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Using Mixtures of Waste Frying Oil and Pork Lard to produce Biodiesel

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***Abstract*—**Studying alternative raw materials for biodiesel production is of major importance. The use of mixtures with incorporation of wastes is an environmental friendly alternative and might reduce biodiesel production costs. The objective of the present work was: (i) to study biodiesel production using waste frying oil mixed with pork lard and (ii) to understand how mixture composition influences biodiesel quality. Biodiesel was produced by transesterification and quality was evaluated through determination of several parameters according to EN 14214. The weight fraction of lard in the mixture varied from 0 to 1 in 0.2 intervals. Biodiesel production yields varied from 81.7 to 88.0 (wt%), the lowest yields being the ones obtained using waste frying oil and lard alone as raw materials. The obtained products fulfilled most of the determined quality specifications according to European biodiesel quality standard EN 14214. Minimum purity (96.5 wt%) was closely obtained when waste frying oil was used alone and when 0.2% of lard was incorporated in the raw material (96.3 wt%); however, it ranged from 93.9 to 96.3 (wt%) being always close to the limit. From the evaluation of the influence of mixture composition in biodiesel quality, it was possible to establish a model to be used for predicting some parameters of biodiesel resulting from mixtures of waste frying oil with lard when different lard contents are used.

***Keywords*—** biodiesel, mixtures, transesterification, waste.

I. Introduction

BIODIESEL consists of a mixture of fatty acid alkyl esters, that can be used as an alternative fuel in compression-ignition engines; it is obtained from renewable resources, such as vegetable oils and animal fats, which makes it biodegradable and non-toxic [1],[2].

Biodiesel might be produced by transesterification, which is a three-step reversible reaction that converts the initial triglyceride into a mixture of alkyl esters and glycerol, in the presence of a catalyst. Currently, biodiesel production is mainly made using virgin vegetable oils and the major obstacle for biodiesel production is the high price of such raw materials. Additionally, the use of food oils for biodiesel production is controversial; reason why studying alternatives is of major importance. Few studies can be encountered regarding the conversion of animal fat. Also, studies regarding the mixture of raw materials for biodiesel production are currently limited. In a study by Meneghetty et al. (2007) [3] the use of castor oil, which had a viscosity of 225.8 $mm^2 s^{-1}$ at 40 ºC was enabled for biodiesel production by mixing it with either soybean oil or cottonseed oil. In a study by Lebedevas et al. (2006) [4] the use of three component mixtures also allowed the reduction of emission and harmful components of the fuel.

The use of wastes as raw materials for biodiesel production has three major advantages: i) do not compete with the food market; ii) recycles waste; and iii) reduces production costs [5]. The great amounts of waste animal fat, produced at several slaughter houses and other meat processing units, might be an attractive and cheap raw material. Other waste materials that can be used for biodiesel production are the waste frying oils [5]-[8]. Due to the scarce availability of these low cost materials, their use at an industrial scale is limited; however, their mixture with other raw materials might be an attractive alternative.

In order to improve the knowledge on this subject, the objective of the present work was: (i) to study biodiesel production using waste frying oil mixed with pork lard and (ii) to understand how mixture composition influences biodiesel quality.

II. Materials and Methods

The waste frying oil was obtained from a voluntary collection system implemented at the Faculty of Engineering and consisted of waste frying oil from different domestic sources. The pork lard was from the brand "*Dilop Carnes*", and was purchased at the market. The reagents used during biodiesel production procedures were: methanol 99.5% (analytical grade, Fischer Scientific), sodium hydroxide powder 97% (reagent grade, Aldrich) and anhydrous sodium sulphate 99% (analytical grade, Panreac). Biodiesel production was performed in three steps, pre-treatment of raw material, synthesis and purification.

A. Pre-treatment of Raw Material

Waste cooking oil was filtered under vacuum, after dehydrated using anhydrous sodium sulphate (left over night) and finally again filtered under vacuum. The pork lard was first heated at 100 ºC to eliminate residual water and after cooled to near the reaction temperature (60 ºC).

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B. Raw materials Characterization

Different properties of the starting raw materials were determined: i) composition (using gas chromatography (GC) according to EN 14103 (2003) and NP EN ISO 5508 (1996)); ii) acid value, by volumetric titration according to the standard NP EN ISO 660 (2002); iii) iodine value, by volumetric titration using Wijs reagent, according to the standard ISO 3961 (1996); and iv) water content, using coulometric Karl Fischer titration.

C. Biodiesel Synthesis

Synthesis of biodiesel was made by transesterification. The mixtures of waste frying oil and lard were prepared considering the increase in the fat fraction of the mixture, varying from 0-1(w/w), in 0.2 intervals. The fat was weighted and added to the reactor, which already contained the necessary amount of oil. A defined amount of methanol (6:1 molar ratio to oil) pre-mixed with NaOH (0.8 (wt %) was added to the reactor, which already had 100 g of the raw material mixture, preheated at the reaction temperature. At this point, the reaction started; the reactor consisted of a 1 L flat-bottom flask immersed in a temperature controlling bath, equipped with a water-cooled condenser and a magnetic stirrer. Reaction occurred for 60 min under vigorous stirring; at the end of the reaction, products were left to settle for 1 hour to allow the separation of the two phases: biodiesel and glycerol.

TABLE I
RAW MATERIALS PROPERTIES INCLUDING: ACID VALUE, IODINE VALUE, WATER CONTENT, FATTY ACID COMPOSITION AND MEAN MOLECULAR WEIGHT

Raw material Properties	**Pork lard**	**Waste frying oil**
Acid value (mg KOH/g)	0.71	0.82
Iodine value (g I_2/100g)	67	117
Water content (wt %)	0.03	0.05
Fatty acid composition (wt %)		
Miristic (C14:0)	1.3	n.d
Palmitic (C16:0)	23.7	8.4
Palmitoleic (C16:1)	2.2	0.2
Heptadecenoic (C17:1)	0.4	n.d
Stearic (C18:0)	12.9	3.7
Oleic (C18:1)	41.4	34.6
Linoleic (C18:2)	15.0	50.5
Linolenic (C18:3)	1.0	0.6
Arachidic (C20:0)	0.2	0.4
Eicosenoic (C20:1)	0.9	0.4
Eicosadienoic (C20:2)	0.7	n.d
Eicosatrienoic (C20:3)	0.2	n.d
Behenic (C22:0)	n.d	0.8
Docosadienoic (C22:2)	n.d	n.d
Lignoceric (C24:0)	n.d	0.3
Mean molecular weight (g mol^{-1})	861.6	877.5

n.d – not detected

D. Biodiesel Purification

Both phases were separated and excess methanol was recovered from each phase, using a rotary evaporator under reduced pressure. Biodiesel was then filtered (S&S, grade 589/1), and washed, first with 50% (v/v) of an acid solution (0.2% HCl) and after repeatedly with 50% (v/v) of distilled water until the pH of the washing water was the same as the distilled water. The filtering stage was adopted due to the fact that it significantly improved the washing stage, reducing emulsion formation. Regarding biodiesel dehydration, different procedures were adopted to evaluate which would be the best one. Such procedures were based on the use of an anhydrous salt and evaporation at reduced pressure under different conditions.

E. Biodiesel Characterization

The biodiesel characterization was made according to the European biodiesel standard EN 14214 (2003). The following parameters were determined: i) acid value, by volumetric titration according to the standard EN 14104 (2003); ii) kinematic viscosity, determined at 40 ºC using glass capillary viscometers according to the standard ISO 3104 (1994); iii) density, determined using a hydrometer method according to the standard EN ISO 3675 (1998); iv) flash point, using a rapid equilibrium closed cup method, according to the standard ISO 3679 (2004); v) copper corrosion, using a copper strip test according to the standard ISO 2160 (1998); vi) water content, by Karl Fischer coulometric titration according to the standard NP EN ISO 12937 (2003); vii) ester and linolenic acid methyl ester contents, by GC according to the standard EN 14103 (2003) and; viii) iodine value, determined from ester content according to annex B of EN 14214 (2003). Regarding to chromatographic analysis, a Dani GC 1000 DPC gas chromatograph (DANI Instruments S.p.A.), with an AT-WAX (Heliflex capillary, Alltech) column (30 m, 0.32 mm internal diameter and 0.25 µm film thickness) was used. The injector temperature was set at 250 ºC, while the detector (FID) temperature was set at 255 ºC. The carrier gas used was the N_2 with a flow of 2 mL/min. Injection was made in a split mode, using a split flow rate of 50 mL/min, the volume injected was 1 µL.

III. Results and Dicussion

A. Raw materials properties

The fatty acid composition and the mean molecular weight (calculated from the composition) as well as some other measured properties of both raw materials are presented in Table 1. Considering the typical fatty acid composition of vegetable oils as determined using GC [9], the waste frying oil composition indicates that both soybean and sunflower oil might be present; the low C18:3 content and the content in C18:1 might indicate that sunflower is present in a higher amount. Much higher acid values have been reported for waste frying oils [5], [10], the low acid value found might indicate smaller degree of both oxidation and hydrolysis

reactions. This can be justified because the waste frying oils were from a domestic source and they might have been exposed to high temperature for short periods [11]. Pork lard also presented a low acid value, probably resulting from pre-treatment processes; however, commonly referred value for commercial lard is slightly higher (1.3 mg KOH/ g fat) [12].

B. Yield

Biodiesel production yields are presented in Table 2. They varied from 81.7 to 88.8 (wt%). The lowest yields were obtained using lard and waste frying oil alone as raw materials and the highest yield resulted from using 80% incorporation of lard in the mixture.

TABLE II
BIODIESEL PRODUCTION YIELDS (WT %) USING WASTE FRYING OIL/LARD MIXTURES AS RAW MATERIALS

Lard fraction (wt)	Yield (wt %)
0	82.2
0.2	87.1
0.4	87.6
0.6	85.2
0.8	88.0
1	81.7

C. Biodiesel Quality

The biodiesel water content is an important parameter because it affects biodiesel oxidation stability [13], therefore influencing the storage life of the fuel. With the objective of selecting an appropriate dehydration method, each sample produced was subjected to a different treatment. The following treatments were performed: 30 wt % of anhydrous salt (AS); or evaporation (163 mbar) including heating at 40 ºC during 45min ($Ev_{40/45}$); heating at 45, 65 and 80 ºC during 1 h 30 min ($Ev_{45/90}$, $Ev_{65/90}$, $Ev_{80/90}$); heating at 90 ºC during 2 h ($Ev_{90/120}$) and; heating at 90 ºC during 3 h 30 min ($Ev_{90/210}$). The standard limit according to EN 14214 is 0.05 % wt and Figure 1 shows the effect of the preformed treatments on the final biodiesel water content. Two samples were used regarding treatment $Ev_{90/120}$ to ensure that such treatment was effective; however, considering the obtained results, evaporation at 90 ºC, 163 mbar and a holding time of 3 h 30 min seemed to be the best to ensure that samples resulting from such raw material mixtures fulfill the European biodiesel standard EN 14214.

As it can be observed in Table 3, all produced samples fulfilled the European standard limit in terms of acid value, kinematic viscosity, density, flash point, copper corrosion, iodine value and linolenic methyl ester content. High flash points indicate effective methanol recovery, which should be reflected in low methanol contents of biodiesel. Among the measured parameters, methyl ester content (purity) was the only one that was not fulfilled by all samples. It was verified that the minimum purity (96.5 wt%) was closely obtained only when waste frying oil was used alone and when 0.2 % of lard

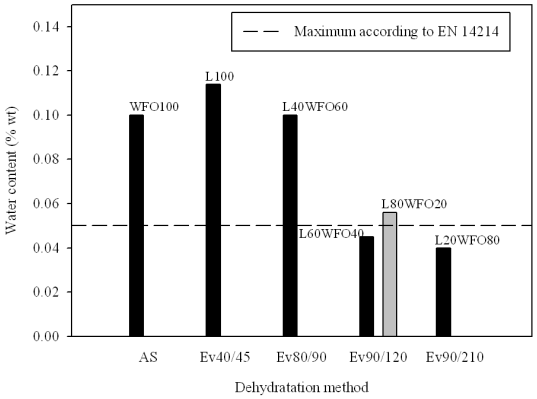

Fig. 1 Water content of biodiesel using different dehydration treatments (nomenclature in the bars refers to sample used and considers percentage of waste frying oil (WFO) and lard (L) used as the raw material)

TABLE III
QUALITY PARAMETERS OF BIODIESEL FROM OIL/LARD MIXTURES AND THE RESPECTIVE STANDARD LIMITS ACCORDING TO EN 14214

Parameter	Results	EN 14214
Acid value (mg KOH/g)	0.04-0.08	<0.5
Kinematic viscosity at 40 ºC (mm^2s^{-1})	4.67-4.77	3.50-5.00
Density at 15ºC ($kg\ m^{-3}$)	875.7-883.4	860-900
Flash point (ºC)	174-179	>120
Copper corrosion (3h/50ºC)	All samples-Class 1a	Class 1
Methyl ester content (wt %)	93.8-96.3	>95.5
Linolenic methyl ester content (wt %)	0.6-1.0	<12.0
Iodine value [a] *(g I_2/100g)*	67-117	<120

[a] from the methyl ester composition.

was incorporated in the raw material (96.3 wt%); however, it ranged from 93.9 to 96.3 (wt%) being always close to the limit (Figure 2).

Concerning the influence of raw material composition in biodiesel quality, it was postulated that the parameter of the biodiesel obtained from the mixture corresponded to the weighted average of the parameter of biodiesel resulting from each component. Therefore:

$$P_{mix} = P_{wfo} X_{wfo} + P_{lard} X_{lard}, \text{ or}$$
$$P_{mix} = (P_{lard} - P_{wfo}) X l_{ard} + P_{wfo} \quad [1]$$

where: P_{mix} – parameter of biodiesel from the mixture, P_{lard} – parameter of biodiesel from the lard, P_{wfo} – parameter of biodiesel from the waste frying oil, X_{wfo} – weight fraction of waste frying oil, X_{lard} – weight fraction of lard.

In fact, a linear correlation was found between some of the quality parameters and the incorporated lard fraction; those parameters were: iodine value, density, methyl ester content and linolenic methyl ester content. Table 4 shows the linear

TABLE IV
FITTING OF SOME QUALITY PARAMETERS OF BIODIESEL FROM OIL/LARD MIXTURES VERSUS INCORPORATED LARD FRACTION - LINEAR REGRESSION PARAMETERS

Parameter	a	b	r^2	*p*-value	P_{wfo}	P_{lard}	P_{lard}-P_{oil}
Iodine value (g I_2/100g)	-50	118	1.000	<0.0001	117	67	-50
Density (kg m^{-3})	-7.4	883.4	0.989	<0.0001	883.4	875.7	-7.6
Viscosity (mm^2s^{-1})	0.02	4.70	0.040	0.705	4.69	4.71	0.02
Methyl ester content (% wt)	-2.5	96.1	0.615	0.0647	96.3	94.4	-1.9
Linolenic methyl ester content (% wt)	0.3	0.6	0.995	<0.05	0.6	1.0	0.3

P_{wfo} – Property of waste frying oil, P_{Lard} – Property of lard, a – slope, b – intercept, r^2 – determination coefficient, *p* –probability value (using an F-test).

regression parameters of the fitting. Such correlations had r^2>0.99 (p<0.05) except in the case of viscosity and methyl ester content. The very low determination coefficient found regarding biodiesel viscosity might be explained by the fact that biodiesel samples obtained from these two raw materials had very similar viscosities and experimental errors were much more reflected. It was possible to verify that, considering the fittings with determination coefficients r^2> 0.99, the slope (a) was similar to the difference between the property in fat and oil (P_{lard}-P_{wfo}); also, the intercept (b) was similar to the property of the oil (P_{wfo}) (differences were less than 3%). Therefore, the results showed that equation 1 might be used to predict the property of biodiesel resulting from mixtures of waste frying oil and lard when different lard contents are used, for the following properties: iodine value, density and linolenic methyl ester content.

The iodine value gives the degree of insaturation of the biodiesel samples. The existence of double bonds might lead to polymerization of glycerides by heating, which could lead to gum formation [14]. As expected, the increase in the lard fraction led to a decrease in the iodine value. This fact indicates that lard might be an attractive raw material to be mixed with vegetable oils such as soybean oil, which alone does not meet the standard specification according to EN 14214.

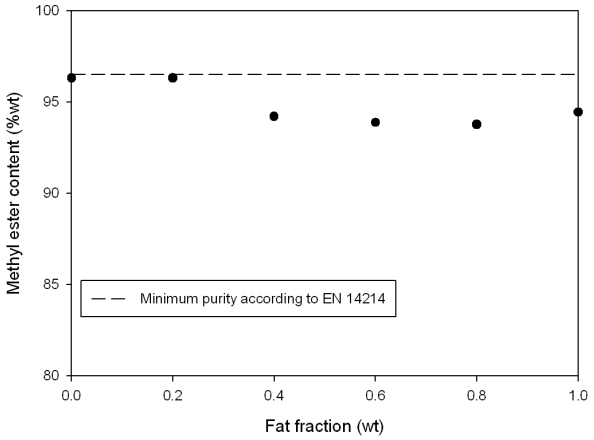

Fig. 2 Methyl ester content (wt %) of biodiesel samples obtained using different mixtures of waste frying oil and lard.

IV. CONCLUSION

Synthesis of biodiesel by transesterification of raw material mixtures considering the incorporation of pork lard in waste frying oil results in yields varying from 81.7 to 88.8 (wt %). Evaporation at 90 ºC, 163 mbar during 3 h 30 min was established as an efficient dehydration method for biodiesel production using such raw material mixtures.

The resulting product met the European biodiesel quality standard EN 14214 in terms of acid value, viscosity, density, flash point, copper corrosion and linolenic acid methyl ester content. Minimum purity was closely obtained only when waste frying oil was used alone and when 0.2 % of lard was incorporated in the raw material; however, it ranged from 93.9 to 96.3 (wt%) being always close to the limit.

It was possible to establish a model to be used for predicting some quality parameters of biodiesel resulting from mixtures of waste frying oil and lard when different lard contents are used. This model states that the parameter of the biodiesel obtained from the mixture corresponds to the weighted average of the parameter of biodiesel resulting from each component and could be applied for the following parameters: iodine value, density and linolenic methyl ester content (linear fittings with determination coefficient r^2>0.99 (p-value<0.05)).

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