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VALORIZATION OF FATS FROM ANIMAL WASTES: BIODIESEL PRODUCTION

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ABSTRACT
Two of the most important concerns regarding planet sustainability are energy management and waste disposal. Renewable energy sources and waste valorization processes are therefore very important. Among biofuels, biodiesel has very good utilization and environmental properties that allow partial or total replacement of diesel fuel. Biodiesel can be produced from residues like waste frying oils and animal fats. The purpose of this work is to produce biodiesel from fat obtained from industrial animal residues: green and lime fleshings from tanneries and slaughterhouses wastes. The fats were previously characterized and some of the samples presented a high acid value. For these materials, an acid esterification step prior to the transesterification reaction was needed, in order to lower the acid value. Transesterification with methanol was performed using sodium hydroxide or sodium methylate as catalysts, at 65ºC. The quality of biodiesel products was assessed by some of EN 14214 Standard parameters. The results show that most of the samples are within the specifications, except for high CFPP. This is typical of biodiesel produced from animal fats that present high saturated fatty acid content. Nevertheless, these products can be used in mixtures with biodiesel from vegetable oils, in order to meet standard specifications.

Keywords: Biodiesel; fleshings; fat waste valorization

INTRODUCTION
Sustainable energy management is a main world concern, considering the fact that fossil fuels supply is limited and energy demand continues to rise. Environmental protection is also a major concern of the International Community, leading to the signature of Kyoto Protocol (1997) where a commitment was made regarding greenhouse gas emissions reduction. Biofuels have therefore gained fundamental importance in this context and are now widely used as alternative to fossil fuels. In the European Union, Directive 2003/30/EC [1] imposes a 5,75% (based on energy content) incorporation of biofuels in all transportation fuels since December 2010. Biodiesel (a fuel

comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats) has very good utilization as well as environmental properties and is commercially used as total or partial replacement of diesel fuel. Although biodiesel can be synthesized from many types of triglyceride containing materials, vegetable oils are the main feedstock used in industry. Presently, the cost of the cereals used to produce these vegetable oils is increasing due to the growing market needs, raising biodiesel costs. Also, this huge cereals demand introduces a sustainability problem for the next coming years and an inacceptable competition with its use as food.

Significant research effort is being dedicated to the search for alternative feedstocks. Among these, residues as waste cooking oils and animal fats present good results as raw materials for biodiesel production [2-4]. Furthermore, this is an environmental friendly disposal option for these residues, while adding value to problematic wastes.

Livestock and poultry related industries generate a large amount of fat containing solid wastes, usually with high disposal costs. In particular, tanning industry generates a high quantity of solid wastes with high pollution level. It is known that only 20% of the hide results in finished products [5]. From an economical and environmental point of view, there is great interest in the valorization of the generated solid wastes.

Some researchers have already studied biodiesel production from animal fat residues, namely chicken fat [6], fleshing oil [7] and poultry meat and bone meal [8].

Traditional biodiesel production processes are based on the transesterification of triglycerides with methanol using an alkaline homogeneous catalyst (NaOH), in batch or continuous plants. This process requires feedstocks with low free fatty acid (FFA) and water contents. Typical animal fats contain from 5% to 30% FFAs [9], and soap formation may occur in considerable amounts (Fig.1) making product separation very difficult.

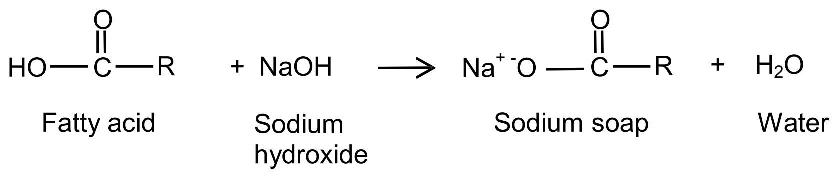

Figure 1. Saponification reaction of free fatty acids.

To overcome this problem, a pretreatment step is usually required to convert the free fatty acids to methyl esters, thereby reducing the FFA level. This treatment consists of an esterification with methanol and sulfuric acid as catalyst, producing methyl esters and water (Fig.2). After this reaction, the treated fat can be transesterified with an alkali catalyst to convert the triglycerides to methyl esters.

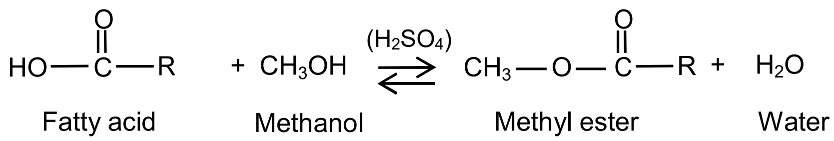

Figure 2. Esterification reaction of free fatty acids.

Besides its high FFA content, another feature of animal fats is that its fatty acid composition shows a more saturated character than vegetable oils, presenting therefore low iodine values. Biodiesel obtained from these raw materials usually presents poor cold flow performance, which could limit its utilization without the use of additives or blending. On the other hand, the high degree of saturation may benefit the oxidation stability of the product [10].

The purpose of this work is to produce biodiesel from fat obtained from four different industrial animal residues and to compare the properties of the products with the European standards. Three types of residues from tanneries (pressure extracted fat from green fleshings and lime fleshings and fat obtained by thermal hydrolysis of lime fleshings) and also fat obtained by thermal extraction of slaughterhouses residue, were chosen as raw materials for this study.

MATERIALS AND METHODS

Fat extraction and characterization

Solid green fleshings and lime fleshings received from a tannery company were heated at 65ºC and then pressed at 41 kg/cm^2 using a mechanical press (Mega KMG-300). A drilled stainless steel cylinder was designed to contain the samples during the pressing process. The extracted fat was filtered to remove solid impurities. These samples were named S1 (fat from green fleshings) and S2 (fat from lime fleshings).
Sample S3 is obtained by thermal hydrolysis of lime fleshings. Sample S4 is fat obtained from slaughterhouses solid residues by thermal extraction.
All samples were characterized for moisture using gravimetric methods and fat content by Soxhlet method. Acid value was determined according to EN 14104 standard and iodine value was determined according to EN 14111 standard.

Biodiesel production

Biodiesel was produced by transesterification with methanol and sodium hydroxide or sodium methylate as catalysts. For samples S2 and S4 it was necessary a pretreatment step with methanol and sulfuric acid prior to transesterification reaction, in order to lower the acid value to less than 5 mg_{KOH}/g_{fat}. The conditions used in this esterification treatment were: 6:1 methanol/fat molar ratio, 1,5% (w/w, based on the fat) sulfuric acid, 2 hours and 65ºC. Products were separated by gravity and acid number of treated fat was evaluated.
Transesterification step was performed at 65 ºC for 2h under stirring, using a 6:1 methanol/fat molar ratio and 1% (w/w, based on the fat) sodium hydroxide.
To test the effect of sodium methylate as an alternative catalyst, sample S3 was also transesterified using 1,5% (w/w, based on the fat) of sodium methylate instead of sodium hydroxide (sample S3-M).
The ester product was separated by gravity and washed with water to remove the catalyst, glycerol and methanol. A final drying step with magnesium oxide was performed, prior to product characterization.

Biodiesel characterization

Ester product quality was evaluated by some of the EN 14214 standard parameters: density by pycnometer method, ester content by gaseous chromatography, viscosity, acid value, iodine value and cold filter plugging point (CFPP) according to standards EN ISO3104, EN14104, EN 14111 and EN 116, respectively.

RESULTS AND DISCUSSION

The results of the characterization of the fats are presented in table 1. Mechanical extraction of the fat seems to be less effective than the other processes, as fat content of samples S1 and S2 are slightly inferior to samples S3 and S4. Low iodine values show the saturated character of animal fats, as expected. High acid values presented by samples S2 and S4 indicate the need for an esterification treatment prior to biodiesel production step. After this treatment, both samples presented acid values below 5 mg_{KOH}/g_{fat} and thus the transesterification reaction was performed.

Table 1. Fat samples characterization.

Sample	Moisture [% w/w, wet basis]	Fat content [% w/w, dry basis]	Acid value [mg_{KOH}/g_{fat})]	Iodine value [$g_{iodine}/100g_{fat}$]
S1	5,5	93,1	0,3	nd
S2	3,1	96,3	10,9	41,3
S3	0,5	99,6	3,7	51,5
S4	0,7	99,9	47,8	nd

nd- not determined

After transesterification reaction and purification, clear light yellow biodiesel sample were obtained, as shown in fig. 3 for samples S1 and S2. Biodiesel characterization results are shown on table 2, as well as EN 14214 standard reference values.

Figure 3. Fat and biodiesel samples. From left to right:
sample S2- fat and biodiesel ; sample S1- fat and biodiesel.

As can be seen, all samples tested produced methyl ester mixtures that are within or very close to the specifications for its utilization as fuel. Low iodine values of raw materials, typical of animal fats, originate high values of CFPP and therefore poor cold flow performance of biodiesel. This limitation can however be overcome by additivation [11] or by blending with biodiesel from vegetable oils.
Regarding the effect of using sodium methylate instead of sodium hydroxide as catalyst, the results do not differ significantly (samples S3 and S3-M). The industrial use of sodium methylate presents some advantages, as it makes unnecessary the mixing step of methanol and hydroxide.

Table 2. Biodiesel properties and EN 14214 standard values.

Sample	**Density [kg/m^3]**	**Viscosity at 40ºC [mm^2/s]**	**Acid value [mg$_{KOH}$/ g$_{fat}$)]**	**Iodine value [g$_{iodine}$/ 100 g$_{fat}$]**	**CFPP [ºC]**	**Ester content [%]**
S1	876	5,0	0,4	nd	2	99,0
S2	878	5,7	0,1	47,9	5	90,0
S3	872	3,5	0,3	50,8	3	97,3
S3-M	872	3,7	0,5	nd	6	99,0
S4	nd	nd	nd	nd	nd	93,3
EN 14214	860-900	3,5-5,0	<0,5	<120	a)	>96,5

nd- not determined ; a) Country and season specific; usually below 0ºC.

CONCLUSIONS

Fat obtained from different industrial animal residues was used as raw material for biodiesel production. As expected in animal fats, some of the samples present high FFA content and a pre-treatment step prior to the transesterification reaction is necessary. Methyl ester mixtures were obtained under the following reaction conditions: reaction temperature: 65 ºC, reaction time: 2h, methanol/fat molar ratio: 6:1, catalyst: 1% (w/w, based on the fat) sodium hydroxide. Product characterization shows that these mixtures are within or close to the specifications of the most important parameters of EN 14214 Standard. The exception is high CFPP values, as usual in biodiesel produced from animal fat. Nevertheless, these products can be used in mixtures with biodiesel from vegetable oils in order to meet standard specifications. This valorization route of residual fat materials is an interesting alternative for biofuel production and also contributes to solve the waste management problem of livestock and poultry related industries.

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