

# Transesterification Reaction Using Zinc Aluminate as Heterogeneous Catalyst and Supercritical Carbon Dioxide

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Biodiesel was produced from waste frying oil (WFO) by transesterification with ethanol and methanol, using supercritical carbon dioxide, as a reaction medium, and a spinel-like zinc aluminate heterogeneous catalyst. The reaction runs were carried out for 2 h taking samples every 30 min, using alcohol:oil molar ratio of 40:1, temperature range of 100 – 200 °C, catalyst dosage of 1- 10 %wt, under 700 rpm stirring. The biodiesel products were analyzed by gas chromatography according to DIN EN 14105. The influence of reaction parameters, such as temperature; catalyst dosage and reaction time in supercritical CO<sub>2</sub>, on the biodiesel yield was discussed. The results showed high yields (>96.5 %) of biodiesel for both ethanol and methanol at 200 °C after 30 min of reaction, showing that the heterogeneous catalyst used contributed to increase in the biodiesel yield in a short reaction time.

## 1. Introduction

Biodiesel is a renewable and environmentally friendly biofuel that can be produced from a range of organic raw materials, including refined or waste vegetable oils, animal fats, and oilseed plants, and is also an important substitute for petroleum-based diesel. The main product of the transesterification process is similar to conventional diesel fuel in terms of its main characteristics, biodegradable and does not contribute to global warming due to the closed carbon cycle (Santana et al., 2012).

The non-catalytic transesterification of vegetal oils using supercritical alcohols has been proposed (SAKA and KUSDIANA 2001). Due to the unique properties of the supercritical fluids (SCF), rate enhancement, high yields and purity can be achieved. In spite of this, the high costs make this method not viable for practical industrial applications (MUPPANENI et al., 2012). The use of co-solvents and catalysts has been also proposed in order to allow the supercritical reaction to be undertaken under milder conditions (YIN et al., 2008). The use of supercritical carbon dioxide, as a reaction medium, instead of supercritical alcohols, seems to be an efficient alternative to operate at milder conditions but just a few works reported on the transesterification reaction under these conditions, frequently using enzyme catalysts. For example, Oliveira and Oliveira (2000) studied the batch ethanolysis of palm kernel oil in supercritical CO<sub>2</sub> using *Lipozyme IM* and *Novozyme 435*. Madras et al. (2004) investigated batch enzymatic methanolysis of various edible and non-edible oils in supercritical CO<sub>2</sub>. Even though packed bed immobilized enzyme reactors have received much attention and employed in several lipid modification applications (Xu et al., 2002), continuous enzymatic biodiesel production in supercritical CO<sub>2</sub> is scarce. Dalla Rosa et al. (2009) conducted continuous enzymatic production of fatty acid ethyl esters from soybean oil in supercritical CO<sub>2</sub>, propane and n-butane. Lubary et al. (2010) reported integrated synthesis and extraction of short-chain fatty acid ethyl esters using supercritical CO<sub>2</sub>.

In a previous paper, a zinc aluminate heterogeneous catalyst was successfully used to synthesize biodiesel (Alves et al., 2013) The present work was carried out in order to study the transesterification of

WFO with ethanol and methanol using this zinc aluminate catalyst in supercritical carbon dioxide, as a reaction medium. The effects of reaction parameters, such as temperature, time and catalyst dosage, were investigated.

## 2. Materials and Methods

### 2.1 Materials and Equipment:

The raw material, waste frying oil (WFO), was received from commercial establishments such as restaurants, hospitals and others in the Salvador city, Brazil. Analytical grade reagents were used: Anhydrous ethanol (99.9% of purity) and methanol (99.9 % of purity) were purchased from Synth®. The gaseous carbon dioxide was obtained from BOC Company with 99.8 % of purity. The experiments were performed in a 4836 Parr stainless steel batch reactor of 300mL capacity, equipped with temperature, internal pressure and stirring controllers to allow the reaction under supercritical carbon dioxide conditions.

### 2.2 Supercritical carbon dioxide transesterification method

The reaction runs were carried out for 2 h taking samples every 30 min, using alcohol:oil molar ratio of 40:1, temperature range of 100 - 200° C, catalyst dosage of 1-10 %wt, under 700 rpm stirring. Ethanol and methanol were used in excess relative to stoichiometric conditions of the reaction, because the transesterification is a reversible reaction. The oil, alcohol and catalyst were weighted, introduced into the reactor and pressurized until 50 bar (CO<sub>2</sub> cylinder pressure). At the reaction temperature, the system was pressurized up to 74 bar at 100 °C, 100 bar at 150 °C and 150 bar at 200 °C. At the end of reaction time (2h), the reactor was cooled down and the samples were withdrawn at room temperature. The insoluble catalyst was recovered by filtration and vacuum dried in an oven at 50 °C. The reaction mixture was introduced into a separation funnel where the glycerin was decanted and the excess alcohol was recovered using a rotary evaporator. The biodiesel samples were characterized as follows.

### 2.3 Biodiesel Characterization

The yield of ethyl and methyl esters, FAEE and FAME, respectively, was determined by a gas chromatographic procedure. The biodiesel aliquots were diluted with n-heptane and the obtained solutions were analyzed by GC (CP 3800A Varian Chrompack) according to DIN EN14105 (Lam & Lee, 2011), with a 30 m long capillary column, Ultimetel VF 5HT (30 m x 0.32 mm x 0.10 µm), He (3 mL min<sup>-1</sup>) as carrier gas, and a flame ionization detector. The column temperature program was as follows: the initial temperature was 50 °C, the first rate was 15 °C min<sup>-1</sup> up to 180°C, the second rate was 7 °C min<sup>-1</sup> up to 230 °C and the third rate was 30 °C min<sup>-1</sup> up to 380 °C with holding time of 10 min. The thermogravimetric analysis of the biodiesel produced from WFO in supercritical CO<sub>2</sub> was evaluated by TG/DTG, using a NETZSCH TG 209F1 analyzer, in air flow (50 mL/min). The sample was heated at 10 °C/min up to 120°C, remained at this temperature for 30 min and then heated up to 1,000 °C .

## 3. Results and Discussion

### 3.1 Effect of temperature, reaction time and catalyst dosage

The effect of reaction time on the yield of fatty acid ethyl esters (FAEE) and fatty acid methyl esters (FAME), at 100 °C, 150 °C and 200 °C, are respectively shown in Figures 1-3.

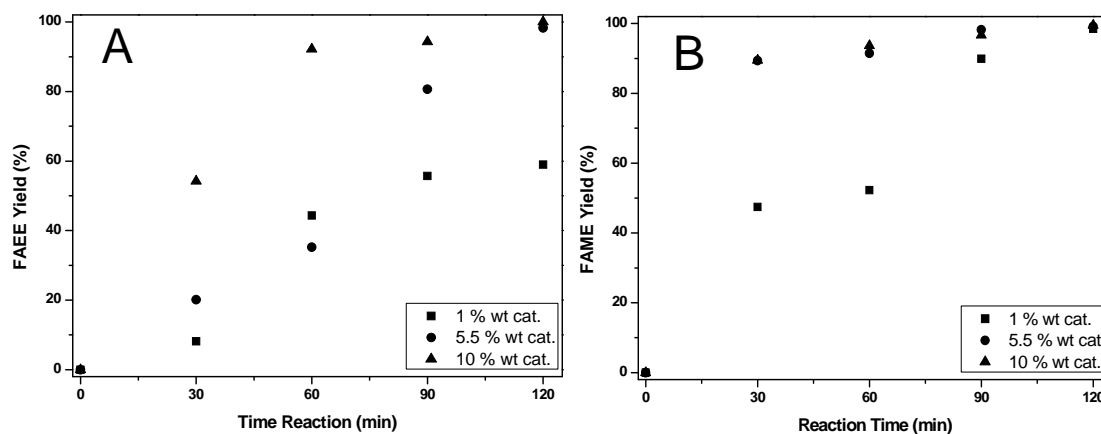


Figure 1: FAEE (A) and FAME (B) yields as a function of reaction time at 100 °C, 74 bar, catalyst dosage 1 – 10 %wt and molar ratio [alcohol : oil] = 40:1

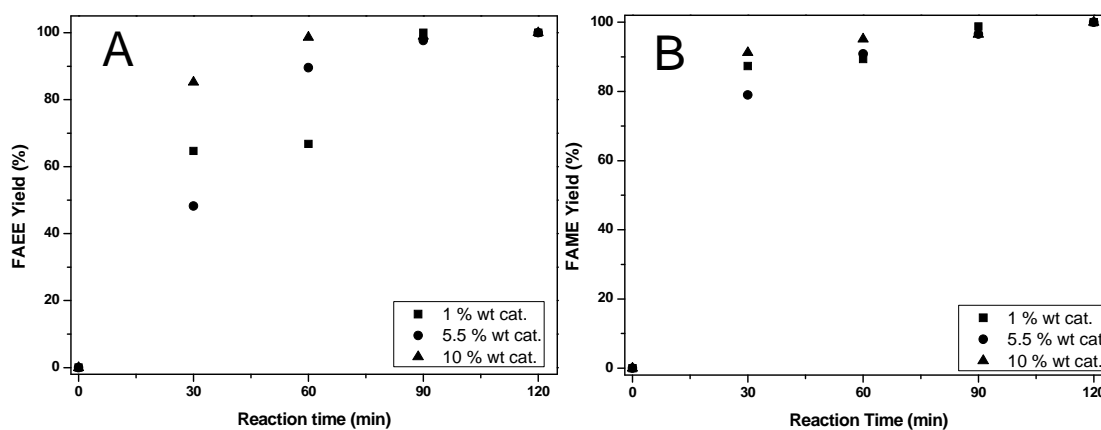


Figure 2: FAEE (A) and FAME (B) yields as a function of reaction time at 150 °C, 100 bar, catalyst dosage 1 – 10 %wt and molar ratio [alcohol : oil] = 40:1

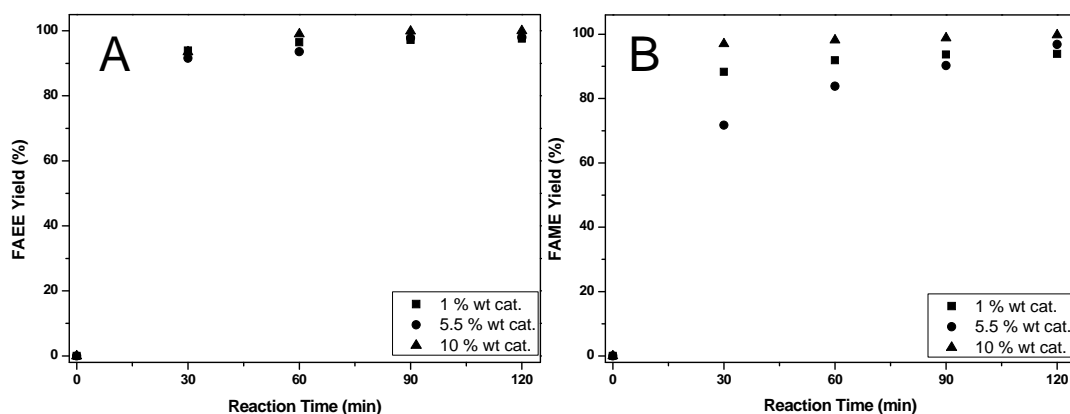


Figure 3: FAEE (A) and FAME (B) yields as a function of reaction time at 200 °C, 150 bar, catalyst dosage 1 – 10 %wt and molar ratio [alcohol : oil] = 40:1.

The results indicate that the ester yields increased with increasing the catalyst dosage for both alcohols at the tested temperatures. For the lowest temperature (100 °C), the influence of reaction time is directly

related to the catalyst dosage and type of alcohol used in the transesterification reaction. Figure 1B shows that the maximal FAME yield was attained at in shorter reaction time and smaller catalyst dosage than that for FAEE, shown in Figure 1A. These findings were interpreted as a consequence of lower carbon chain of methanol which is more easily solubilized in the oil than ethanol in mild conditions, namely, 100 °C and 74 bar (Macaíra et. al, 2010). Thus, FAME yields around 90% were obtained in 30 minutes using either 5.5 %wt or for 10 %wt catalyst dosage. At 150°C and 100 bar, FAME and FAEE yields above 90 % were obtained using 5.5 %wt of catalyst while FAME yields above 95 % and FAEE yields up to 98% were achieved using 10 %wt of catalyst, in 1 hour. The reaction was complete after 120 min for both alcohols and catalyst dosages at these intermediate reaction conditions, as shown in Figure 2. At more severe reaction conditions, namely 200 °C and 150 bar, ethanol act as a co-solvent in higher conditions, assisting the solubility of the reactants in presence of the supercritical carbon dioxide. Thus, as shown in Figure 3, FAEE yields above 93 % were attained using 1 %wt of catalyst, in 30 min, whereas at the same reaction conditions, 93 % FAME yield was attained only after 1 h. Under supercritical conditions, ethanol is preferred over methanol, acting as a reactant and an acid catalyst (VIEITZ et al., 2010 & MUPPANENI et al., 2012). It has been reported that the value of the solubility parameter of methanol/ethanol may decrease and become closer to that of vegetable oil if proper temperature and pressure conditions are employed (Kusdiana & Saka, 2004). Thus, the use of appropriate catalysts and/or co-solvents is more valuable under mild reaction conditions. In general, the variation of the catalyst dosage in the transesterification reaction was more influent for the mild conditions using supercritical carbon dioxide, especially because of the possibility of the formation of more than a single-phase between alcohol and WFO.

### 3.2 Analysis of the thermal stability of the WFO biodiesel

Thermal deterioration and oxidation of biodiesel may affect the quality of the fuel. Considering that the stability of oils depends on their chemical structures, it is appropriate to investigate the stability of the biodiesel synthesized from WFO, a mixture of different edible oils, previously heated at high temperatures. The thermo-oxidative behaviour of oils and biodiesel has been successfully investigated by TG-DTG in an oxidative atmosphere (Jain & Sharma, 2011). The TG-DTG curves of FAEE and FAME, synthesized in supercritical CO<sub>2</sub> at 200<sup>0</sup> C, 150 bar, using 10 %wt Zn<sub>2</sub>O<sub>4</sub> catalyst, are shown in Figure 4A and B, respectively. The weight loss occurred at 116-500°C for FAEE and at 126-560°C for FAME. The thermal events in Figure 6A were assigned to vaporization (up to ~250 C) and combustion (> 380<sup>0</sup>) of ethyl esters while those in Figure 6B were assigned to vaporization (up to ~270 °C) and combustion (> 400<sup>0</sup>) of methyl esters (DANTAS et al., 2007). Chromatographic analysis indicated that ethyl and methyl linoleates were respectively the main components in FAEE and FAME, in accordance with the composition of WFO.

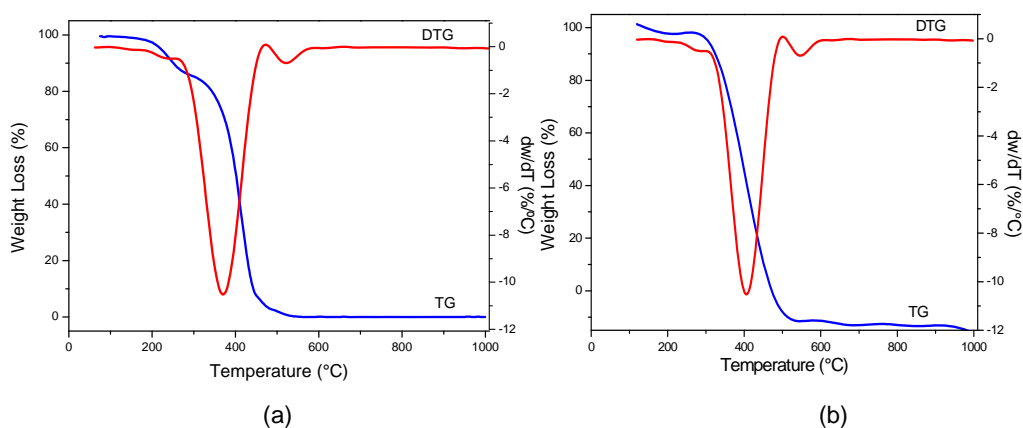


Figure 4: TG/DTG curves in air: FAEE (A) and FAME (B) synthesized from WFO in supercritical CO<sub>2</sub> at 200 °C, 150 bar, using 10%wt Zn<sub>2</sub>O<sub>4</sub> catalyst

### 3.3 Recovered catalyst

In order to investigate the stability of the ZnAl<sub>2</sub>O<sub>4</sub> catalyst under severe reaction conditions (2 h, at 200 C and 150 bar) in supercritical CO<sub>2</sub>, FTIR spectra and XRD patterns of the recovered catalyst were collected. Zinc aluminate was recovered from the reaction mixture by vacuum filtration and dried process at 50 °C. Figure 5 shows the FTIR spectra of recovered ZnAl<sub>2</sub>O<sub>4</sub> catalyst after the transesterification of WFO with ethanol in supercritical CO<sub>2</sub> and that for the new catalyst. Beside the bands assigned to residual esters

and glycerol, the strong bands around  $670$  and  $560\text{ cm}^{-1}$ , assigned to Al–O stretching and O–Al–O bending vibrations of  $\text{AlO}_6$  groups in the spinel structure, and two bands between  $500$  and  $700\text{ cm}^{-1}$ , assigned to the vibrations modes of octahedral and tetrahedral groups indicate that the primary structure of the spinel catalysts was not affected by the operation conditions. The recovered catalyst was yellow colored due to residual organic matter which was properly removed by calcination at  $450\text{ }^\circ\text{C}$  in air flow for 2h. Afterwards, the characteristic white color of catalyst was also recovered. In addition, the  $\text{N}_2$  adsorption-desorption isotherms collected for the calcined powder, shown in Figure 6, correspond to an isotherm Type IV and hysteresis loop type H2, assigned to mesoporous materials. These findings further confirmed that the mesoporous structure of catalyst was preserved after the reaction under pressure as high as 200 bar. On the other hand, the surface area of the recovered catalyst decreased to  $10\text{ m}^2\cdot\text{g}^{-1}$  after calcination, as confirmed by calcination of a new catalyst sample. These last results also suggest that the zinc aluminate catalyst can be reused for several cycles of transesterification reaction using supercritical carbon dioxide, allowing the production of biodiesel from WFO in a less expensive procedure than using homogeneous or enzymatic catalysts.

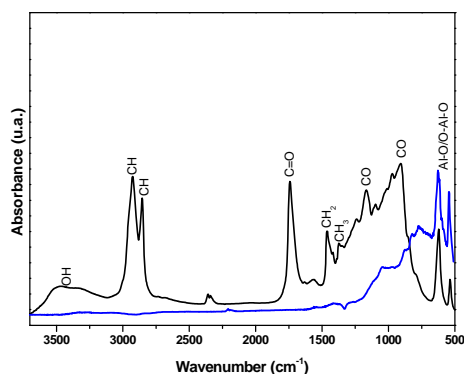


Figure 5: FTIR Spectra of recovered zinc aluminate from transesterification reaction with supercritical  $\text{CO}_2$  using ethanol at  $200\text{ }^\circ\text{C}$  and 10 %wt of  $\text{ZnAl}_2\text{O}_4$  and of fresh catalyst (blue)

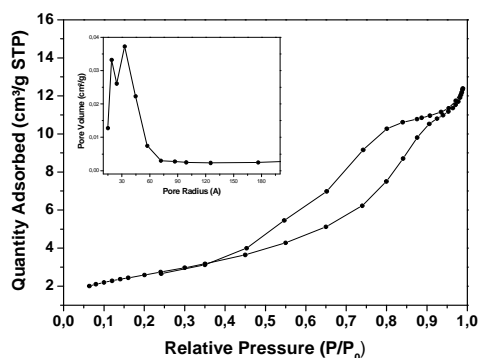


Figure 6:  $\text{N}_2$  physisorption isotherms and the BJH pore size distribution in the recovered  $\text{ZnAl}_2\text{O}_4$  powder

#### 4. Conclusion

Methyl and ethyl esters have been successfully produced from waste frying oil (WFO), by the transesterification reaction in supercritical  $\text{CO}_2$  as a reaction medium, using a  $\text{ZnAl}_2\text{O}_4$  catalyst prepared by combustion reaction. High ester yields were obtained using alcohol:WFO molar ratio = 40, at  $T > 100\text{ }^\circ\text{C}$ , using 1-10 % catalyst: WFO dosages in short reaction time. Experimental results demonstrated that the  $\text{CO}_2$  plays an active role in increasing the mutual solubility of the alcohols tested and waste frying oil at moderate temperatures. Yields above of 96.5% of ethyl and methyl esters were obtained at  $200\text{ }^\circ\text{C}$  using 10 %wt of zinc aluminate in 30 minutes of reaction time. The mesoporous structure of the recovered catalyst was not affected after reaction under severe conditions ( $200\text{ }^\circ\text{C}$ , 150 bar), indicating that it can be recycled and reused. The results presented herein demonstrate that the transesterification of waste frying oil (WFO) with ethanol, in supercritical  $\text{CO}_2$  and in the presence of the  $\text{ZnAl}_2\text{O}_4$  heterogeneous catalyst, is an eco-friendly alternative to produce biodiesel, using renewable and waste raw materials.

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