The Acceleration of Phase Separation by Phase Inversion Transesterification in Alkali-Catalyzed Biodiesel Production

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(Received November 24, 2009; Accepted January 22, 2010)

Conventional alkali-catalyzed BDF production processes have a serious problem because the settling of liquid dispersions after transesterification is slow and requires almost one day. The present study suggests a significant improvement using a simple method called PITE, i.e., strong agitation during transesterification in a fully baffled stirring vessel. The PITE method can invert the dispersions from an alcohol-in-oil (A/O) to an O/A type which settles within 20 seconds. The transesterification reaction immediately reaches its equilibrium after phase inversion, in which the reaction time is less than 2 min. It is estimated from this result that conventional batch-wise BDF production using a 100 L vessel can be replaced by an equivalent continuous operation with a 0.15 L vessel.

1. Introduction

Biodiesel is an alternative fuel for diesel engines, and is one of the most renewable fuels currently available. It can be directly used in most diesel engines without requiring extensive engine modifications [1]. The production of biodiesel fuel (BDF) is rapidly increasing as global BDF production nearly quintupled to nine billion liters during the past four years alone [2]. Nowadays, alkali-catalyzed BDF production processes are globally employed because they have an advantage, i.e., a fast transesterification reaction:

\[
\text{Alkali catalyst} \quad \text{Triglyceride} + \text{Methanol} \rightarrow \text{Mixture of fatty acid esters} + \text{Glycerol} \quad (1)
\]

However, the conventional alkali-catalyzed BDF production processes have a serious problem, a slow phase separation; i.e., the heterogeneous mixture of fatty acid esters and glycerol form emulsions, and requires a long settling time from six to 24 hours [3]. Because of this, batch
operations must be employed, resulting in low productivity thus prohibiting large-scale BDF production. To achieve the goal of large-scale BDF production, the development of continuous operations with quick phase settling is critical. Unfortunately, none of the conventional studies on BDF production processes have focused on the phase separation after transesterification.

It is believed that the emulsions are stabilized by fatty acid soaps preexisting in the system or formed by the reaction between the free fatty acids and the alkali catalyst [1, 4-7]; therefore, to prevent emulsification, mild agitation is extensively employed to provide mixing in the transesterification vessels. However, Kato et al [8] demonstrated that, by using the hexane-water system, mild agitation facilitates the emulsification and lengthens the phase settling time and that, conversely, strong agitation in a fully baffled vessel can cause quick settling within several seconds after cessation of the agitation. In their study, mild agitation forms oil-in-water (O/W) type dispersions, and strong agitation can invert the dispersions from the O/W to the water-in-oil (W/O) type resulting in low energy dissipation due to the low viscosity of the continuous oil phase. Mild agitation in the current transesterification vessels forms alcohol-in-oil (A/O) type dispersions; therefore, strong agitation may invert the dispersions from the A/O to the O/A type due to the low viscosity of the alcohol phase, resulting in quick settling. Although this technique is promising for realizing large-scale continuous BDF production, none of the conventional studies has experimentally examined the possibility of phase inversion transesterification. Hereafter, the phase inversion transesterification is abbreviated to PITE.

The purpose of the present study is to experimentally show that the PITE method can significantly accelerate the phase separation after completion of the alkali-catalyzed transesterification.

2 Phase Inversion Criteria

During the early stage of agitation, a part of the viscous triglyceride (TG) phase forms a stagnant region behind the baffles in the agitation vessel even during strong agitation. Under such a mixing condition, the TG phase is liable to become continuous, because the three alkyl chains involved in the TG molecule are not attracted, and make the alcohol phase interface convex to the TG phase, which thus forms an A/O type dispersion. The alcohol droplets thus formed are divided into smaller ones as the agitation proceeds, becoming a close packed and approaching a steady-state dispersion. Finally, if the alcohol packing is close enough to form a continuous phase and the viscosity of the alcohol phase is much lower than that of the oil phase, the dispersion inverts its type from A/O to O/A, and the energy dissipation of the system decreases. To apply a strong agitation, a fully baffled vessel with a turbine-type impeller should be used to satisfy perfect baffling conditions [9].

The following three criteria are necessary for the occurrence of the phase inversion; i) the agitation must be strong enough, ii) the impeller should be located such as perfect mixing prevails in the vessel, and iii) excess alcohol is present. The first criterion achieves both perfect mixing and the close packing of the alcohol droplets that is required for inversion. The second criterion facilitates perfect mixing, while the third achieves close packing. To satisfy the third criterion, an extra amount of methanol should be added to the TG. Otherwise, the glycerol accumulated in the alcohol phase prevents the phase inversion as the viscosity of the alcohol phase increases. Another advantage involved in the PITE method is that the close packing of methanol droplets facilitates the rate of transesterification, because the interfacial area at the instance of phase inversion significantly increases.
3 Experimental

3.1 Materials
Reagent grade methanol and KOH were supplied by the Kanto Chemical Co. The corn oil and soybean oil were purchased at a daily market. The used rice bran oil was supplied by a restaurant in the Tokyo Metropolitan University. The used oil was filtered before the experiments.

3.2 Apparatus and procedures
Figure 1 shows a schematic diagram of the stirring vessel used in the experiments. The vessel is made of glass, while the impeller and baffles are of stainless steel. Four baffles are present, and the following perfect baffling condition was satisfied [9]

\[ L = (B / D)^{1.2} n_B = 0.35 \]

where B, D and nB, respectively, denote the width of the baffle, the inner diameter of the vessel and the number of baffles. A six-flat-blade turbine type impeller was used. The vessel was located in an air bath kept at 293 ± 1 K. Table 1 lists the experimental conditions. The second column shows the standard conditions used in the experiments.

![Fig 1](image1.png)

Fig 1 A schematic diagram of the 150 mm high stirring vessel: (a) front view, (b) plan view, where B = 10 mm, D = 75 mm and d = 40 mm, impeller blade height and width are 10 and 12 mm, respectively, 1: reactor, 2: vessel, 3: baffle, 4: impeller, 5: methanol, 6: triglyceride.

![Fig 2](image2.png)

Fig. 2 Relationships between the direction of movement of the coalescing interface and the dispersion type during agitation.
Table 1 Experimental conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Standard cond variable range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>293 K</td>
</tr>
<tr>
<td>TG phase volume, VTG</td>
<td>saybean oil, used rice bran oil</td>
</tr>
<tr>
<td></td>
<td>200 ml to 190 – 230 ml</td>
</tr>
<tr>
<td>Methanol phase volume, VM</td>
<td>100 ml to 70 – 110 ml</td>
</tr>
<tr>
<td>KOH</td>
<td>3.68 g to 2 wt% in the TG phase</td>
</tr>
<tr>
<td>Impeller depth, h</td>
<td>–10 mm to -40 to 10 mm</td>
</tr>
<tr>
<td>Stirring speed, N</td>
<td>13.3 s(^{-1}) to 5 – 20 s(^{-1})</td>
</tr>
<tr>
<td>Stirring period</td>
<td>300 s</td>
</tr>
</tbody>
</table>

\(^1\) the height of the impeller from the static methanol–TG interface

A pre-fixed amount of oil and methanol were placed in the glass vessel. The height of the impeller was adjusted to the desired position. After achieving steady state temperature, a given amount of KOH was added and the agitation started at a pre-fixed speed. After five minutes, the agitation was stopped, and the direction of movement of the coalescing interface was observed in order to determine the dispersion type during agitation [8]. As shown in Fig. 2, the coalescing interface moves downward when the BDF droplets coalesce with the light BDF phase accumulated at the top, and goes upward when the alcohol droplets coalesce with the accumulated bottom alcohol phase. Therefore, a downward movement of the coalescing interface means that the dispersion was of the O/A type during agitation and upwards the A/O type.

The upper BDF phase was sampled using a hypodermic syringe, and diluted with 1,4-dioxane, an internal standard. The solution was analyzed by gas chromatography, using a Shimadzu GC-8A with a 15 m DB-1 capillary column at 353 K held for three minutes after the injection following temperature elevation at the rate of 10 K/min to 453 K. The viscosity of the oils was measured by a rotation viscometer made by the HAACKE Co.

4 Results and Discussion

4.1 Dispersions at the beginning of agitation

The dispersion types at the beginning of the agitation were first examined. The dispersion types after cessation of a 15-second agitation were observed for the corn oil under the standard operating conditions given in Table 1 at each stirring speed from 5 to 20 s\(^{-1}\). It was found for all stirring speeds that A/O type dispersions appear at the start of agitation.

Immediately after the start of agitation, only a part of the liquid elements in the vessel was fluidized due to the high viscosity of the oil in which the impeller was immersed. After two seconds, complete fluidization prevailed throughout the vessel, even at 13.3 s\(^{-1}\). To evaluate the emulsification progress, the agitation period was varied from 15 to 60 seconds, and the volume of alcohol that settled at the top during the 150 seconds after the cessation of agitation, \(V_A\), was measured. Table 2 lists the \(V_A\) values versus the agitation period. The settled alcohol was transparent, but the oil phases consisting of corn oil and fatty acid esters were turbid, forming emulsions. Table 2 shows that, even after an agitation period of 15 seconds, 15 % of the methanol had not been emulsified. Therefore, the emulsification gradually proceeds toward a steady dispersion even in the fully fluidized transesterification vessel.
Table 2 Settled methanol volume versus agitation period at 13.3 s\(^{-1}\)

<table>
<thead>
<tr>
<th>Stirring period (s)</th>
<th>(V_{A}^{*}) (cm(^{3}))</th>
<th>methanol phase</th>
<th>TG phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>transparent</td>
<td>turbid</td>
</tr>
<tr>
<td>15</td>
<td>15</td>
<td>transparent</td>
<td>turbid</td>
</tr>
<tr>
<td>30</td>
<td>4</td>
<td>transparent</td>
<td>turbid</td>
</tr>
<tr>
<td>60</td>
<td>0</td>
<td>emulsion</td>
<td>emulsion</td>
</tr>
</tbody>
</table>

\(V_{A}^{*}\): the volume of the alcohol phase settled after 150 seconds from the cessation of agitation

4.2 Phase separation acceleration by PITE

In Fig. 3, the coalescing time, \(t_C\), is plotted versus the stirring speed, \(N\), using corn oil under the standard operating conditions given in Table 1. The coalescing time is defined as the time required for the first appearance of a clear oil-alcohol interface after the cessation of agitation. Figure 3 shows that the dispersion inverts from the A/O to the O/A type with increasing stirring speed. It also shows that the phase inversion significantly accelerates the phase separation, as \(t_C\) decreases from 2600 to 14 seconds, i.e., 1/185. Based on these observations, the phase inversion seems to have occurred after a 90-second agitation, because, at this moment, the liquid mixtures rapidly became transparent, following the swift movement of the fluid elements. As shown in a later section, transesterification was completed within two minutes at \(N = 13.3\) s\(^{-1}\). Therefore, the PITE method can notably accelerate the phase separation after completion of the transesterification reaction.

![Fig. 3 Relationships between N and the coalescing time, t_c, for corn oil at h = 40 mm, V_{TG} = 200 cm^3, V_m = 100 cm^3 and 2 wt% KOH in the TG phase.](image)

The coalescing time without KOH is also plotted in Fig. 3. Figure 3 demonstrates that the phase inversion occurs within a narrow stirring speed range, although the stirring speed at which inversion occurs, \(N_i\), is higher in the absence of KOH than that in the PITE case, because the oil phase in the former case, TG, is more viscous than in the latter case, i.e., fatty acid esters, and requires stronger agitation for inverting the A/O dispersion to the O/A type. Figure 3 clearly demonstrates that, even in the absence of KOH, acceleration of the phase separation occurs under strong agitation. As shown
in Fig. 3, the A/O emulsions with transesterification are more stable than those without KOH, because the lipophilic fatty acid ester molecules adsorbed at the alcohol-oil interface decrease the interface tension and make the alcohol droplets smaller and more stable than those without transesterification. Meanwhile, comparing the two cases of strong agitation, oil droplets coalesce faster in the PITE case than those in the absence of KOH, because the fatty acid ester molecules adsorbed on the interface are liable to form an A/O dispersion, and hence, accelerate the phase separation of the O/A dispersions, resulting in faster coalescence.

In Fig. 4, the \( t_C \) values are plotted versus \( N \) for corn oil, soybean oil and used rice bran oil at \( h = -10 \) mm. Figure 4 also includes (solid lines) the relationship between \( N \) and \( t_C \) for corn oil at \( h = -40 \) mm, as shown in Fig. 3. Figure 4 demonstrates that the acceleration of phase separation by the PITE method successfully occurs in all the tested oils. The \( t_C \) values of the O/A dispersions fluctuate, but are less than 30 seconds. The phase inversion stirring speeds, \( N_i \), were found to be lower at \( h = -10 \) mm than that at \( h = -40 \) mm, because the former can provide a better agitation throughout the vessel.

Fig. 4 N vs. \( t_C \); (−) corn oil at \( h = -40 \) mm, \((\triangle)\) corn oil, \((\times)\) soybean oil, mm, and \((\bullet)\) used rice bran oil at \( h = -10 \) mm.

Fig. 5 Relationships between the volume fraction of methanol and the coalescing time, \((\triangle)\) corn oil, \((\times)\) soybean oil and \((\bullet)\) used rice bran oil.

4.3 Effect of volume fraction and impeller position on PITE

In Fig. 5, the coalescing time is plotted versus the volume fraction of methanol in the corn oil, soybean oil and used rice bran oil under the standard operating conditions given in Table 1. Figure 5 demonstrates that, with an insufficient amount of methanol, the PITE method cannot successfully invert the dispersions from the A/O to the O/A type even with strong agitation at 13.3 s\(^{-1}\), because the viscosity of the alcohol phase is high, and the dispersing alcohol droplets may be too few to be inverted into a continuous phase. Figure 5 shows that a successful PITE method requires more than about 30\% methanol in the perfect-baffling transesterification vessel.

In Fig. 6, the phase inversion stirring speed, \( N_i \), is plotted versus the impeller height, \( h \), for corn oil, soybean oil and used rice bran oil under the standard conditions given in Table 1. The \( N_i \) value was determined from a series of experiments in which varying stirring speeds were employed, as shown in Fig. 3. Figure 6 demonstrates that each oil has a minimum \( N_i \) value near the static
oil-alcohol interface; i.e., \( h = 0 \). It was observed that agitation gradually proceeds throughout the vessel when the impeller height is high above or far below the static interface. In particular, at \( h = -40 \text{ mm} \), the A/O dispersion from the used rice bran oil could not be inverted into the O/A type. The reason may be the high viscosity of the oil. In Fig. 7, the viscosity of oil, \( \mu \), is plotted versus the inverse absolute temperature. Figure 7 shows that, at 293 K, the viscosity of the used rice bran oil is 25% higher than those of the other oils; therefore, as shown in Fig. 6, a successful PITE method for highly viscous oils requires an impeller height just below the static oil-alcohol interface.

- Fig. 6 Relationships between \( h \) and \( N_i \) under standard operating condition, (\( - \triangle - \)) corn oil, (\( \cdot \times \cdot \cdot \)) soybean oil and (\( \bullet \)) used rice bran oil.  

4.4 Reaction rates during PITE

In Fig. 8, the weight fraction of the constituent \( i \), \( w_i \), in BDF originating from the corn oil is plotted versus the reaction time, \( t_R \), measured under the standard operating conditions. The A/O dispersions lasted for about 90 seconds from the beginning of agitation; therefore, the \( w_i \) values at reaction times greater than 100 seconds were examined. After the cessation of a given period of agitation, the settled top oil phase was sampled and analyzed by gas chromatography. Peaks for the heavy components, such as the tri-, di- and monoglycerides, did not appear in the chromatogram, because the retention temperature was low. Two methyl ester peaks for \( \text{C}_{16-0}, \text{C}_{18-0} \) and one peak for \( \text{C}_{18-1} \) to \( \text{C}_{18-3} \) were identified, where \( \text{C}_{i=j} \) denotes the concentration of the methyl ester having a carbon number \( i \) and an unsaturated carbon-carbon double bond number \( j \). Figure 8 shows that the weight fractions of the methyl esters are already constant at 120 seconds; therefore, it is striking that the PITE is fast enough to reach reaction equilibrium when the phase inversion occurs. This is because the large increase in the interface area during the phase inversion significantly accelerates the heterogeneous transesterification. This outcome suggests that the transesterification reaction itself is fast, and the PITE method can successfully eliminate the diffusion controlled time in the heterogeneous reaction. Figure 8 also demonstrates that the amount of methanol increases after 300 seconds due to the occurrence of (A/O)/A multiple dispersions. In fact, when \( t_R > 300 \), the settled oil
phases were turbid. Therefore, the agitation period should not continue for too long after the phase inversion. The PITE method is preferable for the demulsification technique to that using cyclic ethers [10], because the latter requires recovery processes; i.e., distillation, for the added ethers.

4.5 Application of PITE to BDF processes

When the PITE method is applied to industrial processes, a disadvantage involved in the PITE method must be recognized; i.e., a large amount of methanol is required for a successful operation. In conventional KOH-catalyzed BDF processes, the mole ratio of methanol to feed oil is between 5 to 10 [1]. The PITE method requires a ratio of 12, if the volume fraction of methanol is fixed at 0.3 based on Fig. 5. Therefore, although the amount of the excess methanol is not large compared to conventional operations, the excess methanol must be recovered by distillation from both the BDF and alcohol phases using heat energy. The boiling point of methanol is as low as 339 K; therefore, the low-quality heat energy available in chemical plants or municipal incinerators is sufficient. Avoiding the use of pure methanol, an alternative choice in the operation is to recycle the alcohol phase obtained from the settling of the O/A dispersions. Figure 9 is a flow sheet of the recycling process of the alcohol. To verify the applicability of the PITE method, continuous operations with the recycling of the alcohol phase should be experimentally studied in the future.

Most of the current 120 BDF production plants treat 100 liters of oil a day by batch operations [3]. However, the PITE method drastically decreases the volume of the vessel from 100 to 0.14 liter (= 2 min * 100 liter / (24*60 min)), because the time required for transesterification and settling is as short as 2 min as shown in Fig. 8. This is the advantage which enables us to realize the required large-scale continuous BDF production.

Fig. 8 tR vs. w; for corn oil, (×) glycerol, (○) methanol, (△) C16=0, (+) the sum from C18=1 to C18=3, and (●) the sum of methyl esters.

Fig. 9 A schematic diagram of the alcohol recycling process.

5 Conclusions

An improvement in the slow phase settling after transesterification in alkali-catalyzed BDF production processes was experimentally examined. The PITE method, which strongly agitates liquid mixtures during transesterification using a fully baffled stirring vessel, can invert dispersions
from the A/O to the O/A type settling within 20 seconds. The transesterification then attains its equilibrium within two minutes.

References