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METHANOLYSIS AND ETHANOLYSIS OF ANIMAL FATS: A COMPARATIVE STUDY OF THE INFLUENCE OF ALCOHOLS

Biodiesel from animal fats with methanol and ethanol was produced in the presence of sodium methoxide and sodium ethoxide as catalysts. Two samples of pork fats and one natural beef tallow were directly transesterified with a good final product yield: 87.7, 86.7 and 86.3% for methanolysis, and 78.4, 82.6 and 82.7% for ethanolysis, respectively. Methyl ester content was also determined, being higher than 96.5 mass% for all the samples prepared. The presence of natural C17:0 in animal fats makes it necessary to correct the method proposed in the standard EN 14103 (2003). Biodiesel density at 15 °C of the samples was between 870 and 876 kg/m³, within the acceptance range of standard EN 14214, and the dynamic viscosity at 40 °C of the produced biodiesels was in the range of 4.5 to 5.16 mm²/s, also fulfilling requirements of EN 14214 standard. The iodine value is much lower than the superior limit established by EN 14214 standard but oxidation stability (OSI) is lower than the required limit, 6 h, of the standard, which can be attributed to the lack of natural antioxidants in tallows.

Key words: Biodiesel; animal fat; transesterification; ethanolysis; methanolysis.

The growing global emission of carbon dioxide and the progressive reduction of fossil energy resources have been major global concerns for several years now. The use of fuels made from biomass such as biodiesel and bioethanol can help satisfy the need of energy forms with renewable sources.

Biodiesel offers many benefits as an alternative fuel, among which are its derivation from renewable sources as well as its biodegradability and lower ecotoxicity in comparison with petroleum-based diesel. Furthermore, biodiesel has a more favourable combustion emission profile concerning carbon monoxide, particle emission and unburned hydrocarbons [1].

Biodiesel is a mixture of monoalkyl esters of long chain fatty acids derived from renewable lipid feedstock. In order to carry out this reaction, vegetable oils, fresh or used, as well as some kind of animal tallows, are forced to react with a short chain alcohol (methanol or ethanol mainly). Depending on the alcohols used, the products obtained are a mixture of

fatty acid methyl esters (FAME) or fatty acid ethyl esters (FAEE). Biodiesel obtained from ethanol is composed entirely of bio-based materials, making the process more sustainable, but ethanol is currently more expensive than methanol. The most employed vegetable oils for biodiesel industrial production are rapeseed, soybean and sunflower oils [2]. Furthermore, palm oil is considered an excellent feedstock for biodiesel production in tropical countries, such as Thailand, Malaysia and Colombia [2,3]. Beef tallow [4], waste lards and others animal fats [5,6] are also used sometimes in biodiesel production. Biodiesel from these materials doesn't fulfil required properties for its commercialization, so they must be mixed with biodiesel from vegetable oils.

The major problems related to animal fats are the high level of FFA [5] and the poor low temperature properties [7]. Animal fats have a significant content of saturated fatty acids and important properties such as pour point (PP), cloud point (CP) and cold filter plugging point (CFPP) of these biodiesels are usually over reasonable limits and standard specifications (EN 14214). Blending biodiesel from animal fats with biodiesel from vegetable oils is a way to improve these properties with the advantages of low iodine value and higher OSI values. Attending to the differences between FAME and FAEE, Joshi *et al.* [8] report the

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effect on cold flow properties of transesterified soybean oil with various mixtures of methanol and ethanol. They found an improvement of these properties while increasing the FAEE content of the produced mixture of esters. Anyway, mixing is a powerful way to obtain biodiesel with good properties. Additionally, the absence of natural antioxidants in fats makes biodiesel less stable for oxidation. Therefore, the use of this biodiesel obtained from the animal fat without mixing is not recommended.

On the other hand, biodiesel from animal fats has a higher calorific value and cetane number [9,10]. Additionally, important environmental and political advantages are that no competition with the food market is created and that an agricultural or industrial waste product is used instead of thrown away [5].

The most widespread industrial transesterification process is the homogeneous reaction catalyzed by alkali (NaOH or KOH) [11-13]. Other transesterification methods such as the use of acid catalysts (as H₂SO₄) [14,15], enzymes [16,17], heterogeneous catalysts [18-21] or the reaction under supercritical conditions [22,23] have industrial applications or are currently being researched.

Industrial-scale production of biodiesel is already being carried out, but still suffers from a high production cost, which is 1.5 to 3 times higher than production cost for fossil diesel [1,24]. This fact is mainly caused by the cost of fresh vegetable oil feedstocks [25]. For this reason, exploring methods to reduce the production cost of biodiesel, including new raw materials like waste vegetable oils or animal fats have attracted the focus of numerous research papers [9,18,26].

In case of significant FFA content in the oil or fat, special transesterification processes are required. Used cooking oils typically contain 0.4-3.3 mass% FFA, and animal fats contain from 5 to 40 mass% FFA [5,10,27]. When an alkali catalyst is added to these feedstocks, FFA reacts with the catalyst to form soap and water. It has been claimed that up to about 1 mass% FFA the reaction can still be catalyzed with an alkali catalyst, however, other authors reduce this limit to 0.5 mass% [28]. The soap formed during the reaction is either removed with the glycerol or washed out during the water wash. When the FFA level is above 5 mass%, the soap inhibits the separation of the methyl esters and glycerol and leads to the formation of an emulsion during the water washing step [29].

Esterifying FFA to alkyl esters in the presence of an acidic catalyst is a possibility of improving the use of high FFA oils in biodiesel production. Esterification can be carried out with homogeneous acid catalysts

such as sulphuric and p-toluene sulfonic acids [30,31]. Unfortunately, the use of homogeneous catalysts requires additional steps in the process which can reduce the economical yield of biodiesel production with animal fats, such as feedstock.

In this work, reaction yield and several properties of biodiesel produced by direct transesterification of 3 samples of animal fats originated from pork and beef tallow were studied using methanol and ethanol as alcohols. The influence of alcohol in some biodiesel properties such as viscosity, density, iodine number and OSI has been studied.

EXPERIMENTAL

Materials and methods

Several samples were used in this study; commercial edible pork fat (PF), crude pork fat (CPF, from LIPSA company Santa Perpetua de Mogoda, Barcelona, Spain) and natural beef tallow (NBT, from slaughterhouses in Tudela, Navarra, Spain). Fat was extracted from beef tallow by heating it and removing the solid residue. The obtained product was finally filtered and stored.

During the experimental period all raw materials were kept at 4 °C. In order to assure a constant sample composition, raw materials were heated and shaken in order to obtain a liquid homogeneous mixture before storing them.

Reagents used during biodiesel synthesis and purification steps were: methanol (assay (GLC) ≥ 99.9%, Carlo Erba Reagents), ethanol (99%, Panreac), sulphuric acid (96%, Panreac), sodium methoxide (ca. 25 mass% solution in methanol, Sigma-Aldrich), sodium ethoxide (ca. 21 mass% solution in ethanol, Sigma-Aldrich) and Magnesium sulphate (anhydrous, Scharlau). A dissolution of methyl heptadecanoate (standard for GC, Fluka Analytical) in heptane (standard for GC, Fluka Analytical) was used as internal standard for the GC determinations.

Table 1 shows the acid value and the fatty acid composition of the raw materials. Acid value was determined by volumetric titration according to the standard ISO 660 (2002). Fatty acid composition was determined using gas chromatography (GC) according to EN 14103 (2003) and ISO 5508 (1990). The fatty acid compositions of obtained FAEE are also reported and, as expected, no important differences can be observed between FAME and FAEE fatty acid profiles.

The acid value in CPF and NBT exceeds the acidity limit proposed by several authors [26,29] for a direct transesterification. In these cases, a pre-esterification using H₂SO₄ as catalyst is recommended.

Table 1. Acid value and fatty acid profile of used fats

	PF	CPF	NBT	PF	CPF	NBT
	Acid value, mass% FFA					
Fatty acid	0.21	0.97	0.6	-	-	-
	Fatty acid profile, mass%					
	FAME			FAEE		
Capryc (C10:0)	-	-	0.209	-	-	0.171
Lauric (C12:0)	-	-	0.388	-	-	0.339
Myristic (C14:0)	1.410	1.472	4.853	1.346	1.412	4.417
Myristoleic (C14:1)	-	-	0.228	-	-	0.418
Pentadecanoic (C15:0)	0.067	0.050	0.854	0.046	0.032	0.601
Palmitic (C16:0)	26.377	26.762	28.186	26.445	26.798	27.996
Palmitoleic (C16:1)	1.896	2.642	2.031	1.959	2.379	1.937
Margaric (C17:0)	0.415	0.313	1.449	0.390	0.284	1.418
Margaroleic (C17:1)	0.231	0.239	0.365	0.191	0.196	0.309
Stearic (C18:0)	17.114	16.535	23.212	18.558	17.928	24.837
Oleic (C18:1)	35.754	39.140	34.951	36.038	39.257	34.389
Linoleic (C18:2)	13.894	10.464	2.685	12.617	9.677	2.325
Linolenic (C18:3)	1.075	0.772	0.334	1.011	0.640	0.462
Arachidic (C20:0)	0.198	0.205	0.157	0.165	0.173	0.129
Gadoleic (C20:1)	0.667	0.676	0.099	0.597	0.616	0.132
Eicosadienoic (C20:2)	0.448	0.386	-	0.340	0.297	-
Other fatty acids	0.454	0.344	-	0.299	0.313	0.121

However, as shown in this study, the results of a direct transesterification with methanol and sodium methoxide or ethanol and sodium ethoxide as catalysts are very close to the results of a low acidity oil transesterification [32,33].

The following biodiesel properties were evaluated according to EN 14214 (2003), the European biodiesel standard: *λ*) density according to the EN 12185 standard; *ii*) kinematic viscosity at 40°C, using glass capillary viscometers according to the ISO 3104 standard (1994); *iii*) iodine value according to EN 14214 (2003), annex. B; *iv*) OSI according to EN 14112 (2003); *v*) ester and linolenic acid alkyl ester contents, by GC according to the EN 14103 standard (2003); *vi*) water content, by Karl Fischer coulometric titration according to the EN ISO 12937 standard (2003); *vii*) acid value, by volumetric titration according to the EN 14104 standard (2003).

Methyl and ethyl esters were determined using gas chromatography with a flame ionization detector (GC-FID) system, an Agilent 6890 Series GC System gas chromatograph, with a DB-225 MS (Agilent) column (30 m×0.25 mm×0.25 μm). The injector temperature and the detector (FID) temperature were set at 250 °C. The used carrier gas was He with a flow of 1 mL/min. Injection was made in a split mode, using a split flow ratio of 35:1, the volume injected was 1 μL.

The following temperature program was used: 170 °C, then 3 °C/min to 203 °C, then 1.5 °C/min to 214 °C, then 5 °C/min to 230 °C and holding at that temperature for 16 min.

Experimental procedure

The used fats were heated at 70 °C in order to homogenize the mixture previous to the reaction. Synthesis of biodiesel was done by alkaline transesterification in a batch reactor (2000 mL glass vessel) equipped with a mechanical stirrer, a condenser and a thermocouple. The reaction temperature was set to 60 °C for methanolysis and 78 °C for ethanolysis, and stirring speed was set to 600 rpm in order to avoid mass transfer problems.

The reaction conditions were: 6:1 molar ratio of alcohol to fat, 1.0 mass% sodium methoxide or ethoxide, and 3 h reaction time. During the procedure, 500 g of the fat (for all experiments) sample was weighed and transferred into the reactor. When temperature reached 60 or 78 °C for methanolysis and ethanolysis, respectively, MeONa and EtONa, dissolved in the required amount of methanol or ethanol, were added at constant stirring.

Once the reaction was considered complete, the reaction mixture was allowed to decant (2 h for methanolysis and 3 h for ethanolysis) at room temperature.

perature and after that two phases could be identified. The lower phase consisted of glycerol and the upper phase consisted of FAME and FAEE, where the alcohol and the used catalyst are supposed to distribute between both phases.

After the separation step, the alcohol from the biodiesel phase was recovered using a rotary evaporator under reduced pressure (0.2 bar). The obtained biodiesel was washed 3 times with hot (70 °C), acidified (pH 2, sulphuric acid) water to remove residual catalyst, glycerol, alcohol and any soap formed. After separation of the water phase, the biodiesel was dried in a rotary evaporator at reduced pressure, and magnesium sulphate was used to further reduce the biodiesel water content.

RESULTS AND DISCUSSION

Characterization of raw materials

The fatty acid composition of all raw materials is presented in Table 1 in detail. Oleic ester is the dominant one in all cases, up to 34 mass%. A typical characteristic of animal fats is the high amount of saturated esters represented by the presence of palmitic (up to 26 mass%) and stearic (up to 16 mass%) acid alkyl esters. Some minor saturated esters can be found in NBT such as caprylic, lauric, myristic and margaric acid alkyl esters [6]. Table 2 shows the fatty acid compositions of commonly used oils [34]. As can be observed, the saturated esters content for these oils is meaningfully lower in exception to palm oil, which presents a high level of palmitic alkyl ester. Long carbon chain esters such as arachidic, gadoleic and eicosadienoic alkyl esters can also be found in animal fats, especially in NBT. Odd carbon atom number esters can also be found in the transesterified fats, an especially important one being the alkyl heptadecanoate, which is used as an internal standard in the ester content determination. This fact can be explained by taking into account the presence of bacteria in

some animal organisms [35]. Bacteria possess the ability to synthesise odd- and branched-chain fatty acids, consequently ruminant and other animal fats contain odd numbered fatty acids [36].

Esters characterization

Table 3 shows the obtained product yields and the methyl ester content for FAME. Moreover, some final properties of the biodiesel for both, FAME and FAEE are shown: linolenic ester content, density, kinematic viscosity, iodine value, OSI and water content.

Product yield is defined as the weight percentage of the final product (transesterified and purified fat) relative to the weight of fat at the start. They were calculated from the final weight of biodiesel (after all purification steps) and the theoretical material balance, as shown in the following equation:

$$\text{Product yield} = 100 \frac{M_{\text{BIO}} / Pm_{\text{BIO}}}{3M_{\text{FAT}} / Pm_{\text{FAT}}} \quad (1)$$

where M_{BIO} and M_{FAT} are the weight of the obtained biodiesel and the fat, respectively. Pm_{BIO} and Pm_{FAT} are the molar weights of the biodiesel and fat calculated by using the fatty acid profile obtained from the GC analysis and the molar weight of the 4 most abundant components. The results show that all fats (PF, CPF and NBT) can be transesterified with a good final yield using methanol and ethanol as alcohols. The obtained yields for methanolysis reactions are slightly higher than those for ethanolysis. In the case of methanolysis, the solubility of fat in methanol is smaller and the reaction is mass transfer limited at the beginning. On the other hand, the separation of the two phases (biodiesel and glycerol) obtained after the reaction step is quite straightforward, as their miscibility is low. Unlike methanol, ethanol has better solvent properties but the formation of emulsion after the transesterification makes the separation step more complicated and affects the final product yield.

Table 2. Fatty acid composition of commonly used oils [34]

Fatty acid	Rapeseed	Sunflower	Palm	Soybean	Jatropha
Myristic (C14:0)	-	-	-	-	1.4
Palmitic (C16:0)	3.5	6.4	42.6	13.9	15.6
Palmitoleic (C16:1)	-	0.1	0.3	0.3	-
Stearic (C18:0)	0.9	2.9	4.4	2.1	9.7
Oleic (C18:1)	64.1	17.7	40.5	23.2	40.8
Linoleic (C18:2)	22.3	72.9	10.1	56.2	32.1
Linolenic (C18:3)	8.2	-	0.2	4.3	-
Arachidic (C20:0)	-	-	-	-	0.4
Other	0.69	-	1.1	-	-

Table 3. Yield and quality parameters of biodiesel from the used fats

Parameter	FAME			FAEE		
	PF	CPF	NBT	PF	CPF	NBT
Yield, %	87.7	86.7	86.3	78.4	82.6	82.7
Methyl ester content, mass%	96.31 ^a , 98.62 ^b	97.93 ^a , 99.77 ^b	96.95 ^a , 99.43 ^b	>96.5	>96.5	>96.5
Linolenic alkyl ester, mass% (C18:3)	1.075	0.772	0.334	1.075	0.772	0.334
Density at 15 °C, kg/m ³	876.3	873.80	873.31	872.7	871.2	870.3
Kinematic viscosity at 40 °C, mm ² s ⁻¹	4.51	4.57	4.77	5.01	4.98	5.16
Iodine value, gI ₂ /100g	60.0	56.8	37.6	57.9	55.1	36.8
Oxidation stability, h	2.84	6.27	2.56	4.70	8.70	3.60
Water content, ppm	415.3	231.0	358.3	422.7	317.0	349.5

^aWithout correction; ^bwith correction

The methyl ester content for the methanolysis reactions is shown in Table 3. It was measured following the analytical method defined by EN 14214, which uses methyl heptadecanoate (C17:0) as an internal standard, however, this fatty acid exists in animal fats and affects the obtained results. In order to take into account this fact the samples were analysed by GC with and without the internal standard. By applying the correction proposed by Schober *et al.* [37] an increase of the measured biodiesel purity was obtained. The results are in good agreement with other reported data [5] and confirm that the analytical method defined by EN 14214 is not appropriate for purity determination when methyl heptadecanoate is present in the feedstock.

Since commercial biodiesel is produced using methanol as alcohol, no normalized analysis methods for ethyl esters can be found. The use of methyl heptadecanoate as the internal standard for the GC determination does not guarantee a correct ester quantification, but the purity of ethanol based biodiesel has been checked (and considered over 96.5 mass%) by using the GC analysis that confirms that no strange compounds are present in the mixture.

Density values at 15 °C are shown in Table 3 for FAME and FAEE. All biodiesels met the European EN 14214 standard (min. 860, max. 900 kg/m³). FAME densities are slightly higher than FAEE densities but no important differences can be found between them. The obtained data are in good agreement with other published data for both, FAME [4,6,38] and FAEE [39]. An interesting comparison can be made between the densities of fat-made biodiesels and the densities of oil-made biodiesels. Table 4 shows some properties of commonly used oils in the biodiesel production. Density, kinematic viscosity, CFPP (cold filter plugging point) and OSI are shown for both, FAME and FAEE. Comparing Tables 3 and 4 the lower density of fat-made biodiesel can be observed, this fact can be at-

tributed to the presence of higher amounts of low density esters such as palmitic and stearic alkyl esters. These results are in good agreement with those presented by Teixeira *et al.* [40] and Dias *et al.* [41].

Considering the viscosity values shown in Table 3, fatty acid ethyl esters have a higher kinematic viscosity, compared to the values of kinematic viscosity of FAME. The substitution of methanol with higher alcohols is known to increase the kinematic viscosity [42]. Joshi *et al.* [8] found a curvilinear relationship between kinematic viscosity and ethyl ester in a FAME/FAEE mixture. In the present study, two fat-made biodiesels (PF and NBT) exhibit a viscosity value over 5 mm²/s, which is the upper limit for the European standard EN 14214. Table 4 presents the kinematic viscosities of some oil-made biodiesels. Viscosity values for fat-made biodiesel are in general higher than those shown in Table 4 from vegetable oils. This fact is in good agreement with the results reported by Dias *et al.* [41] and Teixeira *et al.* [40] who found a linear dependency between viscosity values and beef tallow biodiesel % in the mixture with soybean made biodiesel.

The iodine values, also shown in Table 3, are significantly lower than those of sunflower oil and soybean oil [43]. Of the three raw materials tested, NBT has the smallest iodine value, which is directly related to the smaller amount of unsaturated compounds, as can be observed in Table 1. These results are in good agreement with the higher unsaturation levels found on vegetable raw materials and other reported values [4, 5]. Joshi *et al.* [8] found higher iodine value in FAME than in FAEE. They propose a mixture in order to reduce high iodine value biodiesels. Similar results are reported by Dias *et al.* [41].

Water and linolenic acid alkyl ester contents meet the European standard for all biodiesels.

Oil stability index (OSI) is an important issue affecting the use of biodiesel. The influence of polyun-

Table 4. Properties of biodiesel from commonly used oils

Property	FAME				FAEE			
	Rapeseed	Sunflower	Palm	Soybean	Rapeseed	Sunflower	Palm	Soybean
Density at 15 °C, g dm ⁻³	888 [33]	880 [33]	875.9 [47]	885 [33]	872-888 [49]	879 [48]	873.8 [46]	882.7 [46]
Kinematic viscosity at 40 °C, mPa s	4.4 [43]	4.2 [43]	4.5 [43]	4.2 [43]	4.7 [49]	-	-	4.6 [8]
CFPP	-10 [43]	-3 [43]	10 [43]	-5 [43]	-	-6 [48]	-	-5 [8]
OSI, h	2 [43]	0.8 [43]	4 [43]	1.3 [43]	-	-	-	6.5 [8]

saturated methyl esters increases the oxidation tendency of biodiesel [44]. It is well known that it is very difficult to meet this limit for biodiesel from commonly used raw materials, unless antioxidants are used. Only two of the obtained biodiesels achieve the minimum limit of six hours for OSI, both produced from CPF with methanol and ethanol.

The relative low stability index reported in Table 3 can be explained by the absence of natural antioxidants in animal fats [45], but reported values are, in general, greater than those for oil-made biodiesel as shown in Table 4 and by Ramos *et al.* [43]. These authors attribute the low OSI of the oil-made biodiesels to the presence of linoleic and linolenic methyl esters due to the position of double bonds in these compounds. Since these compounds have a low amount in animal fats, OSI values are higher for these biodiesels. As seen in Table 3, FAEE displays improved resistance to oxidation compared to FAME. Similar results have been reported by Joshi *et al.* [8] who explain this difference due to the increase in average molecular weight of FAEE compared to FAME.

CONCLUSIONS

Biodiesel synthesis from animal fats was carried out at lab scale by a direct transesterification with methanol and ethanol as alcohols. Good yields, higher than 83 and 78 mass%, were obtained using methanol and ethanol, respectively. The lower yield values in the case of FAEE can be attributed to the problems in the purification step due to the higher inter-solubility of the mixture. Due to the presence of C17:0 in biodiesel as a natural component of animal fats and in light of the results, a correction should be made by the method proposed by EN 14214 for biodiesel purity determination.

The density and iodine values are in the range of the EN 14214 standard for all biodiesels. The obtained iodine values are quite smaller of those for vegetable oil based biodiesel, which is attributed to the presence of high amount of saturated esters. Of the three samples, only the crude pork fat biodiesel shows an OSI high enough to fulfill the requirement of EN

14214 standard. The OSI was higher for the biodiesel produced with ethanol in all samples, however, viscosity values meet the EN 14214 standard for FAME, but FAEE are over this limit.

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NAUČNI RAD

METANOLIZA I ETANOLIZA ANIMALNIH MASTI: UPOREDNO PROUČAVANJE UTICAJA VRSTE ALKOHOLA

Biodizel je dobijen u reakciji animalnih masti sa metanolom i etanolom u prisustvu natrijum-metoksida i natrijum-etoksida kao katalizatora. Dva uzorka svinjske masti i jednog uzorka prirodnog junećeg loja su podvrgnuti direktnoj transesterifikaciji, pri čemu su ostvareni dobri prinosi proizvoda: 87,7, 86,7 i 86,3% za metanolizu, a 78,4, 82,6 i 82,7% za etanolizu, redom. Sadržaj metil-estara je, takođe, određen i bio je veći od 96,5% za sve proizvode. Prisustvo masne kiseline C17:0 u mastima zahtevalo je korigovanje metode predviđene standardom EN 14103 (2003). Gustina biodizela na 15 °C je bila između 870 i 876 kg/m³, odnosno u granicama standarda EN 14214, dok je kinematički viskozitet bio u opsegu 4,5 do 5,16 mm²/s u skladu sa standardom EN 14214. Jodni broj je mnogo niži od granice utvrđene standardom EN 14214, ali je oksidaciona stabilnost niža od zahtevane granice (6 h), što se može pripisati nedostatku prirodnih antioksidanasa u mastima.

Ključne reči: Biodizel; animalna mast; transesterifikacija; etanoliza; metanoliza.