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Biodiesel Production From Poultry Fat

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Abstract

Biodiesel is an alternative fuel to fossil diesel that contributes to diversify energetic sources, as well as to reduce green house gas emissions. Vegetable oils are the most used raw-material, but as they compete with the food market for the use of the soil, new raw-materials need to be developed; the use of low cost feedstock, such as animal fat wastes, can reduce biodiesel production costs, at the same time allowing adding significant value to the wastes. Poultry fat is currently considered a potentially good low cost raw-material for biodiesel production. Previous studies concluded that it is possible to obtain biodiesel obeying the European quality standards through a transesterification reaction of poultry fat wastes at low temperatures, so poultry fat wastes might be extremely appealing as raw-material, because significant reductions of energetic and material costs can be possible. The aim of the present work was to study the transesterification of poultry fat, by focusing on the influence of two reaction variables: stirring rate (400, 800, 1200 rpm) and temperature (30, 45, 60 °C), considering their influence on the quality of the obtained product, namely in terms of kinematic viscosity, acid number, methyl ester content and iodine value. Product yield generally increased with increasing temperature and stirring rate, ranging between 50.13% and 78.01%. Temperature seemed to influence the kinematic viscosity of the product being possible to observe a decrease in viscosity with the temperature increase. Acid values were generally in agreement with EN 14214. Ester content was maximum at the higher temperature studied (60 °C) and higher stirring rate (1200 rpm), being 67.1%. The use of such a low grade raw material using conventional processing was possible but some difficulties were observed probably related with raw material degradation, suggesting that the optimization of storage conditions or an esterification pre-treatment should be conducted.

Resumo

O biodiesel apresenta-se como uma alternativa aos combustíveis fósseis que contribui para a diversificação das fontes de energia, assim como para a redução de emissões gasosas com efeito de estufa. Os óleos vegetais são a matéria-prima mais utilizada para a produção de biodiesel, contudo estes competem pelo uso do solo e torna-se imperioso encontrar novas alternativas; o uso de matérias-primas de baixo custo, como os resíduos de gordura animal, reduzem os custos de produção do biodiesel e ao mesmo tempo permitem a valorização destes resíduos. A gordura de frango é actualmente considerada uma matéria-prima com potencial para a produção de biodiesel. Estudos anteriores concluíram que é possível obter biodiesel de acordo com as normas europeias de qualidade, a partir de resíduos de gordura de frango, realizando uma reacção de transesterificação a baixas temperaturas. Os resíduos de gordura de frango podem ser portanto, extremamente apelativos como matéria-prima, pois possibilitam uma significativa redução de custos energéticos e de material. O objectivo principal deste trabalho foi o estudo da produção de biodiesel a partir de gordura de frango, analisando principalmente a influência da agitação (400, 800 e 1200 rpm) e da temperatura (30, 45, 60 °C), na reacção de transesterificação, considerando a sua influência na qualidade do produto obtido, nomeadamente viscosidade cinemática, índice de acidez, teor de ésteres e índice de iodo. O rendimento da reacção aumentou com o aumento da agitação e da temperatura, situando-se entre 50,13% e 78,01%. A temperatura parece influenciar a viscosidade cinemática do produto, sendo possível observar uma diminuição da mesma com o aumento da temperatura. Os valores do índice de acidez foram na generalidade de acordo com a norma EN 14214. O teor de ésteres foi máximo à temperatura estudada mais elevada (60 °C) e à mais elevada agitação (1200 rpm), sendo 67,1%. O uso desta matéria-prima para a produção convencional de biodiesel foi possível, contudo foram evidenciadas algumas dificuldades, provavelmente relacionadas com a degradação da matéria-prima, sugerindo que a optimização das condições de armazenagem ou um pré-tratamento, realizando uma reacção de esterificação, devem ser efectuados.

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1. Introduction

1.1 Framework

From the 19th century when Industrial Revolution occurred, until now, the world energy resources are based upon fossil fuels. At a global scale, 43% of the energy that is produced by fossil fuels is from oil, 40% from coal and 17% natural gas (Rittman, 2008). Those fossil fuels have some disadvantages such as: (i) concentration in few and problematic regions of the world; (ii) sporadic shortages and imminent risk of running out; and (iii) association with the emission of pollutant gases to the atmosphere (particles, volatile organic compounds, CO_x, NO_x, and SO_x) which are related with impacts on the public health and on the environment, namely, with the greenhouse effect and the global warming (Crabbe et. al, 2001).

Everything suggests that world reserves of oil and the extraction efficiency will decrease over the next 20 to 40 years, but there are still large reserves of coal available, which have been intensively used mainly by developing countries, such as China and India.

Biofuels, renewable fuels derived from biomass, are certainly key contributors for the diversification of energy sources in the transport sector. At present, about 90% of the biofuel market is captured by bioethanol and biodiesel, which have been already applied on a large scale as gasoline or diesel substitutes; these energetic resources are mainly first generation biofuels (Antoni et al., 2007), since their production mainly relies on either simple carbohydrates (sucrose or starch) or edible vegetable oils (palm, soybean, or rapeseed); thus, the exploitation of these cost intensive feedstocks competes with the world food supply, being economically and ethically problematic (Rude and Schirmer, 2009). Due to the low yield of oilseed crops, the current diesel demand cannot be met without a dramatic increase of cultivation areas. Additional conversion of natural habitats into monocultures (e.g., palm plantations in the rain forest) decreases biodiversity and will reduce the natural carbon sink capacity (Fortman et al., 2008; Tilman et al., 2006).

Biodiesel is an alternative fuel similar to fossil diesel, being possible using it alone or in blends with fossil diesel. It is simple to use, biodegradable, non-toxic and, as it is

essentially free of sulphur and aromatics, allows a significative reduction of atmospheric emissions, namely, of carbon compounds.

Biodiesel is constituted by a mixture of fatty acid alkyl esters. The ester composition varies according to the fatty acids present in the triglyceride used as raw material. One molecule of triglyceride chemically consists of three long chains of fatty acids radicals that are ester bonded to a single glycerol molecule (Figure 1); triglycerides are the main components of vegetable oils and animal fats (90-98%) (Dias et al., 2010).

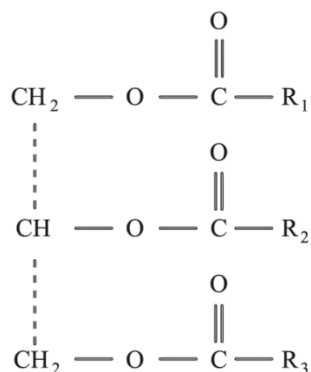


Figure. 1 Triglyceride molecule (R_1 , R_2 and R_3 are the radicals which vary according to the fatty acid composition of the oil) (Dias et al., 2010).

Because different fatty acids have different physical and chemical properties, their profile is probably the most important parameter influencing the physical and chemical properties of the vegetable oil or animal fat.

Different technologies have been reported for the production of biodiesel, such as transesterification, esterification/hydro-esterification (Brito et al., 2008), hydrocracking (Gusmão et al., 1989) and pyrolysis (Arvanitoyannis et al., 2007; Demirbas and Dincer, 2008; Huber and Corma, 2007; Mahler et al., 2008; Tian et al., 2008).

The most common way to obtain biodiesel is the transesterification of vegetable oils or animal fats, mainly due to its simplicity and relative low costs associated. In that reaction, vegetable oils or animal fat react in the presence of a catalyst (usually a base) with an alcohol (usually methanol) to give the corresponding alkyl esters (or for methanol, the methyl esters) of the fatty acids belonging to the triglycerides that constitute the parent vegetable oil or animal fat.

This technical concept of using these oils and fats as raw materials for the production of a renewable diesel fuel is very attractive (Knothe and Gerpen, 2005). Furthermore, the use of low cost feedstock, such as animal fat wastes, can significantly reduce biodiesel production costs, being additionally a friendly environmental alternative to recycle

wastes, adding value to materials that often have reduced or even negative commercial value.

The aim of the present work was to study the transesterification of poultry fat, by focusing on the influence of the reaction variables: stirring rate and temperature, and their influence on the quality of the obtained product.

1.2 Biodiesel Production

Like it was said before, due to its simplicity and relative low cost operation, the most common way to produce biodiesel is through a transesterification reaction; also called alcoholysis, the transesterification is a three-step reversible reaction that converts the initial triglycerides into a mixture of esters (biodiesel) and glycerol, in the presence of a catalyst. During the transesterification reaction, the triglycerides are converted, step by step, into diglycerides, monoglycerides and glycerol; at each step, one mol of ester is produced. The overall reaction is presented in Figure 2.

Usually a homogeneous base such as NaOH or KOH or their methoxides (Vicente et al., 2007) can be used as catalysts. The use of methoxides, such as sodium methoxide, has been demonstrated to be a better option instead of using NaOH or KOH, because they are water free. When NaOH is added with the alcohol, instead of using methoxide, their reaction might lead to water formation and consequently decreases the reaction yield. Therefore, the use of methoxides usually leads to higher quality products and better yields (Alvim-Ferraz, 2009). The disadvantages relate are related with its higher costs and toxicity.

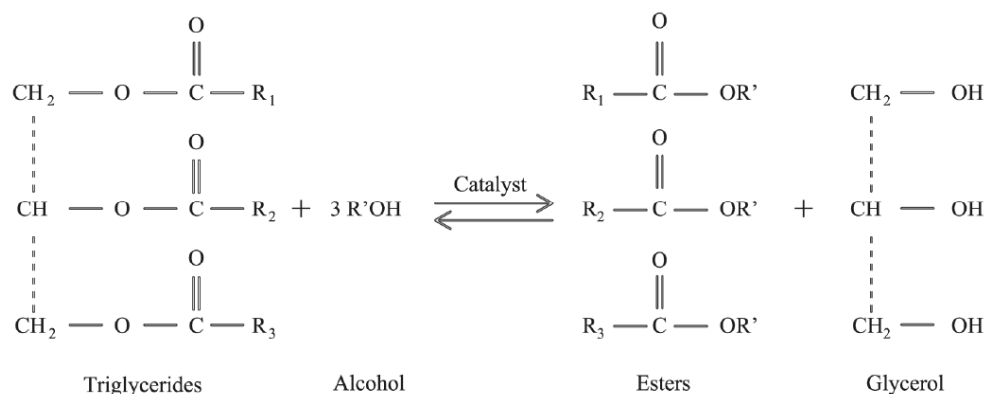


Figure. 2 Transesterification reaction of triglycerides (overall reaction) (Dias et al., 2008).

The transesterification of triglycerides to produce methyl esters and free glycerol was first described in 1852 (Duffy, 1852).

The most widely used alcohol is methanol, reason why sometimes this reaction is called methanolysis. Besides being cheaper, one of the major advantages of using methanol is that the products, fatty acid methyl esters (FAME) and glycerol, can be very easily separated; also important is that biodiesel produced by methanolysis shows very similar properties to fossil diesel (Dias, 2010).

Ethanolysis is also very used due to its environmental friendly process, because ethanol has very low toxicity unlike methanol. However, ethanol presents some problems related to higher difficulty in phase separation, since ethyl esters are much more soluble in glycerol than the corresponding methyl esters; also, residual amounts of water significantly affect product yield, making this process very expensive relatively to methanolysis (Mittelbach et al., 2004).

There are some advanced technologies for the production of renewable diesel substitutes, such as non-catalytic transesterification of vegetable oils or fats, Fischer-Tropsch synthesis of lignocellulosic biomass and hydrotreatment, namely of vegetable oils and/or fats.

Non-catalytic transesterification is one alternative technology for biodiesel production using methanol under supercritical conditions. The reaction is fast, presenting high conversions in short time (50-95% after 10 min reaction), but high temperatures (250-400 °C) and pressures (up to 82.7 bar) difficult its commercialisation due to high production costs and energy consumption (Dias, 2010).

The Fischer-Tropsch Synthesis is used to produce chemicals, gasoline and diesel fuel by converting a syngas (a mixture of hydrogen and carbon monoxide which can be produced from biomass gasification) into a range of hydrocarbons, being therefore an alternative process for the production of liquid fuels. For its application, this technology needs to be integrated in the overall biomass-to-fuel production system (biomass gasification, gas cleaning, water-gas-shift reaction for an optimal H₂/CO adjustment, amongst others); therefore, high investments are expected before the cost of the final products is reduced to competitive levels (Dias, 2010).

Hydrotreatment of vegetable oils can be used to produce liquid alkanes with high cetane numbers (80-100) and improved fuel properties. Hydrotreatment occurs by hydrogenation of the C=C bonds of the vegetable oils. The resulting free fatty acids (FFA), diglycerides, monoglycerides and waxes can go further different pathways to

produce the alkanes. Dehydration/hydrogenation produces a liquid alkane (Dias, 2010). Hydrotreatment is an expensive process because it requires H_2 ; as petroleum refineries already perform hydrotreatment, this technology can be more easily implemented for renewable fuel production in such units.

The application of advanced technologies might be a solution in a long term; however, so far the costs and complexity difficult their application to the production of alternative diesel fuel.

From all the technologies applied, the transesterification has been demonstrated to be the more efficient aiming to reduce the triglyceride viscosity to obtain a product presenting properties similar to those of fossil diesel (Dias, 2010); accordingly, most plants throughout the world use this process for biodiesel production.

Many parameters affect the transesterification reaction to produce biodiesel, such as temperature, methanol/oil molar ratio, mixing rate, catalyst type and amount of catalyst. The optimization of the reaction usually considers the parameters previously referred and also the type of feedstock (Dias et al., 2008).

Considering the homogeneous alkali catalytic systems, the optimum temperature tends to be the one closest to the boiling point of the alcohol used; an excess of alcohol is necessary to promote a good conversion; the mixing rate should be as high as possible to promote the mixture between reactants, which is particularly important because reactants and catalysts (oil, alcohol and catalysts dissolved) constitute a two phase system (Dias, 2010).

Results obtained through the transesterification reaction using different catalytic procedures (including the use of supercritical conditions) are presented in Table 1. It is shown that heterogeneous catalyst is a good option because it is cheaper and according to Table 1 good results are obtained, although the reaction temperature is relatively high. At lower temperature reactions there are three catalyst options: basic, acid and lipase catalyst; the first two are very similar to each other and the most promising seems to be lipase catalyst, but more expensive.

Currently, biodiesel production is performed using virgin vegetable oils as feedstock, which are also used as food resource; accordingly, research is making efforts to find alternative raw materials that do not compete with the food market.

The cost of feedstock is a major economic factor in the viability of biodiesel production (Van Gerpen, 2005); according to some researchers (Krawczyk, 1996; Connemann and Fisher, 1998), approximately 70–95% of the total production cost of biodiesel results

from the cost of raw material. Average international prices of some feedstocks are expressed in Table 2.

According to Table 2, the cheapest feedstocks to produce biodiesel are waste cooking oil (154 EUR/ton), poultry fat (176 EUR/ton) and yellow grease (258 EUR/ton). Yellow grease consists on typically used-frying oils from deep fryers or lower-quality grades of tallow from rendering plants. Consequently, waste oil sources are the cheapest alternative raw materials and despite in less amounts, their use for biodiesel production is fundamental as it simultaneously reduces waste management costs and environmental impacts (Dias, 2010).

Table 1 Comparison of different catalytic procedures for the transesterification (Helwani et al., 2009).

Variable	Basic catalyst	Acid catalyst	Lipase catalyst	Supercritical alcohol	Heterogeneous catalyst
Reaction temperature (°C)	60-70	55-80	30-40	239-385	180-220
Water in raw materials	Interfere with reaction	Interfere with reaction	No influence	-	-
Yields of methyl esters	Normal	Normal	High	Good	Normal
Recovery of glycerol	Difficult	Difficult	Easy	-	Easy
Purification of methyl esters	Repeated washing	Repeated washing	None	-	Easy
Production cost of catalyst	Cheap	Cheap	Relatively expensive	Medium	Potentially cheaper

Table 2 Average international prices for raw materials used as feedstock for biodiesel production in 2007 (EUR/ton) (Demirbas, 2009).

Feedstock	Price
Crude palm oil	374
Rapessed oil	568
Soybeen oil	531
Refined cottonseed oil	539
Crude corn oil	553
Crude peanut oil	614
Crude tea seed oil	354
Waste cooking oil	154
Yellow grease	258
Poultry fat	176

1.3 Biodiesel Quality Control

The raw materials and the production process variables strongly influence biodiesel quality. To ensure and control product quality, standards were established.

Table 3 shows the biodiesel quality parameters according to American and European standards (ASTM D6751, 2002 and EN 14214, 2009) the test methods for each quality parameter determination are also shown. The main quality parameters will be now described in more detail.

1.3.1 Acid value

The acid value is defined as the mass (mg) of potassium hydroxide required to neutralise the FFA present in 1 g of sample (Dias et al., 2008).

Table 3 Biodiesel quality parameters, standards and test methods, according to ASTM D6751 and EN 14214

Quality parameter	Unit	Standards		Test methods	
		ASTM D6751	EN 14214	ASTM D6751	EN 14214
Flash Point	° C	>130.0	>101.0	D93	ISO CD3679e
Kinematic viscosity at 40 °C	mm ² .s ⁻¹	1.9 - 6.0	3.5 - 5.0	D445	EN ISO 3104
Cetane number	-	>47	>51	D613	EN ISO 5165
Sulphated ash content	% (m/m)	<0.020		D874	ISO 3987
Copper strip corrosion	-	<N° 3	Class 1	D130	EN ISO 2160
Acid value	mg KOH.g ⁻¹	<0.80	<0.5	D664	pr EN 14104
Free glycerol	% (m/m)	<0.020		D6584	pr EN 14105m pr EN 14106
Total glycerol	% (m/m)	<0.240	<0.25	D6584	pr EN 14105m
Density	kg.m ⁻³	-	<900	N/A	EN ISO 3675 and EN ISO 12185
Water content	mg.kg ⁻¹	-	<500	N/A	EN ISO 12937
Phosphorous content	% (m/m)	<0.001	<0.01	D4951	pr EN 141101

prEN - Draft European Standard is a standard under development (CEN, 2011)

It is an indicator of biodiesel quality, as well as an indicator of its stability, because the acid value may increase with time as the fuel degrades due to its contact with air or water (Waynick, 2005 and Van Gerpen et al., 2004). The acid value of biodiesel must be $<0.50 \text{ mg KOH.g}^{-1}$ according to the European biodiesel standard ISO 14214.

1.3.2 Kinematic Viscosity at 40 °C

This parameter is an indicator of the oil conversion to esters, because the methyl ester content has been correlated with viscosity. Also, viscosity is related with the chemical structure of raw material; therefore, viscosity of biodiesel from fats is higher than from vegetable oils due to their higher saturation levels (Canakci and Sanli, 2008). High viscosity leads to negative impacts on fuel injector performance (Encinar et al., 2005). The viscosity is one parameter of major importance also for transport purposes, namely to guarantee good conditions for oil flow into pipelines, as well as to predict cold weather behaviour (biodiesel with high viscosity tends to solidify at higher temperatures than the biodiesel with lower viscosity). The range for biodiesel samples according to EN 14214 is $3.5\text{-}5.0 \text{ mm}^2\text{s}^{-1}$ (Dias et al., 2008).

1.3.3 Density at 15 °C

The density, for similar reasons to the viscosity, might be used as an indicator of the completeness of the transesterification reaction (Al-Widyan and Al-Shyoukh, 2002). The injection of the fuel is influenced by the density. The range for biodiesel samples according to EN 14214 is $860\text{-}900 \text{ kg.m}^{-3}$.

1.3.4 Flash Point

Flash point is the temperature at which the fuel ignites when exposed to a flame. The flash point of biodiesel is higher than the one of diesel fuel which makes it safer (Meher et al., 2006). The presence of methanol is indicated by lower flash points and therefore it is a very important parameter to be determined considering handling, storage and safety of the fuel (Encinar et al., 2005; Al-Widyan and Al-Shyoukh, 2002).

According to EN 14214, biodiesel flash point must be $> 120 \text{ °C}$.

1.3.5 Copper Corrosion

Copper corrosion is, by definition, the corrosivity of copper by one liquid. This test is used as a measure of possible difficulties with copper and brass or bronze parts of the

fuel system that might lead to complications. Biodiesel samples according to the European biodiesel standard must be classified as class 1 using a 3 h test at 50 °C.

1.3.6 Water Content

The water content is the ratio between mass of water and the mass of sample. The basic principle for quantification consists in injecting the sample in the analysis recipient of the water analysis apparatus, which anode produces coulometrically iodine for the Karl Fischer reaction (the excess of iodine is detected when all the water is titulated). According to EN ISO 14214 the upper limit for water content is 500 mg.kg⁻¹.

1.3.6 Ester Content

The determination of the ester content of FAME is of major importance for biodiesel intended for use as pure or as a blending component for heating and diesel fuels, it determines the purity of the biodiesel studied and therefore serves to control illegal mixtures and ensure quality. The method according to EN 14103 is used for FAME containing methyl esters between C14 and C24.

1.4 Biodiesel Production from Poultry Fat Wastes

Due to the relative low price of poultry meat, its production has increased significantly in recent years; furthermore, poultry products are not forbidden by any religion which increases its consumption. The major producers of chicken meat in 2009 were the United States of America (15.9 million tons), China (12.1 million tons), Brazil (10.9 million tons) and the European Union 27 (8.6 million tons). Brazil was in 2009 the exporting leading country of chicken meat (3.6 million tons), occupying 15 % of the world market in the production of chicken meat; European Union 27 was the third with 720 thousand tons (ABEF, 2009).

The inventory of animal wastes with potential for biodiesel production in Portugal was of fundamental interest to estimate the production of fat from bovine, swine and poultry (Cardoso, 2009). The Portuguese capacity to produce those fat wastes in 2008 was estimated (Cardoso, 2009; Moreira, 2009; Dias et al. 2008_b); this potential ranged between 46 000 to 57 000 tons. Table 4 shows specifically the amount of poultry fat wastes produced in Portugal, the yields (%) of fat extraction and the potential Portuguese biodiesel production in millions of tons.

Table 4 Potential Portuguese biodiesel production estimated for 2008, considering the Portuguese poultry fat wastes production and extraction efficiency.

Type of waste	Poultry Fat waste (tons)	Yield (%)		Biodiesel Production Potential (millions of tons)
		Fat extraction	Biodiesel Production	
Abdomen, cutting and boning	8500-9400	80	80	5.1
Skin	1300-2700	80	80	8.9-18
Total	9800-12000	80	80	26

It is likely to believe that more consumers lead to an increasing amount of poultry fat wastes resulting from its slaughter; consequently, the recycling of poultry fat wastes has been subject of study, since their incorporation in animal diets was restricted due to the potential transmission of infectious diseases between different animal species (Liu et al., 2007). Poultry fat, for countries such as Portugal that do not have fossil fuel reserves, has the additional advantage of diminishing the demand for imported energy.

As can be seen in Table 4, different parts of poultry can be used for fat extraction, being also possible to consider the feather meal, that is “the product resulting from pressuring clean, undecomposed feathers from slaughtered poultry” according to U.S. Census Bureau (2011). Feather meal contains 2 to 12% of fat, depending upon the type of feathers used; chicken feathers contain approximately 11% of fat, while turkey and duck feathers contain approximately 6.7% of fat (Dale, 1992).

However, the best fat, which is easier extracted and less contaminated, comes from the following three major parts of skin: bottom, body and wings, as shown in Figure 3.

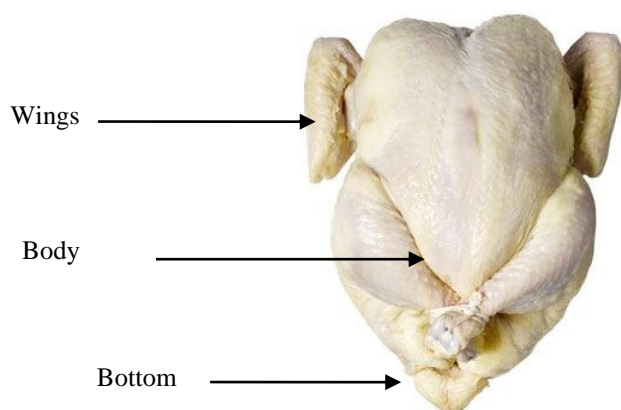


Figure. 3 Major parts of poultry skin for fat extraction aiming biodiesel production.

The global process of biodiesel production from poultry fat is presented in Figure 4:

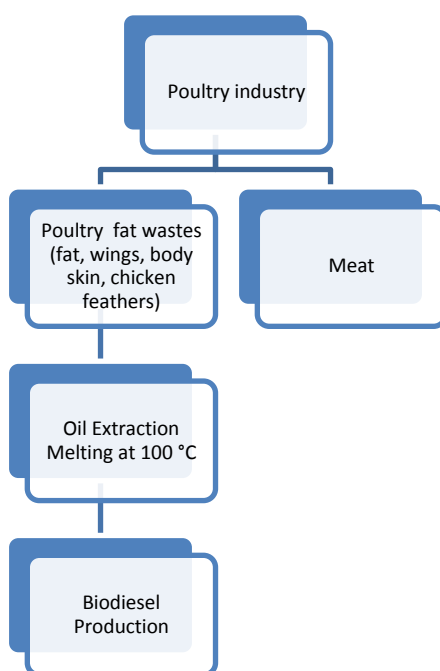


Figure. 4 Schematic representation of the main steps to obtain biodiesel from poultry fat wastes (Adapted from Kondamudi et al., 2009).

2. Literature Revision Regarding Biodiesel Production from Poultry Fat Wastes

The most relevant publications revised until May 2011, which studied biodiesel production from poultry fat wastes are presented in Table 5; the quality of the resulting product is assessed in Table 6.

Moreira et al. (2009) studied biodiesel production from poultry fat by homogeneous alkaline transesterification, evaluating the influence of the reaction conditions, namely temperature, time, methanol to fat molar ratio, concentration and type of catalyst on the yield and quality of the product. The product yield varied from 73 to 86 % (w/w).

Table 5 Studies regarding the production of biodiesel from poultry fat wastes

Reaction Conditions

Raw-Material	Process	T (°C)	Metanol/Fat (molar ratio % w/w)	t (h)	Reaction Conditions			Observations	References
					Catalyst		Stirring		
					Amount (% w/w)	Type			
Chicken Fat	Transesterification	30	6:1	1.5	1	NaOH	vigorous	-	Moreira et al. 2009
Chicken Fat	Transesterification	65	-	0.5	0.4	NaOH	-	-	Wyatt et al. 2005
Poultry Fat	Transesterification	50	1:3	24	25	H ₂ SO ₄	130 rpm	-	Bhatti et al. 2008
Poultry Fat	Transesterification	25	72:1	6-7	1 mmol/15 mL	NCO	-	-	Reddy et al. 2006
Chicken Fat	Transesterification	62	20 + 15	1 + 1	8 H ₂ SO ₄ and 1 NaOH	H ₂ SO ₄ and NaOH	-	-	Guru et al. 2010
Poultry Fat	Transesterification	120	30:1	8	10-20	MgAlH	1417 rpm	-	Liu et al. 2007
Feather meal	Transesterification	70	1:9	1	1	KOH	5000 rpm	Pre-treatment: Fat extraction; FFA remotion; Dehydratation	Kondamudi et al. 2009
Chicken Fat	Transesterification	60	6:1	4	1	H ₂ SO ₄	-	Pre-treatment: acid catalise	Alptekin and Canakci 2010
Duck Fat	Transesterification	65	6:1	3	1	KOH	-	-	Chung et al. 2009
Chicken Fat	Supercritical	400	9:1	6-10*	-	-	-	-	Marulanda et al. 2010
Poultry Fat	Pyrolysis	350-400	-	1.3	absence	absence	-	-	Santos et al. 2010

T- Temperature; t – time; *min

Table 6 Quality parameters studied in the most relevant articles of literature that refer biodiesel from poultry fat wastes.

Quality Parameters									
Density (kg.L ⁻¹)	Kinematic Viscosity (mm ² .s ⁻¹)	Acid value (mg KOH.g ⁻¹)	Total Glycerin (% mass)	Cloud Point (°C)	Yield (%)	Pressure	Flash Point (°C)	Observations	Reference
0.878-0.885	4.52-6.13	0.091-0.24	-	-	78.9-96.3	-	170-178	-	Moreira et al. 2009
-	4.3	0.33	0.101	4.3	-	-	150	-	Wyatt et al. 2005
0.867	0.00625 (kg.m ⁻¹ .s ⁻¹)	0.25	-	-5	99.01	-	-	-	Bhatti et al. 2008
0.869	2.8	-	-	-	89	-	74	-	Guru et al. 2010
-	-	-	-	-	-	100***	-	-	Liu et al. 2007
0.883	4.94	0.22	0.19	-	87.4	-	171.8	-	Alptekin and Canakci 2010
0.864	5.5	0.2	-	-	97.1	-	-	-	Chung et al. 2009
-	-	-	-	-	88	100-300**	-	-	Marulanda et al. 2010
0.84	4.93	114.43	-	-	40	-	-	3 h at 50 °C Copper Corrosion: 2	Santos et al. 2010

*Temperature between 80 and 140 °C; ** bar; ***psi

The authors concluded that it was possible to obtain biodiesel obeying the European quality standards, namely in terms of viscosity and ester content, through a transesterification at 30 °C; as most publications refer that transesterification reaction should be processed between 60 °C and 70 °C, this conclusion showed that waste poultry fat could be extremely appealing as raw material for biodiesel production.

Wyatt et al. (2005) prepared FAME from chicken fat by base-catalyzed transesterification using sodium hydroxide for its use as biodiesel fuel. The results showed that, in comparison with biodiesel produced from soybean oil, the biodiesel obtained from chicken fat showed decreasing NO_x emissions but still an increase in NO_x emissions over those resulting from fossil diesel use. The methyl esters produced from chicken fat had poorer low temperature properties than did the soy methyl esters, due to the highest degree of saturation, which was expected. Such difference was minimized by blending it with fossil diesel (B20). Regarding the other evaluated quality parameters, the quality of the product was satisfactory, their results were: viscosity – 4.3 mm².s⁻¹, acid value – 0.33 mg KOH/g, flash point – 150 °C, free glycerin – 0.04% (w/w), total glycerin – 0.101% (w/w), water and sediment – 0.020% volume, copper corrosion – 1^a, sulfated ash – 0.006% (w/w).

Bhatti et al. (2008) studied the production of biodiesel from chicken tallow using an acid (H₂SO₄) and basic transesterification (KOH). Results showed that acid catalysis led to higher yields. On the other hand, different experimental parameters studied such as amount of catalyst, temperature and time affected the biodiesel production. The yield of biodiesel was found to be highly dependent on the amount of catalyst, increasing with higher quantities of catalyst. At different levels of catalyst concentration, biodiesel yield increased with temperature and the highest yield (99.01%) was obtained at 50 °C. Finally it was also demonstrated that the conversion rate increases with reaction time (24 h).

Reddy et al. (2006) studied the conversion of poultry fat to biodiesel at room temperature (25 °C), results showed that nanocrystalline calcium oxide is an efficient catalyst for the production of environmentally compatible biodiesel fuel in high yields. The biodiesel obtained meets the ASTM D-874 in terms of sulfated ash value but the reaction time was considerably high (6-7 h); the molar ratio of methanol to fat (72:1) was very high too. In that study nanocrystalline calcium oxide (NCO) was used as heterogeneous catalyst (1 mmol dissolved in 15 mL of methanol).

Guru et al. (2010) studied the two step conversion of chicken fat (esterification followed by transesterification) to produce biodiesel. After, an addition of a synthetic Mg additive was studied in terms of its effect on engine performance. Because animal fats, in contrast to edible vegetable oils, have higher pour point, viscosity, flash point, and processing difficulties, magnesium-based additives might be used to improve the economics and feasibility. Magnesium based additives might reduce these parameters, depending on the rate of additive. The results showed that the engine torque did not change significantly with the addition of 10% of chicken fat biodiesel. The exhaust emissions were analyzed being concluded that CO and smoke emissions decreased by 13% and 9% respectively, but NO_x emission increased by 5%. Reduction in smoke emissions was principally based on the higher oxygen content of biodiesel and lower aromaticity and sulphur content, which are advantages of using chicken fat biodiesel.

Liu et al. (2007) analyzed the transesterification of poultry fat with methanol using Mg-Al hydrotalcite (MgAlH) derived catalysts. Transesterification was carried out during 8 h at 120 °C, and 100 psi in Parr 4590 batch reactor consisting of a stainless steel chamber, a glass liner, a three-blade impeller, and a thermocouple. The reactants were always loaded into the reactor at room temperature. A typical molar ratio of methanol to poultry fat was 30:1 and a stirring rate of 1417 rpm was used in all reaction experiments. The catalyst concentration was 10 or 20% (w/w) based on the poultry fat weight.

Kondamudi et al. (2009) described a new and environmentally friendly process for developing biodiesel from commercial feather meal, a waste product of the poultry industry. In this study, the fat was extracted using boiling water and KOH was used to remove the FFA in the form of soap that was separated from the fat content by centrifugation. It was possible to produce between 7 and 11% w/w of biodiesel (on a dry basis). The quality of the biodiesel was tested in accordance to ASTM, and it was similar to the biodiesel made from other common feedstocks, therefore showing the relevance of using such waste raw materials with very low value. Alptekin and Canakci (2010) developed an optimization of the pretreatment process for methyl ester production from chicken fat. In order to avoid the soap formation due to the use of alkali catalyst, an acid catalyst (sulfuric acid) was used before the transesterification. The optimum pretreatment conditions were found to be 20% sulfuric acid, 40:1 molar ratio of methanol to feedstock, 80 min of reaction and 60 °C. The transesterification reaction was further conducted at 60 °C during 4 h, with an alkali catalyst (KOH, 1 %

(w/w)) and the molar ratio of methanol to feedstock was 6:1. After transesterification, the methyl ester yield was 87.4% and the measured fuel properties of the chicken fat met EN 14214 and ASTM D6751 biodiesel specifications.

Chung et al. (2009) studied the biodiesel production by transesterification of duck fat with methanol using an alkali catalysts; the content of FAME, composition and chemical properties were investigated. The FAME content at the reaction conditions was 97% with KOH as catalyst. The highest purity was obtained conducting the reaction between 55 and 85 °C. When methanol was added according to the stoichiometry of the reaction (molar ratio of methanol to triglyceride of 3:1), the FAME content was 75%. The FAME content was increased significantly to 97% for 6:1 molar ratio of methanol to feedstock, obeying the quality standard EN14214. The acid value was 0.56 mg KOH.g⁻¹ before the reaction. After the reaction with methanol the acid value reduced to 0.2 mg KOH.g⁻¹ using KOH as catalyst, therefore obeying the biodiesel quality standard EN14214.

Marulunda et al. (2010) investigated a supercritical transesterification of chicken fat with methanol at various temperatures (350, 375 and 400 °C), pressures (100, 200 and 300 bar), methanol to chicken fat molar ratios (stoichiometric, 3:1 to 12:1), and residence time (3-10 min). The best experimental conditions were obtained under the following conditions: 400 °C, 300 bar, methanol to oil molar ratio of 9:1, and a residence time of 6 min. A good quality biodiesel was obtained with the conditions used; and such conditions might be more attractive to do the scale-up, compared to the experimental conditions at which supercritical transesterification processes are usually conducted, which are high methanol to oil molar ratios (usually 42:1) and high costs associated with pumping and preheating. Because of the high temperatures used in such process, some thermal decomposition products are formed; however, these products can improve certain properties of biodiesel, such as viscosity and cold flow.

Santos et al. (2010) studied the thermal cracking of poultry fat to produce biodiesel. It has been demonstrated that fatty acid wastes from the agribusiness, whatever vegetable or animal, can be transformed into biofuels by thermal cracking. As was already previously said, the search for alternative processes that allow the use of low quality feedstocks became an important subject to the biofuel industry. Pyrolysis experiments were carried out in the absence of catalyst at temperatures ranging from 350 to 400 °C using a bench home-made 5 L stainless steel batch unit. The materials were pyrolyzed for 10 minutes and vaporized. The vapor feed left the reactor with a temperature of

about 200 °C, entering in water cooled heat exchanger. As a result two phases were formed in the reactor, an aqueous fraction and an organic fraction. These two fractions were separated by decantation and the organic phase was distilled by standard laboratory techniques. The yields of fuel using poultry fat were lower than the ones obtained using other studied raw materials: soybean oil and beef tallow. Poultry fat yielded a 20% (w/w) of fuel at distillation temperature fraction higher than 200 °C whereas with the soybean oil a product yield of 56% (w/w) was obtained and with beef tallow 51% (w/w). The presence of steam during the pyrolysis can change the selectivity (Idem et al. 1996); thus, the high moisture content in the poultry waste compared to the other feedstocks, along with the presence of proteins and lipoproteins, might be responsible for the different behavior found during its pyrolysis. The high acid value found in the poultry fat increased the corrosive potential of the resulting fuel causing it to fail copper strip corrosion test and a high carbon residue of the fuel was also observed and attributed to a higher presence of double-bonds in alkyd chains causing polymerizations and incomplete combustion. The density and viscosity of the obtained fuels was in agreement with the standard EN 14214.

Despite the fact that the following literature does not refer specifically biodiesel production from poultry fat wastes, it introduces some important issues related to poultry fat. Therefore, the analysis that will be made from now on are focused on the physico-chemical composition of chicken skin fat, effects of blending alcohols with poultry fat methyl esters on cold flow properties and the storage stability of poultry fat.

Feddern et al. (2010) analyzed chicken fat extraction methods. The yield found for lipid extraction through Soxhlet method was only 14% comparing to 30%, obtained by different methods (Bligh et al., 1959). Amongst the methods with good results, the Bligh and Dyer method with modifications was selected, because it extracted twice more fat from the skin, and avoided changes caused by thermal treatment which occurred in both the hydrolytic methods and thermal extraction using the Soxhlet method.

Joshi et al. (2010) studied the effects of blending alcohols (ethanol, isopropanol and butanol) with poultry fat methyl esters on cold flow properties. Low-level blends of ethanol in fossil diesel are in fact known to reduce harmful exhaust emissions such as particulate matter, hydrocarbons and carbon monoxide as a result of increased fuel oxygenation. The study showed that the low temperature operability, the kinematic viscosity, and the acid value of poultry fat methyl esters were improved with the

addition of some alcohols; on the other hand, the flash point decreased and moisture content increased. The alcohol type did not influence the low temperature performance at similar blend ratios. Blends of ethanol afforded the least viscous mixtures, whereas isopropanol and butanol blends were progressively more viscous, but still in agreement with the EN 14214 requirements. Blends with alcohols failed the flash point specifications found in EN 14214, which should be expected, due to the very low flash point of such alcohols. Butanol blends with poultry fat biodiesel exhibited slightly superior low temperature performance, acid value, flash point and moisture content being suggested as the best option when considering such alcohol-biodiesel blends.

Geller et al. (2008) analyzed the storage stability of poultry fat biodiesel blends with fossil diesel. The stability of biodiesel is an issue of major importance, for example, poultry fat collected in warm summer months may be stored until needed to heat broiler houses in colder winter months. While these fats are being stored they must be relatively stable so that fuel properties will not deteriorate before biodiesel is used. Different poultry fat mixtures (20-80%) were stored for 1 year at bench scale (1 L) under controlled laboratory conditions at 4, 38, 54.4 °C and at ambient room temperature. Poultry fat biodiesel mixtures (20% and 80%) were also stored at pilot scale (946 L) outdoor, at ambient conditions. Viscosity and specific gravity of biodiesel changed very little over 1 year storage period. Sediment accumulation was present in all treatments, with increasing sedimentation correlating with increasing biodiesel concentrations. The addition of anti-oxidant to 100% biodiesel, minimized changes in physical properties and sedimentation over the course of the study. The corrosive effects of biodiesel component require the use of resistant materials in systems designed to store, transport and utilize these fuels; in this study, grey cast iron showed slight corrosion and therefore it was advised not to use it. On the other hand, stainless steel and carbon steel were not susceptible to attack by this biodiesel. This study showed that very little retrofitting is necessary to compensate for physical differences between fuels when switching to biodiesel in systems designed to store, transport and use petroleum fuels.

The study of stirring rate and temperature in the transesterification of poultry fat is extremely important, because recent studies show they have great influence in biodiesel yield. In order to achieve the highest biodiesel yields using waste raw materials, different reaction conditions have been studied. Stirring rate influence was not very studied at the present time, so that is why its study assumes a greater importance.

The present work intended to produce biodiesel from poultry fat adopting the most common reaction conditions in literature and focusing on the influence of stirring rate and temperature and also study their influence on the quality of the obtained product.

3. Material and Methods

3.1 Raw Material Pre-Treatment

Waste poultry fat was provided by two local butcherys: “Talho Carlota”, located in Santa Maria da Feira, and “Talho da Boavista”, located in Porto, Portugal. Fats were melted by heating at a temperature higher than 100 °C and then filtered under vacuum to remove suspended matter.

Using this process, the liquid fat was released and separated from the fat wastes. Being weighted and collected in a plastic box, after kept in the refrigerator to maintain its properties.

After extraction, the fat was melted together at 50 °C and homogenized to perform biodiesel production. The total amount of fat was conserved in two plastic boxes inside the refrigerator.

3.2 Raw Material Characterization

3.2.1 Acid Value

In order to assess the quality of the raw material, the acid value was determined by volumetric titration according to NP EN ISO 660 (2002).

A test portion was dissolved in a solvent (ethanol at 70 °C) and titrated with a 0.1 M solution of potassium hydroxide, using phenolphthalein as an indicator (Figure 5).



Figure. 5 Acid value determination.

3.3 Biodiesel Production

Biodiesel production was performed in two main steps: synthesis and purification. The reagents used in the synthesis and purification of biodiesel were sodium hydroxide powder 97% (reagent grade, Aldrich) and methanol 99.5% (analytical grade, Fisher Scientific).

The reactions were performed in the experimental apparatus shown in Figure 6, located in the fumehood, at the Laboratory for Process, Environmental and Energy Engineering (LEPAE).

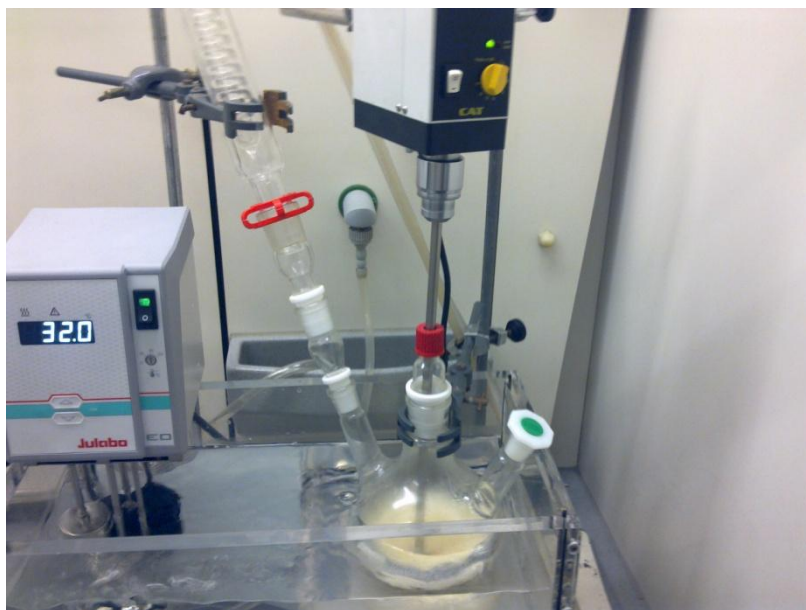


Figure. 6 Biodiesel Production in the laboratorial reactor

Figure 6 shows the reactor used, a round-bottom flask with three entrances, immersed in a thermostatic agitated bath, to maintain the desired temperature. In order to vary the stirring rate, a mechanical stirrer was used. A distillation column was also used to avoid the escape of methanol, and to allow methanol reflux. The reagents were added in the free entrance; and a thermometer was also used during the entire reaction. The reaction started when the mixture of NaOH (97%), dissolved in methanol (95%), was added to the sample.

The following reaction conditions were considered, according to the literature review: 6:1 methanol to fat molar ratio and catalyst amount 1% (w/w). As the mass of fat consider in each reaction was 150 g, the methanol used was 42 mL and the mass of catalyst (NaOH) was 1.5 g. The respective calculations are presented in Appendix A. The reactions occurred for a range of temperatures 30-60 °C and stirring rates of 400-1200 rpm during 1.5 h according to Moreira, 2009.

Biodiesel yield of each reaction was determined based in the follow expression:

$$\text{Biodiesel Yield} = \frac{\text{mass of biodiesel}}{\text{mass of raw material}} \times 100 \quad (1)$$

3.4 Planning of experimental conditions

Quimiometry is a specific area of Chemistry that uses statistically tools and multivariables, like experimental design methods to obtain important information of the chemical systems.

The main objective of optimization is to identify and study the effect of different process variables in the characteristics of a certain product.

The classical methodology is known to study one variable at the time, but as an alternative, the use of methodologies with reaction factorial design, based on the statistical principles of independent variables variation, allow the study of different variables interaction.

Factorial design is based on the simultaneous variation of all the factors in a limited number of levels (high or low). This type of experimental design allows the determination of the interactions between different factors, which leads to a high level of knowledge of the impact of variables on the product.

Experimental conditions were planned using JMP program; 1.5 h was the fixed time for all the reactions; two parameters were considered: temperature and stirring rate, being possible to understand the synergistic effects that could occur. Three different temperatures were considered: 30 °C, 45 °C, 60 °C as well as three stirring rates: 400 rpm, 800 rpm, 1200 rpm. These were selected because very few studies consider studying the reaction rate and the temperature is a key issue considering the energetic efficiency of the process. The experimental planning considered the use of Response Surface Design using Central Composite, the effects of the variables were therefore considered alone and combined.

Table 7 Parameters corresponding to the reactions performed according to JMP for biodiesel production.

Reaction number	Stirring rate (rpm)	T (°C)
1	400	30
2	400	30
3	800	30
4	800	30
5	1200	30
6	1200	30
7	400	45
8	400	45
9	800	45
10	800	45
11	800	45
12	800	45
13	1200	45
14	1200	45
15	400	60
16	400	60
17	800	60
18	800	60
19	1200	60
20	1200	60

After, the mixture of biodiesel and glycerol was placed in a dropping funnel, as shown in Figure 7. Separation occurred during one hour.



Figure. 7 Biodiesel and glycerol separation

After separation methanol was recovered in a rotary evaporator (Figure 8). In that equipment, biodiesel and glycerol phases were subjected to low pressure conditions at 65 °C to facilitate the methanol extraction.



Figure. 8 Methanol recovering in a rotary evaporator.

3.5 Biodiesel Purification

After extracting the excess methanol, biodiesel suffered a washing process (Figure 9) to remove the residual catalyst. First, 75 mL of a diluted solution of HCL (0.2%) was added to the biodiesel, then, the same amount of distilled water was repeatedly used to wash the biodiesel and ensure total removal of acid/base and salts. The washing process was stopped when the initial distilled water pH was similar to the pH of the water after extraction. After this washing process, biodiesel was heated at 90 °C to evaporate the water present.

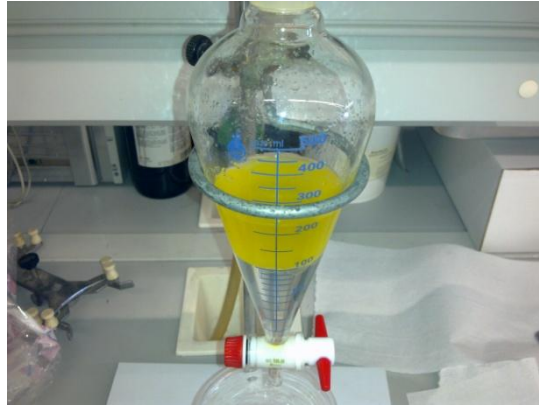


Figure. 9 Biodiesel purification

Finally, the purified product was weighted and placed in the refrigerator.

3.6 Biodiesel Characterization

In order to control biodiesel quality, some of the most important parameters according to ISO 14214 were determined; namely, kinematic viscosity, acid value, methyl ester content and iodine number.

3.6.1 Kinematic Viscosity at 40 °C

The viscosity is the resistance of a fluid to flow under gravity. Viscosity is determined recording the time that a fixed volume of fluid takes to flow under gravity in a calibrated capillary viscometer (Figure 10) at a constant temperature, using a proper bath (Figure 11). This determination was based on the standard reference ISO 3104 (1994).



Figure. 10 Cannon-Fenske Viscosimeter with a total longitude of 250 mm.



Figure. 11 Experimental apparatus – Thermostatic agitated bath with immersed viscosimeters.

When the bath reached the studied temperature, biodiesel was introduced into the viscosimeter and was left there for 10 minutes before the determination, to guarantee the desired temperature to perform the determination.

The time that a certain volume of oil takes to flow between the two marks was recorded. A *pompette* was used in the top part of the viscosimeter to create *vacuum* in the capillary. The oil flow due to the gravity and the flow time should not be lower than 200 seconds according to ISO 3105. Kinematic viscosity results from the product between time and a constant that is associated with the viscosimeter:

$$v = C \times t \text{ (mm}^2 \cdot \text{s}^{-1}\text{)} \quad (2)$$

For each oil, at a defined temperature, determinations were performed considering a maximum error of 0.85%.

3.6.2 Acid Value

The acid value was determined using volumetric titration following EN 14104 (2003), the results were expressed in milligrams of KOH per gram of sample. The procedure for this determination was similar to the described in 3.2.1. but using a mixed solvent, diethyl ether and ethanol.

3.6.3 Determination of methyl esters

Methyl esters were determined using gas chromatography with metil-heptadecanoate as internal standard, according to EN 14103 (2003). This parameter is of extreme importance because it measures biodiesel purity, the results are expressed in mass percentage.

A gas cromatograph Dani GC 1000 DPC (DANI Instruments S.p.A.), with an AT-WAX column (30 m, 0.32 mm internal diameter and 0.25 μm of film thickness) was used (Figure 12).



Figure. 12 Gas chromatograph.

The split injector was maintained at 250 $^{\circ}\text{C}$ and the Flame Ionization Detector (FID) at 255 $^{\circ}\text{C}$. The auxiliary gas used was nitrogen with 2 $\text{mL}\cdot\text{min}^{-1}$ flow. The injection was made in split mode with an injection volume of 1 μL . After the sample injection, a specific temperature program was used: firstly the oven temperature was fixed at 120 $^{\circ}\text{C}$ increasing 4 $^{\circ}\text{C}\cdot\text{min}^{-1}$ until reach 220 $^{\circ}\text{C}$ that was finally maintained during the last 10 minutes.

The samples are prepared in a vial, using 100 mg of biodiesel and 2 mL of a methyl-heptadecanoate solution (10 mg.mL⁻¹ in heptane). In order to analyze biodiesel samples each sample was diluted 8 times.

Then, 1 µL of diluted sample was injected in the chromatograph and by using an appropriate software the methyl esters were identified in a chromatogram comparing the retention times with the times of the respective standards.

The methyl ester percentage values were determined using the expression below:

$$TE = \frac{(\sum A) - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100 (\%) \quad (3)$$

where $\sum A$ corresponds to the total peak areas of methyl esters, from C14:0 to C24:1, A_{EI} is the peak area corresponding to methyl-heptadecanoate (C17:0), C_{EI} is the methyl-heptadecanoate concentration in mg/mL, V_{EI} the methyl-heptadecanoate volume (mL) and the mass of biodiesel in mg is represented by m .

3.6.4 Determination of the content of the methyl ester of linolenic acid

The methyl ester of linolenic acid was determined by gas chromatography using the same method expressed in 3.6.3. The importance of this determination is due to the sensitivity of this particular ester when exposed to the light and oxygen. It was calculated using the expression below:

$$L = \frac{A_L}{\sum A - A_{EI}} \times 100 (\%) \quad (4)$$

Where L represents the linolenic acid methyl ester content, in mass percentage, A_L the peak area that corresponds to linolenic acid. $\sum A$ express the total peak areas of methyl esters from C14:0 to C24:1 and A_{EI} is the peak area that corresponds to methyl-heptadecanoate (C17:0).

3.6.5 Iodine Value Determination

Iodine value determination was performed using the methyl esters composition, according to the Appendix B of EN 14214 (2009). The results are expressed in grams of iodine per 100 g of FAME. The importance of this property is due to its capacity to express the biodiesel unsaturation degree. The iodine value was calculated considering

the individual contributions of each methyl ester. These contributions are referred in Appendix B of EN 14214 (2009) and correspond to a numerical factor. The iodine value is obtained by multiplying each methyl ester factor by the percentage of each methyl ester present in the sample and adding all the values obtained.

4. Results

4.1 Raw-Material Extraction and Characterization

The total mass of oil obtained was 5.097 kg, showing a fat extraction yield of 35% w/w. The amount of extracted fat was higher than the needed for the experiments, for safety reasons.

The acid value of the fat was $5.72 \text{ mg KOH.g}^{-1}$, much higher than expected according to Moreira (2009). Such value shows a relatively high deterioration of the raw-material which might also be responsible for the difficulties in obtaining reproducible results. The acid value calculations are presented in Appendix B.

4.2 Biodiesel Production Conditions and Quality Parameters

Table 8 resumes the quality parameters for all the experiments performed, under different reaction conditions.

Table 8 Reaction conditions for biodiesel production and quality parameters determined

Reaction number	Stirring rate (rpm)	T (°C)	Kinematic Viscosity ($\text{mm}^2.\text{s}^{-1}$)	Acid Value (mg KOH.g^{-1})	Ester content (%)
1	400	30	12.20	0.11	34.7
2	400	30	34.01	0.08	1.6
3	800	30	9.46	0.09	21.1
4	800	30	19.90	1.85	61.1
5	1200	30	31.03	0.07	4.6
6	1200	30	21.84	0.10	19.2
7	400	45	29.02	0.19	5.6
8	400	45	27.19	0.08	5.1
9	800	45	31.07	0.27	7.5
10	800	45	29.73	0.11	6.8
11	800	45	29.83	0.08	7.3
12	800	45	30.91	0.16	10.6
13	1200	45	27.09	0.82	17.4
14	1200	45	21.54	0.06	6
15	400	60	25.53	0.17	9.2
16	400	60	11.31	0.17	10.2
17	800	60	29.30	0.14	12.6
18	800	60	25.75	0.19	46.7
19	1200	60	8.22	0.55	67.1
20	1200	60	10.97	0.41	16.1

In the following subchapters the yield and quality parameters will be analyzed in detail.

4.2.1 Biodiesel Production Yield

From an economical perspective, biodiesel production yield is very important. The yield was determined considering the initial poultry fat mass (150 g) and the mass of biodiesel obtained after the reaction. The yield obtained was calculated using expression (1) and it varied between 50.13% and 78.01%.

There are a few reasons for the low yield achieved: i) formation of emulsions that difficult the washing process during purification; ii) drag of some biodiesel during this phase; iii) presence of water that leads to hydrolyzation of triglycerides and

consequently formation of FFA that react with NaOH forming soaps. Regarding the raw material used, the results show that biodiesel production using acid raw material by conventional process is possible, without any pre-treatment, contrary to the results obtained in other studies; however it brings many operational problems and difficulty the reproducibility of the experiments. Therefore, the storage and the processing of the fat is a key issue.

The influence of temperature and stirring rate on the biodiesel yield was evaluated and also in kinematic viscosity, acid value, methyl ester content and iodine value of the resulting product.

Figure 13 shows the influence of the temperature at different stirring rates. Yield varied between 50.13% and 78.01%, due to the difficulty in obtaining reproducible results, tendencies are difficult to be accessed. However there seems to be a tendency of a higher yield with increasing temperature at the highest mixing rates studied (Figure 13 (b) and (c)); the opposite occurring at the lowest mixing rate (Figure 13 (a)). The lack of reproducibility in the yield might be related with the difficulties observed during separation and purification steps.

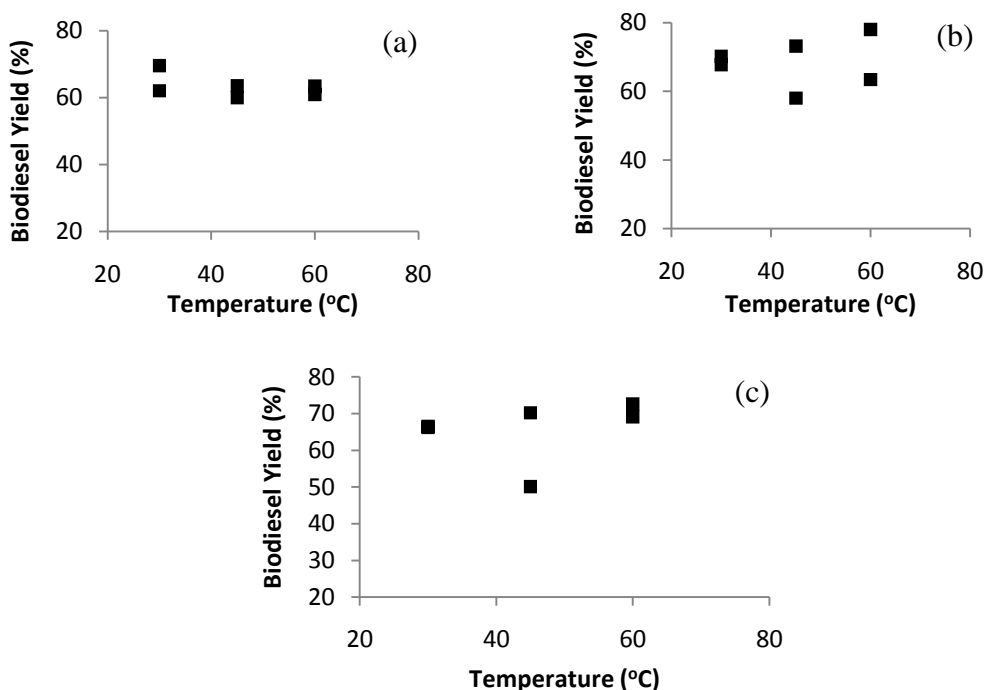


Figure. 13 Influence of temperature in biodiesel yield % (w/w) at: (a) 400 rpm, (b) 800 rpm and (c) 1200 rpm.

Figure 14 shows the variation of yield with the mixing rate at different temperatures. Results showed that: (a) at 30 °C the values were very similar to each other so it seemed that at this temperature the stirring rate had not a great influence; (b) at 45 °C

reproducibility was difficult to achieve and so results were not conclusive; and (c) at 60 °C there seems to have a tendency of increasing in biodiesel yield with increasing stirring rates; nevertheless, the maximum yield was obtained at 800 rpm, being 78.01%. This might indicate that at higher stirring rates, the formation of soaps and emulsions are more likely to occur, leading to yield losses.

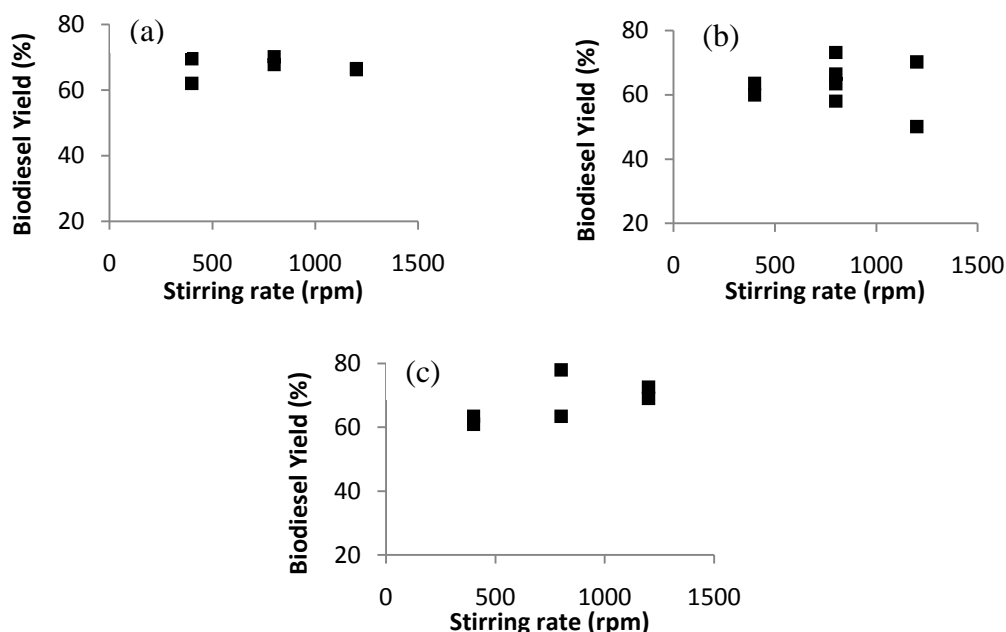


Figure. 14 Influence of stirring rate in biodiesel yield % (w/w) at: (a) 30 °C, (b) 45 °C and (c) 60 °C.

4.2.2 Biodiesel Quality Control

Biodiesel quality control was made by evaluating the kinematic viscosity, acid value, methyl esters content and iodine value following the procedures present in EN ISO 14214. The results obtained are presented in Table 9.

Table 9 Properties of the produced biodiesel

Properties	EN 14214	Range of results
Kinematic Viscosity at 40 °C (mm ² .s ⁻¹)	3.50-5.00	8.22-34.01
Acid value (mg KOH.g ⁻¹)	< 0.50	0.06-1.85
Methyl ester content (% (w/w))	> 96.5	1.6-67.1
Linolenic acid (% (w/w))	< 12.0	not detected
Iodine Value (I ₂ .100g ⁻¹)	< 120	52-96

Observing Table 9 it is possible to understand that there was a significant variation of the quality properties among experiments; showing, that under the conditions studied, such variables influence significantly biodiesel quality. However, in none of the conditions studied it was possible to obtain a product with enough quality to be used 100% as diesel replacer in diesel engines.

4.2.2.1 Kinematic Viscosity at 40 °C

The study of this property is very important because it influences the injection efficiency of the fuel and the combustion itself (Moreira, 2009).

When a fuel has high viscosities, the injection is affected because it leads to a pressure and volume increase, this phenomenon is more significant at low temperatures. The viscosity analysis is also of extreme importance in order to guarantee the good function of some vital parts of the engine, namely fuel atomization and conservation of the lubricated pieces (Moreira, 2009).

Viscosity is higher when the raw material is highly saturated and also, when a high proportion of mono, di and triglyceride exists, which shows lower biodiesel purity (Mittelbach et al., 2004).

The influence of temperature in kinematic viscosity was also evaluated being represented in Figure 15. Viscosities were between 8.22 and 34.01 mm².s⁻¹. By analyzing the three different plots it was possible to see that generally, kinematic viscosity decreased with increasing temperature except at 800 rpm, where results were not conclusive due to high variations observed.

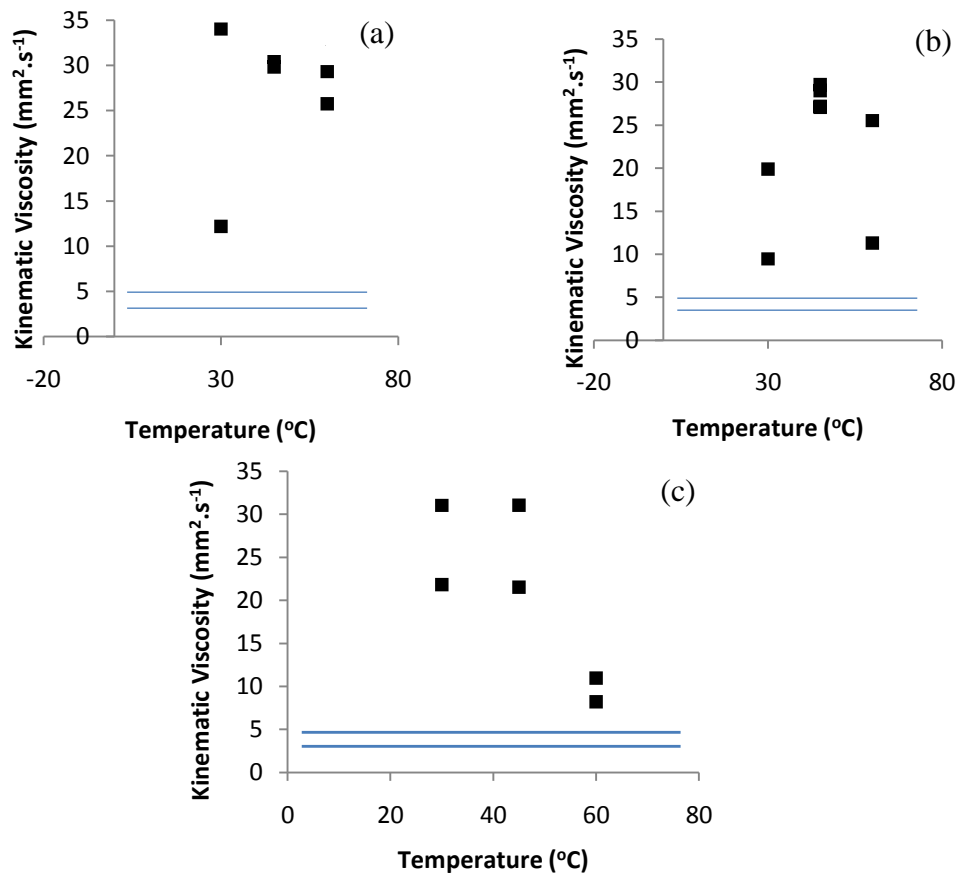


Figure. 15 Influence of temperature in the kinematic viscosity at: (a) 400 rpm, (b) 800 rpm and (c) 1200 rpm.

In Figure 16 it is possible to see the influence of stirring rate in the behavior of kinematic viscosity. The values ranged from 8.22 to 34.01 $\text{mm}^2 \cdot \text{s}^{-1}$: At the lowest temperature (Figure 16 (a)) a high variation of results were obtained. It was however evident that at 60 $^{\circ}\text{C}$, lower viscosities were obtained at higher stirring rates (Figure 16 (c)). Such effect was more evident at the highest temperature studied.

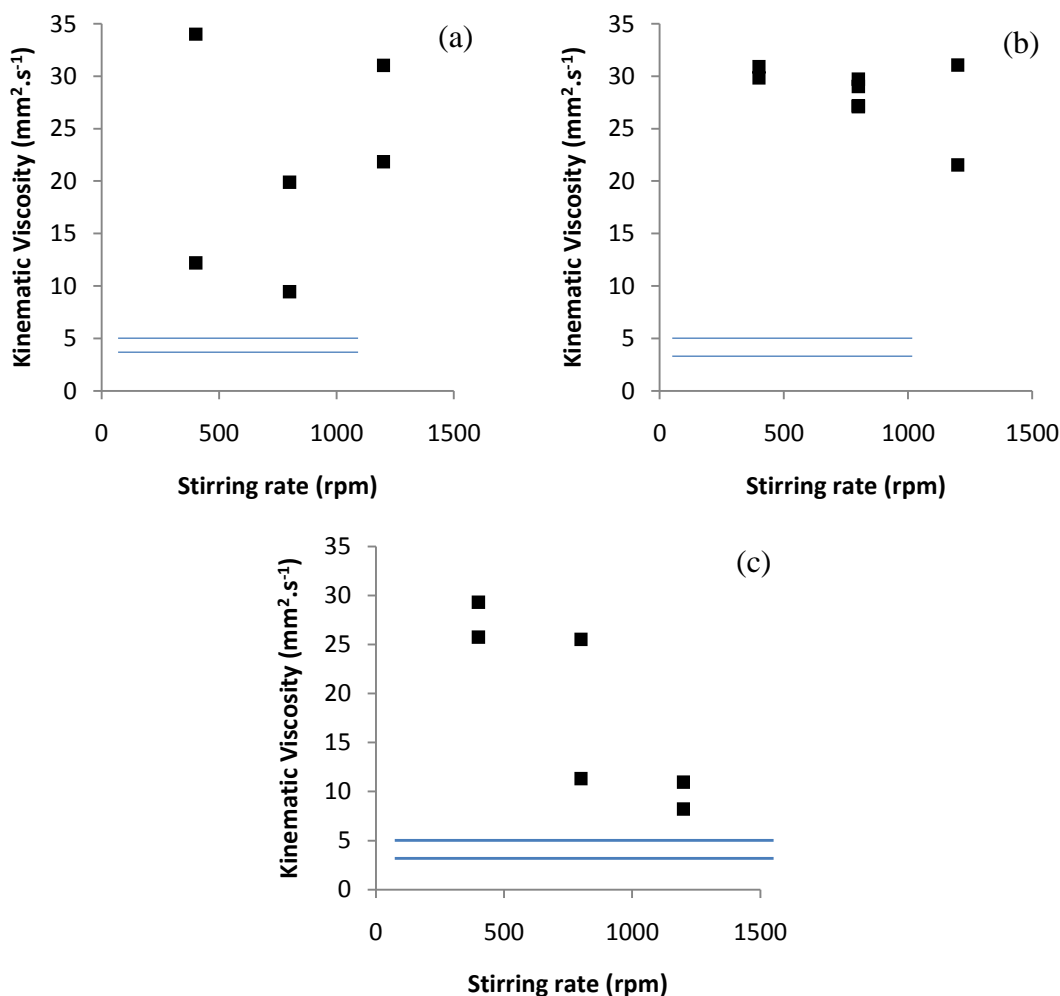


Figure. 16 Influence of stirring rate in the kinematic viscosity at: (a) 30 °C, (b) 45 °C and (c) 60 °C.

Considering all the reaction conditions studied, the lowest viscosity, which indicates higher conversion, was obtained using 1200 rpm at 60 °C, being 8.22 mm².s⁻¹.

4.2.2.2 Acid Value

The amount of FFA present in a sample of fuel affects its acid value.

The acid value varies mostly due to the raw material characteristics and it is also determined to evaluate biodiesel degradation during its storage; higher acid values indicate high biodiesel degradation (Moreira, 2009).

In terms of the acid value, the influence of temperature and stirring rate was evaluated.

Figure 17 shows the influence of temperature in the acid values at different stirring rates are very close to each other and it seemed that temperature did not have a relevant effect on acid value. The lowest acid values were obtained at 400 rpm; however, under all conditions studied, it was possible to achieve values lower than 0.5 mg KOH.g⁻¹ that is the maximum acid value accepted by EN ISO 14214.

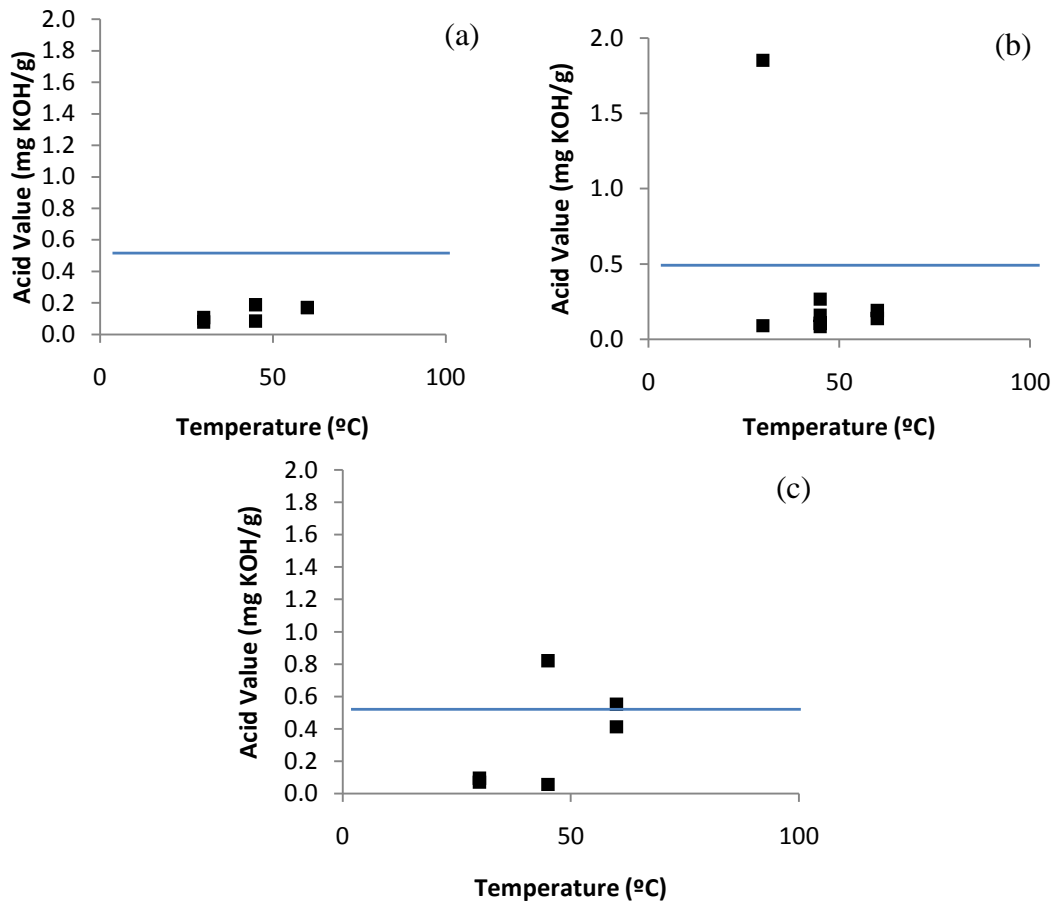


Figure. 17 Influence of temperature in the acid value at: (a) 400 rpm, (b) 800 rpm and (c) 1200 rpm.

In Figure 18 the influence of the stirring rate at different temperatures might be observed. The limit established by EN ISO 14214 was respected by most all biodiesel samples. The differences observed in some replicates might indicate that some of the samples were deteriorated by air, light or temperature conditions during their storage

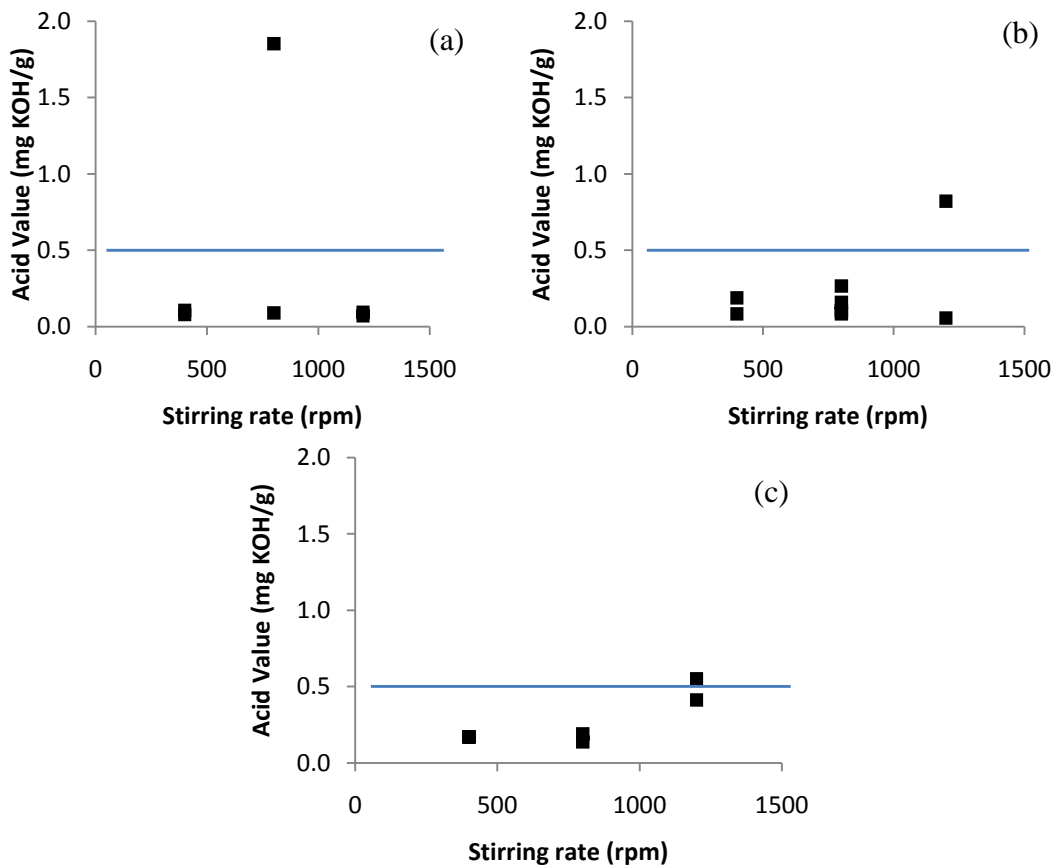


Figure. 18 Influence of stirring rate in the acid value at: (a) 30 °C, (b) 45 °C and (c) 60 °C.

Considering all the reaction conditions studied, when in agreement with the standard EN 14214, the values varied from 0.06 mg KOH.g⁻¹ to 1.85 mg KOH.g⁻¹. The lowest values were obtained when stirring rate was 1200 rpm, at 45 °C.

4.2.3 Biodiesel Composition

Biodiesel composition reflects the raw material composition and was determined using gas chromatography. The mean values for ester composition (%) obtained for each methyl ester as well as the standard deviation are presented in Table 10.

Table 10 Ester composition (%) for each fatty acid.

Methyl Ester of the following fatty acids	Composition (% w/w)	Standard Deviation
Myristic C14:0	0.28	0.26
Palmitic C16:0	24.85	1.49
Palmitoleic C16:1	6.13	0.34
Stearic C18:0	6.23	0.31
Oleic C18:1	41.19	1.11
Linoleic C18:2	20.94	1.53
Linolenic C18:3	< DL (lower than the detection limit)	3.38
Eicosanoic C20:0	0.28	-

The biodiesel saturation degree was calculated based on the sum of saturated fatty acids (C14:0, C16:0, C18:0 and C20:0) and biodiesel unsaturation degree was also calculated based on the sum of unsaturated fatty acids (C16:1, C18:1, C18:2, C18:3). The saturation and unsaturation degree were 31.64% and 68.26% respectively. Oleic fatty acid ester was the one presented in higher quantity.

4.2.3.1 Biodiesel Methyl Ester Content

Methyl ester content expresses biodiesel purity, which according to EN ISO 14214 must be at least 96.5% w/w. This parameter is of extreme importance to avoid illegal mixtures and ensure proper quality.

Lower methyl ester content might be related to: i) reaction conditions established; ii) raw material characteristics; and iii) high presence of impurities in the final product, such as alcohol and residual glycerol. Most impurities are usually removed during biodiesel purification procedures.

The influence of temperature in the ester content was studied being presented Figure 19. The results ranged from 1.6% to 67.1% and it was possible to observe that the highest purity was obtained at 60 °C and also at the highest stirring rate. Usually purity

increases with temperature and mixing rate, so results at lower stirring rates were not expected.

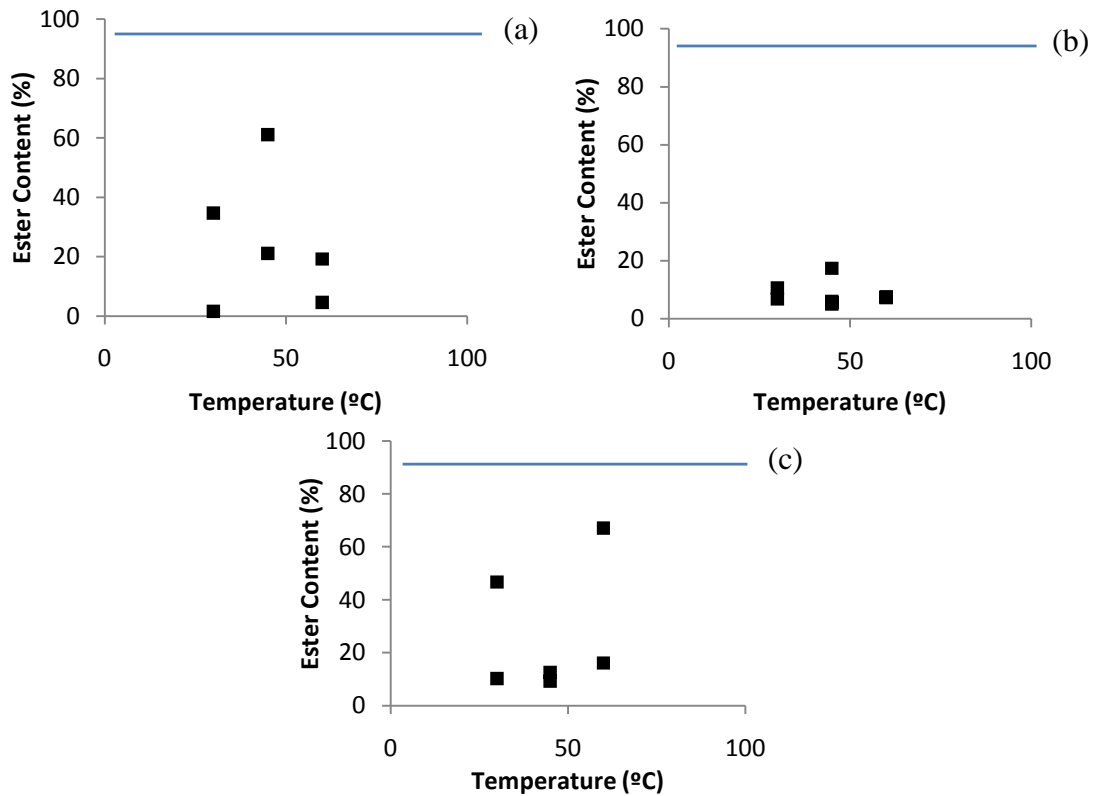


Figure. 19 Influence of temperature in the ester content at: (a) 400 rpm, (b) 800 rpm and (c) 1200 rpm.

Regarding the influence of the stirring rate in ester content at different temperatures, it was verified that the best results (higher ester content) were obtained at higher stirring rates and the clearly effect was more pronounced at 60 °C; the results obtained ranged from 1.6% to 67.1%.

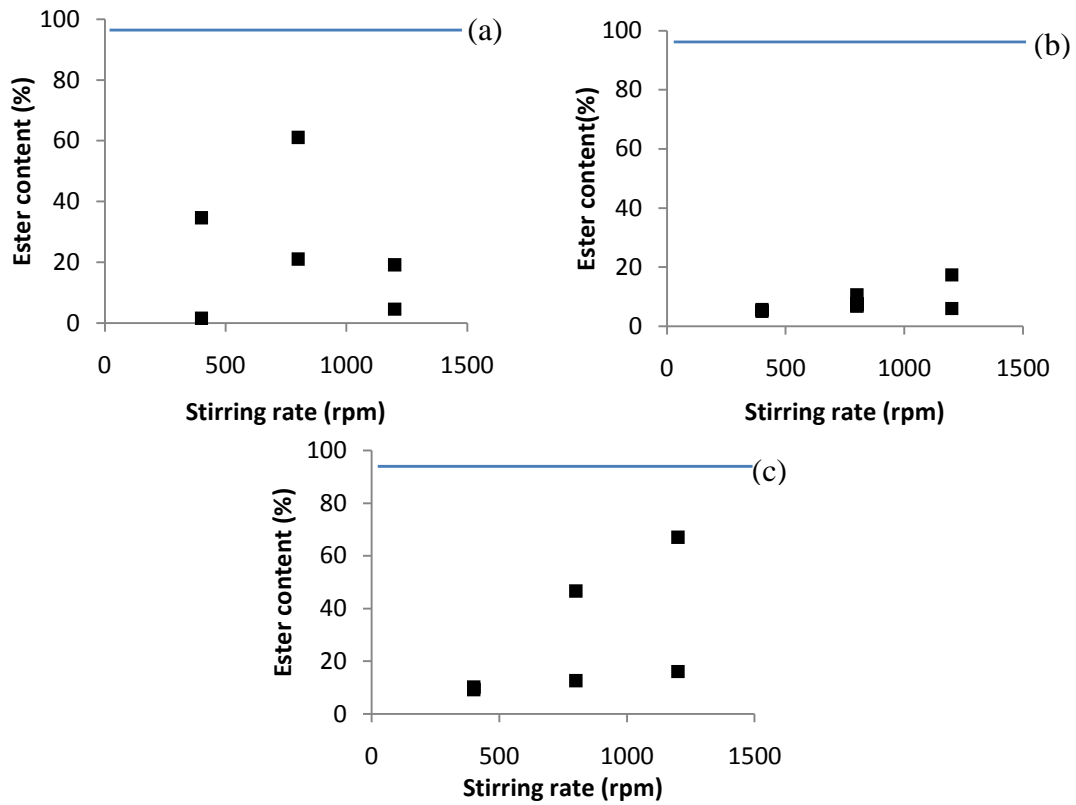


Figure. 20 Influence of stirring rate in the acid value at: (a) 30 °C, (b) 45 °C and (c) 60 °C.

4.2.3.2 Iodine Value

The iodine value measures the biodiesel unsaturation degree. EN ISO 14214 sets 120 g I₂/100 g as the maximum value for this parameter. Generally, when using animal fats as raw materials, due to its lower unsaturation degree, iodine value tends not to be limiting. In Table 11 we can see expressed all values for iodine value and some differences between samples were noticed.

Table 11 Iodine Values of the biodiesel samples

Reaction number	Iodine Value
1	96
2	81
3	77
4	77
5	52
6	76
7	89
8	77
9	77
10	79
11	78
12	78
13	77
14	81
15	76
16	77
17	78
18	78
19	79
20	87

As it can be seen in Table 11, the mean iodine value was below the maximum expressed in the international standard, being 78.5 g I₂.100g⁻¹.

Table 11: Iodine value determined in all samples

	Iodine Value (g I₂.100 g⁻¹)
Average	78.5
Standard deviation	8.05

5. Conclusions

The main conclusions that could be taken from the present work about biodiesel production from poultry fat, were:

It is a good practice to use renewable raw materials to produce biodiesel;

Poultry fat wastes from slaughtering had a fat extraction yield of 35% w/w;

The acid value of the extracted fat was $5.72 \text{ mg KOH.g}^{-1}$, which indicates some degree of degradation;

It was possible to perform basic transesterification of such raw material as opposed to what is mentioned in several studies; however, it was not possible to obtain a product conforming European biodiesel quality standard EN 14214.

Biodiesel yield was between 50.13% and 78.01%; Product yield generally increased with increasing temperature; Product yield generally increased with increasing stirring rates; nevertheless the maximum yield was obtained at 800 rpm, being 78.01%.

It was found a marked influence of the stirring rate and temperature in the yield, viscosity and purity of the obtained product;

Biodiesel samples obtained did not meet the requirements of EN ISO 14214 regarding kinematic viscosity, acid value, ester content;

Biodiesel samples presented an acceptable iodine value according to EN ISO 14214; the mean iodine value was $78.5 \text{ I}_2.100\text{g}^{-1}$.

Reproducibility was an obstacle because it was not maintained for some conditions, due to the low quality (high acid value) of raw material used;

Temperature seemed to influence kinematic viscosity of the product and it was possible to observe a decrease in viscosity with the temperature rise.

Acid values were generally in agreement with EN 14214;

Ester content was maximum at the higher temperature (60 °C) studied and higher stirring rate (1200 rpm), being 67.1%.

The use of such a low grade raw material using conventional processing was possible but difficulties showed that, in order to achieve economical viability of using such inexpensive raw materials and avoid high degree of pre-treatment and associated costs; the storage conditions should be optimized to ensure good quality of the raw material. If not possible, other alternatives should be studied.

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APPENDIX

APPENDIX A

Methanol Volume:

$$M_{fat} = (M_{biodiesel} \times 3) - 4 = (290 \times 3) - 4 = 866 \text{ g. mol}^{-1} \quad (1)$$

$$n_{fat} = \frac{m_{fat}}{M_{fat}} = \frac{150}{866} = 0.17321 \text{ mol} \quad (2)$$

$$n_{methanol} = 6 \times 0.17321 = 1.039261 \text{ mol} \quad (3)$$

$$m_{methanol} = n_{methanol} \times M_{methanol} = 1.039261 \times 32.04 = 33.2979 \text{ g} \quad (4)$$

$$V_{methanol} = \frac{m_{methanol}}{\rho_{methanol}} = \frac{33.2979}{0.79} = 42.15 \text{ mL} \quad (5)$$

Amount of Catalyst NaOH:

$$1 \% (w/w) = 0.01 \times 150 = 1.5 \text{ g} \quad (6)$$

APPENDIX B

Acid Value Calculation:

$$\text{Acid Value} = \frac{56.1 \times 10.2 \times 0.1}{10.00} = 5.72 \text{ mg KOH/g} \quad (7)$$