ONE STEP AND TWO-STEP SYNTHESIS OF FAMES USING WASTE RAW MATERIALS

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ABSTRACT

The production of fatty acid methyl esters (FAMEs), an environmentally friendly diesel substitute, might be conducted using vegetable oils or animal fats as raw materials. At present, biodiesel production is made using virgin vegetable oils as raw materials; however, their high price, which sometimes approaches that of the fossil diesel fuel, is becoming a huge problem. Additionally, the use of food oils for FAMEs production is controversial; reason why studying alternative raw materials is of major importance.

The use of waste raw materials for bioenergy production is very appealing; however, due to the common characteristics of such materials, research is required to enable its application in a larger scale. Aiming the FAMEs production from waste animal fat at a larger scale, the usually high content of free fatty acids of the fats is a limiting factor, because fatty acids react with the catalyst during alkali transesterification, causing the formation of soaps. Because alkali transesterification is still considered the best option from an economic point of view (acceptable temperatures and atmospheric pressure are used), studying alternatives which might be easily adopted in current production process is very important.

In the present study, the production of FAMEs from acid waste lard was studied considering a one-step alkali transesterification reaction and a two step reaction consisting of an acid esterification followed by an alkali transesterification. The two step synthesis was optimized considering the amount of acid catalyst used and the final product quality was evaluated.

The one-step transesterification was ineffective due to the high acidity of the raw material. The proposed two-step reaction was effective to enable acid wastes as single raw materials for biodiesel production with acceptable quality; however, low yields were obtained (65 wt%). The reaction conditions of the acid esterification reaction were selected being 65 ºC, 2.0 wt% H_2SO_4 and 5 h, which allowed obtaining a product with a viscosity of 4.81 $mm^2 s^{-1}$ and a purity of 99.6 wt%. As an alternative to lower the waste lard acidity and enable the one step synthesis, a mixture containing 25% waste lard and 75% soybean oil was used. Alkali transesterification of the mixture resulted in a product with a purity of 99.8 wt% and a yield of 77.8 wt%, showing that, despite the small fat incorporation used, blending might be an interesting alternative to recycle such wastes. Also, because in addition to using conventional and relatively economical processes, some biodiesel properties depending on the raw material composition (such as the iodine value) might even be improved.

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OBJECTIVES

- Enabling waste animal fats instead of virgin vegetable oils for Biodiesel (Fatty acid methyl esters, FAMEs) synthesis;
- Evaluating FAMEs synthesis considering the use of a one-step alkali transesterification reaction and a two step reaction consisting of an acid esterification followed by an alkali transesterification;
- Optimizing first step reaction considering the amount of catalyst used and quality of the final product;
- Evaluating the use of raw material mixtures to enable one-step FAMEs synthesis.

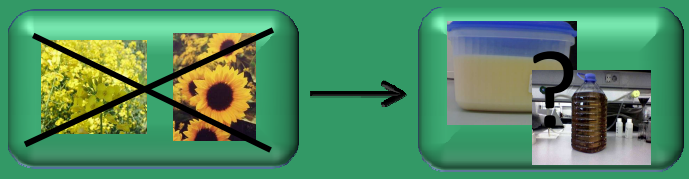
INTRODUCTION

- Raw materials commonly used for FAMEs synthesis: virgin vegetable oils
  - *Advantages*: perform well during alkali transesterification (Reaction B);
  - *Disadvantages*: used for food purposes and expensive.
- Alternative raw materials for FAMEs synthesis: waste raw materials
  - *Three major advantages*: (i) do not compete with the food market; (ii) recycles waste; and (iii) reduces production costs;
  - *Disadvantages*: High acid values present in waste fats (more abundant raw material) does not allow alkali transesterification.

Because alkali transesterification is still the most economically attractive FAMEs synthesis alternative, there is a need to enhance pretreatment of waste raw materials to enable further transesterification

- *Solutions*: fat saponification / esterification (reaction A)
  - *Saponification*: causes the loss of raw material
  - *Esterification*: uses all the raw material

→ Research is required to optimize its application in a larger scale



$$R_1 - COOH + CH_3OH \underset{\text{Catalyst}}{\rightleftharpoons} R_1 - COO - CH_3 + H_2O$$

Reaction A. Esterification of free fatty acids.

$$\begin{matrix} CH_2 - OOC - R_1 \\ CH - OOC - R_2 \\ CH_2 - OOC - R_3 \end{matrix} + 3\ CH_3OH \underset{\text{Catalyst}}{\rightleftharpoons} \begin{matrix} R_1 - COO - CH_3 \\ R_2 - COO - CH_3 \\ R_3 - COO - CH_3 \end{matrix} + \begin{matrix} CH_2 - OH \\ CH - OH \\ CH_2 - OH \end{matrix}$$

Reaction B. Transesterification of oils and fats.

MATERIALS AND METHODS

Pork wastes were collected at a local butchery; fat was extracted by heating, the melted product was separated from the solid residue, and after filtered at reduced pressure.

- Raw material characterization: i) composition by GC (Fig. 1C) (EN 14103 and NP EN ISO 5508); ii) acid value by titration (NP EN ISO 660);
- Biodiesel characterization: : i) acid value by titration (EN 14104); ii) kinematic viscosity using capillary viscometers (ISO 3104) iii) water content by Karl Fischer titration (Fig. 1 D) (NP EN ISO 12937); iv) ester and linolenic acid methyl ester contents by GC (EN 14103); and, v) iodine value (annex B, EN 14214).

Synthesis of biodiesel (Figure 1 A): Esterification + Transesterification

- Esterification conditions (Reaction A): 120.0 g of the dehydrated lard; 55 ºC; 6:1 methanol to fat molar ratio, 5h, H_2SO_4 (1.0 - 4.0% of lard weight);
- Transesterification conditions (Reaction B): esterified product; 65 ºC; 6:1 methanol to fat molar ratio, 1h, NaOH (1% of the esterified product weight).

Products were after decanted (Figure 1B), excess methanol was recovered and catalyst was removed. Final product was dehydrated.

- A waste lard/soybean oil (25/75 (wt%)) was studied as alternative raw material.

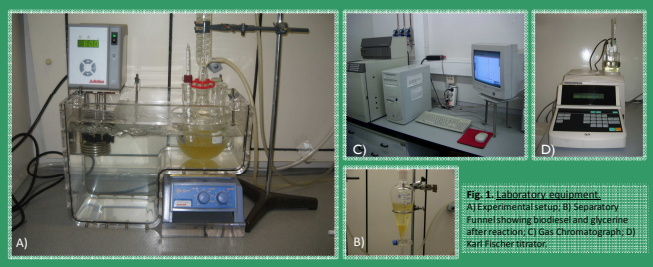


Fig. 1. Laboratory equipment. A) Experimental setup; B) Separatory funnel showing biodiesel and glycerine after reaction; C) Gas Chromatograph; D) Karl Fischer titrator.

RESULTS AND DISCUSSION

- Fat yield was 70 wt%; acid value was 14.57 mg KOH g^{-1} for the waste lard and 0.21 mg KOH g^{-1} for the soybean oil. Basic transesterification of the acid lard was ineffective.
- First reaction step: acid value tended to stabilise after 1h (Fig. 2) indicating reaction completeness within that period.
- Optimization of two-step synthesis considering product quality: Acid value was not within limit (Table 1) at the lowest catalyst concentration (less effective esterification); viscosity and purity were not always fulfilled; other evaluated parameters were in agreement with EN 14214.
- For the same raw material, lower viscosity indicates insufficient methyl ester conversion; catalyst amount needed to be higher than 3wt% (Figure 3A) obtain a viscosity in agreement with EN 14214.
- Purity determination method uses methyl heptadecanoate (C17:0) as internal standard; however, C17:0 might exist in animal fats affecting results. Analysis showed 0.6 wt% of C17:0 (Fig.4) and further corrections were performed. Catalyst amount strongly influenced biodiesel purity, only close to minimum using 3 wt% catalyst (Fig. 3B); therefore, lower viscosities were indicating effective conversions.
- Two-step synthesis enabled the use of acid wastes for biodiesel production; 65 wt% yield was obtained, the same when using a waste lard/soybean oil mixture.
- Alkali transesterification of the mixture: yield of 77.8 wt%; purity of 99.8 wt%.

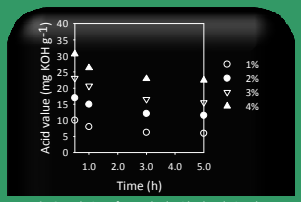


Fig. 2. Evolution of waste lard acid value during the esterification reaction.

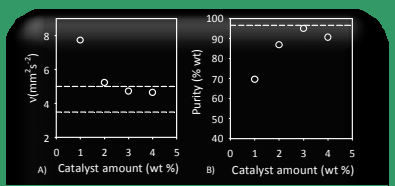


Fig. 3. Viscosity (A) and Purity (B) of FAMEs using different catalyst amounts (6:1 molar ratio of methanol to lard, 55 ºC, 5h (dashed lines indicate minimum and maximum requirements according to EN 14214 for viscosity and minimum for purity)

Table 1: Quality parameters of biodiesel from waste lard and the respective requirements according to EN 14214

Parameter	Results	EN 14214
Water content (mean, wt %)	0.040	<0.05
Acid value (mg KOH g^{-1})		
1 wt % H_2SO_4	1.13	<0.50
Other conditions (mean)	0.142	
Kinematic viscosity at 40 ºC (mm^2s^{-1})	4.64 - 7.73	3.50 - 5.00
Methyl ester content (wt %)	69.6 – 95.0	>96.5
Linolenic methyl ester content (mean, wt %)	1.4	<12.0
Iodine value (mean, g I_2/100g)	77	<120

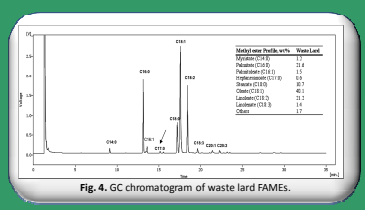


Fig. 4. GC chromatogram of waste lard FAMEs.

CONCLUSIONS

- The one-step transesterification of acid waste lard was ineffective due to the high acidity of the raw material.
- The proposed two-step synthesis enabled acid wastes as single raw materials for biodiesel production; however with low yields (65 wt%).
- Regarding the first step synthesis optimization, the best H_2SO_4 concentration was found to be 3 wt%, which allowed obtaining a product with a viscosity of 4.72 $mm^2 s^{-1}$ and a purity of 95.0 wt%.
- Despite the small fat incorporation used, blending was found to be an interesting alternative to recycle such wastes enabling the use of one-step synthesis.

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