

## ACID OILS IN FAME PRODUCTION

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Received August 7, 2013, Accepted November 25, 2013

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### Abstract

In this paper six new or innovated procedures of fatty acids methyl esters (FAME) preparation from natural triacylglycerols (TAG) with higher acidity are described. The extraction of soaps of free fatty acids (FFA) by a polar solvent such as glycerol (G), but primarily by the G-phase originating from own FAME production, is a simple procedure applicable mainly in small-scale production plants. The effective TAG deacidification is obtained also using FFA vacuum distillation in wiped film evaporators. Preliminary acid-catalyzed FFA esterification with methanol (MeOH) performed before alkali-catalyzed TAG transesterification to FAME allows a simple separation of reaction water, excess of MeOH, and acidic catalyst at appropriate reactant ratios. During FFA esterification at temperatures over 110 °C, ambient pressure and at continuous MeOH feeding to the reaction mixture, advantageous nonequilibrium conditions for effective mass and heat transfer are created. Ethanolamines, used in TAG degumming for technical application, form separable adducts with water and FFA. At high-temperature FFA esterification with G in acid oils, acidic functional groups are blocked. The mentioned procedures are technically feasible and allow decreasing TAG acidity down to 1.0 mg KOH/g or less. Conversion of acyl glycerols to FAME complies with the standard EN 14 214.

**Keywords:** triacylglycerols; FFA; FAME; esterification; transesterification.

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### Abbreviations

AG, acylglycerols; AV, acid value; D, distillate; DEA, diethanolamine; F, feed; FAME, fatty acid methyl esters; FFA, free fatty acids; G, glycerol; GL, glycerol layer; G-phase, glycerol phase from alkali based transesterification of TAG by MeOH; ME, methyl esters; MEA, monoethanolamine; MeOH, methanol; RP oil, oil from rendering plant ; TAG, triacylglycerols; TEA, triethanolamine; UFO, used frying oils; W, distillation residue.

### 1. Introduction

Methyl esters of higher fatty acids are generally accepted as a full-valued and equivalent alternative fuel extractable from renewable sources for diesel engines or as component of blended fuels for such engines. FAME are prepared by alkali-catalyzed transesterification of vegetable oils or animal fats with methanol (MeOH), usually in a two-step process occurring at a temperature up to 65°C and reaction times of about 100 minutes in each of the steps at a various ratio of acylglycerols: methanolic solution of alkaline. In each of the two reaction steps, a separate glycerol-containing phase is formed having a higher density which causes its settling out and shifting the reaction equilibrium towards products.

Acidic components and water, when present in reaction media, exhibit an extremely adverse impact on alkaline catalyst KOH, NaOH or alkaline methoxides. The alkaline catalyst reacts with organic acids producing catalytically inactive alkaline soaps. Due to their emulsifying potential, alkaline soaps are even in the presence of small water quantities able to emulsify the glycerol (G) originated in the reaction preventing thus the products from forming. The water present in alkaline media both decomposes the alkaline methoxide acting as actual catalyst, and causes hydrolysis of acylglycerols to free fatty acids (FFA) being in turn transformed to alkaline soaps exhibiting the above mentioned undesirable effects.

In connection with transesterification, there are some unavoidable water sources. It means that obvious contents of water and acids must be reduced to the lowest reachable values. It follows from common experience that the water content in oil approachable *via* common operations applied in oil preparation should not exceed 0.1% wt. The content of water in MeOH should not be higher than 0.3% wt., i.e. MeOH content should not drop down to less than 99.7%. The used hydroxides are strongly hygroscopic compounds; however, their water content should be of minimum value. The water content in KOH usually reaches 10-15% wt., in NaOH it approaches to 1-2% wt.

The acid value (AV) of the oil used for transesterification may be about 2.0–2.5 mg KOH/g. At higher values - about 4.0 mg KOH/g - a substantial decrease in acylglycerols-to-methyl esters conversion is found together with an increase in glycerol phase formation (G-phase) with a consequence of a lower yield of methyl esters (ME). When the oil AV exceeds 4.5 mg KOH/g, no reaction usually occurs and the separate G-phase is not formed. A state characterized by ceased reaction may happen at a substantially lower AV of the oil or fat feedstock provided that water content in the reaction system is higher. The optimum oil AV is in the range of 1.0–1.5 mg KOH/g, when the conversion reaches 98%; yield of FAME, based on the treated oil quantity, is higher than 96% and within the final treatment raw FAME reflect the technological steps in optimal mode. Such AV may be maintained without any special measures adopted both for stored and pressed oil sources. On the other hand, at low input oil AV (below 0.5 mg KOH/g) some modifications in the catalyst composition need to be employed.

The current increase of production and interest in methyl esters is characterized by high price of crude oil. This fact leads to considerations taking into account such sources of acylglycerols (AG) that are, owing to their parameters such as a higher AV, not suitable for direct utilization in transesterification. A higher level of oil AV may be a consequence of several reasons. Oils occurring in the nature are naturally of acidic character. These oils can be exemplified by palm oil playing a crucial role in both the oil and ME production in the south-east Asia. A high content of saturated palmitic acid with unsuitable low-temperature properties and also a high content of carotenoids are typical for palm oil. Its AV usually ranges from 5 to 15 mg KOH/g. Among its typical features, the high hectare yield and relatively low price should be mentioned. One of the reasons of its increased acidity is improper handling with oil and/or seeds (improper storage) giving rise to hydrolytic processes catalysed by the enzyme lipase. The issue may, however, concern old oxidized oils, oils exposed to water influence at higher temperatures (hydrolysis), waste edible oils/fats, etc. While oil dehydration – water removal – is feasible in practice at a higher temperature and lower pressure in suitable equipment, oil deacidification represents a more serious problem.

Several series of more or less complex and efficient procedures solving the task of oils and fats deacidification preceding their transesterification are described in the literature. For example, a two-step procedure consisting of acid-catalyzed FFA esterification with MeOH to their ME in the first step followed by alkali-catalyzed acylglycerol transesterification with MeOH to FAME performed in the second step [1–7]. In articles dealing with used frying oils (UFO) and other waste TAG as a source of low cost TAG, the process of optimization is solved as well [8–14]. New types of oils and fats, especially those inedible, their properties and specifications are described in [15–19]. Considerable attention is devoted to heterogeneous catalysts, mainly those belonging to solid super acids [20–27]. In an effort to rationalize FAME production from acid oils, accelerating technological steps, such as ultrasonic and microwave techniques are applied [28–32].

This study is aimed at presenting some available technological processes lowering the acidity in the reaction mixture for FAME preparation in particular on the following six directions with real chance of their utilization in the praxis:

- 1) FFA extraction using a polar solvent [33];
- 2) Physical refining by means of vacuum evaporation of FFA [34];
- 3) Preliminary FFA esterification followed by separation of the polar phase with a lower density than that of ester phase [35];
- 4) High-temperature esterification of FFA with MeOH at ambient pressure [36];
- 5) Reaction of FFA with ethanolamines [37];
- 6) High-temperature FFA esterification with G [38].

## 2. Materials and Methods

### 2.1 Materials

Acidic oils and fats used at tests were obtained from collectors of used frying oils and from other local sources. Used chemicals were purchased from Mikrochem Pezinok, Slovakia.

### 2.2 Methods

Known procedures described in commonly available literature were applied for esterification reactions. At each procedure, conditions for reaction water removal from reaction mixture were formed in an effort to shift equilibrium towards direction of product formation. Within transesterification and final treatment of deacidified oils/fats the mode described in [39] was applied.

Conversion of AG into FAME was determined by GL chromatography using the methodology referred to in [40]. The method is based on the comparison of FAME peak areas in the sample before and after the sample treatment with an efficient transesterification agent. Analytic measurements were carried out using the gas chromatograph Chrompack CP 9000 with a flame-ionization detector and a 1.8 m glass packed column of internal diameter of 0.3 cm. 10% SE 30 on Chromatone NAW DMCS, particle size of 0.125–0.16 mm was used as stationary phase. Samples were analyzed isothermally at 250 °C. The injector temperature was 240°C, the FID temperature 270 °C. Nitrogen having the flow rate of 30 cm<sup>3</sup> min<sup>-1</sup> was used as carrier gas.

The ester content was determined by a standard technique according to EN 14 103 involving gas chromatography. The resulting values were obtained by taking the arithmetic average of three measurements.

The AV was determined according to EN 14 104 using 50:50 (v/v) toluene–ethanol solvent.

## 3. Results and Discussion

### 3.1. FFA extraction using polar solvent

Simple and effective deacidification of acidic oil or fat can be obtained through extraction of acidic oils by G-phase having been formed during transesterification, i.e. just within FAME production. Besides G, MeOH, FAME and alkaline soaps, the G-phase contains also free alkalis reacting with acids and forming alkaline soaps concentrated in the G-phase. This mode of deacidification exhibits one more significant advantage. If the oil contains a higher level of moisture, it is transferred into polar G-phase within extraction by the G-phase and becomes automatically dried. Within the modification only those substances participating in the standard process of FAME production are applied. Another advantage lies in the fact that valuable fatty acids are rather transferred into the G-phase in the form suitable for their recovery *via* their decomposition with a mineral acid than became irreversibly lost from the process. Applying a suitable procedure they can be converted to FAME [36]. At some laboratory experiments, oil bleaching following its extraction was observed.

In case of the insufficient alkaline reserve of the G-phase itself based on the AV of the oil feedstock, it can be increased by an addition of concentrated hydroxide solution to the G-phase, e.g. by fortification of the G-phase by alkaline. The quantity of added hydroxide solution must be predetermined based on preliminary testing because of different alkaline reserves of various G-phases. The amount of alkaline to be added to the G-phase used for extraction is calculated stemming from the mass balance taking a lower efficiency of the process into account. It is recommended to perform a control extraction in laboratory scale and to determine the optimum content of alkaline in the G-phase used for the extraction.

Extraction may benefit from a higher temperature about 50°C both in continuous or discontinuous modes providing an intensive short-term contact of both streams. A mixture of the treated oil and the G-phase is settled out without any agitation, the sedimentation may, however, be accelerated in a centrifugal separator. Extraction should provide transparent oil. Subsequent to sedimentation, it is necessary to determine the AV of the upper oil phase. If the value is acceptable, the lower G-phase can be pumped off the reactor and the first step of standard transesterification can be initiated. In case the oil AV is not low enough, the extraction should continue after adding a further volume of the concentrated alkaline solution or also without such an addition in the case of insufficient duration and intensity of mixing.

The mass balance of acidic oils extraction by G-phase is complicated, dependent on several factors and ambiguous. It is obvious that acidic components are transferred from the oil into the G-phase in the form of soap with a consequence of the oil mass loss. Similarly, water transfer into the G-phase will result in the loss of oil mass. On the other hand, MeOH is partly transported from the G-phase to the oil and, in addition, an equilibrium distribution of FAME between the oil and the G-phase can be anticipated; the FAME enter the G-phase owing to the emulsion effects of soaps. The equilibrium conditions are thus determined by several factors. At laboratory experiments, an increase in the mass of extracted oil after the extraction was found in some cases. More frequently, however, a decrease in the oil phase mass by some % was observed.

The AV of the oil introduced to the extraction should be restricted, the limiting AV should not exceed 10-15 mg KOH/g.

Typical conditions applied within such physico-chemical pretreatment of higher AV oils/fats and of AG-to-ME conversion following the standard procedure of ME production and those applied in the ME final treatment are listed in Table 1.

Table 1 Examples of deacidification of oils through extraction by G-phase; G-phase input to TAG = 15 % w/w

Test No.	Input oil, its AV	Fortification of G-phase with alkaline	AV of output oil, mg KOH/g	output G-phase, %	Conversion %
1- 1	UFO, 15.0 mg KOH/g	25% KOH / MeOH, 3.6 g /100g TAG	1.4	144	98.1
2 - 1	UFO, 3.7 mg KOH/g	no fortification	0.5	97	95.9
3 - 1	UFO, 7.1 mg KOH/g	25% KOH / MeOH, 0.4 g / 100g TAG	2.2	107	98.6
4 - 1	Beef tallow, 7.7 mg KOH/g	25% KOH / MeOH, 0.7 g / 100g TAG	1.9	86	99.0
5 - 1	UFO, 11.1 mg KOH/g	25% KOH / MeOH, 2.4 g / 100g TAG	2.5	121	97.4
6 - 1	Palm oil, 11.4 mg KOH/g	20% KOH / MeOH, 3.4 g / 100g TAG	2.5	135	97.0

UFO – used frying oil, AV – acid value; G-phase – G-phase from transesterification

### 3.2 Physical refining of acidic oils in a wiped film molecular evaporator

Another effective alternative mode of pretreatment of acidic oils and fats before their transesterification is their deacidification performed by distillation in a wiped film molecular evaporator, associated with the effective dewatering of the materials. The essence of the method lies in the different volatility of FFA with the molar mass of 270-300 g/mol and that of TAG with the molar mass of 870-900 g/mol. Molecular evaporator allows thus to separate FFA and lipids with a high efficiency.

Molecular distillation is the gentlest method of distillation serving to separate and purify both thermally unstable high-molecular substances and liquids with low vapour tension. If performed continuously in a film evaporator, the characteristic features of molecular distillation may be defined as follows:

- The pressure of incondensable gases in the equipment is rapidly dropped to about  $10^{-1}$ - $10^{+1}$  Pa leading to a reduction in distillation temperature by 200–250°C comparing to that at normal pressure;
- Distance between the surfaces of evaporation and condensation is small (20-50 mm), which in combination with the low pressure gives rise to the high rate of distillation ranging from 20 to 40 g m<sup>-2</sup> s<sup>-1</sup>, and such a rate is interesting for operational practice, too;
- Liquid distribution in a wiped film with a thickness of 0.05-2 mm given the liquid viscosity and feed rate ensure that the liquid dwells on heated surfaces only for a short time varying from some seconds to tens of seconds. This fact, coupled with the lowered operational temperature, results in only negligible yield of decomposition products and in occurrence of the process without almost any thermal decomposition. A marginal partial pressure of oxygen is of key importance from the view of the thermal decomposition.

In the evaporators with wiped film, the liquid forming the film layer of the evaporation surface is continuously stirred by a wiper and uniformly distributed along with the whole evaporator.

This creates advantageous conditions for the mass and heat transfers, as well as the compensation of concentration and temperature gradients originating in the film due to intensive evaporation. Moreover, deposits and resin substances are removed from the evaporation surface attaining thus utilization of the whole evaporation surface. The positive effect of the wiping is reflected in a high evaporation performance approaching  $100 \text{ kg m}^{-2} \text{ h}^{-1}$  at maintaining a minimum level of the thermal decomposition and separation capacity close to theoretical values which are, however, rather low and correspond to one theoretical stage. The evaporator is still of simple design and it is possible to construct large apparatus with the evaporation surface up to  $40 \text{ m}^2$ . Based on the liquid viscosity and quantity, wiper kind and tip speed, an average thickness of the wiped film ranges from 0.1 to 0.5 mm. In the evaporators fitted with a properly designed wiper, liquids with a viscosity up to  $50 \text{ Pa s}$  may be processed.

This separation method profits in the field of oils or fats deacidification from the fact that FFA are obtained as relatively pure substances and can be subsequently used for various purposes. On the other hand, the investment and operational demands represent a drawback side. In practice, there are no limitations relating to oil AV. We apply this technology mainly for physical refining of edible oils [41] and it has been implemented in several technological units. In the framework of ME final treatment, vacuum distillation ensures almost all ME parameters which may be affected in operation within the meaning of standard EN 14 214.

In Table 2, typical conditions of a vacuum evaporator application at oils deacidification, corresponding yields and other data are listed. An evaporation degree of the light acidic fraction usually corresponds to about half of AV of the treated oil.

Table 2 Deacidification of oils and fats using molecular distillation

Test No.	Input oil/fat (F)	AV (F), mg KOH/g	t, °C	p, Pa	D/F.100%	AV (D), mg KOH/g	AV (W), mg KOH/g	Conversion, %
1 - 2	RP oil	41.9	200	20	23.2	175	0.6	98.9
2 - 2	RP oil	27.6	200	30	14.2	182	1.2	98.2
3 - 2	RP oil	32.2	200	60	17.4	180	0.8	99.5
4 - 2	RP oil	38.5	200	70	20.0	181	2.1	96.8
5 - 2	Pelt	36.4	200	10	17.8	187	4.4	-
6 - 2	Rapeseed	34.4	200	5	18.4	160	2.1	98.5
7 - 2	RP oil	30.0	230	15	18	168	0.4	98.8
8 - 2	UFO	7.5	200	20	4.0	170	0.8	97.9
9 - 2	UFO	11.5	200	30	6.5	165	1.3	98.1
10 - 2	UFO	59.0	220	15	32	172	4.0	-
11 - 2	Palm	18.0	200	20	8	178	3.3	94.6
12 - 2	Beef tallow	7.7	200	30	3.5	177	1.9	97.8

RP oil – oil/fat from rendering plant; UFO – used frying oil; F – feed; D – distillate, W – distillation residue; AV – acid value

### 3.3 Preliminary esterification of acidic oil/fat

The process [35] belongs to the group of two-step procedures consisting of acid-catalyzed esterification of FFA with MeOH in the 1st step followed by alkali-catalyzed transesterification in the 2<sup>nd</sup> step. In the procedure, ratios of reactants are favourably applied so as termination of the esterification step is accompanied by the separation of the polar phase containing unreacted MeOH, acidic catalyst and process water as separate liquid phase having a lower density than that of the ester phase. Low density of MeOH (approximately  $790 \text{ kg m}^{-3}$  at  $20^\circ\text{C}$ ) comparing to that of TAG about  $910 \text{ kg m}^{-3}$  at  $20^\circ\text{C}$  is a key element together with a relatively high molar excess of MeOH versus FFA 10:1 to 20:1 which is however, after recalculation to the weight ratio, small. For example, an addition of 17.1 g MeOH to 150 g oil with AV 13.6 mg KOH/g represents a FFA:MeOH molar ratio equal to 1:15 (test 1-3, Tab. 3). Water-MeOH layer containing most of the process water and almost all loaded acidic catalyst can be separated using common procedures and pure MeOH as well as the acidic catalyst can be recovered and both are usable without any further treatment. In case of a heterogeneous acidic catalyst, its replacement does not pose any serious problem. Due to small amounts of the MeOH used at acid esterification within the preliminary stage, the mass of water-MeOH phase introduced into the recovery stage is small as well. Even if the preliminary esterification is not carried

out at optimum conditions, the reaction will still proceed, however, with the need of additional separation operations. When keeping to the optimal state, only sedimentation or final dewatering is to be done. Both, the preliminary esterification and the subsequent transesterification are performed at mildly elevated temperatures and ambient pressure, or at a pressure moderately increased up to 5 bar, i.e. no costly pressure equipment is needed.

Table 3 Acidic catalyzed esterification of FFA in acid oil with MeOH

Test No.	Input oil, its AV	FFA:MeOH, mol/mol	light fraction, AV	AV of output oil	TAG conversion, %
1 - 3	rapeseed oil 13.6 mg KOH/g	1 : 15	14.3 g 49.6 mg KOH/g	1.0 mg KOH/g	98.0
2 - 3	RP oil 32.2 mg KOH/g	1 : 25	59.0 g 9.9 mg KOH/g	0.60 mg KOH/g	97.1

RP oil – oil/fat from rendering plant; reaction conditions: temperature 65 °C, time of the reaction 2 h, atmospheric pressure; catalyst: H<sub>2</sub>SO<sub>4</sub> 0.5 % w/w from TAG mass; AV – acid value

The process may run both in continuous or discontinuous mode. In the esterification stage, other lower alcohol (C2 - C4) may be applied instead of MeOH. The use of MeOH, which is exclusively employed in the subsequent transesterification is, however, preferred. Another advantage consists in purposefully performed removal and disposal of FFA within the preliminary stage, since these acids exhibit an adverse effect in the alkali-catalyzed transesterification. FFA are thus transformed to target FAME in a single step without any necessity of their separation. It leads to a higher yield of FAME based on input oil and/or fat.

### 3.4. High-temperature FFA esterification with MeOH at ambient pressure

Acid-catalyzed FFA esterification with MeOH at ambient pressure and temperature higher than MeOH boiling temperature at the continuous feed of MeOH into reaction media showed that the FFA-to-ME conversion is remarkable higher reaching 99 % within a relatively short time of some tens of minutes at a small 3-4 molar excess of MeOH to FFA at such process arrangement [36].

Table 4 Esterification of FFA with MeOH at ambient pressure Batch of the acidic component 180 g

Test No.	Input AV, mg KOH/g	PTSA, % wt	MeOH, mL/min	<i>t</i> , °C	Output AV/ $\tau$ mg KOH <sup>-1</sup> /min	<i>n</i> (MeOH)/ <i>n</i> (FFA) final
1 - 4	84.5	0.5	0.7	90	1.2/160	17.7
2 - 4	84.5	0.5	0.7	98	2.8/110	12.3
3 - 4	84.5	0.5	0.7	117	3.1/50	5.6
4 - 4	84.5	0.5	0.7	126	2.9/50	5.2
5 - 4	84.5	0.5	1.2	70	1.1/125	24.8
6 - 4	84.5	0.5	1.2	83	2.9/80	15.7
7 - 4	84.5	0.5	1.2	107	2.1/40	21.3
8 - 4	84.5	0.5	1.2	125	2.2/40	7.5
9 - 4	118.0	0.5	0.7	77	3.3/130	10.5
10 - 4	118.0	0.5	0.7	106	2.5/80	6.3
11 - 4	118.0	0.5	0.7	115	2.8/70	5.6
12 - 4	118.0	0.5	0.7	127	2.6/50	4.4
13 - 4	118.0	0.5	1.2	76	3.1/90	13.3
14 - 4	118.0	0.5	1.2	90	3.5/70	10.1
15 - 4	118.0	0.5	1.2	120	1.9/50	7.0
16 - 4	118.0	0.5	1.2	121	1.7/60	9.1
17 - 4	201.5	0.7	0.7	77	2.6/180	5.6
18 - 4	201.5	0.7	0.7	90	2.7/150	4.7
19 - 4	201.5	0.7	0.7	99	3.2/120	3.5
20 - 4	201.5	0.7	0.7	116	2.5/120	3.7
21 - 4	201.5	0.7	2.0	72	2.7/140	8.0
22 - 4	201.5	0.7	2.0	94	2.8/80	4.9
23 - 4	201.5	0.7	2.0	111	2.8/60	3.8
24 - 4	201.5	0.7	2.0	116	2.5/60	3.7
25 - 4	196.0	0	2.0	116	116.3/240	24.0

AV – acid value; PTSA – *p*-toluene sulphononic acid;  $\tau$  - reaction time;



Table 4 summarizes the initial values of AV, *p*-toluene sulphonic acid as catalyst, MeOH flow rate, temperature of reaction mixture, final AV, reaction time and final molar  $n\text{MeOH}/n\text{FFA}$  ratio.

In the esterification procedure acidic component together with the catalyst was inserted into a stirred reactor maintained at a defined temperature. When the required temperature was reached, MeOH started to be pumped into the reactor at the selected rates through a narrow PTFE pipe ending at the bottom of the reactor. Due to evaporation of MeOH, the temperature of the reaction mixture slightly decreased during the MeOH flow. MeOH entered the reactor in the liquid state. Here, in the medium with the temperature about 50-60°C higher than its boiling point it evaporated relatively quickly, and along its journey as vapour through the layer of the reaction mixture to the downward cooler it reacted with FFA. The measurement was completed after reaching a low AV usually around 2-3 mg KOH/g.

The high reaction rate, 2-3 times higher than that at the temperatures close to the boiling point of MeOH is allied to the following factors: the reaction temperature being higher by 50-60°C than the MeOH boiling point, the reaction system is kept far from the chemical equilibrium by high local molar excess of MeOH versus FFA, and efficient dewatering of the reaction system. Non-equilibrated conditions formed in this way are probably the main driving force of the process, increasing its reaction rate. Test No. 25 in Table 4 is repeated test No. 23, but without the use of catalyst. The measurement without the catalyst revealed that the reaction rate of the non-catalyzed reaction is under the same conditions approximately 35 times lower than the rate of the catalyzed reaction.

The presented method of esterification enables to achieve a high conversion of FFA to FAME, exceeding 99 %. Low acidity of the reaction mixture at the end of the reaction reaching the level of 2-3 mg KOH/g corresponds roughly with the contribution of the catalyst, and subsequent to extraction with water it can decrease below 1 mg KOH/g. At the end of the reaction the reaction mixture contains no free MeOH or water. Low acidity of the final reaction mixture is also acceptable from the point of view of its utilisation as fuel for diesel engines with modified engine periphery for two fuel systems [42]. The maximum allowed acidity of 0.5 mg KOH/g for this application can be ensured for example by the adsorption on alumina or by neutralization with  $\text{Ca}(\text{OH})_2$  and filtration. High excesses of MeOH in order to achieve FFA-to-ME conversion over 99 % of are not necessary and the consumption of MeOH corresponds with the molar ratio of MeOH: FFA between 3:1 and 4:1. Described convenient process set-up can be applied both in the batch and continuous productions. In comparison with classical set-up of esterification, it represents significant rationalization and intensification.

### 3.5 Ethanolamines used for deacidification and drying of rapeseed and sunflower oils

Pure vegetable oils can be used as alternative fuel for standard unmodified diesel engines, provided the oil viscosity has been lowered by heating before they enter the fuel injection system [42]. In its role as diesel fuel a vegetable oil has to have, among other parameters, a low acidity and low contents of phosphorus and alkaline earth metals Ca+Mg. Such parameters can be achieved by appropriate partial refining of oil by degumming. Three common ethanolamines: monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA) were used as degumming agents for removing non-hydrolyzable phospholipids from crude rapeseed and sunflower oils. Among the studied ethanolamines, MEA is the most effective for the removal of phosphorus. After degumming with MEA (0.5 wt. %), the phosphorus content dropped down from 445 to 3.5 ppm in rapeseed oil and from 163 to 2.2 ppm in sunflower oil. After oil treatment with MEA (1.0 wt. %), the residual content of Ca and Mg decreased from 136 to 4.2 ppm, and from 55.4 to 1.1 in rapeseed oil. In sunflower oil the values of Ca and Mg decreased from 23.9 to 1.5 ppm and from 24.6 to 1.0 ppm. The advantage of this oil treatment process is that it takes place at ambient temperature, results in lower production costs and simpler technology.

Crude rapeseed and sunflower oils contain small amount of FFA up to 1.0 wt. %, reflected in their AV of up to about 2.0 mg KOH/g. During the degumming using ethanolamines, neutralization of FFA in oil takes place in a single step together with the degumming process. Ethanolamines and FFA may combine together to form the ethanolamine salts of fatty acids. The salts precipitate, and can be removed by centrifugation. These ethanolamine salts may

play an important role in converting the non-hydrolyzable oil-soluble complexes with divalent metal ions Ca and Mg into more hydrolyzable species. Ethanolamine salts of fatty acids may also form complexes with divalent metal ions and contribute to their removal from the oil. TEA reduced the AV of rapeseed and sunflower oils but not as efficiently as did MEA and DEA. Moreover, the ethanolamines are weak bases and do not saponify the TAG. Tab. 5 shows the effect of ethanolamines on AV decreasing of rapeseed and sunflower oils.

Table 5 Effect of ethanolamines on AV decreasing of rapeseed and sunflower oils

Test No.	Crude input oil	AV of tested oils, mg KOH/g		
		Rapeseed 1.07 ± 0.2	Sunflower 1.35 ± 0.1	
1 – 5		0.5	0.20 ± 1.8 × 10 <sup>-2</sup>	0.24 ± 1.8 × 10 <sup>-2</sup>
2 – 5	MEA % wt.	2	0.07 ± 9.0 × 10 <sup>-3</sup>	0.10 ± 1.2 × 10 <sup>-2</sup>
3 – 5		4	0.02 ± 5.3 × 10 <sup>-3</sup>	0.02 ± 7.1 × 10 <sup>-3</sup>
4 – 5		0.5	0.21 ± 2.2 × 10 <sup>-2</sup>	0.25 ± 2.2 × 10 <sup>-2</sup>
5 – 5	DEA % wt.	2	0.07 ± 5.0 × 10 <sup>-3</sup>	0.09 ± 1.2 × 10 <sup>-2</sup>
6 – 5		4	0.02 ± 2.7 × 10 <sup>-3</sup>	0.02 ± 4.2 × 10 <sup>-3</sup>
7 – 5		0.5	0.54 ± 4.1 × 10 <sup>-2</sup>	0.67 ± 1.9 × 10 <sup>-2</sup>
8 – 5	TEA % wt.	2	0.17 ± 7.1 × 10 <sup>-3</sup>	0.29 ± 5.2 × 10 <sup>-3</sup>
9 – 5		4	0.07 ± 4.2 × 10 <sup>-3</sup>	0.12 ± 2.3 × 10 <sup>-3</sup>

MEA – monoethanolamine; DEA – diethanolamine; TEA – triethanolamine

The obtained results show that the degumming of vegetable oils with the use of ethanolamines is a suitable operation for treating vegetable oils destined for direct use as fuel for diesel engines. The low P content is important because of the correct function of the emission catalyst; the presence of Ca and Mg, as ash-forming components, is undesirable. This operation is also suitable for the pre-treatment of vegetable oils for FAME preparation by alkali-catalyzed transesterification of vegetable oils with MeOH.

The benefit of the presented process is that it takes place at temperatures 20 to 30°C with sufficient efficiency without requiring extra energy, resulting in lower production costs, time savings and simpler technology. The used agent is an easily available and inexpensive substance. The addition of water at the end of treatment does not increase its content in the final treated oil, because its excess is bound to the complex ethanolamine phospholipids, or ethanolamine-FFA, and can be removed together with these polar substances from the oil environment by sedimentation or centrifugation. The energy and equipment intensive process of drying oil are thus avoided.

### 3.6 High temperature FFA esterification with G

The acidity of vegetable oils and animal fats stems from FFA which form part of TAG and in the free form are present as products of hydrolysis, frequently catalysed by the enzyme lipase. FFA react with alkaline catalyst producing catalytically inactive alkaline soaps. There are also natural TAG, e.g. palm oil, with the acidity about 15 mg KOH/g. The permitted AV limit of TAG for transesterification is usually up to 3.0 mg KOH/g as a maximum. At higher acidity values the reaction either does not occur and two distinct phases are not formed, or it occurs with a low yield and low TAG-to-FAME conversion. In case of the use of vegetable oils or animal fats as fuel for engines with the periphery adapted for two-fuel regime [42] a higher acidity may cause corrosion. For such application the standard DIN V 51 605 allows the acidity up to 2.0 mg KOH/g as a maximum.

As mentioned above, TAG acidity can be decreased by several ways, apart of other routes also through neutralization of the oil by aqueous solution of alkali lye. This procedure, used within the production of edible oils, can be applied only at low oil AV, since the formed alkaline soaps emulgate oil in water and cause its substantial loss and ecological issues.

In this connection, a new procedure to lower TAG acidity was elaborated by pre-esterification of oils and fats having AV ranging from 3 to 50 mg KOH/g with glycerol in aqueous or alcohol solution of alkali lye [38]. The reaction occurs at temperature 100-200 °C and pressure 1-50 kPa during 1-10 hours. The method offers an advantage to replace pure G for neutral salt-water



solution of G containing 75-95 % wt. G, 2-10 % wt. water, 2-8 % wt. salts, and 1-8 % wt. MeOH named as G-layer. The salt-water solution is obtained as the bottom layer after decomposition of the G-phase originated from alkaline-catalyzed transesterification of TAG with MeOH. As for operating facilities, the procedure is simple and modest, basically it represents a single-step synthesis.

The final treatment of the product consists of sedimentation or centrifugation, and scrubbing of oil or fat layer with water. The yield is high and by-products are environmentally friendly. The key step lies in adding alkaline hydroxide to acidic oil or fat. This forms a small amount of soaps playing subsequently the important role of emulsifying agent and providing good contact of mutually non-miscible reactants G and FFA. FFA being in the form of soaps do not participate in esterification with G and are scrubbed from the reaction mixture by water. With the aim to reach maximum yield of AG from the present fatty acids, only small amount of alkaline hydroxide is used. Here, alkaline hydroxide does not function as catalyst, the esterification is acid-catalyzed by hydrogen cations of the free fatty acids. The G-phase formed in FAME production is decomposed by a strong mineral (e.g. phosphoric, sulphuric, or hydrochloric) acid, so as pH of the salt-water solution of G is about 4.5 and its AV about 0.9-2.2 mg KOH/g. The original G-phase is transformed at decomposition by mineral acid to so-called G-layer, which is neutral salt-water solution of G, containing after partial removal of water, salt and MeOH usually 75-95 % wt. G, 2-10 % wt. water, 2-8 % wt. salts, and 1-8 % wt. MeOH. The present salts, originating from both the esterification catalyst in FAME production and the treatment of originally acidic salt-water solution of G, do not interfere the esterification. Due to partial evaporation of water from the G-phase, part of the dissolved salts crystallizes and is removed from the system, which leads to an increase in G concentration. During water evaporation almost all MeOH is removed as well. The temperature and pressure are set optimally in order to reach the average rate of the reaction at a minimum G evaporation and effective water removal from the system. The esterification is completed in nearly water-free media, G is separated from the present solid inorganic salts by sedimentation or centrifugal separation and can be used in a new cycle. The final product is water-free oil/fat phase with AV of 0.1-1.0 mg KOH/g, suitable for using the oil/fat in alkaline transesterification to FAME or as fuel in engines with the periphery modified for two-fuel regime. The residual ash content less than 0.1 %, which is a crucial requirement for the above mentioned use in engines with two-fuel regime, is provided applying extraction of oil/fat phase after esterification by aqueous solution of low-concentrated ethanol or propan-2-ol. This extraction results also in the removal of G from the modified oil/fat. The measured data are gathered in Table 6.

Table 6 Catalyzed esterification of FFA in acid oil with G

Test No.	Input oil, its AV	Type of G, G:FFA, mol/mol	50% NaOH, wt. %	Reaction conditions, t, p, τ	Output oil, its AV
1 - 6	used frying oil 12.6 mg KOH/g	Refined 99 % G 1 : 0.091	0.20	200 °C, 1.6 kPa, 5 h	0.30 mg KOH/g
2 - 6	rapeseed oil 13.6 mg KOH/g	GL, 93 % G 1 : 0.25	0.15	180 °C, 3.2 kPa, 4 h	0.60 mg KOH/g
3 - 6	rapeseed oil 10.1 mg KOH/g	GL, 80 % G 1 : 0.18	0.15	180 °C, 3.2 kPa, 4 h	0.35 mg KOH/g
4 - 6	rapeseed oil 13.6 mg KOH/g	GL, 80 % G 1 : 0.25	0.10	200 °C, 3.2 kPa, 5 h	0.35 mg KOH/g

G - glycerol; GL - G-layer, t - temperature; p - pressure; τ - reaction time; AV - acid value

Using the above mentioned procedure, AV of oil/fat phase is reduced to 0.3-0.5 mg KOH/g. The ash content ranges from 0.4 to 0.6 % wt. Its content can be substantially reduced down to 0.10-0.16 % wt. through the extraction of oil/fat phase by 1-5 % aqueous solution of ethanol or propan-2-ol.

Data in Table 6 demonstrate the applicability of FAME production as an alternative fuel for diesel engines also from waste oils and fats with a high acidity, which are not suitable for alkali-catalyzed transesterification of TAG by usual procedures.

#### 4. Conclusion

Utilizing the developed effective and environmentally friendly deacidification procedures in the systems of TAG enables almost unlimited full-valued processing of vegetable oils and animal fats in the production of FAME attaining all the parameters stipulated by the standard EN 14 214, with a possible exemption of low-temperature properties and iodine value. A wide choice of procedures allows to apply an optimal modification for a particular customer.

#### Acknowledgement

Support of the Slovak Grant Agency, Grant VEGA No. 1/0539/13 is acknowledged.

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