

# Hydrolysis of Waste Frying Oils in Subcritical Water for Biodiesel Production by Esterification Using a Heterogeneous Catalyst

Luciana P. Toralles<sup>a\*</sup>, Carine T. Alves<sup>b</sup>, Ednildo A. Torres<sup>a</sup>, Heloysa M.C. Andrade<sup>c</sup>, Fernando L.P. Pessoa<sup>d</sup>, Silvio A.B. Vieira de Melo<sup>a</sup>

<sup>a</sup>Programa de Engenharia Industrial, Escola Politécnica, Universidade Federal da Bahia, Rua Prof. Aristides Novis, 2, Federação, 40210-630, Salvador-BA, Brazil.

<sup>b</sup>Universidade Federal do Recôncavo da Bahia, Feira de Santana-BA, Brazil

<sup>c</sup>INCT Energia e Ambiente, CIENAM, Universidade Federal da Bahia, Rua Barão de Jeremoabo s/n, Ondina, 40170-115, Salvador-BA, Brazil

<sup>d</sup>Universidade Federal do Rio de Janeiro, Escola de Química, Departamento de Engenharia Química, Centro de Tecnologia, bloco E, Ilha do Fundão, Rio de Janeiro, Brasil  
[lucianatoralles@gmail.com](mailto:lucianatoralles@gmail.com)

Waste frying oils have become a material of great interest for various routes of biodiesel production. This study investigates waste frying oils (WFO) under subcritical hydrolysis to generate free fatty acids for biodiesel production using zinc aluminate as heterogeneous catalyst. WFO were pre-treated to reduce particulate material and saponified compounds present in the raw material. Their kinematic viscosity, fatty acid composition and proton Nuclear Magnetic Resonance (NMR+) were determined, which identified strong similarities between WFO and refined soybean oil. Through the fatty acid composition analysis of WFO, a molecular weight of 873 g/mol was obtained and linoleic acid was identified as the main component in the tested oil. The hydrolysis experimental runs were conducted over a range of temperatures between 200-250 °C. Once hydrolysis reactions were completed, a significant increase in the acid value was observed for all samples. After phase separation, a subsequent ethyl esterification of free fatty acids obtained from hydrolysis was carried out at 100 °C and 150 °C, using 10:1 and 20:1 as ethanol:oil molar ratio. The biodiesel produced by subcritical water hydrolysis and esterification was analysed by Gas Chromatography (GC). The results showed that this route provides an effective contribution towards the feasibility of alkyl ester production by esterification of free fatty acids using a zinc aluminate catalyst.

## 1. Introduction

In recent years the continuous growth in greenhouse gas emissions, especially CO<sub>2</sub>, sulfur and aromatic hydrocarbons has been mainly due to the considerable increase in the consumption of fossil fuels. To reduce the amount of these emissions and mitigate future environmental impacts, renewable energies research has grown stronger and it has been well developed in many countries (De Jong, 2013). Among the alternative fuels proposed, biodiesel stands out as a promising way to reduce certain emissions (Janaun and Ellis, 2010), as well as reduce the global dependence on petroleum reserves. The possibility of large-scale production of biofuels is becoming a reality all over the world. It has stimulated the development and improvement of routes for biodiesel production. Among the advantages of this biofuel are its characteristics of being non-toxic, biodegradable and coming from renewable vegetable oils. Therefore, biodiesel is considered an environmentally sustainable fuel.

Today the required biodiesel specifications are defined by global standards, such as those of the American Society for Testing and Materials, ASTM D 6751, which states the limit values of biodiesel acidity and

composition. There are different methods to achieve the required quality of biodiesel. Generally, this biofuel is produced by transesterification of triglycerides with the use of methanol or by esterification of free fatty acids obtained by a prior hydrolysis (Saka et al., 2006). Within these two methods, biodiesel can be produced from non-catalytic or catalytic reactions, with homogeneous or heterogeneous processes (Hassan and Kalam, 2013). Furthermore, in recent studies experiments in subcritical water (Ju et al., 2013) and / or supercritical alcohol (Sawangkeaw et al., 2011) with and without carbon dioxide (Maçaira et al., 2011, Nascimento et al., 2013) have performed well in biofuel production.

When water is maintained at temperatures within the range of its boiling point (100 °C) and its critical point (374 °C) and kept in the liquid state, this is referred to as the subcritical water condition. For the hydrolysis of the oil, subcritical water presents higher solubility in the oil due to the modification of its properties, such as a reduction in its dielectric constant with increasing temperature (Carr et al., 2011). Thus, water in subcritical conditions in hydrolysis acts both as a reactant and as a solvent for a reaction (Pinto and Lencas, 2006, King et al., 1999). In this context, it is also worth noting that according to studies by Alenezi et al., (2010) and Milliren et al., (2013), as the free fatty acids are formed in the hydrolysis reaction of vegetable oils, they act as acid catalysts and are able to accelerate their own reaction.

This study aims to investigate the feasibility of using waste cooking oils to obtain free fatty acids for biodiesel production through a hydrolysis reaction with subcritical water followed by ethyl esterification using zinc aluminate as a heterogeneous catalyst. In the hydrolysis reaction, the influence of operating parameters on the reaction yield was observed through the analysis of the products obtained. Through the characterization and use of waste cooking oil as a source for the production of biodiesel, this work contributes to the development of an entirely new environmentally benign route for biodiesel production.

## 2. Experimental

### 2.1 Materials and Equipment

Waste frying oils were obtained from donation by local bars and restaurants in the city of Salvador, Brazil. Analytical reagents for esterification and acid value characterization were purchased from Vetec Química Fina Ltda in commercial grade, including anhydrous ethanol (99.9% purity), diethyl ether (99.9% purity) and potassium hydroxide (99.9 % purity).

Before hydrolysis, the WFO was filtered in order to eliminate particulate materials and other impurities in the process. The hydrolysis and esterification reactions were carried out in a Büchiglasuster stainless steel batch reactor, Model li2, of 100 mL capacity, fitted with internal pressure, stirring and temperature controllers.

### 2.2 WFO Characterization

After filtration, the acid value of WFO was determined by titration in approximately 8.8 mgKOH/g of WFO. The composition of fatty acids presents in WFO was also analysed by gas chromatography (GC 3800A Varian) as shown in Table 1. A molecular weight of 873 g/mol was calculated and cinematic viscosity of 56 cSt was obtained.

Table 1: Fatty Acid Compositions of WFO

Fatty Acids	Nomenclature	Sample 01 (%)	Sample 02 (%)	Soybean Oil (%)
C16:0	Palmitic Acid	11.33	11.48	12.50
C18:0	Stearic Acid	3.53	3.53	0.65
C18:1 $\omega$ 9 cis	Oleic Acid	22.71	21.73	27.81
C18:1 $\omega$ 9 trans	Elaidic Acid	1.49	1.43	-
C18:2 $\omega$ 6 cis	Linoleic Acid	54.82	55.67	54.19
C18:2 $\omega$ 6 trans	Linolelaidic Acid	0.18	0.16	-
C18:3 $\omega$ 3	Linolenic Acid	5.62	6.00	4.67
C20:0	Eicosanoic Acid	0.32	-	-

### 2.3 Hydrolysis Reactions

A 100 mL stainless steel batch reactor equipped with a gas liner was used for the subcritical hydrolysis reactions (Büchiglasuster, Model li2). Temperature reaction was analysed at 200 and 250 °C, where the reactor jacket provided rapid heating. The tested weight ratio of water to WFO was 1:1 and 2:1. Both reactants were added to the reactor under nitrogen pressure to ensure the subcritical condition of the water.

During reactions, the pressure was always maintained above water saturation pressure, suggesting a minimal vaporization. The stirring speed set point was 500 rpm for all runs. Reaction time was set at 30 and 60 min to evaluate the progress of the hydrolysis process. No catalyst was used in this step due to the water subcritical condition, which provides water as a reactant and solvent able to act as an autocatalytic agent of the hydrolysis of triacylglycerides.

## 2.4 Catalyst Synthesis and Characterization

Combustion reaction method was applied to generate the catalyst zinc aluminate by the using of p.a. grade reagents, zinc and aluminium nitrates, as starting materials, and urea, as fuel. The stoichiometry of the total oxidizing and reducing valences of the reagents provided the basis to calculate the appropriate amounts of the metal nitrates and urea aiming to obtain maximum energy release. The batches were prepared in a vitreous silica basin and directly heated in the furnace up to the temperature of 400 °C until the ignition process, which the zinc aluminate was synthesized in a foam form. In order to remove any volatile product, the foam material was heated at 500 °C for further 20 min and then sieved in the range of 0.149–0.105 mm.

The obtained powder was characterized by FTIR spectra using a Perkin Elmer Spectrum BX spectrometer, TGA analyses (Shimadzu H-50 system), X-ray diffraction (Shimadzu 6000 diffractometer, CuK $\alpha$  with a Ni filter and scanning rate of 2° 2 $\theta$  min<sup>-1</sup>, in a 2 $\theta$  range of 20–60 °). Nitrogen adsorption isotherms collected in a Micromeritics ASAP 2020 system defined the BET specific surface area and the pore volume of the catalyst. NH<sub>3</sub>-TPD and TPD-CO<sub>2</sub> (temperature programmed desorption of ammonia or carbon dioxide) profiles were analysed in the temperature range of 20–800 °C, at a heating rate of 10 °C min<sup>-1</sup>, using a Micromeritics 2720 system.

## 2.5 Esterification Reactions

The samples with higher acid values obtained from hydrolysis reactions were used to perform the esterification reactions. Due to the high availability and low toxicity, anhydrous ethanol was applied to perform esterification of the free fatty acids produced in the hydrolysis in this work. Zinc aluminate catalyst was tested as obtained by the combustion reaction method. The reactions were carried out in the same reactor (Bunchiglasuster, Model li2). The reaction time was set for 120 min, where the temperature set points were 100 and 150 °C. The tested molar ratio of alcohol to WFO were 10:1 and 20:1, the catalyst to oil weight ratio was 5 % under 500 rpm stirring for all runs.

## 2.6 Sample Characterization

The acid value was determined by titration for all samples obtained to investigate the changes that occurred in the reactions. Furthermore, the yield of ethyl esters produced by this route was determined by gas chromatography. According to DIN EN 14105 procedure, biodiesel aliquots were analysed by GC (G3440A CG/MS Agilent). Using Helium flow of 1 mL/min as a carrier gas and triple-axis detector in a 30 m long DB-WAX column (30 m x 0.250 mm x 0.25  $\mu$ m), the characterization was performed. The column temperature began at 60 °C, where the sample remained for 2 min. The first rate was 10 °C/min up to 200 °C and the second rate was 5 °C/min up to 240 °C, where the sample remained at this temperature for 7 min.

# 3. Results and Discussion

## 3.1 Subcritical Hydrolysis Experiments

The influence of temperature, weight ratio of water to WFO and residence time in the yield of subcritical WFO hydrolysis was investigated. The subcritical hydrolysis reactions were carried out from 30 to 60 min runs and their products were analysed by titration. The temperature reaction ranged from approximately 200 to 250 °C for water:oil weight ratio of 1:1 and 2:1 under 500 rpm stirring. In the subcritical hydrolysis reaction, the decomposition of triglycerides into free fatty acids (FFA) is expected. The formation of FFA is verified by higher acid values and darker colour acquired. The yields of FFA produced by subcritical hydrolysis were plotted as a function of residence time of the reactions as shown in Figure 1. The yields of FFA are dramatically higher when the subcritical hydrolysis were carried out at 250 °C. The influence of residence time showed the most considerable changes at lower temperatures (200 °C). Furthermore, the water:oil ratio was not very significant at the temperatures tested. In general, the yield of FFA increased with temperature growth and longer residence time. The highest yield was obtained using water:oil weight ratio of 1:1 at 250 °C in a 60 min reaction run. Based on the previously showed characterization of WFO, the amount of FFA produced by the subcritical hydrolysis reactions were also quantified (%) in terms of the most representative fatty acids identified by gas chromatography. According to its tested acid value, before hydrolysis only 4.5 % of the fatty

acids were available for esterification. After hydrolysis, a considerable increase of the acid value was verified and the amount of FFA available for esterification was calculated again. Figure 2 illustrates the amount of FFA in percent of acid value found for the different tested conditions as a function of residence time. Figure 3 presents the obtained conversion of hydrolysis reactions at both temperatures and ratios calculated from the amount of FFA generated. As a result, the sample hydrolysed at 250 °C using water:oil weight ratio of 1:1 for 60 min reaction demonstrated 95 % conversion, providing the highest amount of FFA available for esterification of all samples, as shown on Figure 3.

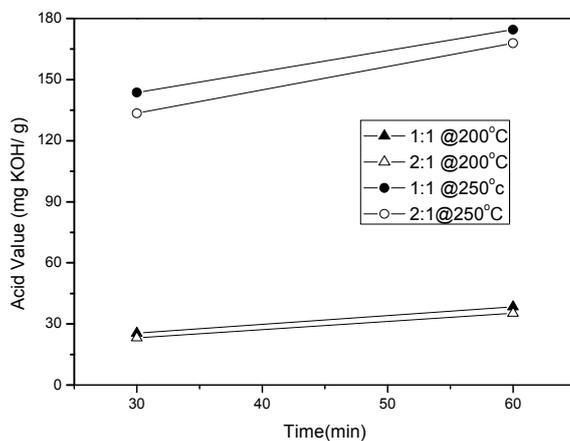


Figure 1: Acid value (mg KOH/g oil) of the hydrolysed oil in subcritical water at 200 °C and 250 °C

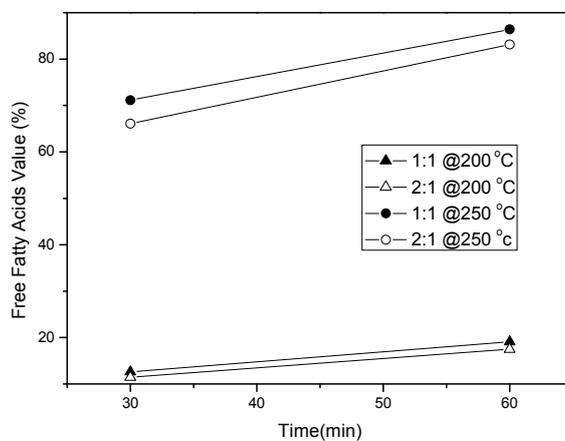


Figure 2: Percent of FFA available for esterification after subcritical hydrolysis at 200 °C and 250 °C

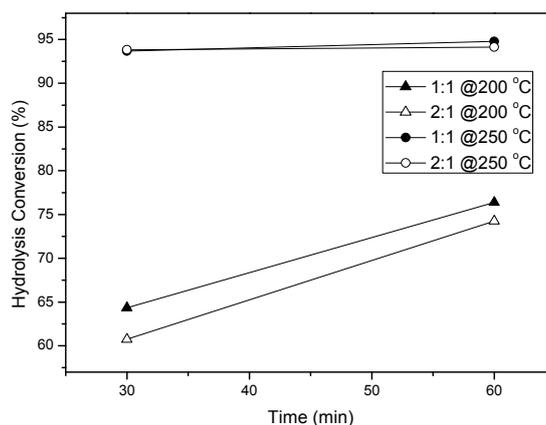


Figure 3: Conversion of Hydrolysis Reaction of WFO Experiments

### 3.2 Esterification Experiments

In the second step of this process, the hydrolysed oil obtained from the first step underwent ethyl esterification for biodiesel production. The influence of the temperature and alcohol:oil ratio was investigated. Experiments were carried out for 120 min under 500 rpm stirring and 5 % wt. catalyst of the initial amount of oil for all reaction runs. Temperature range was between 100 to 150 °C, for 10:1 and 20:1 of alcohol:oil ratio. In order to recover the catalyst vacuum filtration was performed and then the samples were dried at 105 °C to eliminate alcohol excess and generated water. The samples produced were analysed by gas chromatography and conversion was calculated according to the new acid value of the produced samples. High ester yields was obtained from reaction runs at 150 °C using 20:1 alcohol:water ratio. It was assumed that an increase in the alcohol excess helps to maintain the fluidity of the catalyst. Also, according to Alves et al. (2013) the utilization of high alcohol excess provides high yields and allows the recovery of zinc aluminate for further reactions. As shown in Figure 4, esterification reaction temperatures represents a stronger influence in ester yields when compared to the tested molar ratios. It was also observed that as the temperature increases, the tested molar ratios presented significant changes in ester yields.

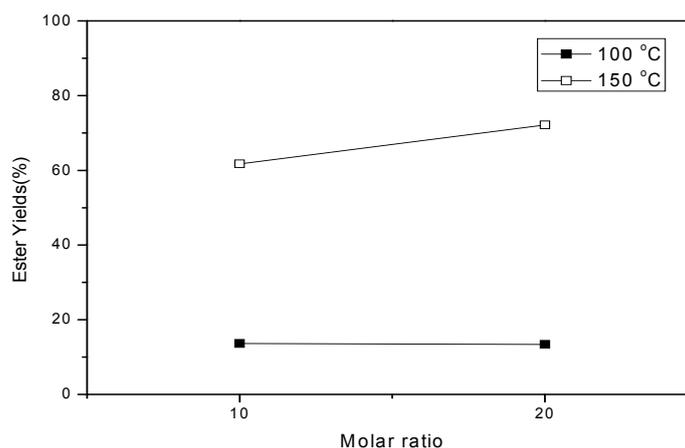


Figure 4: Influence of molar ratio on the esterification reaction with ethanol at the tested temperatures

In order to identify the produced esters, gas chromatography was performed in all samples. Ethyl esters peaks were clearly identified by the method applied. In all samples, there were three strong ester peaks identified at approximately 18, 21 and 22 min. The first identified peak represents the hexadecanoic acid ethyl ester, formed from palmitic acid. At approximately 21 min it was identified the (9)-octadecenoic acid ethyl ester,

being ethyl oleate. Finally, the third and highest peak was identified after approximately 22 min, representing the linoleic acid ethyl ester, which was the most abundant acid in the tested WFO. During this same period it was also verified smaller peaks of octadecanoic acid ethyl ester and 9,12,15-octadecatrienoic ethyl ester, being namely stearic acid ethyl ester and linolenic acid ethyl ester, respectively. All highlighted peaks corroborates with the most abundant free fatty acids identified in WFO characterization. As a result of a non-complete reaction, in this gas chromatography method it was also identified smaller peaks of residual free fatty acids, being the n-hexadecanoic acid the most featured peak identified at 26 min.

#### 4. Conclusion

Subcritical hydrolysis of waste frying oil followed by ethyl esterification using zinc aluminate as a catalyst was an effective method for biodiesel production. This two-step process achieved high free fatty acids yields (95 %) using 1:1 water:oil weight ratio at 250 °C in subcritical hydrolysis for 60 min and ester yield of 75 % using 20:1 alcohol:oil at 150 °C for 120 min. In both steps the influence of the temperature was stronger than the tested ratios. The main ethyl esters produced from WFO identified by gas chromatography were in agreement with WFO composition. The results showed that this two-step process using waste frying oil represents an alternative route for biodiesel production.

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