

# RESIDUAL LARD FAT: A GOOD ALTERNATIVE AS BIODIESEL RAW MATERIAL

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## 1 INTRODUCTION

Liquid biofuels are a growing resource of great interest and are complementary to petrol-based fuel. Biodiesel is an environmentally friendly liquid fuel that can be used in any diesel engine without any modifications. In addition, it is less contaminating and of a more renewable nature than conventional petroleum diesel fuel. Biodiesel is defined, according to The American Society for Testing and Materials (ASTM), as monoalkyl esters of long chain fatty acids (FAME) derived from a renewable lipid feedstock, such as vegetable oil or animal fat (Zhang et al. 2003).

Nowadays, the searching of alternative vegetable oily raw materials to product biodiesel has redirected the research towards animal fats. The shortage of the conventional raw materials has conducted to think the perfect raw material will be an animal fatty waste. In biodiesel production, to obtain high quality product at the same time good yields, is really important to repay the production costs. As far as their fatty acid compositions are concerned, animal fats have certain disadvantages with regard to quality due to the fact that the high saturated fatty acid content causes problems in winter operations. On the other hand, the high degree of saturation yields excellent fuel properties, specifically with regard to heating value and cetane number (Mittelbach et al. 2004).

Residual or reused lard fat contains mainly triglycerides although it is frequently to found free fatty acids (FFA), solids and diminished compounds as polar-compounds due to the previous utilisation. Due to the high acid value, the fat needs pre-treatment for alkaline transesterification. If the FFA level exceeds 0.5 wt.%, saponification hinders separation of the ester from glycerine and reduces the yield and formation rate of FAME because of alkaline catalyst consumption (Berrios et al. 2007; Canakci et al. 2001). So if FFA esterification is carried out with methanol and acid catalyst to obtain FAME, the final yield will be slightly increased. A factorial design of experiments has been applied because it allows the simultaneous consideration of many variables at different levels and the interactions between those variables, using a smaller number of observations than conventional procedures. This technique has several advantages and has been used extensively to develop different transesterification processes (Da Lima et al. 2006; Vicente et al. 2007).

Because FAME cannot be classified as biodiesel until the EN 14214 Standard specifications (2008) are met, the purification stage is essential. The purity level of the biodiesel has a strong effect on fuel properties and on engine life. The most common process of purification is water washing.

The aim of this work has been the utilisation of residual lard fat as new raw material in biodiesel production. Subsidiary objectives have been optimizing some reaction conditions in the two used process: esterification and transesterification.

## 2 MATERIALS AND METHODS

The raw material used in this paper was residual lard fat, with an acid value of 3.144 mg KOH·g<sup>-1</sup> oil. Table 1 shows the most important characteristics of this residue, after water washing and centrifugation. 99.5% pure methanol, sulphuric acid (95-98% purity) and potassium hydroxide (85% purity) used as catalyst for esterification and transesterification respectively, were purchased from Alcoholes del Sur, S.A. (Spain) and Panreac (Spain), respectively. The gas chromatography reference standards were obtained from Fluka (Sweden). All the determinations were made with a method in accordance with the requirements from EN 14214 Standard (2008).

The experimental set-up used for esterification and transesterification were identical to that previously employed in other papers (Berrios et al. 2007; Berrios et al. 2010), which allow to control agitation speed and temperature. In addition, pressure can be controlled in esterification reactor.

In previous studies (Berrios et al. 2007; Zhang et al. 2003) similar esterification conditions were reported. Esterification tests were carried out at 600 rpm, with H<sub>2</sub>SO<sub>4</sub> as the acid catalyst at a concentration of 5 wt.%

(relative to total acidity as oleic acid), using a methanol/oleic acid mole ratio of 60:1 and two different temperatures (60 and 80 °C). The reaction development was checked by the acid value determination (EN 14214, 2008) in samples taken from the reactor at several intervals.

The transesterification conditions were taken from the background literature (Darnoko et al. 2000; Tomasevic et al. 2003). Transesterification tests were carried out at 60°C, with a methanol/oil mole ratio of 6:1, several agitation speeds (from 400 to 800 rpm) and three alkaline catalyst concentrations (KOH) of 0.6, 0.9 and 1.2 wt.%. The transesterification development was checked by the determination of the content of methyl esters (EN 14214, 2008) in samples taken from the reactor at several intervals.

The purification stage was performed with water washing (2 extraction steps with tap water at 10 wt.%) in order to fulfil the requirements of EN 14214 Standard (2008).

A factorial design of experiments was applied to find out the influence of the operational conditions of the transesterification process. The experimental design applied to this study was a full 3<sup>2</sup> factorial design (two factors each at three levels). The response selected was the FAME concentration (C, % m/m) at 20 minutes. The factors were selected according to the background literature (Berrios et al. 2007; Vicente et al. 2007), the chemistry of the system and previous studies. The factors chosen were agitation speed (revolutions per minute, rpm) and catalyst concentration (% wt). Factor levels were chosen by considering the operational limits of the experimental set-up and preliminary tests. Experiments were run at random to minimize errors due to possible systematic trends in the variables (Vicente et al. 2007). The experiments were carried out in duplicate for experimental error estimation. The use of analysis and factorial design of experiments allowed us to express the FAME concentration as a polynomial model.

**TABLE 1 Chemical analysis of residual lard fat**

Tests	Results (wt.%)	Tests	Results (wt.%)	Tests	Results (wt.%)
Ash content	0.17	Monoglycerides	0.11	Triglycerides	84.82
Moisture	1.24	Diglycerides	4.76	Others	7.32
Free fatty acids (FFA)	1.58				

### 3 RESULTS AND DISCUSSION

#### 3.1 Esterification

The elimination of FFAs relies on the well-known esterification reaction:



which is catalysed by acids. In this work, R<sub>1</sub> was a linear chain of 13–23 carbon atoms containing a variable number of unsaturations depending on the particular origin of the raw material, and R<sub>2</sub> was a methyl radical.

This reaction is heterogeneous (methanol is non-soluble in residual lard fat), so it requires agitation in order to avoid mass transfer taking control of the process. In this work, a speed of 600 rpm was used to examine the influence of the temperature on the conversion of FFA to FAME, because this value was found to have no further effect on the reaction rate in previous research (Berrios et al. 2007).

The methanol/oleic acid mole ratio was set at 60:1 and the H<sub>2</sub>SO<sub>4</sub> concentration was 5 wt.% as was checked in previous research. Figure 1 shows the removal of free fatty acids versus time. It was found that the reaction rate increased when the temperature rose. In all the tests, the equilibrium of the reaction was observed. The temperature increase caused the decrease of oil viscosity, improving the contact between reactants. The reaction time to obtain oil, with an acid value below 1 mg KOH·g<sup>-1</sup> oil (FFA level of 0.5 wt.%) was reduced considerably. These improvements were possible thanks to the characteristics of the experimental set-up. Similar results were obtained at different temperatures. But the reaction time was reduced from 2 hours to 1 hour when temperature was increased from 60 to 80 °C.

Table 2 shows some chemical characteristics of esterified residual lard fat, where it can be observed that the triglyceride content did not show any significant variation because the formation of FAME from triglycerides in the esterification reaction is slower than in the transesterification step. Thus, diglycerides and monoglycerides appeared from the breakage of triglycerides. However, the fatty acid content decreased up to the recommended value in the background literature.

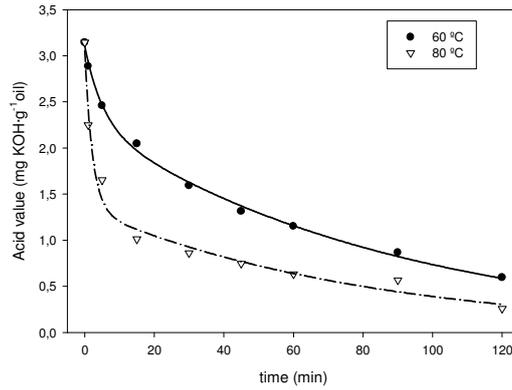


FIGURE1 Removal of free fatty acids versus time

TABLE 2 Characterization of esterified residual lard fat

Tests	Results (wt.%)	Tests	Results (wt.%)	Tests	Results (wt.%)
Moisture	0.85	Monoglycerides	1.65	Triglycerides	81.02
FFA	0.13	Diglycerides	5.87	Others	5.58
FAME	4.90				

### 3.2 Transesterification

To choose the adequate response in the factorial design, several tests were carried out with different levels of catalyst concentration and agitation speed. In all the experiments, atmospheric pressure and a temperature of 60°C were used for economic and technical reasons. A methanol lard mole ratio of 6:1 was selected according to the background literature (Darnoko et al. 2000; Tomasevic et al. 2003). The reaction time for all the experiments was 1 hour in order to observe when the FAME concentration was approximately constant. In this way, the selected response was FAME concentration at 20 minutes as can be observed in Figure 2.

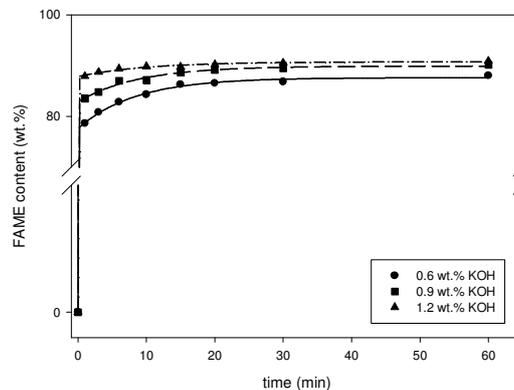


FIGURE1 FAME concentration versus time

The response was fitted to the factors through a general linear model (GLM). In the GLM, the following expression was obtained:

$$FAME_{conc} = 78.068 + 0.007 g \text{ Agitation speed} + 8.653 g \text{ Catalyst}_{conc} - 0.003 g \text{ Agitation speed} g \text{ Catalyst}_{conc} \quad Eq.(1)$$

Statistical analysis of the experimental range studied shows the catalyst concentration as the most important factor in the response. The agitation speed also has an influence. Both of them have a positive influence. The interaction between them is not very significant but has a negative influence (see Eq. (1)). In this way, the FAME concentration increases when the values of these variables increase. However, from 600 rpm and 0.9% wt KOH, the improvement does not justify more catalyst and energy consumption.

Biodiesel purification was run by liquid-liquid extraction at 2 steps and 10 wt.% tap water and drying under vacuum, obtaining a high quality final product. Anaerobic co-digestion has been proposed as a viable option to valorise the glycerol and the generated wastewater. Table 3 shows the characterization of the final product.

**TABLE 3 Characterization of the final product**

Tests	Results	EN 14214
Acid value (mg KOH·g <sup>-1</sup> oil)	0.216	<0.500
Density at 25 °C (g·cm <sup>-3</sup> )	0.871	0.860-0.900
Kinematic viscosity at 40 °C (mm <sup>2</sup> ·s <sup>-1</sup> )	4.89	3.50-5.00
FAME content (wt.%)	89.3	>96.5
Linolenic acid methyl ester content (wt.%)	0.5	<12.0
Water content (mg·kg <sup>-1</sup> )	463	<500
Triglyceride content (wt.%)	0.05	<0.20
Diglyceride content (wt.%)	0.24	<0.20
Monoglyceride content (wt.%)	0.67	<0.80

#### 4 CONCLUSIONS

The most suitable conditions to produce biodiesel from residual lard fat were: pre-treatment of esterification with 600 rpm, 80 °C, 5 wt.% H<sub>2</sub>SO<sub>4</sub> and 60:1 methanol/oleic acid mole ratio and transesterification at 60°C, 6:1 methanol – lard mole ratio, 600 rpm and 0.9% wt KOH. Although the product was not fulfilled all the requirements of EN 14214 Standard, it could be an interesting way to treat an environmental residue.

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