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ESTERIFICATION OF OLEIC ACID IN A SEMI-BATCH BUBBLE REACTOR FOR BIODIESEL PRODUCTION

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Abstract - A semi-batch bubble reactor has been developed to produce fatty acid ethyl ester (biodiesel) by acid-catalyzed esterification of oleic acid with superheated ethanol vapor. In this paper, the effects of reaction temperature (110, 130 and 150°C), ethanol volumetric flow rate (1.35, 2.50 and 3.65 mL/min) and vapor bubble size on the reactor performance were evaluated. The results demonstrated that temperature and volumetric flow rate have significant effects on the chemical reaction, gas phase solubility and mass transfer limitations. In addition, the free fatty acid conversion velocity was increased by approximately 56% when a microporous stainless-steel tube was employed to generate and distribute the vapor bubbles inside the reactor, which allowed the process to reach 95% conversion in approximately 40 minutes for the operating temperature of 150°C and volumetric flow rate of 2.5 mL/min.
Keywords: Biodiesel; Esterification; Bubble reactor; Oleic acid; Ethanol.

INTRODUCTION

Biodiesel is a fuel composed of mono-alkyl esters derived from long chain fatty acids, which are typically produced from vegetable oils and animal fats (Silva et al., 2017; Van Gerpen, 2005). Because of its non-toxicity, biodegradability and production from renewable resources, biofuel has been regarded as an alternative to conventional diesel. Due to the considerable amount of oxygen present in its composition, biodiesel can be blended with petrodiesel at specific concentrations and used without any modification to the diesel engine (Shahid and Jamal, 2008), reducing the emission of carbon monoxide and unburned hydrocarbons (Chavan et al., 2015).

The majority of biodiesel produced worldwide is obtained by reacting oils and fats with methanol (MeOH) to produce fatty acid methyl esters (FAME) by transesterification and esterification, where the reaction pathway is chosen according to the amount of free fatty acid (FFA) present in the lipid feedstock (Borges and Díaz, 2012; Kulkarni and Dalai, 2006; Deng et al., 2010; Leung et al., 2010). In lipids containing high acid content, acid-catalyzed esterification is widely used as a pretreatment step to lower the amount of FFA and prevent soap formation in base-catalyzed transesterification (Chai et al., 2014; Chen et al., 2012; Wang et al., 2007; Zullaikah et al., 2005; Ramadhas et al., 2005). The esterification consists of the reaction of a FFA with a short chain alcohol to produce fatty acid ester and water.

$$R_1-\overset{\overset{O}{\|}}{C}-OH + ROH \overset{acid}{\rightleftharpoons} R_1-\overset{\overset{O}{\|}}{C}-OR + H_2O \quad (1)$$

fatty acid alcohol fatty acid ester water

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Since esterification is a reversible reaction, the accumulation of water in the reactor limits the conversion of FFA to biodiesel. However, the complete removal of the by-product water from the reactor content shifts the reaction equilibrium towards the products, increasing biodiesel yield (Lucena et al., 2011).

Recently, gas-liquid reactors have been designed to produce biodiesel. Studies have shown that bubble column reactors are more efficient and versatile for biodiesel production and process intensification (Joenialingsih et al., 2014; Stacy et al., 2014; Joenialingsih et al., 2012; Leonard et al., 2015; Wulandani et al., 2015; Hagiwara et al., 2015). Joelianingsih et al. (2014) developed a bubble reactor to evaluate the reactivity of the main FFA found in oils and fats at 250 °C by feeding superheated methanol vapor bubbles to the reactor at a rate of 4 g/min in the absence of catalyst. The authors reported 48% conversion for oleic acid in 60 minutes of reaction. Stacy et al. (2014) studied the performance of a bubble column reactor to produce biodiesel by acid-catalyzed esterification of oleic acid with superheated methanol vapor at 120 °C and ambient pressure. The effect of methanol volumetric flow rate and alcohol feed quality were evaluated. The results showed that 98% conversion were obtained in less than 2h for experiments using pure methanol and containing 10% of water by volume.

An important feature of gas-liquid reactors is the potential for process intensification, which is highly associated with the effect of the bubble size. In gas-liquid reactors, the mass transfer rate can be enhanced by reducing the size of the gas bubbles in contact with the liquid phase. Wulandani et al. (2015) reported that biodiesel production rate in a bubble column reactor was increased by about 7.7-fold when different configurations of gas spargers were used to reduce the size of the gas bubbles and improve their distribution throughout the liquid phase.

Most of studies on biodiesel production in gas-liquid reactors use MeOH as the vapor phase due to its high reactivity. However, ethanol (EtOH) may be regarded as a major substitute for MeOH, especially in countries like Brazil, considered as one of the world's largest producers. Furthermore, the second-generation ethanol produced from sugarcane bagasse may be employed to produce a completely sustainable biodiesel if lipid feedstocks such as waste cooking oil are used instead (Dias et al., 2012).

This paper studies the esterification of oleic acid in a semi-batch bubble reactor using superheated ethanol vapor. Oleic acid is one of the major FFAs found in most vegetable oils and fats, corresponding to 22–30% of soybean oil composition (Fan and Eskin, 2015). The effect of reaction temperature (110 – 150°C) and ethanol volumetric flow rate (1.35 – 3.65 mL/min) were evaluated. In addition, the influence of the bubble size on reactor performance was evaluated by using two different static gas spargers: a stainless-steel dip tube and a microporous tube.

MATERIALS AND METHODS

Chemicals and materials

Oleic acid was used as FFA feedstock for all experiments in this paper. Oleic acid (analytical standard), anhydrous ethanol (99.5 %) and sulfuric acid were purchased from Sigma Aldrich and used without further purification. Sodium hydroxide (98.4 %) and phenolphthalein were used for acid/base titration. A stainless-steel dip tube with inner diameter of 1/4" and a microporous stainless-steel tube (Figure 1) with diameter of 23 mm, height of 9.6 mm and porous diameter of 2.0 μm was used to feed ethanol vapor bubbles into the reactor.

Figure 1. Stainless-steel microporous tube with porous diameter of 2.0 μm.

Bubble reactor for catalytic esterification

Figure 2 shows a schematic of the experimental apparatus used in the esterification study, which is composed of a three-neck round-bottom flask (1) with capacity of 250 mL, a heating mantle (2) and a cooling system containing a condenser (3), thermostatic bath (4) and a flask (5) to promote condensation, cooling and storage of the condensed exiting vapors, respectively. The reactor was equipped with a temperature indicator (TI) and stainless-steel tubes (inner diameter of 1/4") responsible for feeding superheated EtOH vapor (solid line) and nitrogen (dashed line) from the gas cylinder (6). In addition, a pump (7) and a tubular heater (8) equipped with a temperature controller (TC) were used to feed and vaporize the liquid EtOH from the alcohol storage glass flask (9), respectively.

Oxidative stability of oleic acid

The oxidative stability of oleic acid was evaluated prior to conducting the esterification experiments. A

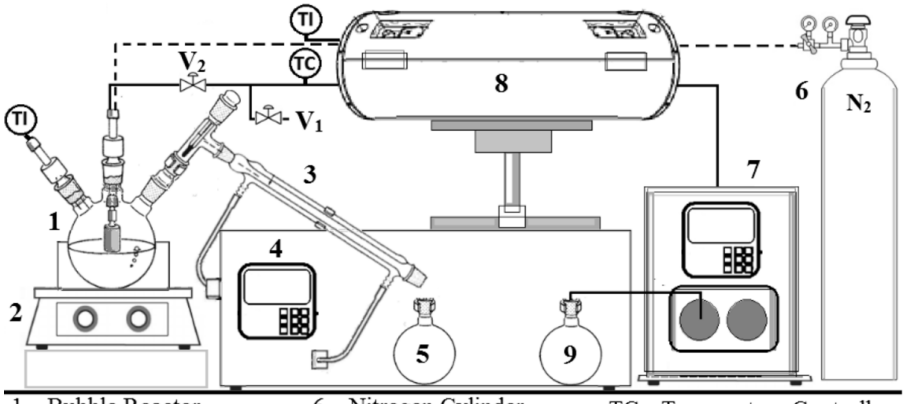

Figure 2. Schematic of the semi-batch bubble reactor for catalytic esterification of FFAs.

fixed amount of oleic acid was added to the reactor and heated under normal and inert conditions, where nitrogen was used as inert gas. The change in oleic acid appearance and the occurrence of vaporization below its normal boiling point (360°C) was observed and taken as indications of FFA degradation.

Experimental procedure and conditions

The reactor was initially charged with 150 g of oleic acid and heated to the reaction temperature (110, 130 and 150 °C) at ambient pressure. Liquid ethanol was continuously pumped from the alcohol storage glass flask to the tubular heater at different volumetric flow rates (1.35, 2.50 and 3.65 mL/min). At the beginning, valve-2 was closed to prevent any liquid ethanol from entering the reactor, while valve-1 was kept open until all alcohol was superheated. After complete vaporization, valve-2 was open to start the reaction by feeding superheated ethanol and then valve-1 was closed. For all experiments, the superheated vapor temperature was set to the reaction temperature, which was controlled by a PID controller attached to the alcohol line.

A solution catalyst was prepared by mixing sulfuric acid in 2 mL of ethanol. The amount of sulfuric acid used to prepare the catalyst solution was equal to 0.1% of the FFA mass loaded to the reactor. During the process, some amount of ethanol is transferred from the vapor bubbles to the liquid phase and reacts with oleic acid to form water and ethyl oleate. Since the reactor operates at temperatures greater than 100 °C, the water formed during the reaction is continuously evaporated and exits the reactor along with any unreacted ethanol. The vapor phase exiting the reactor was condensed and collected in the glass container.

Liquid samples were collected from the reactor at fixed time intervals (10–15 min) and used for analysis to determine the amount of unreacted FFA in the reactor. To evaluate the effect of the vapor bubble size on reactor performance, experiments were performed using a stainless-steel dip tube with inner diameter of 1/4”’ and a 2.0-μm stainless-steel microporous tube to generate the bubbles.

FFA conversion analysis

Oleic acid conversion was determined by base titration. An aqueous solution of sodium hydroxide (0.5 M) was prepared and tested against an acid standard before being used. Each sample collected from the reactor was dissolved in ethanol and a few drops of phenolphthalein solution (1% in ethanol) was added to indicate the end point of the titration. The method used for determining the percentage of free fatty acid in a sample is a procedure similar to AOCS Ca 5a-40 (AOCS, 2009). The experimental FFA conversion at each time was calculated by Eq. (2).

$$X_{exp} = 1 - \frac{C_{FFA}(t)}{C_{FFA,0}} \tag{2}$$

where $C_{FFA,0}$ and C_{FFA} are the molar concentrations of FFA at the beginning of reaction and at time t, respectively.

Kinetic model

The kinetics of the acid-catalyzed esterification reaction in the semi-batch bubble reactor were evaluated. Since the reactor was operated at temperatures above 100°C and ambient pressure, the rate of the reverse reaction becomes negligible due to the continuous removal of the by-product water through evaporation. Therefore, the rate of disappearance of oleic acid in the reactor may be described by a first order reaction with respect to both FFA and EtOH:

$$-\frac{dC_{FFA}}{dt} = kC_{EtOH}C_{FFA} \tag{3}$$

where k is the rate constant and C_{EtOH} is the ethanol molar concentration (mol/L). In the semi-batch mode operation, EtOH is continuously fed to the reactor as vapor bubbles and reacts with the FFA after being absorbed. Due to the fast dynamics of the gas phase in the reactor, the concentration of EtOH in the gas phase does not change appreciably and may be considered as constant throughout the process (Joelianingsih et al., 2008). After rearrangement and integration of Eq. (3), the calculated FFA conversion with time is expressed as follows:

$$X_{calc}(t) = 1 - \exp(-k't) \tag{4}$$

where $k' = kC_{EtOH}$. The effective rate constants of each experiment were determined by minimizing the sum of squared residuals (SSR) of the experimental and calculated conversions:

$$\min SSR = \sum_{i=1}^{N} \left(X_{i,exp} - X_{i,calc} \right)^2 \tag{5}$$

where N is the number of data points for each experiment. The genetic algorithm available in MATLAB was used to minimize Eq. (5).

RESULTS AND DISCUSSION

Oxidative stability results

The oxidative stability of oleic acid was evaluated. The oleic acid heated under normal conditions became dark brown after reaching 90°C (Figure 3a). After a few minutes, the whole amount of FFA in the reactor was totally deteriorated and the occurrence of vaporization and the deposit of solid particles at the bottom of reactor was observed after reaching 130°C, indicating that the molecules of FFA were degraded during heating. On the other hand, oleic acid heated under inert conditions exhibited no changes in its appearance and no vaporization or solid particle deposit was observed in the whole temperature range evaluated (25–200°C) (Figure 3b).

The set of results obtained in the oxidative stability analysis shows that oleic acid is very susceptible to oxidation when exposed to oxygen and high temperatures. Studies have shown that the main factor responsible for degradation of unsaturated oils and fats is autoxidation (Holman and Elmer, 1947; Farmer et al., 1942; Cosgrove et al., 1987; Gardner, 1989), a chain reaction that occurs in the presence of oxygen, which is initiated by free radicals created by thermal decomposition of lipid molecules (Eq. (3)):

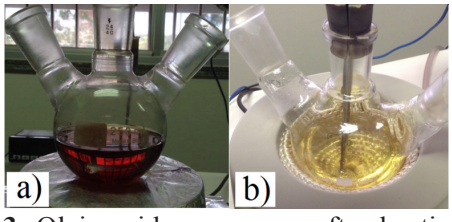

Figure 3. Oleic acid appearance after heating under (a) normal conditions (25 – 130°C) and (b) inert conditions (25 – 200°C).

$$\begin{aligned}
&\text{Initiation:}\\
&RH \rightarrow R\bullet + H\bullet\\
&\text{Propagation:}\\
&R\bullet + O_2 \rightarrow ROO\bullet\\
&ROO\bullet + RH \rightarrow R\bullet + ROOH\\
&\text{Termination:}\\
&2ROO\bullet \rightarrow \text{Nonradical products} + O_2
\end{aligned} \tag{6}$$

where RH represents the unsaturated fatty acid, R• is the carbon-centered radical generated by the abstraction of the hydrogen atom, ROO• is the peroxyl radical formed by the reaction of the carbon-centered radical with oxygen and ROOH is the hydroperoxide (Gardner, 1989; Monirul et al., 2015). Therefore, inert conditions were required to work with oleic acid due to its vulnerability to autoxidation when exposed to high temperatures in the presence of oxygen and all esterification experiments were performed under a continuous flow of nitrogen gas.

Hydrodynamics of the vapor bubbles

The hydrodynamics of the vapor bubbles generated by the static gas spargers was evaluated. Figure 4 shows the ethanol vapor bubble distribution in oleic acid for the tests performed with the dip tube and microporous tube. As can be noted in Figure 4a, for the same volumetric flow rate (3.65 mL/min), a small number of bubbles was created by the dip tube. It was observed that a significant amount of bubbles merged with each other during contact and formed single bubbles with larger sizes (bubble coalescence). Those bubbles were able to overcome the lipid column resistance more easily and reach the top of the column in a relatively short period of time. On the other hand, Figure 4b shows that the microporous tube was able to generate a significantly higher number of bubbles with homogeneous distribution throughout the entire lipid phase. The size of the vapor bubbles was substantially reduced, and coalescence was only observed at the bottom edge of the microporous tube due to its arrangement in the column. Unlike the previous test with the dip tube, the smaller bubbles generated by the microporous tube presented a much lower ascending velocity, which increased the contact time between the phases, enhancing the rate of absorption. The

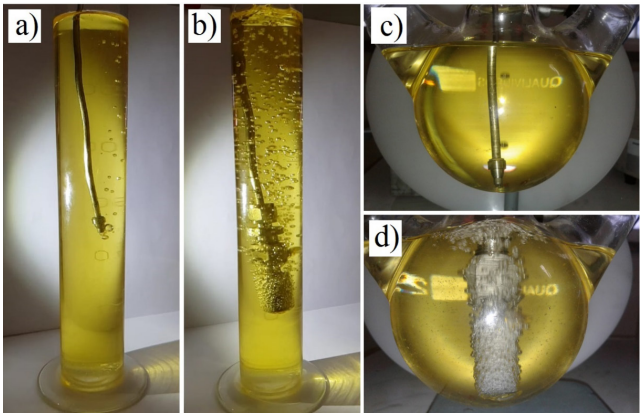

Figure 4. Ethanol vapor bubble distribution in oleic acid: (a) glass column and dip tube, (b) glass column and porous tube, c) round-bottom flask and dip tube and (d) round-bottom flask and porous tube.

microporous tube was therefore chosen as the primary gas sparger for the esterification experiments.

Effect of alcohol flow rate

Pure EtOH was pumped out of the storage glass flask at three different flow rates (1.35, 2.50 and 3.65 mL/min) and fed to the reactor after being vaporized and superheated. Figure 5 displays the effect of ethanol volumetric flow rate on oleic acid conversion using the microporous tube to generate the vapor bubbles. The curves in Figure 5a-c show that conversion is faster at higher ethanol flow rates, but slower at lower flow rates. The charging rate of ethanol seems to have an important effect on reactor performance and this can be explained by mass transfer considerations.

In a bubble reactor, some amount of EtOH from the vapor bubbles needs to be transferred to the liquid phase before reaction takes place. At higher flow rates, the turbulence generated by the bubbles inside the reactor is responsible for creating a more vigorous and intense mixing, which reduces mass transfer resistance in the liquid phase and contributes to a higher mass transfer rate of EtOH from the vapor phase.

As observed in Figure 5a, slower conversions are obtained at the lowest EtOH flow rate. Although the results may be explained by the previous discussion, another reason for slower conversions is the amount of EtOH available in the reactor. At low charging rates, smaller amounts of EtOH will be available to be transferred to the liquid phase, and this may cause the process to be limited by mass transfer. Stacy et al. (2014) reported similar results for experiments performed with MeOH, where nearly linear conversion curves were obtained at even lower flow rates (0.20 mL/min), indicating that the alcohol supply may limit the process and lead to longer reaction times.

At flow rates of 1.35 mL/min, all experiments achieved conversions higher than 97% in about 2 hours of reaction, while experiments conducted at 2.50 and 3.65 mL/min required 45–70 min to achieve

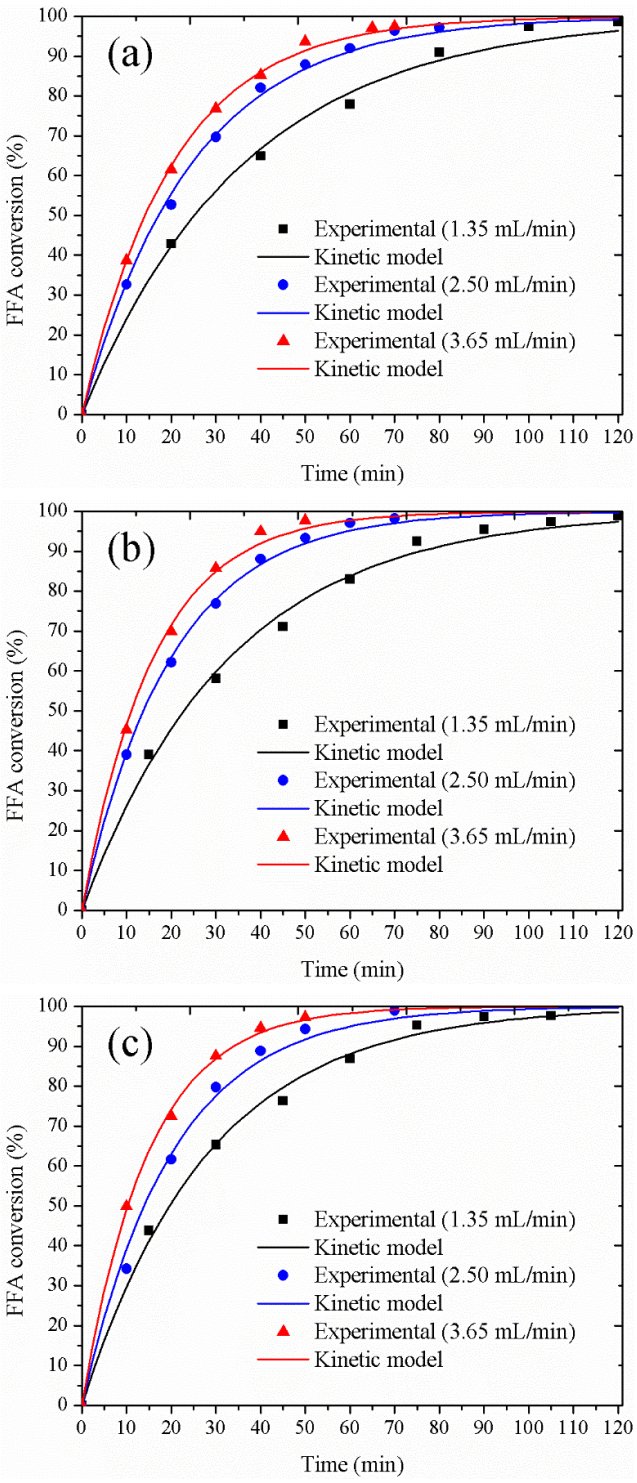

Figure 5. Effect of ethanol volumetric flow rate on oleic acid conversion at different temperatures: (a) 110 °C (b) 130°C and (c) 150 °C.

the same value. The conversion profiles obtained for experiments at 2.50 and 3.65 mL/min show that there is a smaller difference between the conversions measured at the same time in comparison with experiments at 1.35 mL/min. This observation indicates that EtOH flow rates higher than 3.65 mL/min may have no effect on reaction time for a given reaction temperature.

Effect of temperature

Figure 6 shows the effect of reaction temperature based on the time required to achieve 95% conversion of FFA using the microporous tube. The major effect of temperature is observed for the experiment performed at 3.65 mL/min, where the time to convert 95% of oleic acid was reduced from 60 to 42 minutes when the temperature was increased from 110 to 130°C. On the other hand, the conversion time was barely affected when the temperature was varied from 130 to 150°C at the higher volumetric flow rates (2.5 and 3.65 mL/min). One must expect that higher temperatures would always lead to faster reaction and shorter reaction times. However, the temperature of the vapor phase, which was set to the reaction temperature for all experiments, must be considered to analyze the results. Indeed, elevating the reaction temperature leads to higher kinetic constants and faster reaction rates in the liquid phase. However, gas solubility tends to decrease as temperature is increased (Battino and Clever, 1966; Rettich et al., 1981; Wilhelm et al., 1977), which means that the concentration of EtOH available in the liquid phase to react will be lower and no significant reduction in conversion time will be observed. Therefore, higher vapor phase temperatures may cause a negative impact on reducing the time to convert FFA and must be set with caution to avoid low reactor performance and optimize the effect of the operating variables. Kocsisová et al. (2005) showed that acid-catalyzed esterification using MeOH at reaction temperatures about 20 – 60°C above its boiling point was effective to achieve high conversions (higher than 99%) of FFAs in relatively short periods of time.

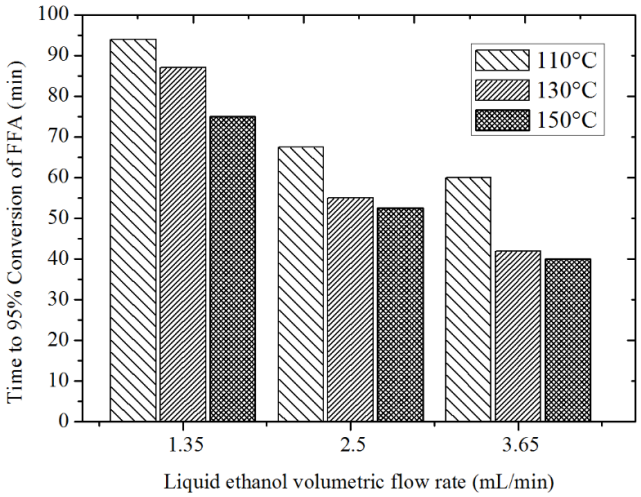

Figure 6. Effect of reaction temperature on FFA conversion.

Experimental data of oleic acid esterification with superheated MeOH vapor at similar conditions was used for comparison. Figure 7 shows the conversion profile obtained by Stacy et al. (2014) at 3.50 mL/min of MeOH and 120°C, which is compared to the results obtained in this work at 130°C and EtOH volumetric flow rate of 3.65 mL/min.

According to Figure 7, the conversion profiles obtained in both experiments are identical and present the same FFA consumption velocity, reaching the steady state level in about 50 minutes. Considering that both experiments in Figure 7 were conducted at approximately the same volumetric flow rate, it was observed that an increase of 10°C in reaction temperature with respect to the experiment of Stacy et al. (2014) was enough to make the FFA consumption rate of both experiments identical. It is worth pointing out that the experimental data used for comparison were obtained by two completely different reactor geometries. Table 1 shows the main characteristics

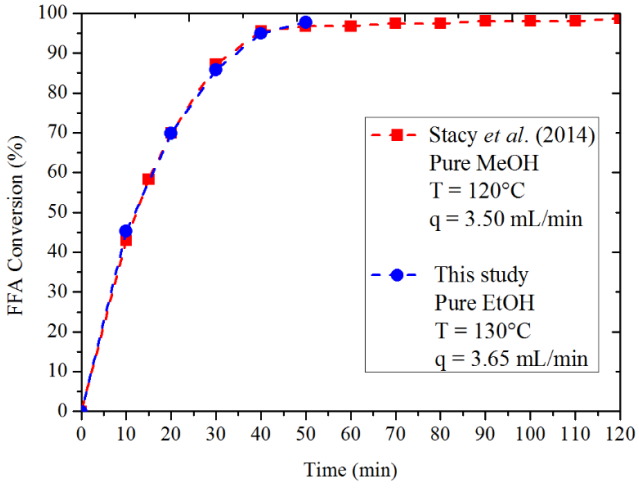

Figure 7. Comparison between experimental conversions of oleic acid esterification with superheated methanol and ethanol vapor at different temperatures and similar volumetric flow rates.

Table 1. Specifications of the reactors used in experiments shown in Figure 7.

Reactor's characteristics and specifications	This study	Stacy et al. (2014)
Type of reactor	Bubble reactor	Bubble column reactor
Glassware	Three-neck round-bottom flask	Jacketed glass column
Reactor diameter (cm)	8.40	2.54
Height of reactor (cm)	-	45.72
Gas sparger	microporous tube	-
Volume of FFA (mL)	170	180
Type of catalyst	sulfuric acid	sulfuric acid
% of catalyst (g cat/g FFA)	0.1	0.1

and specifications of the two reactors used in the experiments shown in Figure 7.

The specifications and conditions in Table 1 show some advantages of the bubble column reactor over the bubble reactor used in this work. The column type geometry increases the contact time between the vapor and liquid phase, since MeOH needs to pass through a lipid column of about 36-cm height, according to the bubble column diameter displayed in Table 1. The higher residence time of the vapor bubbles inside the reactor increases the rate of mass transfer of MeOH and results in higher amounts of alcohol available in the oil phase to react with FFA.

Although the experiments of Stacy et al. (2014) used a more reactive alcohol and a more advantageous reactor geometry, the results obtained in this work showed that FFA esterification can be carried out in the developed bubble reactor with almost the same efficiency as in bubble column reactors, even when a less reactive alcohol is used.

Effect of bubble size

The conversion profiles obtained for experiments performed with the dip tube and microporous tube at the same operating conditions are shown in Figure 8. For all conditions of temperature and volumetric flow rates evaluated, FFA conversion was found to be faster for experiments performed with the microporous tube. According to Figure 8a-b, for the experiments conducted at 110°C/1.35 mL/min and 130°C/2.5 mL/min, FFA conversion was approximately 10% higher than the values obtained with the dip tube for each experimental point. On the other hand, for the highest temperature (150°C), the effect of the bubble size became more evident and FFA conversion was found to be approximately 30% higher than the values obtained with the dip tube for all experimental points over the whole range of volumetric flow rate (Figure 8c-e). The comparison between the average conversion velocity of FFA obtained for the experiments performed with the dip tube and microporous tube is shown in Table 2.

Table 2. Average conversion velocity of FFA at different vapor bubble size.

Operating conditions		FFA average conversion rate (mmol/L·min)		Ratio of FFA average conversion rates
T (°C)	q (mL/min)	6.35-mm dip tube ($-r_1$)	2.0-µm microporous tube ($-r_2$)	$(-r_2)/(-r_1)$
110	1,35	24.1	26.0	1.079
130	2.50	40.9	44.5	1.088
150	1.35	21.6	29.5	1.364
150	2.50	38.4	59.7	1.555
150	3.65	44.6	61.6	1.381

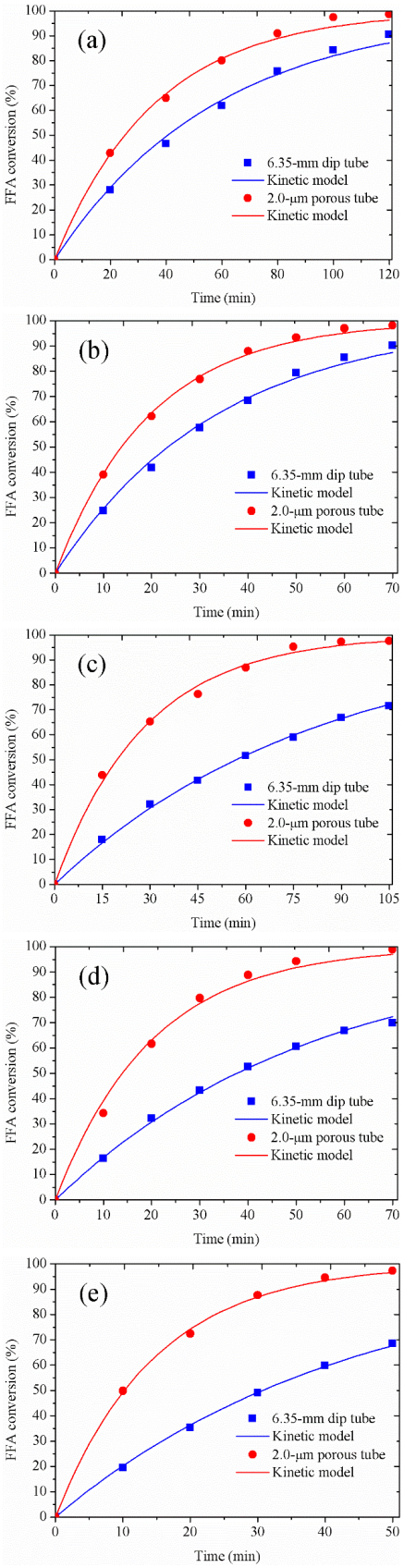

Figure 8. Effect of vapor bubble size on FFA conversion at (a) 110°C/1.35 mL/min; (b) 130°C/2.50 mL/min; (c) 150°C/1.35 mL/min; (d) 150°C/2.50 mL/min and (e) 150°C/3.65 mL/min.

Table 3. Estimated effective rate constants at different operating conditions

T (°C)	q (mL/min)	$k'_{porous\ tube}$ (min^{-1})	$R^2_{porous\ tube}$ (%)	$k'_{dip\ tube}$ (min^{-1})	$R^2_{dip\ tube}$ (%)
110	1.35	0.0275	99.54	0.0171	99.49
110	2.50	0.0405	99.78	-	-
110	3.65	0.0492	99.90	-	-
130	1.35	0.0304	99.59	-	-
130	2.50	0.0505	99.86	0.0297	99.57
130	3.65	0.0630	99.73	-	-
150	1.35	0.0354	99.67	0.0122	99.87
150	2.50	0.0499	99.40	0.0184	99.79
150	3.65	0.0679	99.91	0.0226	99.93

According to Table 2, the FFA average conversion velocity increased about 7.9 and 8.8% by using the microporous tube at the experimental conditions of 110°C/1.35 mL/min and 130°C/2.50 mL/min, respectively. At the highest temperature (150°C), the velocity of FFA consumption increased approximately 36, 56 and 38% when the microporous tube was used at 1.35, 2.50 and 3.65, respectively. The values of the effective rate constants estimated by fitting the kinetic model to the experimental data are displayed in Table 3.

According to the results presented in Table 3, for the conditions of 110 °C/1.35 mL/min and 130°C/2.50 mL/min, the effective rate constants obtained for the experiments performed with the porous tube are about twice the values found by using the dip tube. On the other hand, for the temperature of 150°C, the values of the estimated rate constants for the experiments carried out with the porous tube are approximately three times the values obtained with the dip tube under the same operating conditions. The results show that the distribution and size of the vapor bubbles in the reactor are relevant hydrodynamic parameters that are intrinsically associated with the intensification of the process.

The results presented in Figure 8 and Tables 2-3 corroborate the previous discussion about mass transfer limitations. The conversion of FFA became faster because the higher population of microscopic bubbles generated by the microporous tube increases the average surface area in contact with the lipid content, which decreases the mass transfer resistance and favors the transference of EtOH to the liquid phase to react. Other authors have investigated the effect of the bubble size on gas-liquid reactor performance and reported that smaller bubbles are preferred, since the larger bubbles have larger velocities, which decrease the contact time between the phases and contribute to higher amounts of unreacted alcohol vapor leaving the reactor (Wulandani et al., 2015; Michele and Hempel, 2002; Behkish et al., 2002).

CONCLUSIONS

A bubble reactor for FFA esterification was developed and used to produce fatty acid ethyl esters (FAEE) by reacting oleic acid with superheated ethanol vapor. Oxidative stability analysis of oleic acid showed that all experiments should be performed under inert conditions due to its susceptibility to autoxidation, the main factor responsible for lipid degradation at high temperatures in the presence of oxygen. The effect of volumetric flow rate, temperature and vapor bubble size was evaluated. The bubble reactor was able to achieve FFA conversions of 95% in about 40 minutes. The results showed that all of the operating variables evaluated presented significant effects on the time to convert FFA and that the temperatures of the liquid and vapor phases must be appropriately set to achieve better results and avoid low reactor performance. The use of the 2.0-μm stainless-steel microporous tube was effective in generating higher populations of microscopic vapor bubbles and increased the average FFA conversion rate by about 56% with respect to the experiments performed under the same conditions with a dip tube. Therefore, the bubble reactor developed was shown to be robust for conducting acid-catalyzed esterification of FFAs with superheated EtOH vapor, being as efficient as the bubble column reactors used for esterification of lipids with superheated MeOH vapor, which is more reactive than ethanol.

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