

# Esterification of acetic and oleic acids within the Amberlyst 15 packed catalytic column

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**Abstract**—A packed column system was used to study the esterification of acetic and oleic acids by the macro-porous acidic resin, Amberlyst 15. All reactions were at a constant temperature (75 °C) and catalyst mass (3 g). The impact of column flow rate conditions and the molar fatty acid to ethanol feedstock ratio on ester production is reported. The maximum ester production was noted at a flow rate of 0.25 mL/min. The maximum observed ester yield for acetic acid ( $95.2 \pm 0.5\%$ ) and oleic acid ( $43.8 \pm 1.3\%$ ) was observed at an acid:ethanol molar ratio of 1 : 3 and 1 : 1, respectively. The difference in yield indicates the importance of the fatty acid chain length to the reaction.

Keywords: Heterogeneous Column, Fatty Acid, Esterification, Amberlyst 15, Percent Conversion

## INTRODUCTION

Concerns over availability, environmental impacts and cost of petroleum-based diesel have increased interest in biodiesel production. Biodiesel, which is composed of long chain fatty acid mono-alkyl esters, is produced by the reaction of fatty acids (esterification) or triglycerides (transesterification) with an alcohol (methanol or ethanol) in the presence of a catalyst. As a bio-based fuel, it is a safer and more sustainable alternative to petroleum-based diesel [1-5]. This alternative fuel can be used in transportation vehicles when blended with petro-diesel up to 20% [6]. Biodiesel can also be used to produce electricity in current generator systems with minimal modifications [7].

Biodiesel production cost and ease depend upon feedstock quality. Transesterification and esterification of high quality feedstocks is straightforward and results in high biodiesel yield. However, use of high quality feedstocks increases production cost. Switching to lower quality feedstocks, such as waste cooking oil, offers potential cost savings, but requires additional processing steps. Therefore, both the high costs of biodiesel production using high quality lipid feedstocks and challenges of additional processing of lower quality feedstocks are barriers to industrial production [8-12].

While the cost of high quality feedstock accounts for 60-75% of production costs in conventional processing [10], other costs impacting production include maintaining the reaction temperature and/or pressure, the cost of the alcohol, and cost of the catalyst. Conventional biodiesel production relies on the use of liquid-phase homogeneous catalysis at high temperatures, often approaching the boiling point of the alcohol, or pressures to produce high yields. However, homogeneous catalysts, such as sodium hydroxide for transesterification or hydrochloric acid for esterification, are con-

sumed during the reactions and pose safety and handling concerns [13,14]. Alternatively, solid-phase heterogeneous catalysts can be recovered and regenerated during the production process and have reduced safety concerns. Heterogeneous catalysts used in biodiesel production are well studied and include carbonates, oxides, and ion exchange resins [15-19].

While heterogeneous catalysts have been well characterized for esterification, the majority of available research has used batch reaction systems [20-22] to determine the impact of catalyst mass and reaction temperature on esterification [23-25]. In this research a continuous flow through column system containing Amberlyst 15 (a macro-porous acidic resin) was employed to study esterification of acetic and oleic acid. We investigated the ability of the heterogeneous catalyst column system to produce esters at low temperature and atmospheric pressure at constant catalyst mass and reaction temperature. Specifically, the objectives of this research were to determine the effect of i) column flow rate, ii) fatty acid:ethanol molar ratio, and iii) fatty acid chain length on ester yield.

## EXPERIMENTAL METHODS

### 1. Materials

Ethanol (99.8% purity) was purchased from BDH (Dubai, UAE). Oleic acid (>99% purity) was purchased from Merck (Darmstadt, Germany). Acetic acid (99.8% purity), Amberlyst 15, sodium hydroxide, phenolphthalein, and potassium bromide were purchased from Sigma Aldrich (St. Louis, USA). All chemicals were used as received. Vendor characterization of the Amberlyst 15 catalyst used in this research reports that the catalyst is dry, macro-porous, and spherical with BET surface area of  $29.69 \text{ m}^2/\text{g}$ , a porosity of 0.36 mL pore/mL bead, and average pore diameter of 240 angstrom [26].

### 2. Methods

#### 2-1. Column Experiments

Fig. 1 shows the layout of the column system used in the experiments. The system consisted of two hot plates with magnetic stir-

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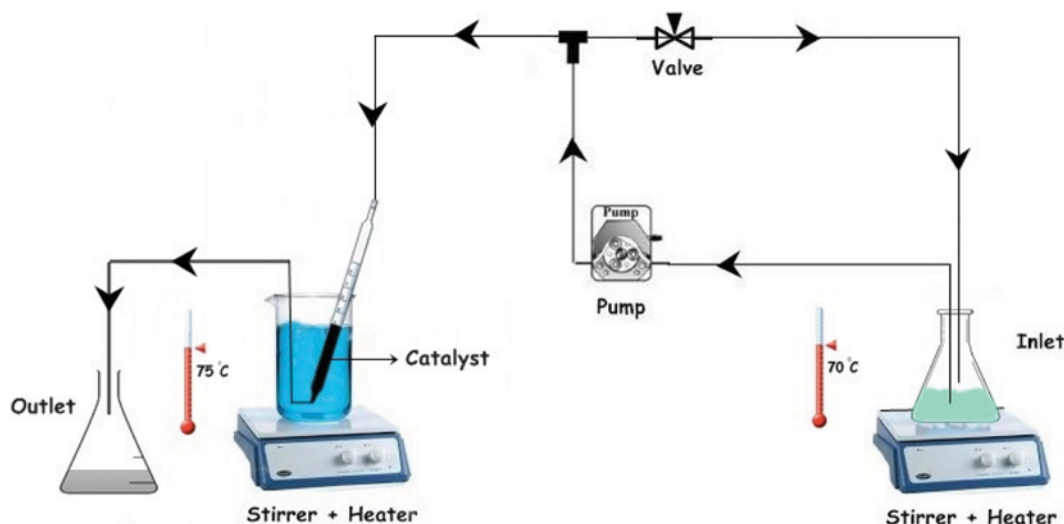


Fig. 1. Layout of the continuous flow through Amberlyst 15 catalytic column system used in this research.

ers, a pump, the Amberlyst 15 packed catalytic column, two thermometers, heat resistant tubing (4 mm internal diameter), tubing joints, a flow control valve, a diverter, a 2 L beaker, a feedstock flask, an effluent flask, and a measuring cylinder.

The feedstocks, consisting of acetic acid and oleic acid, were mixed with ethanol in a flask equipped with a magnetic stirrer and pre-heated to 70 °C using a stirring hot plate. The pre-heated reaction mixture was then pumped through the catalytic column. The column consisted of a 10 mL pipette filled with 3 grams catalyst (occupying approximately 4.7 mL of the pipettes volume). Glass wool was plugged on both ends of the pipette to keep the catalyst compacted within the column. The pre-heated feedstocks were passed directly through the column without any column pre-wetting. The flow rate through the column was set and varied using an in-line flow control valve with a diverter. The excess diverted flow was returned to the pre-heated feedstock flask. The column reaction temperature (75 °C) was maintained by operating the column in a hot water bath heated by the hot plate. Due to continuous water evaporation from the hot water bath, the water level was maintained by adding pre-heated (75 °C) water to the hot water as needed.

The effects of feedstock flow rate, fatty acid:ethanol molar ratio, and fatty acid chain length were each investigated. The magnitude of the effect was quantified by monitoring column effluent for ester production by measuring the acid value. For the flow rate experiments, the flow rate was varied (0.25, 0.5, and 0.70 mL/min) while keeping the feedstock composition (1 : 3 acetic acid : ethanol) constant. For the fatty acid : ethanol molar ratio experiments, the ratios of acetic acid : ethanol and oleic acid : ethanol were varied (1 : 1, 1 : 3, and 1 : 5) while keeping the flow rate (0.25 mL/min) constant. A comparison of the results was used to demonstrate the impact on esterification due to fatty acid chain length. Each individual column experiment was 150 minutes. Column effluent samples were acquired at  $t=0$ , 15, 30, 60, 90, 120, and 150 minutes.

While the regeneration and reusability of Amberlyst 15 resin was previously demonstrated [27], an experiment was run to evaluate the impact of column regeneration by ethanol washing in the column system [28]. For the regeneration experiment, two sets of col-

umns each processing the 1 : 3 acetic acid:ethanol feed were evaluated at flow rates of 0.5 and 0.7 mL/min. One column set was washed with ethanol and the other was not. Fresh 1 : 3 acetic acid:ethanol feeds were then run through each column set and the column effluent was again monitored for 150 minutes.

## 2-2. Analytical Measurements and Calculations

Ester formation within the column system was observed by measuring the acid value of both the feedstock and the column effluent. Acid value was determined on 2 g samples taken from the feedstock or the column effluent following AOCS titration Method Ca 5a-40 [29,30]. The calculations used to determine the acid value and the corresponding ester formation (represented as percent conversion of FFA in the samples) are provided in Eqs. (1) and (2) [30].

$$\text{acid value} = \frac{\text{mL NaOH} \times \text{NaOH normality} \times 28.2}{\text{sample weight}} \quad (1)$$

% FFA conversion

$$= \left[ \frac{\text{feedstock acid value} - \text{column effluent acid value @ } t=n}{\text{column effluent acid value @ } t=n} \right] \times 100 \quad (2)$$

BET surface area and porosity for the catalyst used in the experiments was conducted at a relative pressure range of 0.00-0.30 using a Micromeritics Gemini VII system to check the vendor Amberlyst 15 characterization. The sample was initially degassed at 100 °C for five hours. Weight hourly space velocity (WHSV) of the feedstock passing through the packed catalytic column was determined by using the concept of "mass flow per unit mass of catalyst." WHSVs at three different flow rates were calculated following Eq. (3).

$$\text{WHSV} = \frac{\text{mass flow/catalyst mass}}{(\text{flow rate} \times \text{density})/\text{catalyst mass}} \quad (3)$$

FTIR was used to confirm the structure of reactants and products. 3 mg of the sample was mixed with 300 mg of potassium bromide to make a pellet that was then analyzed using PerkinElmer FTIR spectrometer.

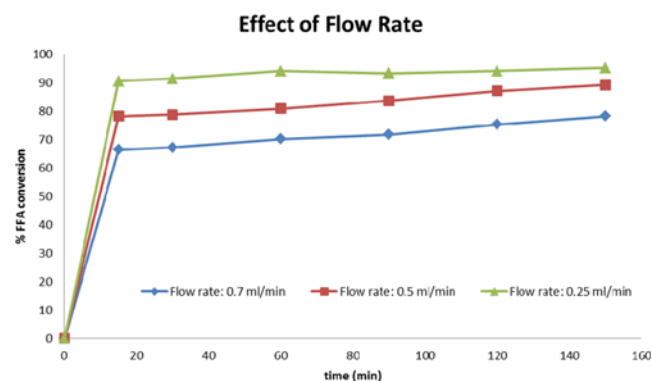
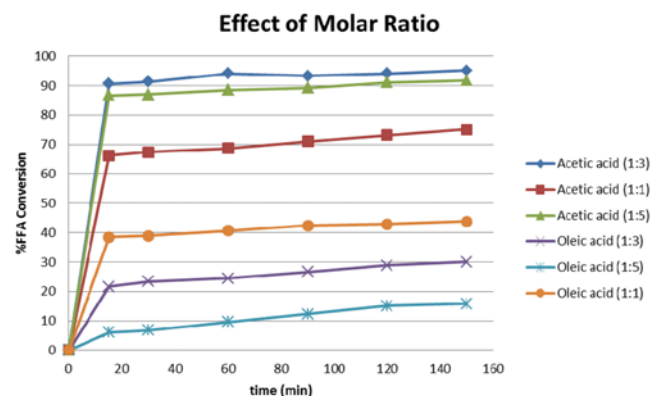
**Table 1. Weight hourly space velocity (WHSV) through the packed catalytic column**

	Flow rate (ml/min)	Density (g/ml)	WHSV (hr <sup>-1</sup> )	Percentage conversion after 2.5 hrs
Acetic acid-ethanol (1 : 3) feedstock	0.70	0.84	11.76	78.23
	0.50	0.84	8.40	89.25
	0.25	0.84	4.20	95.16
Oleic acid-ethanol (1 : 1) feedstock	0.25	0.79	3.95	43.81
Mixture of acetic acid-ethanol (1 : 3) and Oleic acid-ethanol (1 : 1) feedstock	0.25	0.81	4.05	71.02

## RESULTS AND DISCUSSION

Column experiments were at 75 °C and atmospheric pressure to demonstrate the use of Amberlyst 15 in a less energy intensive column system [31,32]. Prior to starting the experiments the vendor-supplied characteristics of Amberlyst 15 were confirmed. The measured BET surface area was 29.68 m<sup>2</sup>/g and Barrett-Joyner-Halenda adsorption average pore width (4V/A) was 20.34 Å. Table 1 provides the WHSVs at three different flow rates.

Fig. 2 shows the effect of column flow rate on ester formation. Ester formation increased as the feedstock flow rate through the column decreased (95.2±0.5% conversion at 0.25 mL/min com-

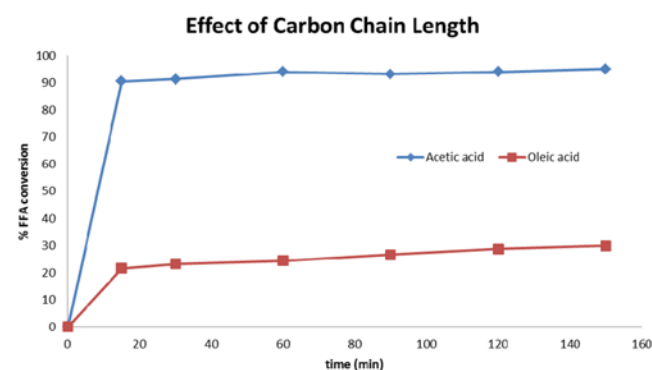
**Fig. 2. Effect of flow rate on acetic acid esterification at molar ratio=1 : 3, temperature=75 °C, and a catalyst mass=3 grams.****Fig. 3. Effect of acetic acid:ethanol and oleic acid:ethanol molar ratios on esterification at a flow rate=0.25 mL/sec, temperature=75 °C, and a catalyst mass=3 grams.**

pared to only 78.3±1.7% at 0.7 mL/min). For all flow rates, maximum yields occurred within the first 15 minutes. Only a marginal increase in yield was noted the longer the column was operated. The reduced yield observed after the first 15 minutes was caused by moisture production during the reaction. Moisture hinders the approach of acetic acid to the catalyst surface and slows esterification [33].

Fig. 3 shows the effect of the acetic acid : ethanol and oleic acid : ethanol molar ratios on ester formation. Different patterns were observed for each acid, dependent upon the molar ratio evaluated. For acetic acid, the percent conversion of feedstock to esters ranged from 75.2±1.2% at 1 : 1 molar ratio to 95.2±0.5% at 1 : 3 molar ratio. An observed conversion of 91.9±0.7% was observed for the 1 : 5 molar ratio. These findings suggest that sufficient ethanol must be present for the reaction to proceed, but an excess amount of ethanol floods the catalyst reaction sites and impacts ester formation [21].

For oleic acid, the opposite trend was observed. Ester formation decreased as the volume of ethanol increased. Observed conversion ranged from 15.8±2.1% at a 1 : 5 molar ratio to 43.8±1.3% for the 1 : 1 ratio. For oleic acid, as the ethanol content increases, ethanol adheres to the catalyst surface, causing reduced catalytic activity.

Fig. 4 shows the effect of fatty acid chain-length on ester formation. Esterification of acetic acid (C-2) produces higher ester yields compared to esterification of oleic acid (C-18) under the same conditions. The modeling software, Molecular Operating Environment (Chemical Computing Group, Inc.), was used to model the bond length of oleic acid and acetic acid to demonstrate this relationship. Based upon the model, the bond lengths of oleic and acetic

**Fig. 4. Effect of carbon chain length on esterification at a flow rate=0.25 mL/sec, molar ratio=1 : 3 acid:ethanol, temperature=75 °C, and a catalyst mass=3 grams.**

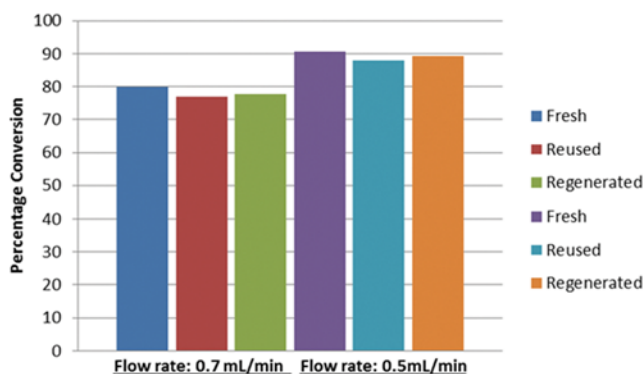


Fig. 5. Comparison of ester formation on fresh catalyst, regenerated catalyst (washed with ethanol), and reused catalyst (not alcohol washed) to demonstrate reusability.

acid are 22.46 Å and 3.83 Å, respectively. Comparing these bond lengths with Amberlyst 15's average pore diameter (240 Å), the model and experimental data indicate that acetic acid is able to access more of the catalyst surface in comparison to the larger oleic acid molecule.

Fig. 5 demonstrates the limited impact of ethanol washing for regeneration. Within these experiments a nominal increase in ester formation occurred when the column was ethanol washed and then reused. No nominal increase was observed when reusing the column without the ethanol wash. However, esterification yields were similar for fresh and reused Amberlyst, with or without an ethanol wash. These results demonstrate that Amberlyst 15 has a long service life.

FTIR was applied as a secondary confirmation of ester formation. Fig. 6 shows the results of FTIR for a mixture of acetic acid,

oleic acid and ethanol (at a 1:1:4 molar ratio), and the column effluent (determined to be esters) produced after esterification. As observed within the FTIR spectra, fatty acids demonstrate higher percentage transmittance in comparison to their respective esters. The first main dip is in the spectrum range of 2,800–3,000  $\text{cm}^{-1}$ . This dip represents the C-H and =C-H stretching frequencies. A second prominent dip is observed in the 1,700–1,800  $\text{cm}^{-1}$  range due to the presence of carbonyl (C=O) group. The presented FTIR results confirm esterification of acetic and oleic acid based on functional groups observed in the spectra of the feedstock versus the column effluent. These results are in agreement with earlier reported findings [34,35].

## CONCLUSIONS

Amberlyst 15 facilitated esterification of acetic and oleic acids in a continuous flow packed column system. The feedstock flow rate through the column has a direct impact on ester formation, with slower flow rates allowing for more feedstock catalyst contact time and higher ester yields. The acetic acid:ethanol and oleic acid:ethanol molar ratios were also observed to impact ester formation. For acetic acid, ester formation increased as ethanol increased. For oleic acid, ester formation decreased as ethanol increased. The highest ester yield for acetic acid ( $95.2 \pm 0.5\%$ ) and oleic acid ( $43.8 \pm 1.3\%$ ) was observed at an acid:ethanol molar ratio of 1:3 and 1:1, respectively. The difference in chain length between acetic (C-2) and oleic (C-18) acids also impacted ester yield in the column system. Acetic acid yielded higher ester formation compared to oleic acid under the same operating conditions. Acetic acid is able to approach more sites on the surface of the resin (in comparison to oleic acid) due

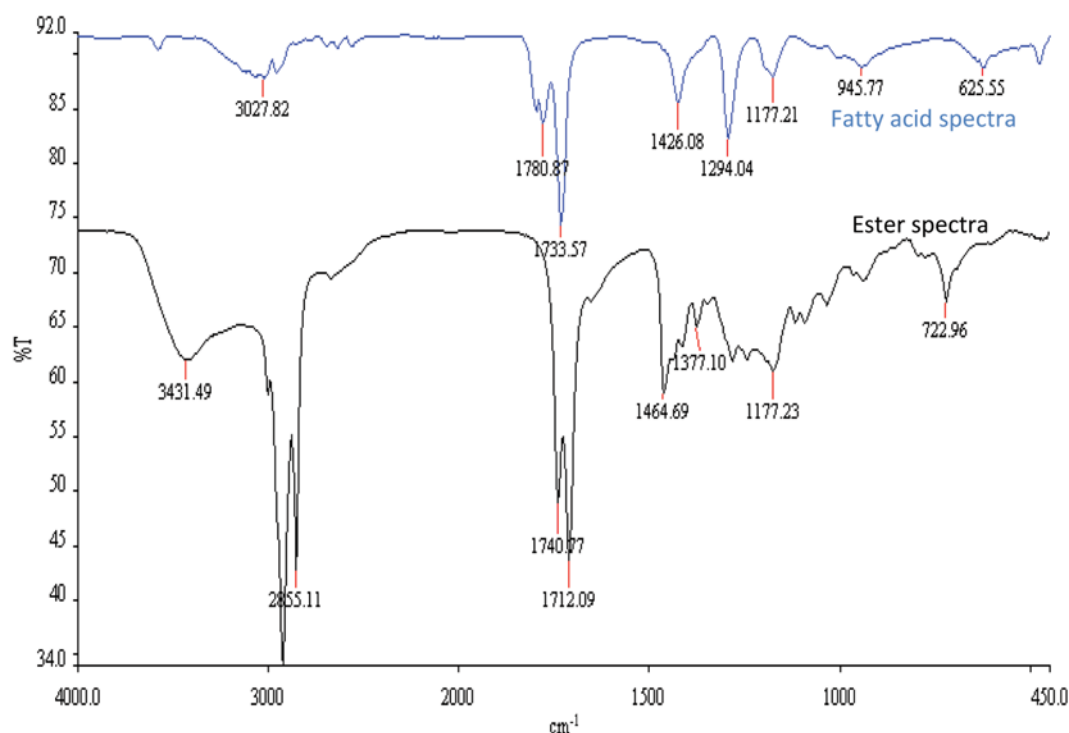


Fig. 6. FTIR spectra of feedstock (a mixture of oleic and acetic acids and ethanol) and column effluent (esters).

to acetic acid's smaller molecular size. Overall, the findings of this research confirm the use of a low pressure and low temperature operated continuous flow Amberlyst 15 catalytic column for esterification.

## NOMENCLATURE

Å : angstrom [s]  
 AOCS: American oil chemist's society  
 BET : Brunauer-Emmett-Teller  
 C-H, =C-H : carbon-hydrogen bonds  
 C-2 : a two carbon chain length  
 C-18 : an eighteen carbon chain length  
 cm : centimeter  
 FFA : free fatty acids  
 FTIR : Fourier transform infrared radiation  
 g : gram [s]  
 m<sup>2</sup> : meter squared  
 min : minute  
 mL : milliliter  
 mm : millimeter  
 NaOH : sodium hydroxide  
 t : time  
 WHSV : weight hourly space velocity  
 % : percent

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