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"Pushing and pulling" the equilibrium through bubble mediated reactive separation for ethyl acetate production†

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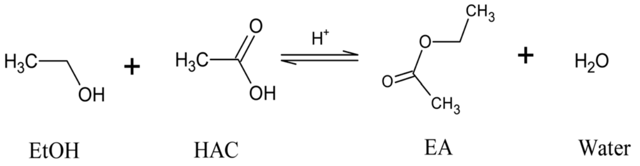
Esterification, a reaction extensively used in chemical processing, is limited by the establishment of kinetic equilibrium, *i.e.* marginally exer/endergonic. The reaction is generally slow with low yield making downstream separation cost intensive. A new heterogeneous contacting method for the synthesis of ethyl acetate through fine bubbles tests the hypothesis that reactive distillation can "pull" the reaction nearer to completion, reducing the downstream separation requirements. It achieves a high yield of ethyl acetate, 79.9% in 35 min, as compared with 64% conversion in 350 min using a conventional method. The kinetics of esterification reaction under bubbly flow conditions are studied – entirely different from the conventional bulk model. The alcohol is fed as vapor within the bubbles which means alcohol is always in deficit, providing an opportunity to convert an equilibrium limited reaction to nearly irreversible one. As the bubbles flow upwards, the reaction proceeds at the "skin" of the bubble. If the esterification reaction occurs at or near the microbubble interface, ethanol is in large *excess* in the bubble phase, as acetic acid is well below its boiling point in the liquid phase. By Le Chatelier's principle, the local excess ethanol will *push* the equilibrium towards completion. Similarly, removal of water and ethyl acetate *via* the "dry" bubble *pulls* the equilibrium towards completion.

1. Introduction

An equal amount of revenue, both capital and operational, if not more, is spent on the separation of the products or increasing their concentration than the cost of the reaction/reactor. Over the past few decades, several technologies have been developed to achieve higher conversions of mass transfer or kinetic equilibrium limited reactions. These processes require large separation and recycling units for high purity products.[1] Esterification, as an example, finds various applications in the process industry.[2] These reactions are generally very slow and catalyzed by the homogeneous acid catalyst to increase the rate of reaction.[3–5] In conventional esterification processes, kinetic and mass transfer limitations are key constraints, due to the inherent nature of the mixing of reactants in bulk in homogeneous phases. However, an entirely different approach has been developed in this article to increase the rate of the reaction and conversion. The study is focused on a core hypothesis – (1) increasing the interfacial area between the reactant would increase the mass transfer and hence the rate of reaction and (2) simultaneous separation of the reactant and product would move the reaction in the forward direction increasing the conversion of the overall reaction.[6] To examine the proposed hypothesis, ethyl acetate (EA) production was selected as an example, due to its increasing global demand.[7]

EA is one of the most important traditional solvents used for the production of adhesives, inks, resins, coatings, paints, flavors and different fragrances.[8] Commercially, EA is produced through the Fischer esterification process, where acetic acid (AcOH) and ethyl alcohol (EtOH) react to form EA in the presence of a homogeneous catalyst[9] as shown in eqn (1).



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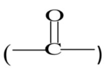
The Fischer esterification process is the most cost-effective option with the highest selectivity and conversion compared to the acetylene–AcOH process and dehydrogenation of EtOH.[7,10,11] Separation and purification of EA from the reaction mixture is inherently an energy-intensive process.[7,12,13] The reversible nature of Fischer esterification poses equilibrium constraints which control the process economics. Significant research has been carried out, both modeling[14–21] and experimental,[22–25] to manipulate the equilibrium during the esterification process. Several solutions have been proposed to improve the energy and cost-effectiveness for EA production such as reactive distillation (RD), pressure swing reactive distillation (PSRD) and RD with a divided wall column. These processes were limited due to the size of the column, formation of azeotropes or low EA recovery.[26] Despite recent developments in reactive distillation, there are many practical constraints for the commercialization of RD technologies in EA recovery and purification.[27]

To address these constraints in conventional processes,[26] a simple process yet achieving high mass transfer through fine bubbles, due to their larger surface area to volume ratio, has been proposed in the current study. The bubble-mediated mass transfer has already been reported for various chemical engineering operations and processes.[28–30] Finer bubbles, not even microbubbles, can push esterification reactions to completion using Le Chatelier's principle.[31] Research in the field of ethyl acetate production has been focused on altering process configuration and parameters to improve the kinetics but in vain. However, the kinetic limitation can be overcome by enhancing the mass transfer thereby "cheating" the equilibrium.[31,32] In this research work, esterification has been carried out in a bubble reactor with EtOH entering in the form of bubbles (vapors). The equilibrium in conventional esterification establishes as the reaction is carried out in bulk. Even in the presence of excess alcohol, the system always establishes equilibrium. However, when alcohol is fed in the form of vapors, as hypothesized, the reaction occurs on the skin of the bubble. Since, the bubbles are fine with sizes varying approximately between 200–800 microns, the amount of alcohol present in a single bubble is very low. Subsequently, the alcohol filled bubble reacts instantly with protonated AcOH. Since, alcohol is not mixed in bulk and the amount of alcohol present in a bubble is small, the equilibrium is not established, providing the opportunity to convert an equilibrium limited reaction to a nearly irreversible one.

The esterification reaction between an alcohol and carboxylic acid can only proceed after the carbonyl group  $(-\overset{O}{\overset{\|}{C}}-)$ has been protonated making the reaction slow. However, we propose to premix AcOH and a catalyst ensuring AcOH is ready to react as soon as it comes into contact with EtOH. The reaction temperature was set at 80 °C which is greater than the boiling point of EtOH and less than water warrants the separation of unreacted EtOH from the reaction mixture, hence, shifting the reaction in the forward direction. To the best of our knowledge, this production process for ethyl acetate has not been reported in the literature elsewhere.

2. Experimental

Reagent grade AcOH was purchased from DAEJUNG Chemicals, Korea. Pure EtOH (99.8%) was purchased from Merck Chemicals, Germany, and sulphuric acid (99.8%) reagent grade was purchased from PURE Lab Chemicals, Thailand.

The experimental setup is shown in Fig. 1. The calculations for molar ratio and related parameters are given in Table 1. Sulfuric acid (99.8%) was used as the catalyst. For every set of experiments, AcOH and the catalyst were premixed at 80 °C and 600 rpm for a different duration of time (0–100 min). Different molar ratios of AcOH and EtOH were studied and corresponding volumes were calculated using eqn (2) and 3. EtOH was heated in a 500 ml round bottom flask using a heating mantle and fed through a grade 1 sintered borosilicate diffuser with a porosity of 90 to 150 microns, in the form of bubbles. The total volume of the reactor was 0.692 dm^3. Temperature and pressure in the flask were continuously monitored using a thermocouple (Digital Thermometer, CE) and a bourdon gauge (WIKA range 0 to 300 mbar). The temperature of the EtOH in the flask was maintained at boiling point ~78 °C and controlled by a thermostat in a heating mantle while the pressure remained constant at 25 mbar gauge. The reaction temperature was maintained at 80 °C using a silicone rubber beaker heater (Brisk Heater Corporation, USA). The products were condensed using a water-cooled condenser at the downstream. The water flow rate was adjusted to ensure complete condensation of all product vapors. Catalyst loading was studied from 0.5 to 1.5 wt% of AcOH. AcOH head in the reactor was analyzed from 10 mm to 65 mm. All experiments were conducted three times for subsequent error analysis.

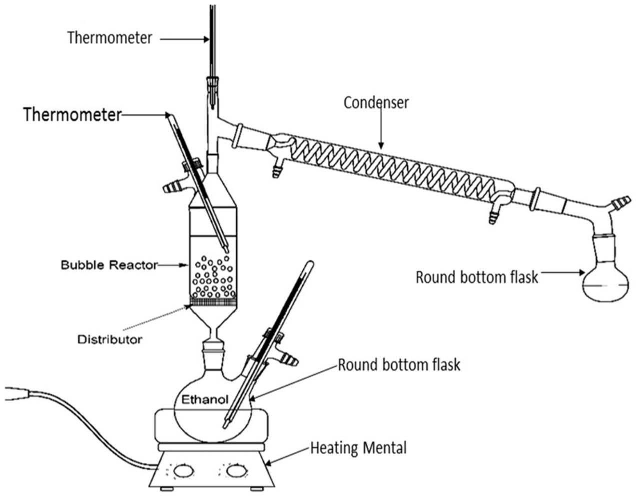


Fig. 1 Assembly for EA production.

Table 1 Properties and calculation used in kinetic studies

Acetic acid	Quantities	Units
Moles used	2	Moles
Molecular weight	60.01	g mol^{-1}
Mass	120.02	g
Density	1.049	g ml^{-1}
Volume	114.4	ml
Ethanol		
Moles used	4	moles
Molecular weight	46.06	g mol^{-1}
Mass	184.24	g
Density	0.789	g ml^{-1}
Volume	233.5	ml

$$\text{Volume for AcOH} = \frac{\text{moles of AcOH} \times \text{MW of AcOH}}{\text{Density of AcOH}} \quad (2)$$

$$\text{Volume for EtOH} = \frac{(\text{moles of EtOH} \times n) \times \text{MW of EtOH}}{\text{Density of EtOH}} \quad (3)$$

where $n = 1, 2, 3$, *etc.*

Experiments to investigate kinetics were carried out at 80 °C in which 2 moles of AcOH [corresponding volume] and 4 moles [corresponding volume] of EtOH were used. H_2SO_4 (0.5 wt% of AcOH) was used as the catalyst. It took 35 minutes to feed total ethyl alcohol in AcOH in the form of bubbles at 1.025 bar. The samples were taken at a regular interval of five minutes.

Samples were analyzed using a 1260 Agilent HPLC system equipped with UV/vis. The HPLC system was controlled by Chem-station software. The temperature of the column was set at 40 °C and the wavelength was set at 200 nm. The analytical column was Agilent Zorbax C8, particle size 5 μm and 250 mm × 4.6 mm. The mobile phase used for HPLC analysis included 0.03 mol L^{-1} H_3PO_4 in H_2O and acetonitrile in a ratio of 88 : 12 v/v. A 20 μL sample volume was injected.[33] A calibration curve was constructed by linear regression of the observed peak area *versus* concentration. The calibration curve for all concentration ranges was described by a linear equation with a correlation coefficient >0.99.

$$y = 0.0002(x) + 0.0161 \quad (4)$$

Conversion of AcOH was calculated according to

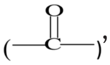
$$\text{Conversion} = \frac{\text{moles of AcOH converted}}{\text{moles of AcOH fed}} \quad (5)$$

3. Reaction kinetics

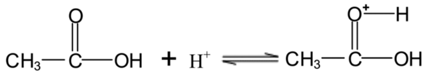
In the bubble reactor, EtOH enters in the form of bubbles and moves into AcOH in the liquid phase. Now the rate of reaction will depend on both mass transfer and chemical reaction step resistances.

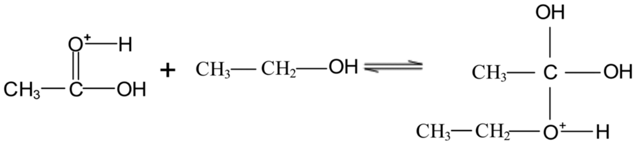
$$a\ \text{EtOH} + b\ \text{AcOH} \rightleftharpoons c\ \text{EA} + d\ \text{Water} \quad (6)$$

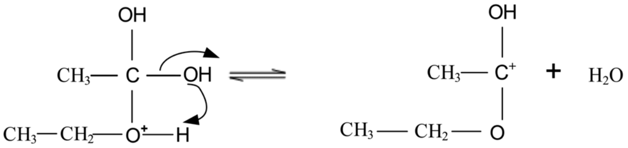
$$a\ \text{A} + b\ \text{B} \rightleftharpoons c\ \text{C} + d\ \text{D} \quad (7)$$

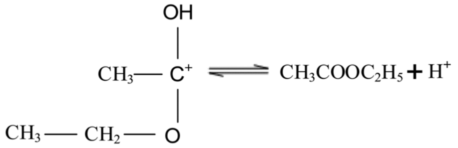
where a, b, c, and d are stoichiometric constants for EtOH, AcOH, EA, and water, respectively. Developing a strong understanding of the kinetics is important to explain the results in later sections of the article. The mechanism of the esterification reaction is shown below eqn (8)–(13). The reaction starts with ionization of sulphuric acid into ions as shown in eqn (8). In eqn (9), AcOH is protonated. Eqn (10) shows the nucleophilic substitution and is the rate-limiting step.[34] Eqn (11) and (12) show the charge transfer to and from central C of the carbonyl group , respectively, and formation of EA. The eliminated proton (H^+) combines with HSO_4^- to regenerate H_2SO_4 which subsequently participates in next cycle of reaction. These steps are fast due to the protonation reaction.[35]

$$H_2SO_4 \rightleftharpoons HSO_4^- + H^+ \quad (8)$$


$$CH_3-C(=O)-OH + H^+ \rightleftharpoons CH_3-C(=O^+-H)-OH \quad (9)$$


$$CH_3-C(=O^+-H)-OH + CH_3-CH_2-OH \rightleftharpoons CH_3-C(OH)(OH)-O^+(H)-CH_2-CH_3 \quad (10)$$


$$CH_3-C(OH)(OH)-O^+(H)-CH_2-CH_3 \rightleftharpoons CH_3-C^+(OH)-O-CH_2-CH_3 + H_2O \quad (11)$$


$$CH_3-C^+(OH)-O-CH_2-CH_3 \rightleftharpoons CH_3COOC_2H_5 + H^+ \quad (12)$$

$$HSO_4^- + H^+ \rightleftharpoons H_2SO_4 \quad (13)$$

As compared with the volume of EtOH, it is assumed, that the AcOH concentration does not drop appreciably within the liquid film. So the concentration of AcOH remains constant throughout. In general, the reaction follows a first order or second order kinetics depending on process configuration when carried out in bulk.[36,37] However, for reaction occurring on the skin of the bubble, the kinetics are different that need to be analyzed.

To investigate whether the reaction is diffusion controlled or kinetics controlled in the bubble reactor, the Hatta number (M_H) was calculated. If $M_H > 1$ then the reaction occurs in the film and the bubble surface area is the controlling rate factor. If $M_H < 1$ then no reaction occurs in the film, and the bulk reaction becomes the controlling factor. The equations used for the M_H number are shown below.[38,39]

$$M_{\mathrm{H}} = \frac{\sqrt{(D_{ab})_{\mathrm{T}}\, k\, C_{\mathrm{b}}}}{k_{\mathrm{bl}}} \tag{14}$$

where, k is the rate constant, k_{bl} is the liquid film coefficient and D_{ab} is the diffusion coefficient of EtOH and AcOH. D_{ab} at 25 °C was calculated using eqn (15) and at 80 °C using eqn (16).[40]

$$(D_{ab})_{T=25\,°\mathrm{C}} = 6.02\times10^{-5}\left(\frac{V_b^{0.36}}{\mu_b^{0.61} V_a^{0.64}}\right) \tag{15}$$

$$(D_{ab})_T = 4.996\times10^{3}\,(D_{ab})_{T=25\,°\mathrm{C}}\exp\left(\frac{-2539}{T}\right) \tag{16}$$

For a bubble size less than 2 mm mass transfer coefficient in the liquid film (k_{bl}).[41]

$$k_{\mathrm{bl}} = 0.31\left(\frac{(D_{ab})_T\,\rho_{\mathrm{b}} g}{\mu_{\mathrm{b}}}\right)^{\frac{1}{3}} \tag{17}$$

where, T is the reaction temperature. M_H was calculated to be 4 which is greater than 1 confirming the reaction on the skin of the bubble is kinetically dominant. The order of the reaction was calculated using the enhancement factor (E).[38]

$$E = M_{\mathrm{H}}\left(1 - \frac{M_{\mathrm{H}} - 1}{2E_{\mathrm{i}}}\right) \tag{18}$$

where, E_i is the infinite enhancement factor. E_i was calculated using eqn (19).[38]

$$E_{\mathrm{i}} = 1 + (D_{ab})_T\left(\frac{C_{\mathrm{B}} H_{\mathrm{A}}}{b\, P_{\mathrm{A}}}\right) \tag{19}$$

where H_A is Henry's constant, P_A is the partial pressure of EtOH and C_B is the concentration of EtOH. The calculated enhancement factor was approximately equal to M_H indicating that the reaction follows pseudo-first order kinetics.

The rate law of the bubble-mediated esterification reaction was calculated using eqn (20).

$$-r_{\mathrm{A}} = \frac{1}{\dfrac{1}{k_{\mathrm{A}}\sigma} + \dfrac{H_{\mathrm{A}}}{a\sqrt{(D_{ab})_{\mathrm{T}}\, k C_{\mathrm{B}}}}} P_{\mathrm{A}} \tag{20}$$

where, k_{Ag} is the mass transfer in the gas film coefficient and P_A is the overall pressure. The values of the rate constant (k), mass transfer gas film coefficient with the interfacial area (σ) per unit volume of the column/reactor ($k_{Ag}\ \sigma$) and liquid film coefficient (k_{bl}) under bubbly flow conditions are 0.0016 kmol $s^{-1}\ m^{-3}$, 2.486×10^{-3} kmol $s^{-1}\ m^3$ Pa and 1.74×10^{-4} ms^{-1}, respectively, and calculated using the graph between concentration and time as shown in Fig. 2.[41]

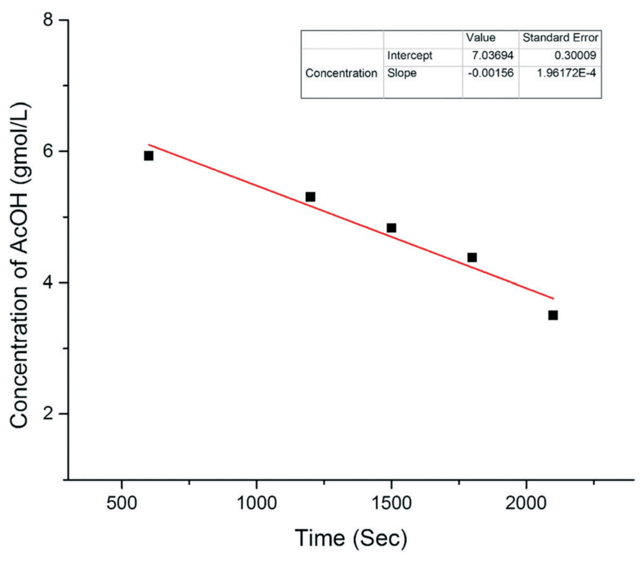
The overall rate of the bubble-mediated esterification reaction is shown in eqn (21).

$$-r_{\mathrm{A}} = \left(3.332\times10^{-5}\right)\left(P_{\mathrm{A}}\times101\,325\right)\left(\sqrt{C_{\mathrm{b}}}\right) \tag{21}$$

4. Analysis and discussion

The experimental results shown in Fig. 3 indicate the concentration of EA in the reactor and condensate. There is a steady rise in the concentration of EA. The increasing trend clearly has two linear parts. The first line follows a rather steep slope for the initial 15 minutes followed by a steady increase in the concentration for the remaining period of time.

The difference between the conventional reaction system and reactions occurring on the skin of the bubble at the interface of vapor phase alcohol and liquid AcOH must be noted before discussing the results. In conventional systems,



		Value	Standard Error
	Intercept	7.03694	0.30009
Concentration	Slope	-0.00156	1.96172E-4

Fig. 2 Concentration and time effect on the production of EA.

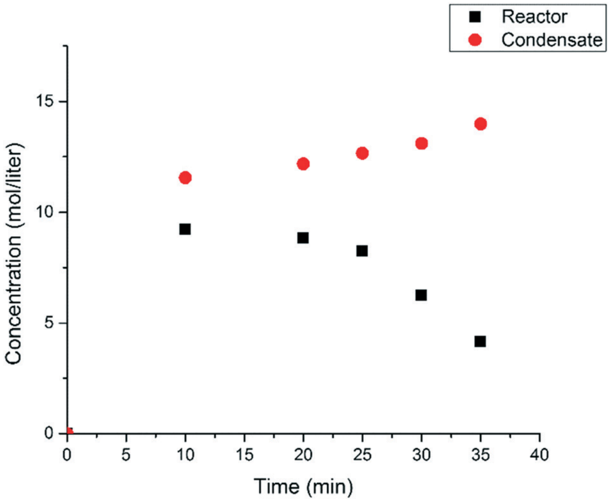


Fig. 3 Concentration of EA in the reactor and condensate.

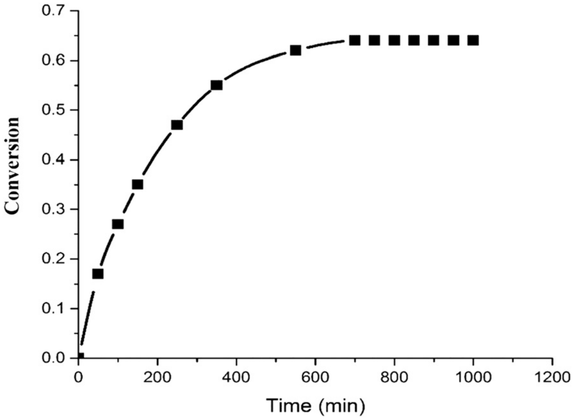


Fig. 4 Conversion of AcOH for a molar ratio of 1:1 at 80 °C with H_2SO_4 used as the catalyst.[7]

the required amounts of alcohol, acid, and catalyst are mixed together and the reaction occurs in the bulk. The diffusion coefficient of ethyl alcohol in AcOH is very high—of the order of 10^9 m^2 s^{-1} for all percentages of ethyl alcohol in AcOH.[42] The reaction, however, does not proceed unless the AcOH is protonated by the catalyst. The reaction, in this case, is essentially controlled by kinetics and equilibrium is established at an overall conversion of 65%. In RD, the non-catalyzed reaction reaches 20% conversion in the RD column for 1000 min reaction time.[7] For catalyzed reactions, several studies have been carried out for the RD column with most of them showing equilibrium at 64% conversion for 1000 min reaction time. Conversion in a typical RD column along with time is shown in Fig. 4.

However, in a bubble reactor, the alcohol is fed in the form of bubbles which means that there was never a sufficient amount of alcohol to establish the equilibrium, providing the opportunity to convert an equilibrium limited reaction to nearly irreversible one. As the bubbles flow upwards, the reaction proceeds on the "skin" of the bubble. Furthermore, if the esterification reaction occurs at or near the microbubble interface, ethanol is in large excess in the bubble phase, as acetic acid is well below its boiling point in the liquid phase. By Le Chatelier's principle, the local excess ethanol will drive the equilibrium towards completion. Similarly, removal of water and EA *via* the "dry" microbubble pulls the equilibrium towards completion.

Fig. 3 shows that during the first ten minutes of reaction, the concentration of EA in the condensate and in the reaction mixture is approximately equal which implies that the amount of EA formed is partially vaporized and partially remains in the reactor. The bubbles would keep on rising and the reaction would keep on occurring until all of the alcohol in the bubble has reacted or has achieved equilibrium with respect to the AcOH present at the bubble interface. The latter becomes less plausible as the bubble rises and interacts with "fresh" AcOH all the time and pushing the reaction in the forward direction according to Le Chatelier's principle. After ten minutes, the rate of production of EA slows down. At this point, almost 28% of the required amount of ethyl alcohol has already been consumed. Because of the high diffusion of ethyl alcohol to AcOH, part of the alcohol would have dissolved in AcOH. This is the point where, we hypothesize, that the reaction in the bulk would start contributing to the reaction mechanism. However, the equilibrium is still not established as shown by the continuous increase in the conversion of AcOH. The bubble would finally burst at the top releasing unreacted alcohol, water, and EA which are condensed from the top. This means that the reaction mixture in the reactor would never have enough amount of alcohol to establish equilibrium in the reactor.

As shown in Fig. 5, 66.01% conversion in the first 10 min and 79.95% conversion in 35 min. There are multiple reasons for achieving higher conversions in a short period of time.

The experiment was carried out at 80 °C with a 1:2 molar ratio using 0.5 wt% of H_2SO_4 to AcOH. There are examples in the literature showing higher conversions and a shorter period of time than conventional methods for EA production.

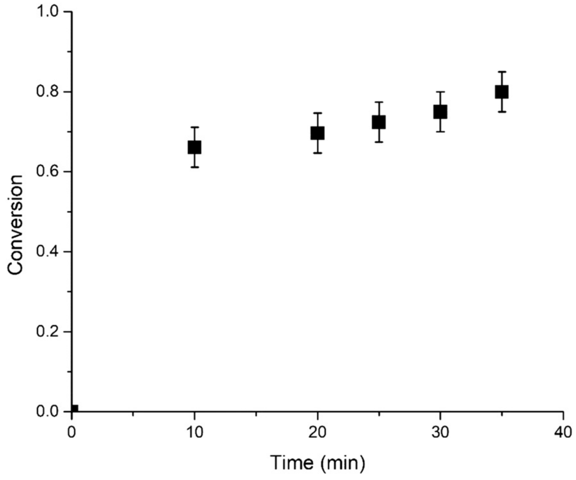


Fig. 5 Experimental result of AcOH conversion.

In 2000, Baris *et al.* studied esterification using an ion exchange resin as a catalyst at 80 °C for 350 min. The results showed that for a molar ratio of 1 : 1, the conversion of AcOH reached 60% and reached 70% for a 1 : 2 molar ratio.[22] In 2012, Rathod reported 65% conversion using 1 to 5% catalyst at 70 °C for 350 min for a molar ratio of 1 : 1.[43] In 2014, Desilva performed esterification with heterogeneous catalyst Trilete SCR (50 g L^{-1}) at 80 °C for 350 min and showed 60% conversion using 1 : 1. These results can be improved to 80% in 35 min for a molar ratio of 1 : 2 with 0.5% H_2SO_4 loading.

One of the prime reasons for higher conversion in a shorter period of time is the removal of the protonation step in the bubble reactor. As discussed above, AcOH is first protonated by H^+ which makes it labile for subsequent alkyl radical attack—nucleophilic substitution. Since AcOH was premixed with the catalyst before introducing it into the reactor, esterification can be initiated as soon as it comes across with ethyl alcohol in the vapor phase increasing the rate of reaction. Also, ethyl alcohol in the vapor phase carries latent heat of vaporization which would facilitate overcoming the activation energy barrier.

Internal mixing is also responsible for the larger rate of reaction. Mass transfer inside a bubble is enhanced by the internal circulation as shown in Fig. 6.

Due to internal circulation, acetic acid from the boundary moved inside the bubble which will enhance the reaction rate of esterification and mass transport.[44,45]

The size of the bubbles entering the reactor is significantly important for the rate of reaction and conversion. As reported in the literature,[6,29] microbubbles have shown higher mass transfer, rate of reaction and surface energy. The real benefit of using small bubbles comes from their larger ratio of surface area to volume. In all interfacial reactions, transport processes such as heat and mass transport are dependent on the surface area and in the dispersed phase; the surface area is proportional to the flux. So, decreasing the bubble size would increase the surface area thereby increasing the transport process and hence the reaction rate.[44] Also a smaller bubble has a larger residence time compared to larger bubbles. Thus, smaller bubbles have high momentum transfer to liquid drag along with them.[29] A higher flow rate, inherently, results in a larger bubble diameter. Also at larger flow rates, bubbles tend to coalesce and formed even larger bubbles shifting the flow regime from laminar to turbulent. Generally, the size of the bubbles is reduced with the decrease in the flow rate of the gas.[29] As discussed in a previous study[46] and shown in Fig. 7 the size of the bubbles reduces with the decrease in the flow rate.

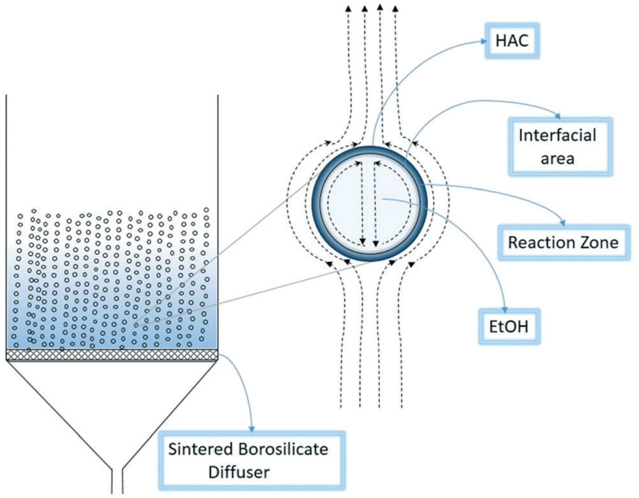


Fig. 6 Internal circulation of a microbubble.

The flow rate used in the current experiment was 6 ml min^{-1} making it safe to assume that a larger number of the bubbles produced would be in the micrometer range. As reported recently,[31] with an increase in microbubble number density, the conversion was increased. The smaller bubble size increases the interfacial area leading to a higher rate than that of ref. 29. The higher conversion of reaction can also be explained by the synergetic effect of smaller bubbles. Ethyl alcohol was fed in the form of vapor in bubbles, as explained above. When the bubbles burst they had taken away a significant amount of EA with themselves shifting the equilibrium in the forward direction and ensuring that non-equilibrium conditions prevail in the reactor.

The molar ratio of EtOH with AcOH was varied at 80 °C with 0.5 wt% catalyst loading w.r.t to AcOH as shown in Fig. 8. Using a higher molar ratio, the overall conversion tends to increase. In the first 10 min, for all three molar ratios, the increase in conversion was maximum. The conversion to AcOH slows down as discussed above. The AcOH : EtOH molar ratio of 1 : 3 gives a maximum conversion of 0.84 in 35 min of reaction time.

Catalyst loading has a predominant effect on AcOH conversion as shown in Fig. 9. Larger catalyst loading means a higher number of H^+ ions are available to protonate AcOH, resulting in higher conversion. A maximum conversion of 91% was achieved using 2 wt% of the catalyst for a molar ratio of 1 : 2 at 80 °C. To monitor the effects of the increased interfacial area because of feeding alcohol in the form of bubbles, and compare it with the control experiment at the same experimental scale, two separate experiments were conducted. The first experiment was carried out without the catalyst using similar experimental conditions and configurations as discussed. The second experiment was conducted without the catalyst using the conventional method – alcohol and acetic acid mixed and stirred at 80 °C for 35 min. Conversion using the bubble reactor without the catalyst was found to be 13.9% while using the conventional system, the overall conversion was only 1%. The comparison signifies the effect of reactions occurring on the skin of the bubble clearly indicating that the current process is more efficient than the conventional process.

Premixing of AcOH with the catalyst is an essential aspect for increasing conversion. Premixing ensures that AcOH is already labile for subsequent methyl radical attack ($-CH_3$). The experiment without pre-mixing shows the lowest conversion

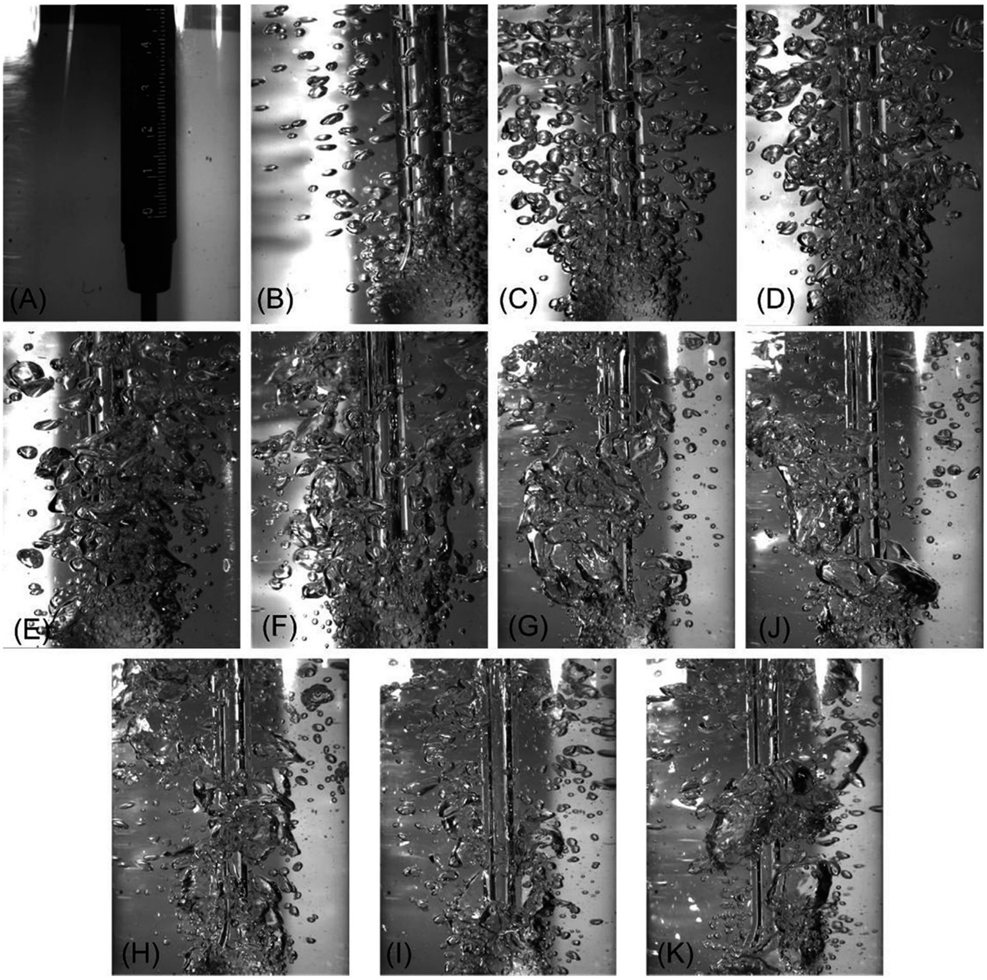


Fig. 7 Bubble size at different flow rates (A: scale, B: 0.2 L min^{-1}, C: 0.4 L min^{-1}, D: 0.6 L min^{-1}, E: 0.8 L min^{-1}, F: 1 L min^{-1}, G: 2 L min^{-1}, H: 3 L min^{-1}, I: 4 L min^{-1}, J: 5 L min^{-1}, K: 6 L min^{-1}.[44]

of 0.35 and with premixing the maximum conversion achieved is 0.8 at a 1 : 2 molar ratio, temperature of 80 °C, and 0.5 wt% catalyst. The results are shown in Fig. 10. As premixing time increases, the effect of protonation is more predominant. However, after 40 min of premixing, the

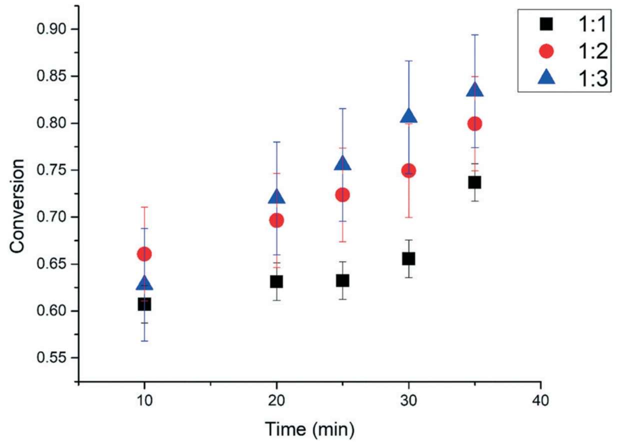


Fig. 8 Effect of the molar ratio of AcOH and EtOH on ethyl acetate production.

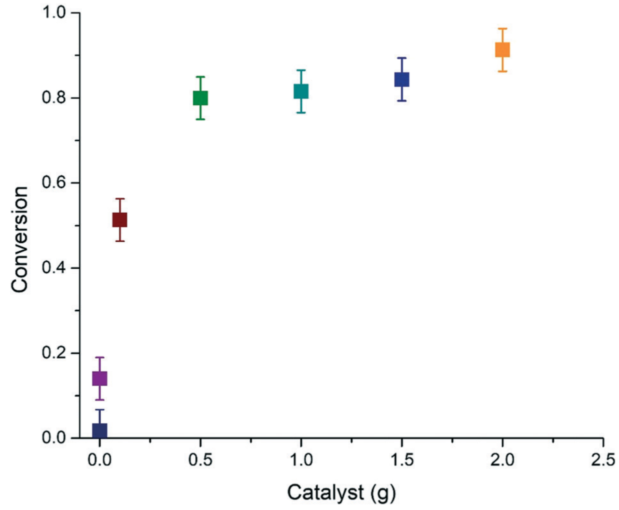


Fig. 9 Effect of the catalyst amount on ethyl acetate production.

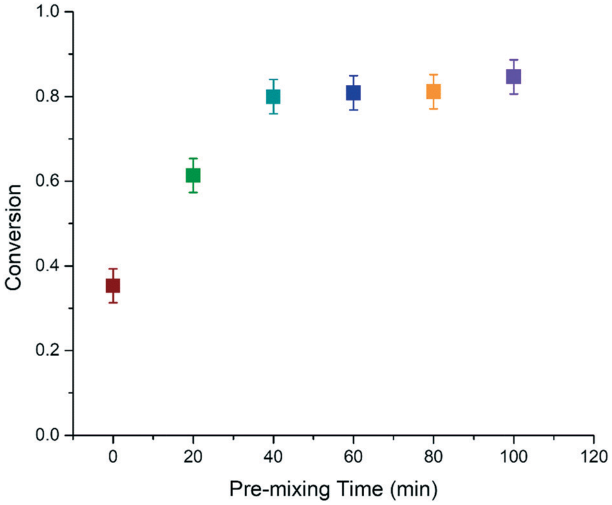


Fig. 10 Pre-mixing on EA production.

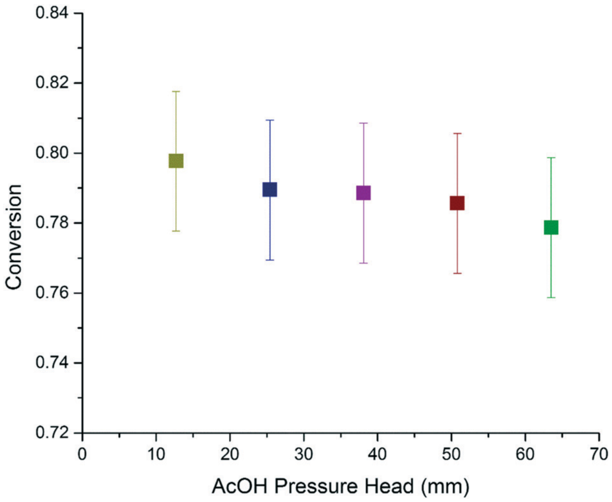


Fig. 11 Effect of the head in the reactor on EA production.

conversion remains almost similar, indicating that protonation has reached the saturation limit.

One of the important questions is to find out the required residence time of a bubble in the reactor. The residence time in the reactor was studied by varying the amount (head) of AcOH in the reactor. Fig. 11 indicates that the conversion is not affected by increasing the head in the reactor which implies that the reaction reaches equilibrium with the head as low as 10 mm. For the minimum and maximum head of 12.7 mm and 63.5 mm almost 79% and 77% conversion was achieved, respectively. The alcohol in the bubble reacts as soon as it comes into contact with protonated AcOH. The reaction proceeds and equilibrium is established around 10 mm as increasing the head does not significantly increase the conversion. This implies that reducing the head using a thin film reactor can enhance the conversion.

5. Conclusion

Production of EA is an energy-intensive process with conventional processing due to equilibrium limitations. EA was produced by feeding EtOH in the vapour phase in the form of bubbles into liquid phase AcOH. The conversion in the current study was found to be 65.8% in the first 10 min and 79.95% conversion in 35 min which is significantly higher as compared to 65% in a typical RD column. This supports the hypothesis that simultaneous bubble induced acid catalysis, with reactive distillation to the bubble phase of the water vapor, pulls the reaction closer to completion. The major factors yielding higher conversions are thought to be premixing of AcOH with the catalyst, dosing of ethyl alcohol in the form of finer bubbles which allow non-equilibrium conditions to prevail in the reactor and facilitating the separation of EA from the reactor. It is noted that the system can be improved by ensuring a larger number density of microbubbles using a cost-effective method for their injection. The rate of reaction indicates that the bubble size was the controlling factor—the smaller bubble size increases the interfacial area and the reaction equilibrium moves in the forward direction. By increasing the molar ratio, the conversion of the process also increases beyond the best conversion achieved in the current experimentation for 1 : 3. For catalyst loading the best conversion achieved 2 wt% of AcOH but the most optimal wt% was 0.5. The premixing study shows that the optimal premixing time is 40 min for the current reaction. Increasing the head slightly reduced the concentration showing that the reaction has already achieved equilibrium around 10 mm head.

Conflicts of interest

There are no conflicts to declare.

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