

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

185,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Role of Mass-Transfer Interfacial Area in the Biodiesel Production Performance of Acid-Catalyzed Esterification

Devjyoti Nath, Adisorn Aroonwilas and
Amornvadee Veawab

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/65657>

Abstract

This work investigated the role of mass-transfer interfacial area in the biodiesel production using the acid-catalyzed esterification process. The interfacial area between alcohol and oil feedstock was determined by conducting acid-catalyzed esterification experiments using methanol and oleic acid (as free fatty acid) under ranges of five process parameters: reaction temperature (45–65°C), agitation speed (200–400 rpm), methanol-to-oil ratio (3:1–9:1 mol/mol), catalyst concentration (0.5–2.0%), and concentration of free fatty acid (5–30%). Effects of these parameters on the biodiesel conversion rate and the interfacial area were quantified. An empirical correlation for the interfacial area was developed as a function of process parameters. Results show that the enhancement of biodiesel production rate is attributed to reaction kinetics and/or interfacial area. The interfacial area is the sole contributor to the increase in biodiesel production rate due to the increase in methanol-to-oil ratio and agitation speed. Both kinetics and interfacial area contribute to the increase in biodiesel production rate due to the reaction temperature and catalyst concentration. The interfacial area plays negligible role in the change in biodiesel production rate due to the free fatty acid content.

Keywords: biodiesel, esterification, mass-transfer interfacial area, reactor design, hydrodynamics, parametric effects

1. Introduction

Energy use is considered to be the most fundamental requirement for various human activities, especially in the industrial, transportation, and agricultural sectors. Among different kinds of

fuels, petroleum constitutes the majority of the world's energy supply. However, petroleum is a finite and nonrenewable energy source, which has already caused serious environmental pollution. Therefore, a sustainable, affordable, and environmentally friendly alternative to petroleum is urgently needed.

Biodiesel is considered to be an important alternative to conventional petroleum-based diesel [1]. It is nontoxic, and biodegradable, offers lower emissions of a number of air pollutants, can be used in typical diesel engines without any major modifications, and has greater lubricity than conventional diesel, thus reducing corrosion in diesel engines [2]. Biodiesel can be used in its pure form called B100 (100% biodiesel) or in a blend with different proportions of conventional diesel fuels. Common blends include B20 (20% biodiesel and 80% conventional diesel), which are much closer to diesel fuel properties than B100 and B5 (5% biodiesel and 95% conventional diesel).

In the typical biodiesel production process, the catalyzed transesterification or esterification reaction is carried out in a multiphase reactor where the two immiscible chemical reactants (oil feedstock and alcohol-containing catalyst) are brought into contact using different agitation or mixing mechanisms. Because the cost of biodiesel production depends heavily on the cost of raw materials, using low-quality feedstocks such as waste cooking oils or nonedible oils instead of high-quality feedstocks will significantly reduce the biodiesel production cost. However, low-quality feedstocks have high content of free fatty acids (FFAs), which can react with the alkaline catalyst and produce soaps. This side reaction in the alkali-catalyzed transesterification process will reduce the catalyst efficiency and the biodiesel conversion rate. Additionally, the formation of soaps will make the later purification process difficult. As a result, the undesired side reactions caused by FFAs will increase the cost of biodiesel production. Therefore, when using low-quality feedstocks for biodiesel production, the content of FFAs must be reduced to an acceptable level (typically below 1% according to references [3–5]) before the alkali-catalyzed transesterification process. One efficient method for removing the FFAs from feedstocks is esterification, where the FFAs react with alcohol to form ester and water as products.

Due to the nature of the multiphase reaction, the efficiency or rate of biodiesel production relies heavily on two primary factors: (i) the kinetics of catalyzed transesterification or esterification reactions and (ii) the hydrodynamics of liquid-liquid mixing promoted by reactor design and operation. In order to arrive at a high-efficiency and optimized biodiesel reactor, these two fundamental features must be understood. To date, a large quantity of biodiesel research works has been carried out in many different aspects, such as production rate and the quality of biodiesel products derived from different feedstocks, kinetic studies to find optimal reaction conditions for achieving higher yields, and use of enzyme and heterogeneous catalysts as an alternative to the conventional homogeneous catalysts [6–11]. Most kinetic works reported biodiesel conversion profiles as a function of reaction time under specific reaction conditions and for specific types of reactor design and operation. As such, the reported kinetic data essentially reflect the combined performance of both reaction kinetics and hydrodynamics of liquid-liquid reaction systems.

Despite its importance to the development of high-performance reactors, the knowledge of hydrodynamics or mass-transfer interfacial area (a_e) between the two immiscible reactants during biodiesel reaction is very limited. Only one study by Stamenkovic et al. [12] relates to the interfacial area in the biodiesel production process. In their work, the effect of agitation intensity during the base-catalyzed transesterification of sunflower oil was investigated under a specific reaction condition, that is, 20°C and alcohol-to-oil ratio of 6:1. There are no other studies reporting the interfacial area for the acid-catalyzed reaction system.

Therefore, the objectives of this work are: (i) to extend knowledge of interfacial area formed between immiscible reactants during the acid-catalyzed esterification reaction which can be used for the design of a high-efficiency reactor, (ii) to investigate the role of process parameters on interfacial area in the esterification process, and (iii) to develop an empirical correlation for interfacial area estimation as a function of process parameters. To achieve these objectives, a series of esterification experiments were performed using a stirred reactor operated under variable ranges of reaction conditions (**Table 1**). The experimental results were obtained in forms of free fatty acid (FFA) conversion profiles which were subsequently used for determining the interfacial area values.

Process parameter	Range
Reaction temperature (°C)	45–65
Agitation speed (rpm)	200–400
Methanol-to-oil ratio (mol:mol)	3:1–9:1
Catalyst concentration (wt%)	0.5–2.0
Free fatty acid concentration (%)	5–30
Type of free fatty acid	Oleic acid
Type of catalyst	Sulfuric acid

Table 1. Summary of test conditions for esterification experiments.

2. Methods

2.1. Materials

Two sets of chemicals were used in the experiments: (i) reactants and an acid catalyst for the esterification reaction and (ii) supporting chemicals for liquid sample analysis. For esterification experiments, canola oil was used as the base ingredient of oil feedstock. Oleic acid (90%) from Sigma-Aldrich (Oakville, Ontario) was used as the representative of free fatty acids (FFAs) commonly found in the feedstock. A predetermined amount of oleic acid was added to the base canola oil in order to simulate low-quality feedstock. Sulfuric acid (98%) was used as the acid catalyst, and methanol (99.98%) was chosen to represent the alcohol reactant. Both sulfuric acid and methanol were purchased from Fisher Scientific (Ottawa, Ontario). For liquid sample

analysis, toluene (99.9%), isopropyl alcohol (99.9%), and potassium hydroxide (0.1 N) were used for titrations to determine the acid number or FFA content of the oil phase.

2.2. Experimental setup

The mass-transfer interfacial area (a_e) and reaction kinetics between oil feedstock and methanol were determined by carrying out esterification experiments in a bench-scale reaction system. As shown in **Figure 1**, the reaction system consists of a 500-mL glass reactor that is jacketed for heating/cooling (Ace Glass Inc., USA), a mechanical agitator powered by a variable-speed drive (Cole-Parmer, Canada), and a water bath with a temperature controller/circulator (Cole-Parmer, Canada). The reactor was designed for operating pressures and temperatures of up to 35 psig and 100°C, respectively. The reactor head has three connecting ports: one for the mechanical agitator, one for sampling collection, and one for temperature measurement. A glass bearing with PTFE coupling was connected to the reactor head to accommodate the agitator. The sampling port was equipped with a silicone rubber septum, thus making possible the collection of liquid samples without interrupting the reaction progress. A K-type thermocouple connected to a handheld meter was used for monitoring reaction temperature. During the experiments, a heating medium (i.e., water from the temperature-controlled water bath) was circulated through the reactor jacket in order to keep reaction temperature constant.

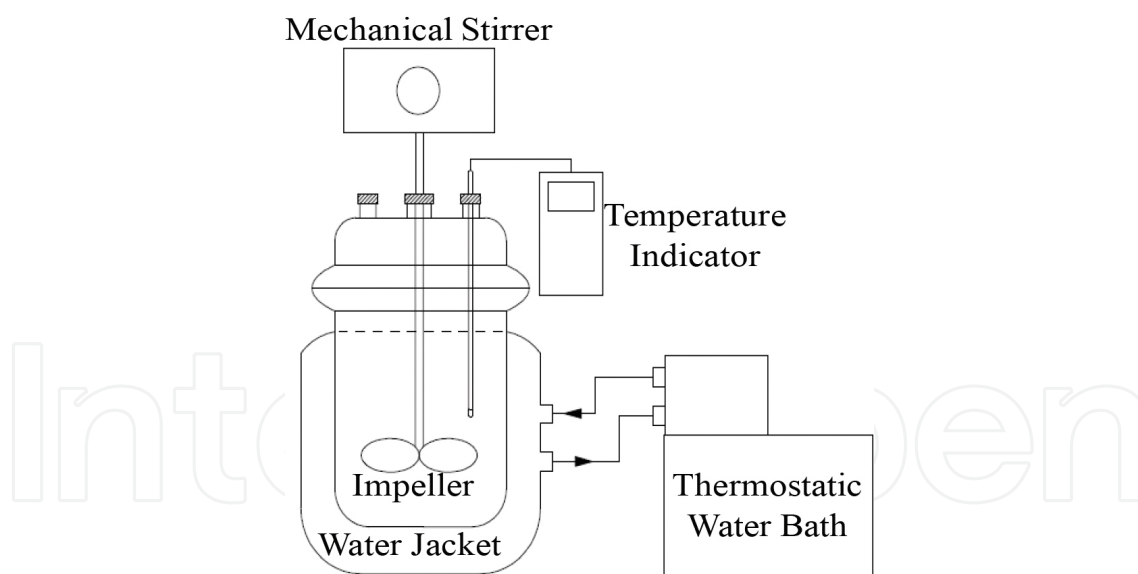


Figure 1. A schematic diagram of the bench-scale reaction system for esterification experiments.

2.3. Experimental procedures

The experiments were conducted in two different modes: (i) esterification tests with a well-defined interfacial area between oil feedstock and methanol, and (ii) esterification tests with the complete mixing between the two reactants. The first mode of experiments provided the

true kinetic features of the esterification reaction, while the second gave the reaction performance that integrates both kinetic and hydrodynamic effects of the reaction system.

For the experiments with a fixed interfacial area (first mode), the canola oil was mixed with oleic acid to simulate a low-quality feedstock containing different levels of FFA. A 250 mL of the prepared feedstock was then transferred into the 500-mL glass reactor and maintained at a desired reaction temperature. An impeller or agitator was placed in the middle of this oil phase and set at a particular mixing speed in order to keep the oil phase homogenized but yet the oil-surface undisturbed. Meanwhile, a predetermined amount of H_2SO_4 (catalyst) was mixed with methanol to form a catalyst/methanol mixture with a desired catalyst concentration. For each experimental run, a 93 mL of catalyst/methanol mixture was used to ensure an excessive amount of methanol (more than 40 mol/mol ratio) available for reacting with FFA in the oil phase. Prior to the reaction, the catalyst/methanol mixture was heated to the desired reaction temperature in a water bath. Once the reaction temperature was reached, the methanol mixture was transferred into the glass reactor to start the esterification reaction. In order to keep the interface between the oil phase and the methanol phase undisturbed, a separating funnel was used to smoothly transfer the preheated catalyst/methanol mixture into the reactor. For each experiment, the reaction temperature was controlled by the water bath. The reaction was timed until it reached its equilibrium. During the experiment, a series of samples were collected from the oil phase at different time intervals. Each sample was transferred into a test tube and then immersed in cold water at 4°C to quench the reaction immediately. For better separation of the final mixture, the samples were centrifuged for 5 min at 3000 rpm, and then, the top layer sample was collected and sent for analysis.

For the experiments with the complete mixing (second mode), each esterification experiment also began with the preparation of low-quality feedstock by mixing canola oil and oleic acid at a specific ratio. The FFA content of the prepared feedstock was analyzed in terms of acid number in accordance with the ASTM D974-04 standard, the details of which are provided in the next subsection. Following the preparation, a known amount of feedstock was charged to the reactor and heated to the desired reaction temperature with an accuracy of $\pm 1^\circ\text{C}$. The feedstock was also stirred by the agitator at a fixed speed. Once the reaction temperature was reached, a predetermined amount of methanol/sulfuric acid mixture (with a given catalyst concentration) was rapidly injected into the reactor to start the esterification reaction. Prior to injection, this alcohol/catalyst mixture was preheated to the reaction temperature in order to avoid unwanted fluctuation in reaction temperature, especially at the beginning of the test. Each experimental run was carried out for at least 70 min at the desired temperature and agitation speed. A series of liquid samples (3 mL) were collected from the reactor at a regular time interval during the experiment. These liquid samples were then analyzed for their acid number so as to determine the depletion of FFA as a function of time.

2.4. Sample analysis

A 3-mL liquid sample collected from the reactor was transferred to a test tube where 6 mL of de-ionized water was added. The tube was then capped and shaken vigorously to promote complete contact between water and the sample. This allowed the methanol and catalyst to

combine with water, thus separating them from the sample. After being shaken, the test tube was placed in a centrifuge operating at 4000 rpm for 10 min. The centrifugal force helped develop two liquid layers, that is, the top layer for oil and the bottom layer for a mixture of water, methanol, and catalyst. The top layer was then withdrawn from the test tube for FFA content analysis by ASTM D974-04. A 2-mL sample was taken from the oil phase, weighed for its mass, and then dissolved in a 100-mL titration solvent (a mixture of toluene, water, and isopropyl alcohol with a volumetric mixing ratio of 100:1:99). Then, p-naphtholbenzein (the titration indicator) was added into the sample which was eventually titrated with 0.1 N potassium hydroxide (KOH) solution. Results from titration were then used for calculating the acid number (in mg KOH/g oil) based on the following equation:

$$\text{Acid number} = \left(\frac{(A - B) \times M \times 56.1}{W} \right) \quad (1)$$

where A is the volume of KOH solution required for the titration of the sample in mL, B is the volume of KOH solution required for the titration of 100 mL of titration solvent in mL, M is the molarity of the KOH solution, and W is the weight of the sample in grams. The acid number was then converted to a FFA content value.

2.5. Data analysis

Data obtained from each esterification experiment were composed of a set of FFA content values (or acid numbers) taken at different reaction times. These data were subsequently used for determining mass-transfer interfacial area (a_c) formed during esterification reaction. The following demonstrates how kinetic and mass-flux equations were used for the analysis of a_c .

The rate of esterification reaction is essentially the rate of FFA conversion into fatty acid methyl ester (FAME). With the stoichiometric ratio of 1:1, the conversion rate can be expressed as a function of reactant concentrations (i.e., C_{FFA} for free fatty acid and C_{Alc} for alcohol):

$$\text{rate} = -\frac{dC_{FFA}}{dt} = kC_{FFA}C_{Alc} \quad (2)$$

where k is the reaction rate constant varying with reaction temperature. Because an excess amount of alcohol for reaction was used in this experimental study, the conversion rate can be rewritten in the pseudo-first-order form:

$$\text{rate} = -\frac{dC_{FFA}}{dt} = k'C_{FFA} \quad (3)$$

where k' is the pseudo-first-order constant (kC_{Alc}). It should be noted that, in an immiscible reaction system (i.e., oil and alcohol), the reaction rate also depends upon the measure of dispersion or interfacial contact between two immiscible reactants. Due to the involvement of the interface between oil and alcohol, the rate of FFA conversion can also be expressed in terms of the mass-transfer flux of FFA (N_{FFA}):

$$-\frac{dC_{FFA}}{dt} = a_e N_{FFA} \quad (4)$$

where a_e is the interfacial area per unit volume of the reaction system. By combining Eqs. (3) and (4), the mass-transfer flux can be written as a function of FFA concentration:

$$N_{FFA} = \left(\frac{k'}{a_e} \right) C_{FFA} \quad (5)$$

Because the magnitude of constant k' is proportional to the degree of contact between oil and alcohol, the $\left(\frac{k'}{a_e} \right)$ ratio in Eq. (5) can be considered to be a constant value, suggesting that mass-transfer flux, N_{FFA} , at a given C_{FFA} concentration should have a fixed value. Then, Eq. (5) can be rewritten as:

$$N_{FFA} = \left(\frac{k'}{a_e} \right) C_{FFA} = \left(\frac{k'}{a_e} \right)_{Ref} C_{FFA} = \text{constant} \quad (6)$$

where $\left(\frac{k'}{a_e} \right)_{Ref}$ is the ratio derived from the reference esterification experiments with the well-defined interfacial area (the first mode experiments). With a known N_{FFA} flux, Eq. (4) can be rewritten as:

$$-\frac{dC_{FFA}}{dt} = a_e \left(\frac{k'}{a_e} \right)_{Ref} C_{FFA} \quad (7)$$

Integrating the above equation results in the following equation:

$$\ln \left(\frac{C_{FFA,0}}{C_{FFA}} \right) = a_e \left(\frac{k'}{a_e} \right)_{Ref} t \quad (8)$$

where $C_{FFA,0}$ is the initial FFA concentration. To determine a_e under a given reaction condition, a plot between $\ln\left(\frac{C_{FFA,0}}{C_{FFA}}\right)$ and reaction time (t) was developed using the experimental data. The values of the $\left(\frac{k'}{a_e}\right)_{Ref}$ ratio were obtained as a function of reaction temperature and catalyst concentration and reported in a separate work. [13]

3. Results and discussion

3.1. Parametric effects on FFA conversion rate and mass-transfer interfacial area

3.1.1. Effect of reaction temperature

The effect of reaction temperature was observed from the experiments carried out at three different temperatures: 45°C, 55°C, and 65°C and for oil feedstock containing 5%, 15%, and 30% FFA. Other experimental conditions were fixed at 0.5 wt% H_2SO_4 catalyst, 6:1 methanol-to-oil ratio, and 300 rpm agitation speed. Results in **Figure 2a, b** show that the conversion of FFA proceeded rapidly at the beginning of the reaction period. As much as 80% conversion (based on initial FFA concentration) was observed within the first 20 min. Then, the conversion rate diminished significantly when FFA conversion approached the plateau. Both figures also show that the FFA conversion rate (or slope of FFA conversion profiles at the first reaction period) increased with reaction temperature regardless of the initial FFA concentration. The increasing conversion rate was quantified and presented in terms of percent improvement compared to the conversion rate at 45°C, as shown in **Figure 3**. It appears that the conversion rate could be enhanced as much as 160% when the reaction temperature was raised from 45 to 65°C. Both kinetic and hydrodynamic factors (a_e) contribute to the rate improvement. Between the two factors, the kinetics plays the major role in controlling the conversion of FFA.

As for the role of temperature on a_e , results in **Figure 2c** show that a_e increases with temperature. The a_e could increase approximately 30 - 60% when the temperature increases from 45°C to 65°C. This is due to the decrease in liquid density and viscosity with increasing temperature. The dependence of density and viscosity of oil on temperature was previously reported by [14, 15]. According to [16], the rate of any reactions in an immiscible liquid-liquid system is controlled by the mass transfer of chemical species across the interface between the two liquids. For the FFA esterification, mass-transfer interfacial area is dependent upon the dispersion level of methanol in the oil feedstock, which is usually controlled by mixing characteristics (e.g., flow, shear, and turbulence). Such mixing characteristics are ultimately dependent upon physical properties, especially the density and viscosity of liquids. This is supported by the fact that Reynolds number (Re) is a function of density and viscosity [17]. Therefore, an increase in reaction temperature causes the density and viscosity of liquids to drop, thus allowing methanol to easily disperse in oil.

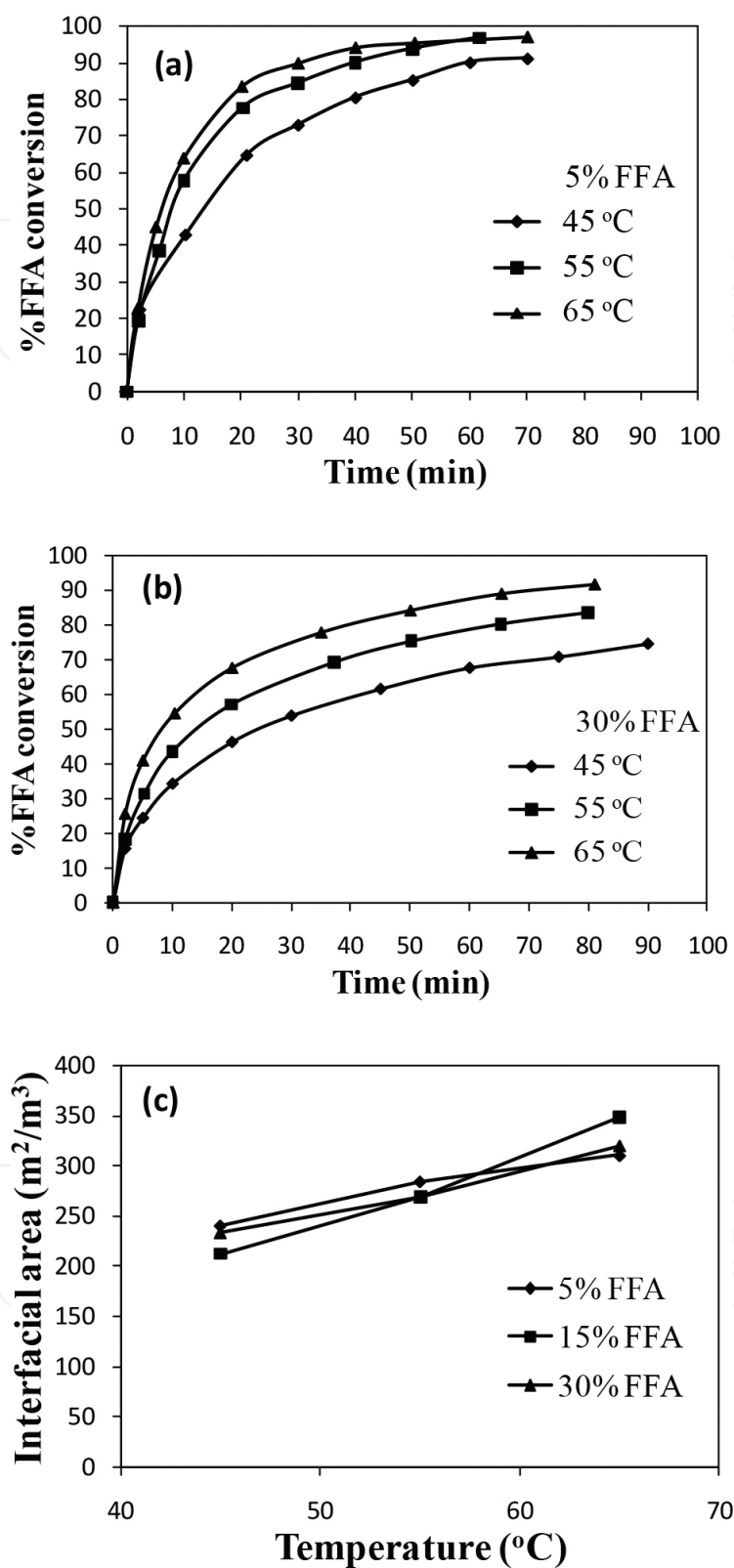


Figure 2. Effect of temperature on esterification performance: (a) FFA conversion profiles for initial FFA concentration of 5%; (b) FFA conversion profiles for initial FFA concentration of 30%; and (c) interfacial area at different temperatures (300 rpm agitation speed, 0.5 wt% of catalyst, 6:1 methanol-to-oil ratio).

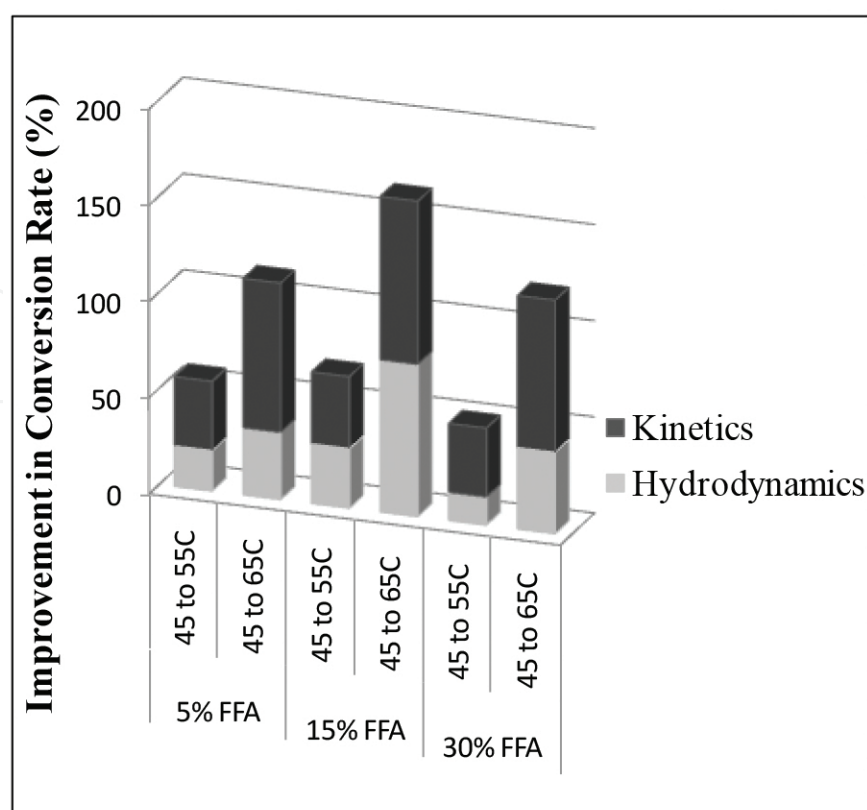


Figure 3. Hydrodynamic and kinetic contributions for effect of reaction temperature on FFA conversion rate (300 rpm agitation speed, 0.5 wt% of H_2SO_4 , and 6:1 mol/mol methanol-to-oil ratio).

3.1.2. Effect of methanol-to-oil ratio

The effect of methanol-to-oil ratio was investigated under 0.5 wt% H_2SO_4 , 300 rpm agitation speed, 45°C and 65°C reaction temperature, for three different FFA concentrations (5%, 15%, and 30%). It was found that methanol-to-oil ratio has a significant impact on FFA conversion performance. An increase in methanol-to-oil ratio enhances the conversion rate for all test conditions. From **Figure 4a, b** FFA conversion rate could be improved by as much as 30 - 35% when methanol-to-oil ratio increases from 3:1 to 9:1. The increasing conversion rate is due to a significant increase in interfacial area a_e . As shown in **Figure 4c, d**, the area a_e increases by 2.1 5.3 times when methanol-to-oil ratio increases from 3:1 to 9:1. This is due to the greater amount of methanol available for dispersion in the oil phase.

Based on the analysis shown in **Figure 5**, the improvement in FFA conversion rate due to increasing methanol-to-oil ratio is primarily caused by a_e , not reaction kinetics. This is because the increasing methanol-to-oil ratio leads to more dispersion of methanol, which in turn provides a greater interfacial area for esterification reaction. On the contrary, increasing the amount of methanol in oil does not result in any changes in concentration of methanol at the reaction interface; thus, the reaction kinetics is unaffected.

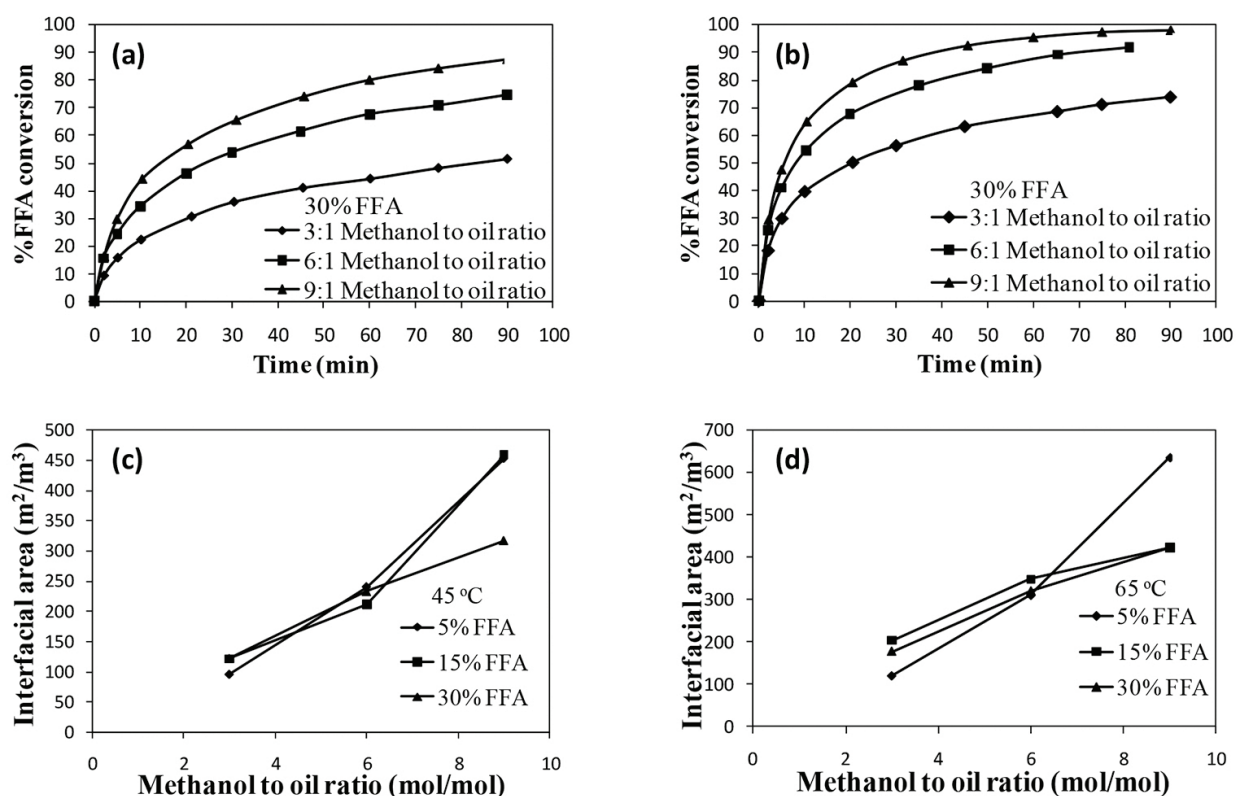


Figure 4. Effect of methanol-to-oil ratio on esterification performance: (a) FFA conversion profiles at 45°C for initial FFA concentration of 30%; (b) FFA conversion profiles at 65°C for initial FFA concentration of 30%; (c) interfacial area plotted against methanol-to-oil ratio at 45°C; and (d) interfacial area plotted against methanol-to-oil ratio at 65°C (300 rpm agitation speed, 0.5 wt% of catalyst).

3.1.3. Effect of agitation speed

The effect of agitation speed on FFA conversion was investigated by varying the agitation speed from 200 to 300 rpm and further to 400 rpm. The investigation was done for three different FFA concentrations (5%, 15%, and 30%) at 0.5 wt% H_2SO_4 , 6:1 methanol-to-oil ratio, and 45°C and 65°C. Results show that agitation speed has an impact on FFA conversion performance. As shown in **Figure 6a, b**, increasing agitation speed from 200 to 300 rpm leads to a significant increase in the conversion rate. For instance, the rate could be improved by 150% at the reaction temperature of 45°C for oil feedstock containing 5% FFA (**Figure 7**). However, it should be noted that raising agitation speed further from 300 to 400 rpm leads to only a small increase in the rate of FFA conversion. It is apparent that the improvement under fixed reaction conditions (excluding agitation speed) was solely caused by an increase in a_e , not reaction kinetics. Raising agitation speed induces more turbulence, thereby creating smaller size methanol droplets in oil and in turn providing a greater a_e for esterification reaction. The increase in a_e is evidenced in **Figure 6c, d**.

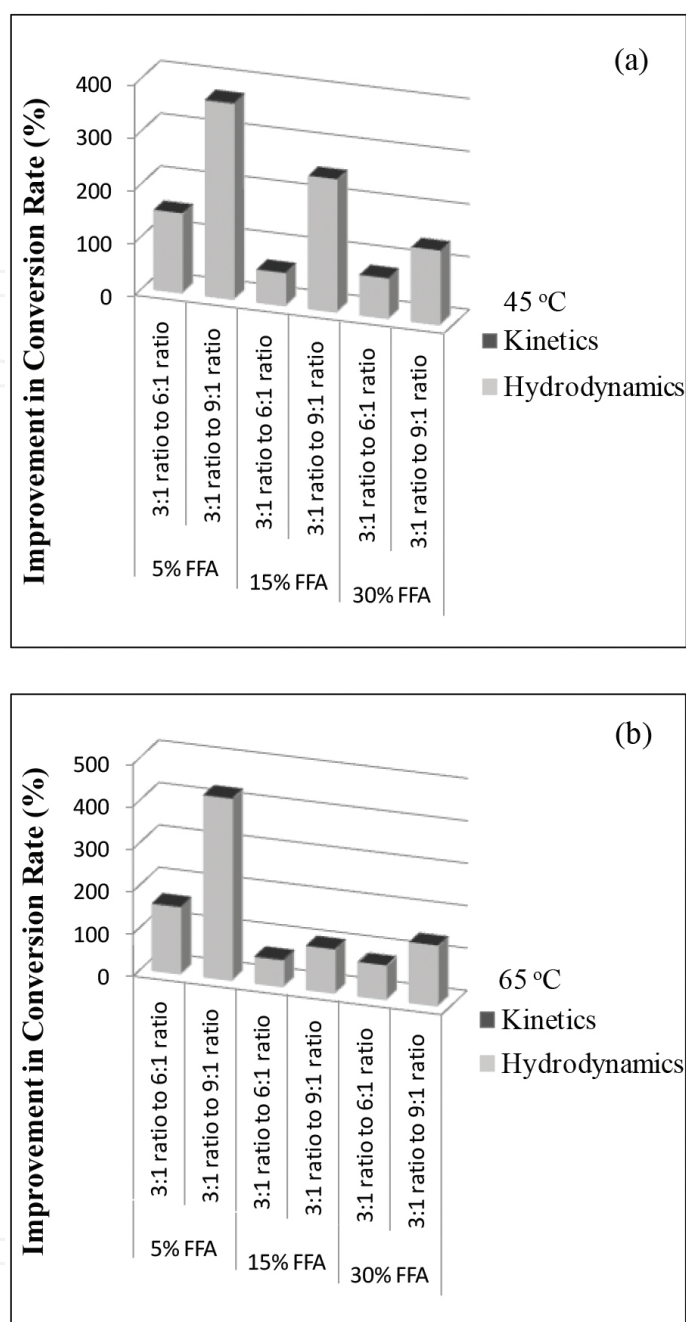


Figure 5. Hydrodynamic and kinetic contributions for the effect of methanol-to-oil ratio on FFA conversion rate: (a) reaction temperature of 45°C; (b) reaction temperature of 65°C (test conditions = 300 rpm agitation speed and 0.5 wt% of H_2SO_4).

It should be noted that the degree of rate improvement also depends on reaction temperature. This exhibits an interaction effect between agitation speed and temperature. The effect of agitation speed at a lower reaction temperature (45°C) is much greater than the effect at the higher temperature (65°C). This behavior can be explained by comparing the magnitude of interfacial area formed at these two temperatures. From **Figure 6c, d** it can be seen that the higher temperature (65°C) tends to offer a greater area, a_v , than the lower temperature (45°C)

does. This is due to the reduction in density and viscosity of liquid mixtures with an increase in temperature. Therefore, increasing agitation speed at 65°C, where the higher a_e is already established, does not yield a much greater improvement in conversion rate.

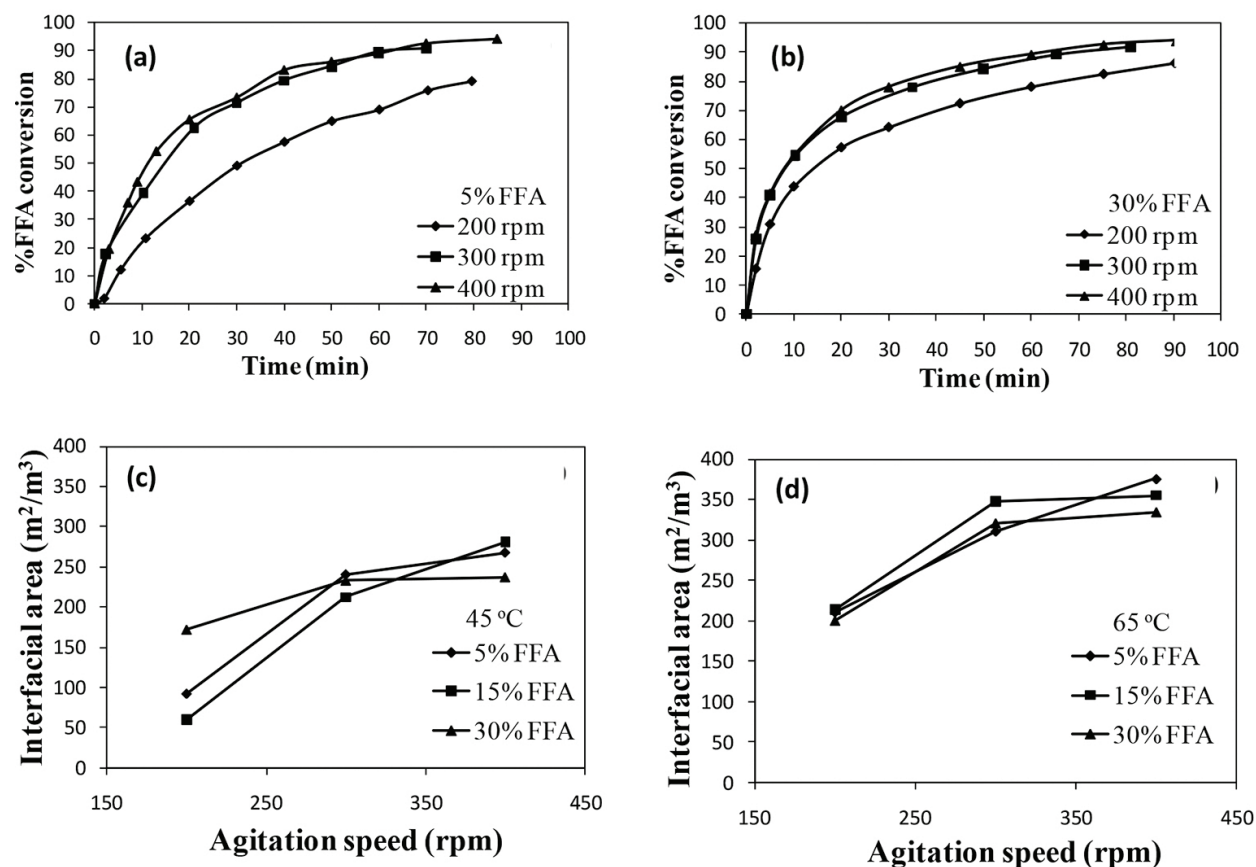


Figure 6. Effect of agitation speed on esterification performance: (a) FFA conversion profiles at 45°C for initial FFA concentration of 5%; (b) FFA conversion profiles at 65°C for initial FFA concentration of 30%; (c) interfacial area plotted against agitation speed at 45°C; and (d) interfacial area plotted against agitation speed at 65°C (6:1 methanol-to-oil ratio, 0.5 wt% of catalyst).

As mentioned previously, raising agitation speed beyond 300 rpm does not have much impact on the conversion rate of FFA. This can be explained by considering the conventional power correlation for agitated reaction. According to McCabe et al. [18], the power number, N_p , for the typical stirred reactor (i.e., an index that reflects friction preventing the impeller rotation) tends to decrease with the Reynolds number (Re), especially at low and moderate turbulence regions, while it remains virtually unaffected by the Reynolds number under highly turbulent conditions. This suggests that the effect of agitation speed should be gradually diminished with the increasing level of system turbulence. This behavior was observed in this work. The a_e increases considerably due to the significant reduction in friction on the impeller when agitation speed increases from 200 to 300 rpm. However, when agitation speed increases from 300 to 400 rpm, despite the increase in turbulence, the friction on the impeller does not diminish much further. This indicates that the friction may reach its minimum for a given system

geometry that accounts for the design and dimensions of the reaction system as well as the type of fluid in the reactor. As such, the degree of mixing does not improve, causing the interfacial area, a_e , to remain unchanged. This in turn results in the stabilization of the FFA conversion rate.

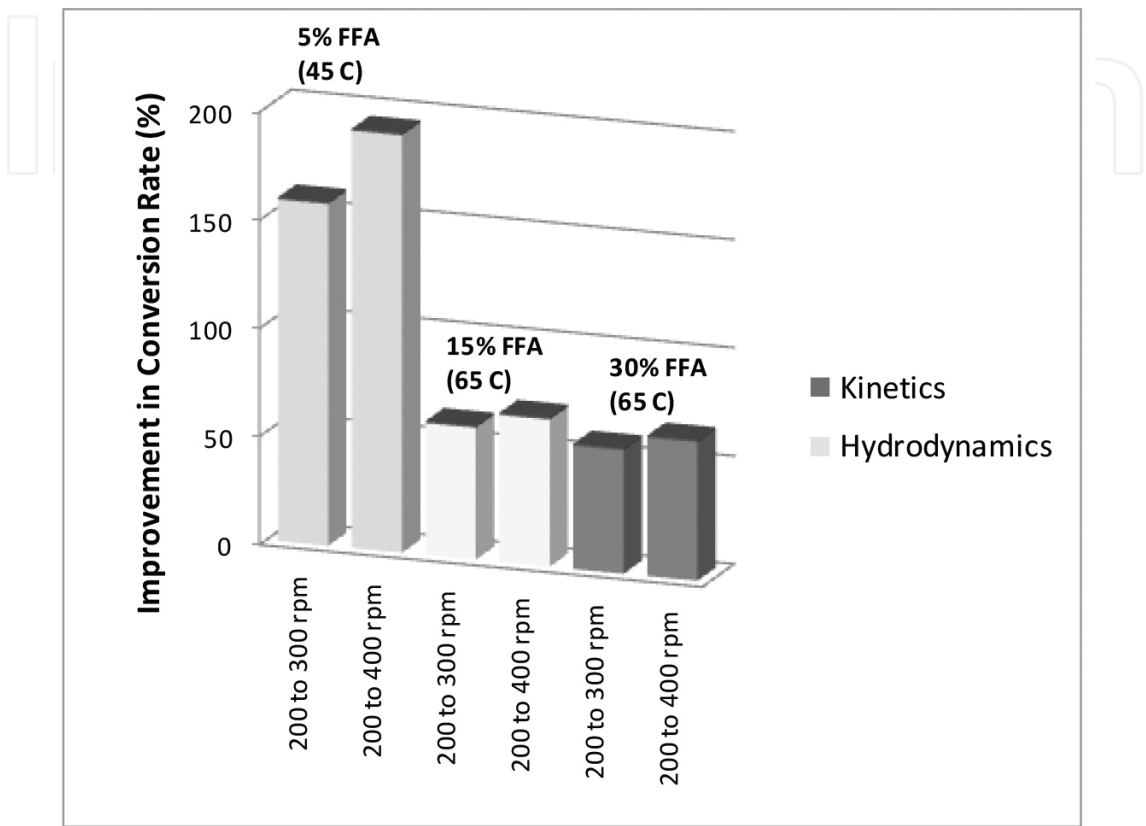


Figure 7. Hydrodynamic and kinetic contributions for the effect of agitation speed on FFA conversion rate (0.5 wt% of H_2SO_4 and 6:1 methanol-to-oil ratio).

3.1.4. Effect of catalyst concentration

The effect of catalyst concentration was studied by varying H_2SO_4 concentration from 0.5 to 2.0 wt%. The effect was examined for three FFA concentrations (5%, 15%, and 30%) and two reaction temperatures (45°C and 65°C) at 6:1 methanol-to-oil ratio and 300 rpm agitation speed. Results in **Figure 8a, b** show that an increase in H_2SO_4 concentration leads to an enhancement of FFA conversion performance for all test conditions. For instance, the conversion rate can be improved by 70% when H_2SO_4 concentration increases from 0.5 to 2.0 wt% at 45°C. Both hydrodynamics and kinetics were found to contribute to such improvement as shown in **Figure 9**. The hydrodynamic contribution (or an increase in a_e) results from the reduction in liquid viscosity. Note that the hydrodynamic contribution is not as significant as the kinetic contribution at a higher temperature (i.e., 65°C). This is supported by the results in **Figure 8c, d** which show that the change in a_e with H_2SO_4 concentration is relatively small at the higher temperature.

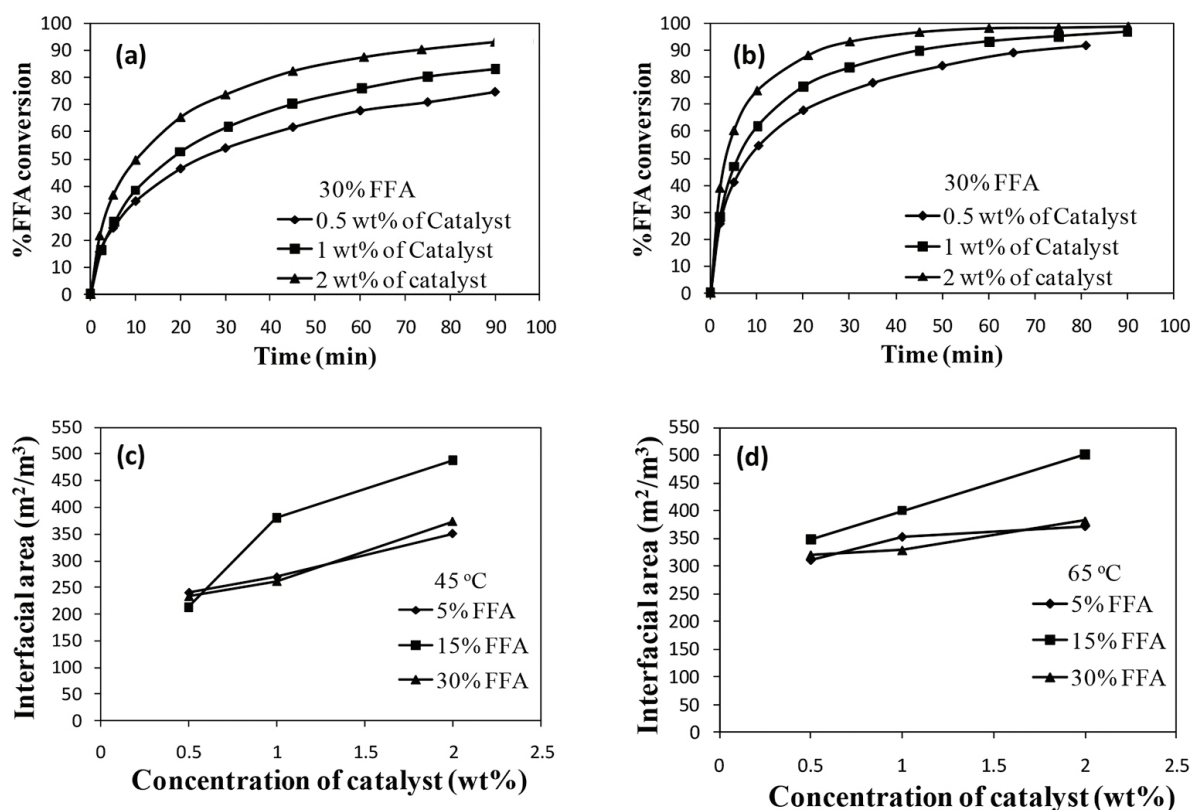


Figure 8. Effect of catalyst concentration on esterification performance: (a) FFA conversion profiles at 45°C for initial FFA concentration of 30%; (b) FFA conversion profiles at 65°C for initial FFA concentration of 30%; (c) interfacial area plotted against catalyst concentration at 45°C; and (d) interfacial area plotted against catalyst concentration at 65°C (300 rpm agitation speed, 6:1 methanol-to-oil ratio).

3.1.5. Effect of FFA concentration in oil feedstock

The effect of FFA concentration was examined over ranges of operating conditions, that is, 45 - 65°C reaction temperature, 200 - 400 rpm agitation speed, 3:1 - 6:1 methanol-to-oil ratio, and 0.5 - 2.0 wt% catalyst concentration. The results in **Figure 10** show that FFA concentration plays an important role in the FFA conversion performance. An increase in FFA concentration causes the conversion rate to decrease. However, it should be noted that the hydrodynamics of the reaction system in this case does not contribute to the changes in FFA conversion rate since the interfacial area, a_e , does not vary with FFA concentration in oil (**Figure 11**). It seems that the unaffected a_e is a result of the invariable physical properties of oil feedstock. According to Kulkarni et al. [19] and Zhou et al. [20], the viscosity and density of canola oil (base ingredient of oil feedstock) and oleic acid (FFA) are in similar ranges. The density of canola oil and oleic acid is 0.912 and 0.90 g/mL, while the viscosity of canola oil and oleic acid is 33.4 and 34.8 cP, respectively. Due to the similar properties of the two ingredients, increasing FFA concentration from 5 to 30% does not considerably alter the viscosity and density of the oil mixture. The unchanged oil properties help establish the stable turbulence level within the reaction system, thus keeping the interfacial area, a_e , relatively unchanged.

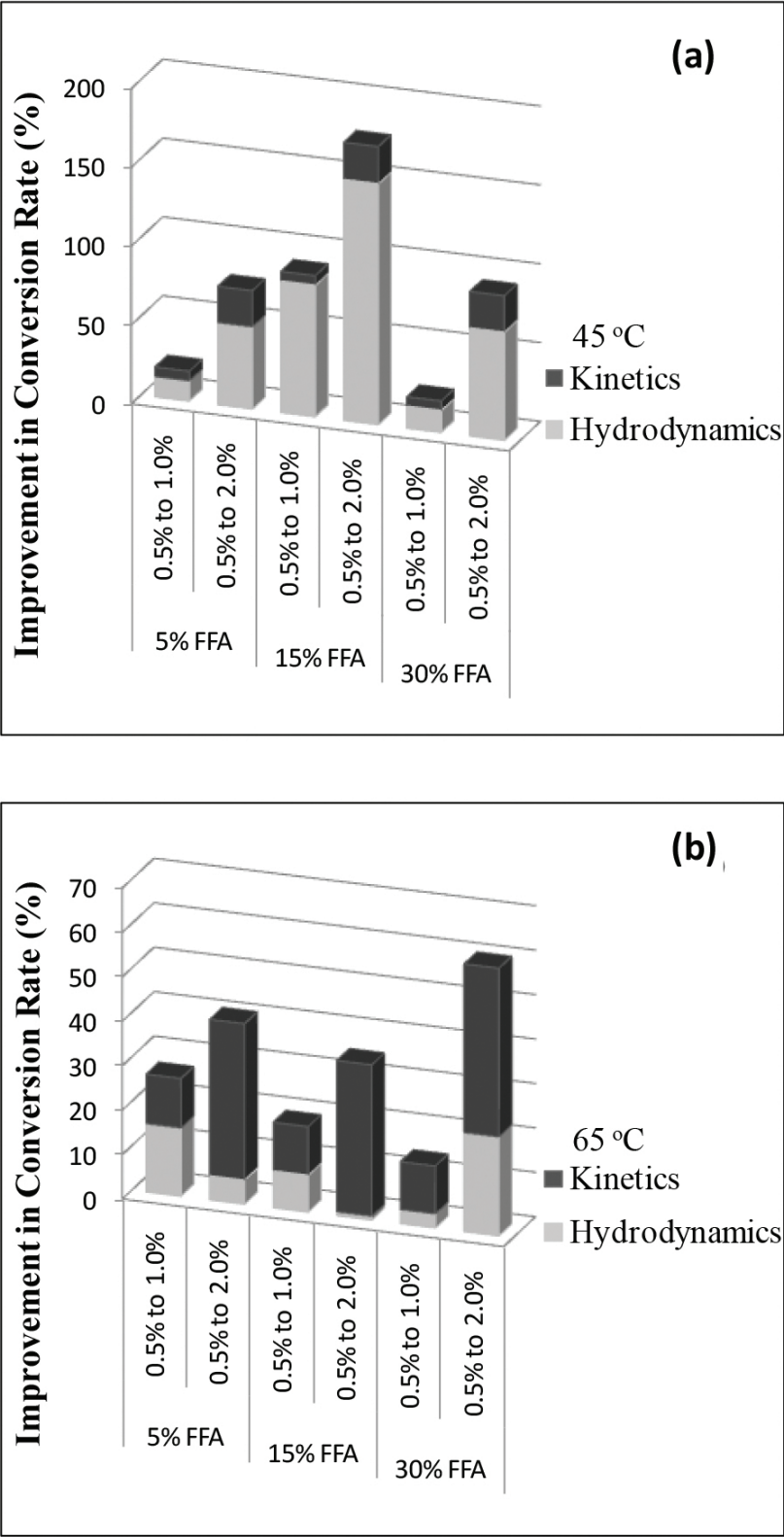


Figure 9. Hydrodynamic and kinetic contributions for the effect of catalyst concentration on FFA conversion rate: (a) reaction temperature of 45°C; (b) reaction temperature of 65°C (test conditions = 300 rpm agitation speed and 6:1 methanol-to-oil ratio).

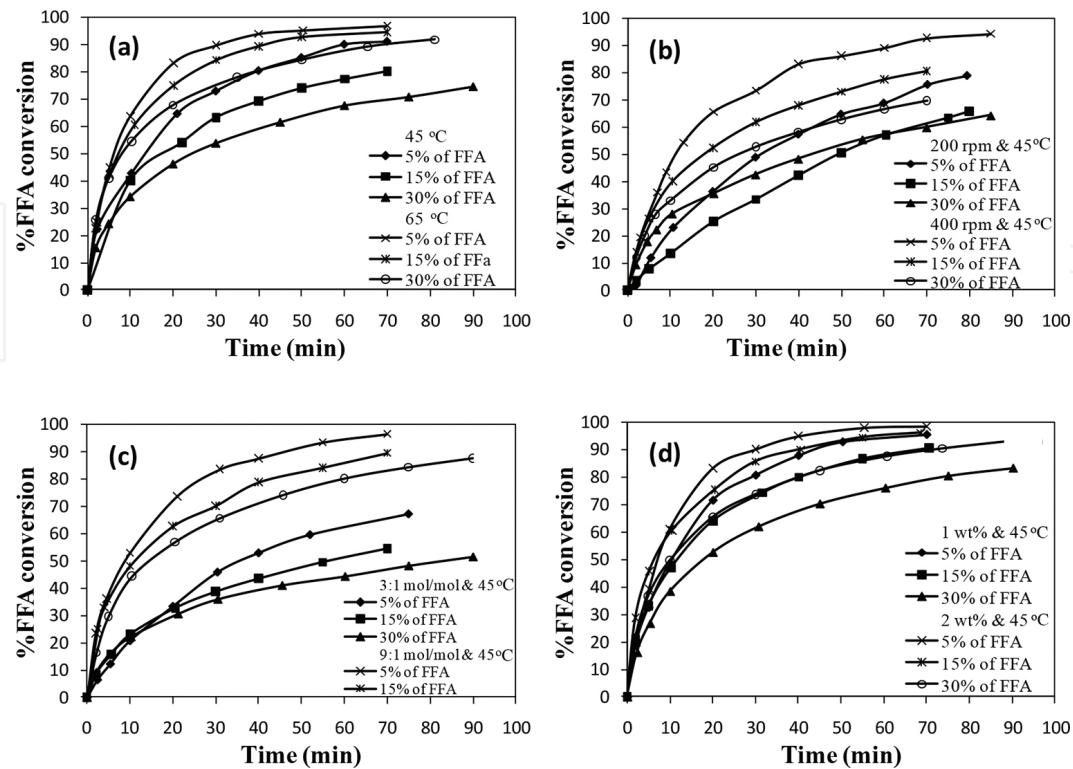


Figure 10. Effect of FFA concentration on esterification performance: (a) based on temperature data series; (b) based on agitation speed data series; (c) based on catalyst concentration data series; and (d) based on methanol-to-oil ratio data series.

3.2. Empirical correlation for mass-transfer interfacial area

The effects of process parameters on the interfacial area reported earlier were correlated in the form of an empirical equation that would facilitate the design of a biodiesel reactor. Development of the correlation was focused primarily on four important parameters controlling the interfacial area between methanol and oil feedstock, that is, reaction temperature, agitation speed, methanol-to-oil ratio, and catalyst concentration. Firstly, the effect of each process parameter was regressed individually to arrive at the best mathematical expression offering simplicity and the lowest data deviation. Four types of mathematical expressions were considered in this screening step: linear, exponential, logarithmic, and power forms. It was found that most parametric effects can be described by linear expressions, except for the effect of agitation speed, the nonlinear behavior of which can be expressed well by the logarithmic equation. Values of average absolute deviation (%AAD) and R^2 derived from individual regressions are summarized in **Table 2**.

Based on the selected equations in the screening step, an overall empirical correlation that combines all four parametric effects was formulated and expressed in the following form:

$$a_e = k_1 T + k_2 \ln(n - k_3) + k_4 R + k_5 C + k_6 \quad (9)$$

where k_1 to k_6 are correlation constants, T is reaction temperature in K, n is agitation speed in rpm, R is methanol-to-oil ratio in mol/mol, and c is catalyst concentration in wt%. The calculated interfacial area (a_e) is presented in m^2/m^3 units. Based on all experimental data obtained in this study, a computer-software package called “NLREG” was used for regression to arrive at values of correlation constants (k_1 to k_6) as listed in **Table 3**. It should be noted that this empirical correlation is capable of predicting methanol-oil interfacial area with an average absolute deviation (AAD) of 12%. A good agreement between the calculated a_e values and experimental data can be observed from a parity plot in **Figure 12**, which shows a R^2 value of 0.88.

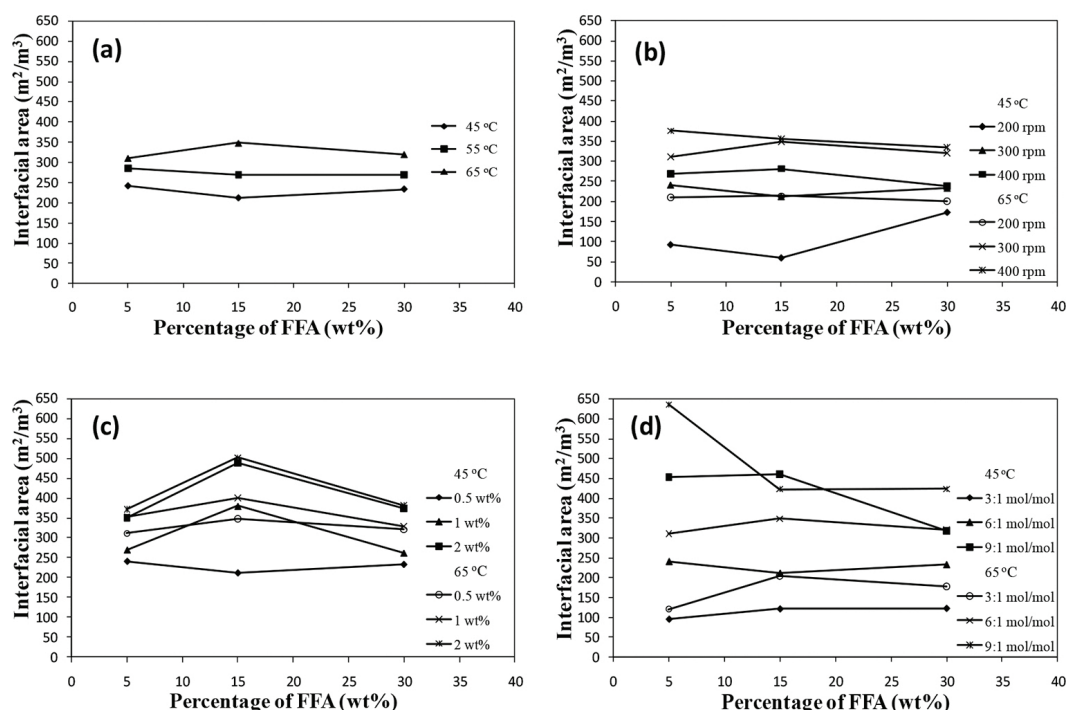


Figure 11. Effect of FFA concentration on mass-transfer interfacial area: (a) based on temperature data series; (b) based on agitation speed data series; (c) based on catalyst concentration data series; and (d) based on methanol-to-oil ratio data series.

Process parameter	Mathematical expression	%AAD	R^2
Temperature (T)	$a_e = k_1 T + k_2$	4.06	0.91
Methanol-to-oil ratio (R)	$a_e = k_1 R + k_2$	13.34 (45°C)	0.89 (45°C)
		14.68 (65°C)	0.82 (65°C)
Agitation speed (n)	$a_e = k_1 \ln(n - k_2) + k_3$	16.81 (45°C)	0.83 (45°C)
		3.64 (65°C)	0.96 (65°C)
Catalyst concentration (c)	$a_e = k_1 c + k_2$	11.09 (45°C)	0.69 (45°C)
		11.09 (65°C)	0.48 (65°C)

Table 2. Results of individual regressions for parametric effects.

Correlation constant	Value
k_1	3.85
k_2	32.50
k_3	198.04
k_4	51.98
k_5	53.01
k_6	-1465.72

Table 3. Correlation constants for Eq. (9).

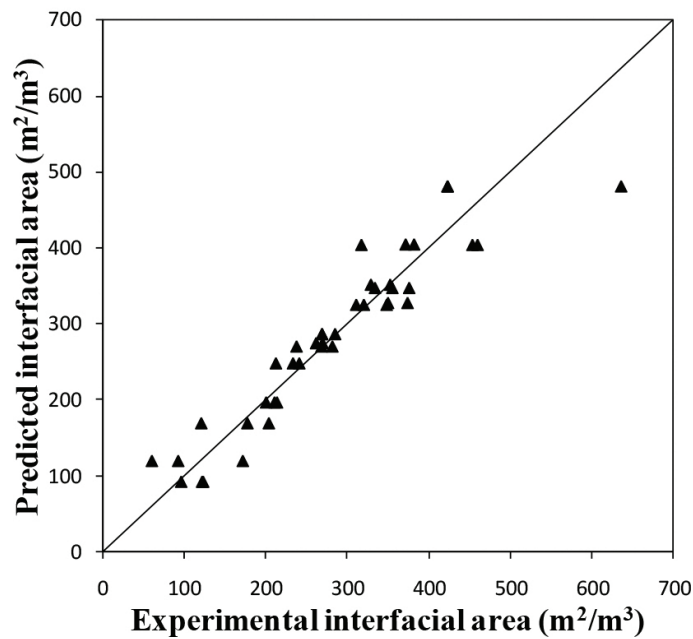


Figure 12. Parity plot between experimental data and calculated interfacial area.

4. Conclusions

Mass-transfer interfacial area plays an important role in the performance of acid-catalyzed esterification-based biodiesel production. Increasing the interfacial area enhances rate of biodiesel production (or rate of free fatty acid conversion). The magnitude of the interfacial area varies with process parameters, except free fatty acid content in oil feedstock. The interfacial area increases with increasing reaction temperature, agitation speed, methanol-to-oil ratio, and catalyst concentration, thus resulting in the increase in biodiesel production rate.

The increase in the biodiesel production rate may or may not be solely attributed to the available interfacial area. It can be attributed to both reaction kinetics and interfacial area. The interfacial area is the exclusive contributor to the increase in the biodiesel production rate when the agitation speed or the methanol-to-oil ratio increases. Both interfacial area and kinetics

contribute to the enhancement of biodiesel production rate when the reaction temperature or the catalyst concentration increases.

Acknowledgements

The authors would like to thank the Natural Sciences and Engineering Research Council of Canada (NSERC) and the City of Regina for their financial support and collaboration.

Author details

Devjyoti Nath, Adisorn Aroonwilas and Amornvadee Veawab*

*Address all correspondence to: veawab@uregina.ca

Energy Technology Laboratory, Faculty of Engineering and Applied Science, University of Regina, Regina, Saskatchewan, Canada

References

- [1] Santacesaria E, Tesser R, Di Serio M, Guida M, Gaetano D, Garcia Agreda A. Kinetics and mass transfer of free fatty acids esterification with methanol in a tubular packed bed reactor: A key pretreatment in biodiesel production. *Industrial and Engineering Chemistry Research*. 2007; 46(15): 5113–5121.
- [2] Bhatnagar A K, Kaul S, Chhibber V K, Gupta A K. HFRR studies on methyl esters of nonedible vegetable oils. *Energy Fuels*. 2006; 20: 1341–1344.
- [3] Freedman B E H P, Pryde E H, Mounts T L. Variables affecting the yields of fatty esters from transesterified vegetable oils. *Journal of the American Oil Chemists' Society*. 1984; 61(10): 1638–1643.
- [4] Liu K S. Preparation of fatty acid methyl esters for gas-chromatographic analysis of lipids in biological materials. *Journal of the American Oil Chemists' Society*. 1994; 71(11): 1179–1187.
- [5] Ma F, Clements L D, Hanna M A. Biodiesel fuel from animal fat: ancillary studies on transesterification of beef tallow. *Industrial and Engineering Chemistry Research*. 1998; 37(9): 3768–3771.
- [6] Sendzikiene E, Makareviciene V, Janulis P, Kitrys S. Kinetics of free fatty acids esterification with methanol in the production of biodiesel fuel. *European Journal of Lipid Science and Technology*. 2004; 106: 831–836.

- [7] Berrios M, Siles J, Martin M A, Martin A. A kinetic study of the esterification of free fatty acids (FFA) in sunflower oil. *Fuel*. 2007; 86: 2383–2388.
- [8] Aranda D A G, Santos R T P, Tapanes N C O, Ramos A L D, Antunes O A C. Acid-catalyzed homogeneous esterification reaction for biodiesel production from palm fatty acids. *Catalysis Letters*. 2008; 122: 20–25.
- [9] Thiruvengadaravi K V, Nandagopal J, Bala V S S, Kirupha S D, Vijayalakshmi P, Sivanesan S. Kinetic study of the esterification of free fatty acids in non-edible *Pongamia pinnata* oil using acid catalyst. *Indian Journal of Science and Technology*. 2009; 2(12): 20–24.
- [10] Berrios M, Martin M A, Chica A F, Martin A. Study of esterification and transesterification in biodiesel production from used frying oils in a closed system. *Chemical Engineering Journal*. 2010; 160: 473–479.
- [11] Yadav P K S, Singh O, Singh R P. Palm fatty acid biodiesel: process optimization and study of reaction kinetics. *Journal of Oleo Science*. 2010; 59(11): 575–580.
- [12] Stamenkovic O S, Lazic M L, Todorovic Z B, Veljkovic V B, Skala D U. The effect of agitation intensity on alkali-catalyzed methanolysis of sunflower oil. *Bioresource Technology*. 2007; 98: 2688–2699.
- [13] Zhou L. Reaction kinetics of biodiesel production by using low quality feedstock [thesis]. University of Regina: Canada; 2013.
- [14] Ceriani R, Goncalves C B, Rabelo J, Caruso M, Cunha A C C, Cavaleri F W, Batista E A C, Meirelles A J A. Group contribution model for predicting viscosity of fatty compounds. *Journal of Chemical Engineering Data*. 2007; 52: 965–972.
- [15] Ceriani R, Paiva F R, Goncalves C B, Batista E A C, Meirelles A J A. Densities and viscosities of vegetable oils of nutritional value. *Journal of Chemical Engineering Data*. 2008; 53: 1846–1853.
- [16] Paul E L, Atiemo-Obeng V A, Kresta S M. *Handbook of Industrial Mixing: Science and Practice*. New Jersey: John Wiley & Sons Inc; 2004.
- [17] McCabe W L, Smith J C, Harriott P. *Unit Operations of Chemical Engineering*. 5th ed. New York: McGraw-Hill Inc; 1993.
- [18] McCabe W L, Smith J C, Harriott P. *Unit Operations of Chemical Engineering*. 7th ed. New York: McGraw-Hill Inc; 2005.
- [19] Kulkarni M G, Dalai A K, Bakhshi N N. Transesterification of canola oil in mixed methanol/ethanol system and use of esters as lubricity additive. *Bioresource Technology*. 2007; 98: 2027–2033.
- [20] Zhou Z, Li M, Yan Y. Viscosity of oil and surfactant binary solution. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2000; 175: 263–266.

