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Sustainable Production of Biodiesel from Tallow, Lard and Poultry Fat and its Quality Evaluation

Mata, T. M.[1], Cardoso, N.[3], Ornelas, M.[3], Neves, S.[1] and Caetano, N. S.[1,2]

[1]LEPAE - Laboratory for Process, Environmental and Energy Engineering / Faculty of Engineering (FEUP), University of Porto, R. Dr. Roberto Frias S/N, 4200-465 Porto, Portugal
[2]Chemical Engineering Department, School of Engineering (ISEP), Polytechnic Institute of Porto (IPP), R. Dr. António Bernardino de Almeida S/N, 4200-072 Porto, Portugal
[3]Department of Chemistry, Faculty of Sciences, University of Porto (FCUP), R. do Campo Alegre S/N, 4169-007, Porto, Portugal

This work aims to study the viability of producing biodiesel or fatty acid methyl esters (FAME) from waste animal fats of tallow, lard and poultry fat and to evaluate them according to the quality requirements defined by the European Standard EN 14214 (2003). Accordingly, tallow methyl esters (TME), lard methyl esters (LME) and poultry fat methyl esters (PME) were produced and characterized, showing that some quality parameters did not comply with the European standard limits (e.g. acid value, kinematic viscosity, CFPP, and concentration of group I of metals). Thus, blends of B20 (20% biodiesel mixed with petroleum diesel) were made and evaluated for these parameters. Results show that it is viable to produce biodiesel from these feedstocks and their reaction yields may vary from 76.8% to 91.4%, being the lowest value for poultry fat biodiesel. Although results show that it is not possible to use 100% of biodiesel from these animal fats in vehicle engines, blends of 20% biodiesel are viable to be used as fuel with some advantages, such as improved cold-flow properties.

1. Introduction

The original diesel engine to run on vegetable oil was projected by Dr. Rudolph Diesel. He used peanut oil to fuel the engine and presented it at the World Paris Exhibition of 1900 (Nitschke and Wilson, 1965). The major problem associated with the use of pure vegetable oils as fuels for diesel engines is the high-fuel viscosity in compression ignition engines (Demirbas, 2008).

Considering the fact that the supply of fossil fuels will decrease in future as the energy demand will continue to grow rapidly, the search for alternative renewable fuels has gained fundamental importance. Also, the environmental concerns regarding greenhouse gas emissions and the commitment of the International Community to significantly reduce emissions, formalized by the Kyoto Protocol adopted in December 1997, triggered the need to find more sustainable alternatives to fossil fuels.

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Biodiesel is a mixture of fatty acid esters obtained by transesterification of vegetable oils or animal fats with a low molecular weight alcohol and with glycerol as a by-product as shown in Figure 1.

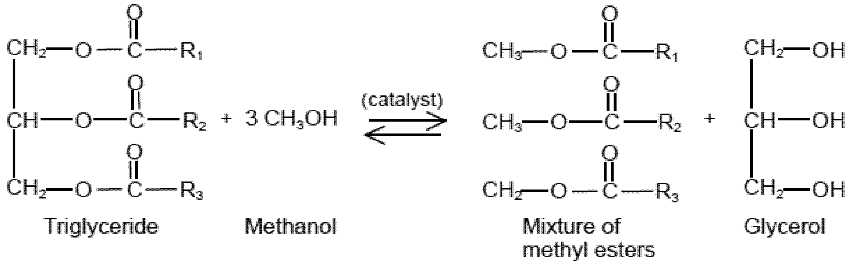

Figure 1. Transesterification reaction of vegetable oils or animal fats

Biodiesel can be used in compression ignition engines as an alternative to diesel fuel with almost none modifications of the vehicle engines. It has become more attractive due to its potential environmental benefits (e.g. to reduce global warming) and since it can be obtained from renewable energy sources, such as vegetable oils and animal fats, with other advantages of being biodegradable and non-toxic (Meher *et al.*, 2006; Gerpen, 2005). In fact, currently biodiesel is mainly produced from a wide range of edible vegetable oils (e.g. rapeseed, soy, sunflower, or palm oil). However, since these feedstocks are also used in the food market and their prices are expected to increase even more in future (USDA, 2007), biodiesel from these feedstocks will be less competitive than fossil fuels what will be the main hurdle to its commercialization. For this reason, in the last few months, most of the Portuguese biodiesel plants had no choice than to stop their production. This concern encouraged the use of low-price waste sources for biodiesel production, which cannot be used in human food, such as waste animal fats from the meat and/or fish processing industries.

Biodiesel produced from animal fats represent an environmental friendly and lower cost alternative. Currently, studies about animal fats esterification and transesterification to biodiesel, do not explain all the difficulties inherent to the process. Therefore, analytical characterization of different animal fats and resulting biodiesel are essential. In this sense, this work aims to assess the viability of using three types of waste animal fats (tallow, lard and poultry fat) for biodiesel production and to evaluate its quality, by comparison with the limits defined by EN 14214 (2003), as well as to evaluate some quality parameters of the waste animal fats, such as acid value, iodine value, kinematic viscosity and higher heating value.

2. Materials and Methods

2.1 Raw Materials Preparation and Characterization

Waste animal fats of tallow, lard and poultry fat were collected from slaughterhouses and meat processing companies. At the laboratory, they were melted and filtered in order to obtain the fat and remove gums, protein residues, and suspended particles. Then, the following properties of these fats were determined:

- Acid value determined by volumetric titration according to NP EN ISO 660 (2002) standard;
- Iodine value determined by volumetric titration and using a Wijs reagent according to ISO 3961 (1996) standard;
- Kinematic viscosity determined at 40 °C using a glass capillary viscometer (Cannon-Fenske routine viscometer of series 200) according to the EN ISO 3104 standard; and
- Higher heating value of the fats determined using an oxygen bomb calorimeter.

2.2 Biodiesel Synthesis

There are several routes to obtain biodiesel from lipidic feedstocks. In this work TME, LME and PME were prepared following a standard procedure and a methanol to oil molar ratio of 6:1. Thus, for 500g of animal fat approximately 150mL of Methanol and 4g of homogeneous alkali-catalyst (KOH) were used. The reaction mixture was stirred for about two hours in a thermostatic bath at a constant temperature of 60ºC. After this period, the resulting biodiesel was separated from glycerol and then washed. The washing was done in a first step with 50% (v/v) of a weakly acid water solution, prepared with o-phosphoric acid, and then with just deionized water until pH around 7. For biodiesel dehydration an anhydrous adsorbent was added, the mixture was stirred during 15 minutes and then filtered to remove the adsorbent from the final purified biodiesel.

2.3 Biodiesel Characterization

FAME quality parameters and their corresponding blends with diesel were tested according to the quality requirements of EN 14214. Thus the following parameters were evaluated:
- Acid value, by volumetric titration according to the standard EN 14104 (2003);
- Kinematic viscosity, determined at 40 °C using glass capillary viscometers according to the standard ISO 3104 (1994),
- Density, determined at 15ºC using a hydrometer method according to the standard EN ISO 3675 (1998),
- Flash point, determined using a rapid equilibrium closed cup method according to the standard ISO 3679 (2004),
- Copper corrosion, using a copper strip test according to the standard ISO 2160 (1998);
- Water content, by Karl Fischer coulometric titration according to the standard NP EN ISO 12937 (2003);
- Ester and linolenic acid methyl ester contents determined by gas chromatography (GC) according to the standard EN 14103 (2003);
- Iodine value, determined by volumetric titration and using Wijs reagent according to the standard EN 14111 (2003); and
- Higher heating value determined following the standard ASTM method D-240-87: Standard test method for heat of combustion of liquid hydrocarbon fuels by bomb calorimeter.

The chromatographic analysis was performed using a Dani GC 1000 DPC gas chromatograph (DANI Instruments S.p.A.) equipped with an AT-WAX (Heliflex capillary, Alltech) column (30m, 0.32mm internal diameter and 0.25μm film thickness). The injector temperature was set to 250°C, while the flame ionization detector (FID) temperature was set to 255°C. The carrier gas used was N_2, with a flow of 2mL/min.

Injection was made in a split mode, using a split flow rate of 50mL/min (split ratio of 1:25), and the volume injected was 1µL.

2.4 Biodiesel-Diesel Blends (B20)

FAME obtained from the three types of waste animal fats were mixed with petroleum diesel on a volume basis, i.e. a ratio of 1:4 (v/v) of biodiesel to diesel, yielding blends of B20 (20% biodiesel mixed with diesel). This blends percentage was chosen since in Portugal it is possible to commercialize B100 and blends up to B20 according to national legislation. Also, the purpose of blending was to understand if all the quality parameters would fulfill the standard EN 14214 (2003) without the need of using further additives. Blends were characterized following the same procedures described above for biodiesel.

3. Results and Discussion

3.1 Raw Materials Properties

The acid and iodine values and the higher heating values of the three types of animal fats were determined as shown in **Errore. L'origine riferimento non è stata trovata.**.

Table 1. Characterization of waste animal fats

Parameter	Tallow	Lard	Poultry fat
Acid Value (mg (KOH)/g fuel)	1.07	0.63	0.56
Iodine Value (g/100g)	45.3	77.9	76.7
Kinematic Viscosity at 40ºC (mm^2/s)	46.37	39.53	41.06
Higher Heating Value (MJ/kg)	38.90	39.49	39.62

An higher acid value is shown for tallow fat, which may indicate a higher degree of oxidation and occurrence of hydrolysis reactions (Knothe, 2007).

3.2 Biodiesel properties and composition

Tallow methyl esters (TME), lard methyl esters (LME) and poultry fat methyl esters (PME) were characterized according to the several quality requirements defined by EN14214 (2003). Table 2 shows the results of this characterization and the respective standard limit value of each quality parameter.

Results in Table 2 show that the reaction yields varied from 76.8% to 91.4%, being the lowest value for poultry fat biodiesel. Also, the several quality parameters evaluated for the three different types of biodiesel (TME, LME, and PME) are according to the EN 14214 standard limits, except for the acid value of PME, kinematic viscosity, concentration of group I of metals (Na+K), CFPP for TME and LME, and the ester content. The lower ester content may be due to the lack of improvement of the biodiesel production process (Nebel and Mittelbach, 2006).

In order to obtain a fuel quality complying with all the required parameters blends of B20 (20% biodiesel mixed with diesel) were made and evaluated. After blending the different types of biodiesel, the parameters that did not fulfill the European standard limits were tested again and the results are shown in Table .

Table 2. Characterization of biodiesel (B100) from tallow, lard and poultry fat

Parameter	TME	LME	PME	EN 14214 limits
Yield (%)	90.8	91.4	76.8	-
Acid value (mg KOH/g fuel)	0.20	0.22	0.55	<0.5
Water content (mg/kg)	374.2	184.0	1201.0	500
Iodine value (g I/100g)	44.4	75.6	78.8	<120
Copper strip corrosion (3 h/50°C)	Class 1	Class 1	Class 1	Class 1
Flash point (ºC)	171	147	172	>120
Kinematic viscosity at 40ºC (mm^2/s)	5.35	5.08	6.86	3.50-5.00
Density (kg/m^3)	870	873	877	860-900
CFPP (ºC)	10.0	5.0	3.0	<5.0
Group I metals (Na+K) (mg/kg)	2.0	17.2	46.8	<5.0
Higher heating value (MJ/kg)	40.23	40.10	39.58	-
Ester content (% w/w)	82.5	85.1	67.25	>96.5
Myristic acid (14:0)	12.63	4.38	-	-
Palmitic acid (16:0)	31.03	39.80	30.08	-
Stearic (18:0)	16.39	8.69	5.95	-
Oleic (18:1)	36.58	28.98	47.03	-
Linoleic (18:2)	3.37	14.74	15.55	-
Linolenic (18:3)	-	27.87	1.39	-

Table 3. Quality Parameters of B20 blends

Parameter	B20			Diesel
	TME	LME	PME	
Kinematic Viscosity at 40ºC (mm^2/s)	3.10	3.15	3.28	2.69
CFPP (ºC)	-10.0	-6.0	-8.0	-5.0
Group I Metals (Na+K) (mg/kg)	0.6	1.6	23.9	2.4
Higher Heating Value (MJ/kg)	44.62	44.58	44.71	46.00

Table shows that only the blend B20 made with PME doesn’t comply with the standard limit for the group I of metals (Na+K). However, an improvement of the biodiesel production procedures is expected to solve this problem.

CFPP values have greatly reduce after blending, being even lower than for petroleum diesel alone. Earlier studies also reported a decrease in CFPP after blending biodiesel with petroleum diesel (Dunn, 2009). The slow cooling or crystallization of these blends may be explained as a consequence of the interactions between the saturated mono-alkyl esters molecules and the non-polar petroleum diesel chains. X-ray diffraction studies have shown that at low temperatures these molecules form bi-layered structures with polar carboxylic head-groups aligned head-to-head and next to each other in the crystal interior (Dunn, 2009). These kinds of structures make it difficult and therefore decrease the temperatures required for crystal formation.

4. Conclusions

This work studied the viability of producing biodiesel from three types of waste animal fats (tallow, lard and poultry fat). The quality of the obtained biodiesel was evaluated according the EN 14214, showing that none of the biodiesel types match all the European standard limits in all the evaluated parameters. Therefore, biodiesel B100 (100% biodiesel) from these feedstocks cannot be used is vehicle engines without further additives introduction. For this reason B20 blends were made by mixing 20% biodiesel with petroleum diesel. The parameters that did not fulfill the requirements for biodiesel B100 were tested again for these blends, showing that all the TME, LME and PME are good alternatives as blending components for petroleum diesel with improved cold-flow properties. The concentration of group I metals (Na + K) can be a problem for PME commercialization even in blends; however this may be solved by adjusting the production procedure in order to remove these metals.

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