a resolution of 1 cm^{-1} with the following features: Noise/signal ratio, min. 60000:1; Acuracy of wave number, 0.01 cm^{-1}@ 2,000 cm^{-1}; Spectral resolution 0.9 cm^{-1}; Spectral range 7500-350 cm^{-1}; Interferometer aligned 60 degrees high energy; Detector RT-DLATGS; IR detector include an integrated A/D convertor; Software OPUS.

Results and discussions

The methanolysis of fatty acid triglycerides consist in a set of successive reversible reactions, which are presented schematically below:

$$TG + M \rightleftharpoons DG + FAME$$

$$DG + M \rightleftharpoons MG + FAME$$

$$MG + M \rightleftharpoons G + FAME$$

MG is the most valuable product from the mixture of esters resulted in the process of methanolysis. Therefore it is desirable to obtain MG in larger concentrations and respectively DG and TG in concentrations as low as possible.

Experimental study which was followed in this paper, was established by preliminary experiments in order to determine the range of variation for the main technological parameters. Thus, it was found that the use of only amino derivatives in relatively low concentrations (1-3 % ratio to vegetable oil) lead to unacceptable results. Also, the presence of guanidine carbonate in higher concentrations than 0.1% ratio to the amount of vegetal oil determine a too much increase of FAME concentration compared to that of MG.

The following amino derivatives were tested for their catalytic activity of methanolysis reaction: N,N-dimethylethanolamine, n-butylamine, N,N-diethyl-ethanolamine, morpholine, diethylamine, ethylenediamine.

In table 1 it is observed that, when the amino compounds: N,N-dimethylethanolamine, n-butylamine and N,N-diethylethanolamine are used, the results are unsatisfactory, and that the concentration of MG and FAME in the ester fraction from methanolysis is low.

Table 2 shows the composition of ester fractions resulted in methanolysis, using a catalyst system consisting of 0.1% guanidine carbonate and 1-2% morpholine, at different time intervals. The particular case of 2% morpholine catalytic system is illustrated in figure 1. At a concentration of 12.44% MG and 49.55% FAME, ester fraction begins to show interest for their further separation.

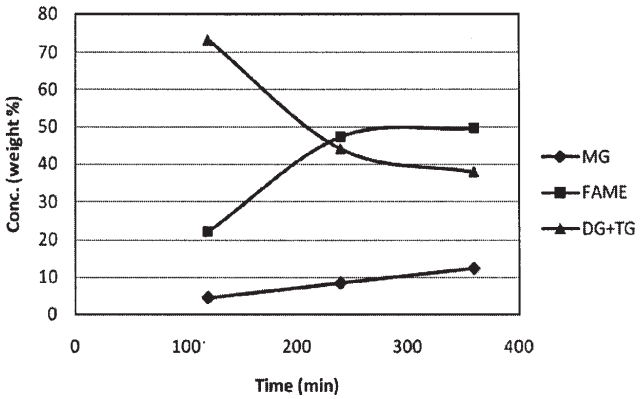


Fig. 1 Ester fraction composition in catalytic system with 2% morpholine

Replacement of morpholine with diethylamine in the catalytic system lead to positive results, as shown in table 3 and fig. 2. When it is used the catalytic system guanidine carbonate 0.1% and 2% diethylamine, ester fraction contains 16.56% MG and 62.35% FAME, after a reaction time of 480 min.

Among the catalytic systems tested, the most powerful proved to be the system containing 0.1% guanidine carbonate and 2% ethylenediamine, as reflected in table 4, respectively figure 3. After a 360 min methanolysis reaction time, it was noticed a stagnation of concentration for MG and FAME, around a value of 21.32%, respectively of 64.42%. It is not recommended to increase the concentration of ethylenediamine to 3%, because it can't bring a significant improvement.

Separation of FAME and MG by distillation in a Short Path Distillation Plant type KDL 5 has been made in three stages process. In the first stage volatiles were removed, in the second stage a FAME fraction and the bottom fraction 1 are separated, and in the third stage the bottom fraction 1 was separated in two fractions: MG and the bottom fraction 2.

No.	Amino derivatives	Conc. (wt. % *vs.* oil)	Reaction time, [minutes]	Ester fraction composition		
				FAME [wt.%]	MG, [wt. %]	DG + TG, [wt. %]
MG 1	N,N-dimethylethanolamine	2	240	31,81	6,34	61,85
MG 2	n-butylamine	2	240	30,62	6,80	62,58
MG 3	N,N-diethylethanolamine	2	240	40,94	3,45	55,61
MG 4	N,N- diethylethanolamine	2	360	44,24	6,22	49,54

Table 1
BEHAVIOUR OF CATALYTIC SYSTEM WITH AMINO DERIVATIVES

No.	Conc. (wt. % *vs.* oil)	Reaction time, [minutes]	Ester fraction composition		
			FAME [wt. %]	MG, [wt. %]	DG + TG, [wt. %]
MG 5	1	240	52,40	7,49	40,11
MG 6	2	120	22,21	4,55	73,24
MG 7	2	240	47.31	8,55	44,14
MG 8	2	360	49,55	12,44	38,01

Table 2
ESTHER FRACTION COMPOSITION FOR CATALYTIC SYSTEMS WITH MORPHOLINE

No.	Conc. (wt. % *vs.* oil)	Reaction time, [minutes]	Ester fraction composition		
			FAME [wt. %]	MG, [wt. %]	DG + TG, [wt. %]
MG 8	1	240	47,95	7,89	44,16
MG 10	2	120	41,60	7,25	51,15
MG 11	2	240	50,11	13,29	36,60
MG 12	2	360	57,55	15,28	27,17
MG 13	2	480	62,35	16,56	21,09
MG 14	4	240	36,88	8.37	54,75

Table 3
ESTHER FRACTION COMPOSITION IN CATALYTIC SYSTEMS WITH DIETHYLAMINE

No.	Conc. (wt. % *vs.* oil)	Reaction time, [minutes]	Ester fraction composition		
			FAME [wt. %]	MG, [wt. %]	DG + TG, [wt. %]
MG 15	1	240	56,50	12,94	30,56
MG 16	1	360	59,83	16,32	23,85
MG 17	2	120	33,10	11,94	54,96
MG 18	2	240	46,82	17,91	35,27
MG 19	2	360	64,42	21,32	14,26
MG 20	2	480	65,24	21,54	13,22
MG 21	3	360	66,42	20,28	13,30
MG 22	3	480	65,98	20,77	13,25

Table 4
ESTHER FRACTION COMPOSITION IN CATALYTIC SYSTEMS WITH ETHYLENEDIAMINE

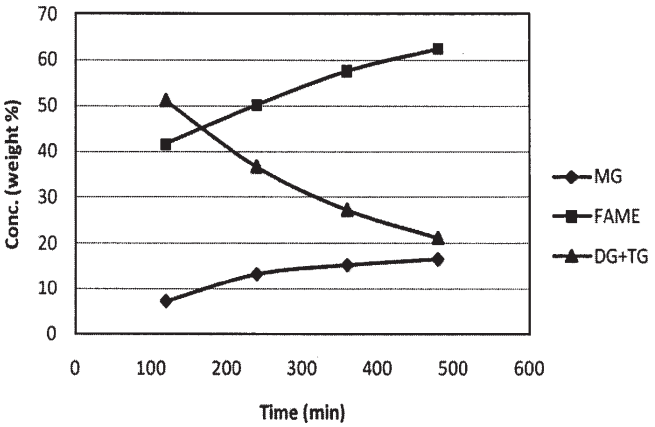


Fig. 2 Ester fraction composition variation in catalytic system with diethylamine

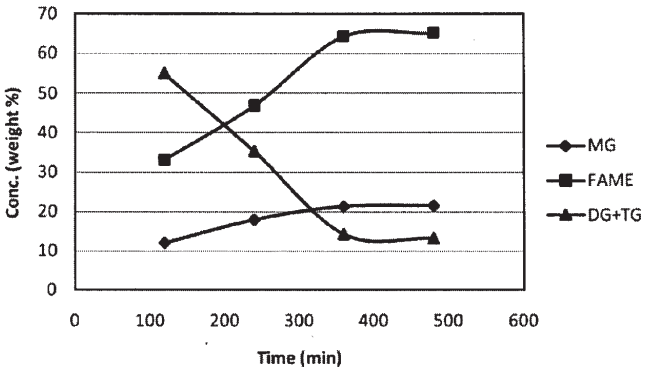


Fig. 3 Ester fraction composition in catalytic system with ethylenediamine

Table 5 shows the main operating parameters of Vacuum Short Path Distillation Plant type KDL 5, for separation of FAME and MG in three stages. Common parameters for all three stages were:

- Feed flow : 1000 mL / h
- Temperature of cold trap : -190°C (made with liquid nitrogen)

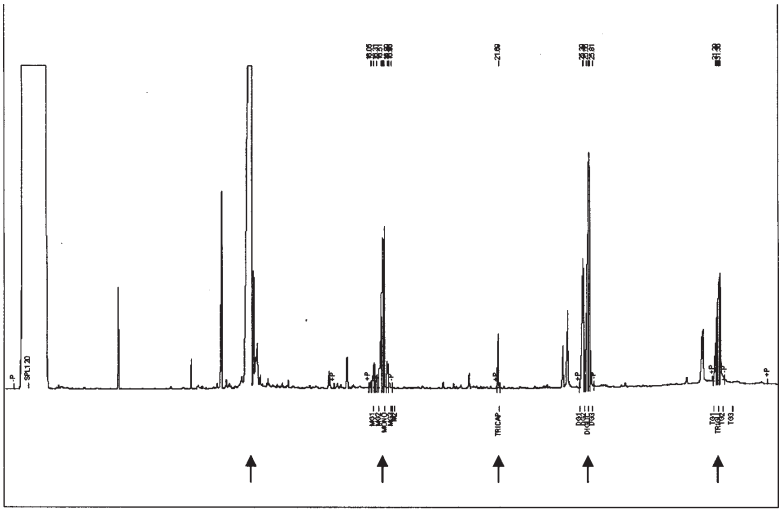
In figure 4 it is presented GC chromatogram of an ester fraction in which its components are detailed: FAME, MG, DG, TG. In tables 1-4 it was shown the composition of ester fractions, for different catalytic systems, analyzed by GC. The ester fraction compositions, obtained by using different catalytic systems, were determined by gas chromatography and are presented in tables 1- 4.

The MG fraction separated on Short Path Distillation Plant type KDL 5 was analyzed by the same GC method. After its redistillation, MG fraction has a purity of 98.8%. "Molecular fingerprint" FTIR ν(cm $^{-1}$): 3402.76, 2924.51, 2854.32, 1736.86, 1175.23, 1047.77, 723.64.

This so purified product could be used as a food emulsifier in pastries, in the preparation of ice cream, mayonnaise, chocolate, creams, etc., or as raw material

No.	Parameter	U.M.	Stage 1	Stage 2	Stage 3
1.	Feed temperature	°C	40	50	60
2.	Evaporator temperature	°C	105	155	210
3.	Residue temperature	°C	70	120	165
4.	Depression (vacuum)	bar	$8x10^{-3}$	$4x10^{-4}$	$2x10^{-6}$
5.	Rotation speed of the wiper basket	$min.^{-1}$	355	360	375

Table 5
THE MAIN OPERATING PARAMETERS OF SHORT PATH DISTILLATION PLANT TYPE KDL 5, FOR SEPARATION OF FAME AND MG



FAME MG TRICAPROIN DG TG

Fig. 4 Chromatogram of ester fraction - peaks details, FAME, MG, DG, TG

to obtain biodegradable surfactants (MG ethoxylate, sulfonate, etc.).

The FAME fraction separated on Short Path Distillation Plant type KDL 5 was analyzed by GC method with methyl heptadecanoate as internal standard. After redistillation, FAME fraction had a 99.2% purity. The product meets all quality requirements according to SR EN 14214 and can be used as biofuel, known as biodiesel. FAME fraction could be used like eco-friendly solvent and as raw material in fabrication of a wide use biodegradable surfactants (ethoxylated fatty acid methyl esters, sulphonated methyl esters, fatty alcohols, fatty acid alkanolamides, alkaline salts of fatty acids, etc.).

Conclusions

Is was established a method for obtaining fatty acid methyl esters and monoglycerides, by methanolysis of fatty acid triglycerides using homogeneous nonalkaline catalysts. The best results were obtained with a catalytic system containing 0.1% guanidine carbonate and 2% ethylenediamine (wt. % *vs.* vegetable oil) for 6 h reaction time. The ester mixtures resulted from methanolysis were separated by high vacuum short path distillation resulting in high purity fatty acid methyl esters and monoglycerides. Intermediate and final products have been analyzed by GC and FTIR methods.

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