

CONTINUOUS AND CIRCULATED BATCH PROCESSES FOR ESTERIFICATION OF FREE FATTY ACIDS BY NOVOZYM 435 IN EXPANDED BED REACTOR: A CASE STUDY OF PALM FATTY ACID DISTILLATE

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ABSTRACT

An effective process for esterification of free fatty acids (FFA) by Novozym 435 in expanded bed reactors was developed. Oleic acid and palm fatty acid distillate (PFAD) were used as FFA. In the circulated batch process, Novozym 435 was reusable for 22 cycles with an FFA conversion greater than 90%. Furthermore, in the continuous process using four expanded bed reactors connected in series, FFA conversions from the esterification of oleic acid and PFAD with a total residence time of 80 min were 93.5% and 88.5%, with the overall productivity of about 1000 g and 940 g fatty acid methyl ester (FAME) litre⁻¹ hr⁻¹, respectively.

Keywords: biodiesel, palm fatty acid distillate, esterification, expanded bed reactor.

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INTRODUCTION

Alternative and renewable fuels are widely explored and expected to ease fossil fuel demand. Among these alternative fuels, biodiesel is attractive because it is renewable, biodegradable and non-toxic. It can be blended with petroleum-based diesel due to its similar properties (Lee *et al.*, 2010; Chongkhong *et al.*, 2007). Biodiesel is produced from animal fats, vegetable oils, waste cooking oil or free fatty acids (FFA) (Chen *et al.*, 2009; Fjerbaek *et al.*, 2009) and alcohols using a transesterification or esterification process depending on the major feedstock of triglycerides or FFA. Methanol is the most widely used alcohol in biodiesel production attributed to its low cost and high reactivity compared to those of longer-chain alcohols with higher nucleophilicity and its lower steric hindrance than ethanol (Fjerbaek

et al., 2009; Chongkhong *et al.*, 2009; Zhao *et al.*, 2014). Chemicals such as sulphuric acid (H₂SO₄) and potassium hydroxide (KOH) are widely used as catalysts for biodiesel production (Marchetti *et al.*, 2007). However, enzymes are also potentially useful catalysts because they are compatible with several types of raw materials, reusable, energy efficient and produce less wastewater compared to processes using acid or base catalysts (Fjerbaek *et al.*, 2009).

Novozym 435 is an interesting enzymatic catalyst for biodiesel production. Novozym 435 from *Candida antarctica* lipase B, is produced by the submerged fermentation of *Aspergillus* microorganisms immobilised in a macroporous acrylic resin, and shows an effective performance compared to other immobilised lipases (Tamalampudi, 2008; José *et al.*, 2013; Yang *et al.*, 2014). Furthermore, Novozym 435 catalyses transesterification and esterification processes with mild operating conditions (Arroyo *et al.*, 1999). Nevertheless, enzymatic biodiesel production is more expensive than those using chemical catalysts owing to the high price of enzymes (Chen *et al.*, 2009). Therefore,

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improving the productivity of biodiesel and the reusability of enzymatic catalysts is important for commercialisation and industrialisation (Chen *et al.*, 2011). Selection of the appropriate reactor type and operating conditions are major criteria for biodiesel production (Behzadi and Farid, 2009). Packed bed reactors have been extensively investigated for the use in industrial scale applications (Royon *et al.*, 2007; Chen *et al.*, 2009; Lee *et al.*, 2010; Wang *et al.*, 2011). The packed bed reactor is a widely used reactor for heterogeneous catalysis because the catalyst can be easily reused without separation from the reactor effluent. Besides, the mechanical shear stress that affects enzyme deactivation in a continuous stirred-tank reactor can be prevented. Moreover, a packed bed reactor provides higher reaction performance (Chang *et al.*, 2007; Chen *et al.*, 2009; Fjerbaek *et al.*, 2009) and lower operating costs than other batch processes.

Oleic acid is an unsaturated fatty acid that is the most widely distributed and abundant fatty acid in nature. It is monounsaturated fatty acid and is stable to thermal oxidation than many other unsaturated fatty acid components. Oleic acid is a major component in many low cost raw materials such as canola oil, palm oil, jatropha oil, rapeseed oil, soyabean oil, tallow and yellow grease (Anwar and Garforth, 2016). It has been used as a representative FFA in many studies on esterification.

In South-east Asia, biodiesel is produced from palm oil and its products is promoted as a renewable biofuel (Winayanuwattikun *et al.*, 2008; Choo and Wafti, 2015; Pannilawithana and Pathirana, 2017). Palm fatty acid distillate (PFAD), a by-product of palm oil refineries and lower in cost than palm oil, is an alternative low cost feedstock for next generation palm biodiesel in South-east Asia (Chongkhong *et al.*, 2009; Yujaroen *et al.*, 2009). The esterification of PFAD can thus help reduce the production cost of biodiesel. Previously, esterification process for the production of biodiesel from PFAD has been developed using mild acid catalysts, *i.e.* sulphonic acids (Choo and Wafti, 2015). PFAD mainly consists of a mixture of FFA up to 93%-97% with a small percentage of mono-, di-, and triglycerides (Mulalee *et al.*, 2015; Natthapon and Krit, 2015); therefore, at the same weight, PFAD can produce more biodiesel as compared to palm oil. Malaysia is one of the largest producers of palm oil and almost 700 000 t yr⁻¹ of PFAD were produced in Malaysia (MPOB, 2010). In January 2008-January 2010, the price difference between refined, bleached and deodorised (RBD) palm oil and PFAD is USD 100-USD 680 t⁻¹ (Cheah *et al.*, 2010). According to the market price generated by collecting market price data from the Malaysian Palm Oil Board from January 2014 until May 2016, the average prices of RBD palm oil, olein, stearin and PFAD relative to crude palm oil (CPO) price was 105.0%, 106.2%, 99.6% and 92.1%, respectively (Solikhah *et al.*, 2017).

The present work aims to develop the esterification process of FFA (oleic acid and PFAD) and methanol using Novozym 435 as a biocatalyst from a batch process in our previous work (Mulalee *et al.*, 2015) into circulated batch and continuous processes in expanded packed bed reactors. Important operating factors affecting FFA conversion, such as the feed volumetric flow rate, the amount of enzyme loading and the bed-to-catalyst volumetric ratio were investigated in a circulated batch process using a single packed/expanded bed reactor and then applied in the continuous process using multiple-expanded bed reactors connected in series. The efficiency of the enzymatic biodiesel production was evaluated.

MATERIALS AND METHODS

Materials and Chemicals

Novozym 435 (Lipase B from *Candida antarctica*, EC 3.1.1.3, a non-specific lipase immobilised on macroporous acrylic resin) was purchased from S M Chemical Supplies Co, Ltd (Bangkok, Thailand). The diameters of the particle beads were in the range of 0.3-0.9 mm with an approximate density of 0.4 g ml⁻¹. All other chemicals used in this work, oleic acid, methanol, KOH and phenolphthalein, were analytical grade and purchased from local suppliers in Thailand. PFAD was obtained from Patum Vegetable Oil Co. Ltd, Pathum Thani, Thailand.

Circulated Batch Process Using Packed/Expanded Bed Reactor

A cylindrical glass column with an inner radius of 2.5 cm and a height of 10.0 cm was used as the reactor. The total working volume of the reactor was 50-100 cm³. The bottom of the reactor (~40 cm³) was used as a reservoir for stirring the feed mixture with a magnetic bar (No. 5) at 600 rpm to homogenise the mixture. Novozym 435 was packed in a bed of an aluminum net covered with cotton fabric. The biocatalyst bed was packed inside the reactor. The optimal operating conditions for the esterification of oleic acid and alcohols by Novozym 435 from our previous study (Mulalee *et al.*, 2015) were applied in this study. The reaction temperature was maintained at 45°C, and the enzyme loading was 5% w/w of FFA. A mixture of 100 g of oleic acid and methanol at an FFA-to-alcohol molar ratio of 1:2 was thoroughly mixed and maintained at 45°C in a feed tank. The mixture was continuously fed into the reservoir of the reactor using a peristaltic pump at a constant flow rate. The mixture flowed upwards through the biocatalyst bed from the bottom to the top of the reactor, and the effluent was recycled into the agitated feed tank until the reaction reached equilibrium.

The schematic diagram of esterification by Novozym 435 in the circulation batch process by packed/expanded bed reactors is shown in Figure 1. Figure 1a demonstrates a circulated batch expanded bed with volumetric ratio of bed to catalyst of 1:1 at enzyme loading of 5% w/w of FFA. Figure 1b demonstrates an expanded bed reactor with volumetric ratio of bed to catalyst of 2:1 at enzyme loading of 5% w/w of FFA. Figure 1c demonstrates a doubly expanded bed reactor with volumetric ratio of bed to catalyst of 2:1 at enzyme loading of 10% w/w of FFA. The effluent was collected every hour to determine the FFA conversion. The effects of important factors such as volumetric flow rate, residence time and the amount of enzyme loading on the FFA conversion were investigated.

Continuous Process Using Expanded Bed Reactors Connected in Series

The circulated batch process described in the previous section was developed into a continuous process consisting of multiple expanded bed reactors

connected in series, in which the effluent from the top of each reactor directly flowed into the bottom of the next one. The schematic diagram of continuous esterification of FFA and methanol by Novozym 435 in the expanded bed reactors connected in series is shown in Figure 2. When a steady state was reached, the effluent of each reactor was collected to determine the FFA conversion at each stage.

Biodiesel Conversion Analysis

The percentage of FFA conversion was determined by titration with 0.1 M KOH solution using phenolphthalein as the indicator. The FFA conversions were calculated from the titration volumes of the KOH solution (Mulalee *et al.*, 2013). The reported values were the average values of each duplicate set. The titration was repeated three times for each sample and the data from each set had a small standard deviation (less than 1%). From the experiments in the continuous operation, after the steady state, three samples were taken from each reactor for the analysis of FFA conversion. The

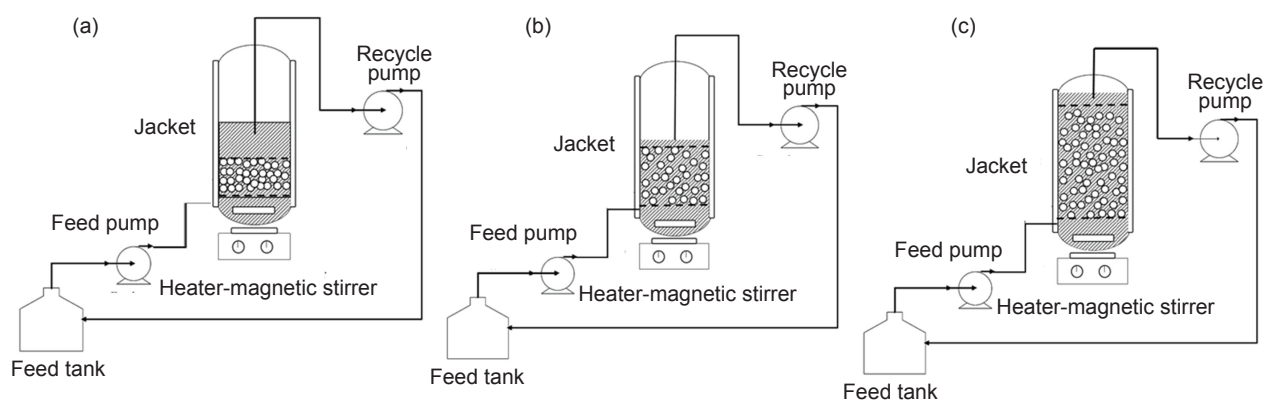


Figure 1. Schematic diagram of the esterification of free fatty acid (FFA) and methanol catalysed by Novozym 435 in the circulated batch process. (a) A packed bed reactor with volumetric ratio of bed to catalyst of 1:1, (b) an expanded bed reactor with volumetric ratio of bed to catalyst of 2:1 and, (c) a doubly expanded bed reactor with volumetric ratio of bed to catalyst of 2:1.

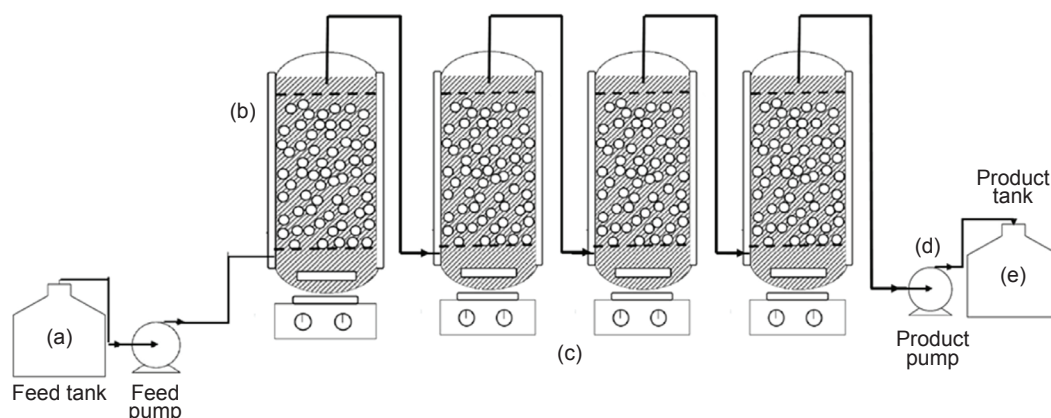


Figure 2. Schematic diagram of the esterification of free fatty acid (FFA) and methanol catalysed by Novozym 435 in the continuous process using four expanded bed reactors connected in series, consisting of (a) feeding tank, (b) a multiple-position hot plate stirrer, (c) four expanded bed reactors connected in series, (d) peristaltic pumps, and (e) a product tank.

calculation for FFA conversion from the titration method was calculated by the following equation (Chai *et al.*, 2014).

$$\text{FFA conversion (\%)} = \frac{(\text{Initial FFA} - \text{final FFA})}{\text{Initial FFA}} \times 100$$

where, *Initial FFA* is initial acid value at time $t = 0$ (mg KOH g^{-1}) and *Final FFA* is final acid value (mg KOH g^{-1}) at time $t = t$.

The results were confirmed by the fatty acid methyl ester (FAME) yield analysed by nuclear magnetic resonance (NMR) spectroscopy (Varian Inova, 500 MHz, Lexington, MA, USA) (Tariq *et al.*, 2011). The samples were sent to Research Instruments, Department of Chemistry, Faculty of Science, Chulalongkorn University for the determination of FAME conversion by NMR technique. The FAME yield was analysed by NMR 500 MHz with CP/MAS solid probe and Nano probe (Varian version INOVA, Lexington, USA). NMR analysis was performed by dissolving the sample in CDCl_3 . The dissolved sample was transferred to a NMR tube. All solid material must be removed from the solution before it was placed in the NMR tube. Then, the NMR tube was inserted into a sample turbine. Spectra were recorded on a Varian Mercury-500 spectrometer operating at 500 MHz at room temperature. The FAME content was determined by the ratio of the area of peaks associated with the methyl ester (3.65 ppm) and methylene group protons (2.26 ppm) (Hajar *et al.*, 2009). The equation for FAME (%) determination has shown below.

$$\text{FAME (\%)} = 100 \times \frac{2A_{\text{Me}}}{3A_{\text{CH}_2}}$$

where FAME (%) is FAME yield of esterification; A_{Me} is the integration value of the methoxy protons

of the methyl esters, A_{CH_2} is the integration value of α -methylene protons and 2, 3 are proton numbers in the methylene and methoxy groups, respectively. Spectra analysed by NMR are shown in *Figure 3*.

According to the comparison between FFA conversion from the titration and FAME conversion from $^1\text{H-NMR}$, we could confirm that the change of FFA was from the esterification reaction to convert FFA to FAME. The productivity was calculated based on the amount of FAME obtained (g) from FFA conversion per reaction time (hr) per reactor volume (litre). Molecular weight (MW) of oleic acid and PFAD were 282.5 and 265.5, respectively (Natthapon and Krit, 2015). MW of methyl ester from oleic acid and PFAD were 296.5 and 279.5, respectively.

RESULTS AND DISCUSSION

Circulated Batch Esterification of Oleic Acid Using a Packed/Expanded Bed Reactor

Effect of feed volumetric flowrate on FFA conversion.

The effect of feed volumetric flow rate ranging from 4-6 ml min^{-1} on the FFA conversion in the packed bed reactor was investigated. The experiment was performed in a packed bed reactor under recycling flow of the effluent as shown in *Figure 1a*. The optimal operating conditions from our previous work (Mulalee *et al.*, 2015) were applied as follows: reaction temperature of 45°C , molar ratio of oleic acid to methanol at 1:2 and Novozym 435 loading at 5% by weight of oleic acid. *Figure 4a* shows the effect of the feed volumetric flow rate on the FFA conversion of oleic acid. The FFA conversion rate increased as the feed flow rate increased from 4-5 ml min^{-1} because the higher flow rate caused a higher external mass transfer rate (Chattopadhyay and Sen, 2013). The FFA conversion reached a maximum of 90.6% at a flow rate of 5 ml min^{-1} within 8 hr. However, when the volumetric flow rate was increased from 5-6 ml min^{-1} ,

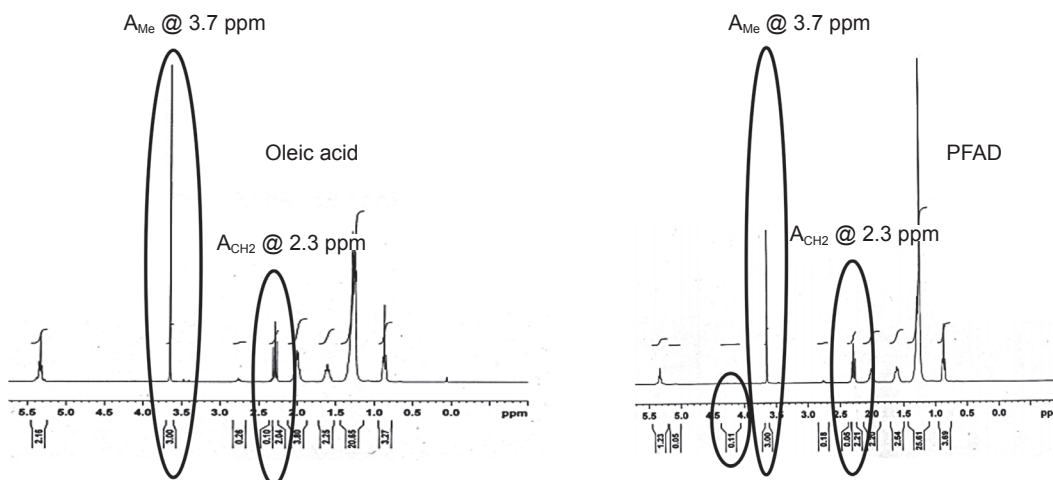


Figure 3. The H-nuclear magnetic resonance (NMR) spectra of fatty acid methyl ester (FAME) and free fatty acid (FFA) of esterification of oleic acid (left) and palm fatty acid distillate (PFAD) (right) with methanol catalysed by Novozym 435.

the reaction rate decreased and the equilibrium time was extended from 8-9 hr. A similar effect of feed flow rate on FFA conversion has been observed previously in a study of the transesterification of vegetable oil in a packed bed reactor using immobilised lipase and a circulation process (Hajar *et al.*, 2009; Lee *et al.*, 2010). At a low flow rate, the FFA conversion was limited because of the mass transfer resistance at the liquid-film layer. However, at a high flow rate, the contact between the substrate and enzyme active sites was insufficient and could cause a low FAME yield (Halim *et al.*, 2009). The shear stress of the high flow could also damage the immobilised biocatalyst (Wang *et al.*, 2011).

Effect of volumetric ratio of bed to catalyst on FFA conversion. To study the effect of contact time of the reaction under the feed flow rate of 5 ml min⁻¹, the volumetric ratio of bed to biocatalyst was increased from 1:1 to 2:1 as shown in Figures 1a and 1b respectively. In this case, the reactor bed was expanded, the contact time in the bed was doubled, and the biocatalyst could move freely within the bed. This operation has the advantages of increased contact area and time between the substrate and catalyst. As shown in Figure 4b, the initial rate of esterification in the expanded bed with the volumetric ratio of bed to catalyst at 2:1 was higher than that in the bed with the 1:1 ratio. However, the equilibrium conversions of both systems were almost the same. Previously, an expanded bed reactor packed with active ion-exchange resin catalyst was successfully developed for the continuous biodiesel production (Shibasaki-Kitakawa *et al.*, 2007; 2010). As the expanded bed enhances the initial reaction rate, it was used for the following studies.

Effect of enzyme loading on FFA conversion. To improve the FFA conversion, the optimal enzyme loading for the reaction in the expanded bed was determined. In our previous batch study in 250-ml mixing flasks (Mulalee *et al.*, 2015), the optimal enzyme loading of Novozym 435 was 5% w/w of FFA. Here, the enzyme loading in the expanded bed was increased to 10% w/w of FFA to observe the effect on the FFA conversion. The volumetric ratio of bed to biocatalyst was 2:1. A schematic diagram of the process is shown in Figure 1c. Figure 4c shows that when the enzyme loading was doubled from 5% to 10% w/w of FFA, the initial conversion rate and the equilibrium conversion were significantly enhanced. An FFA conversion of 96.7% was obtained using 10% w/w of Novozym 435, which was about 7% higher than that obtained at 5% w/w of Novozym 435. Moreover, the equilibrium time was reduced from 7-8 hr to 5 hr. As the ratio between enzyme and substrates is higher in the expanded bed reactor compared with that in the batch reactor, a higher reaction performance was achieved (Chang *et al.*,

2007). The optimised reactor was then studied for reusability.

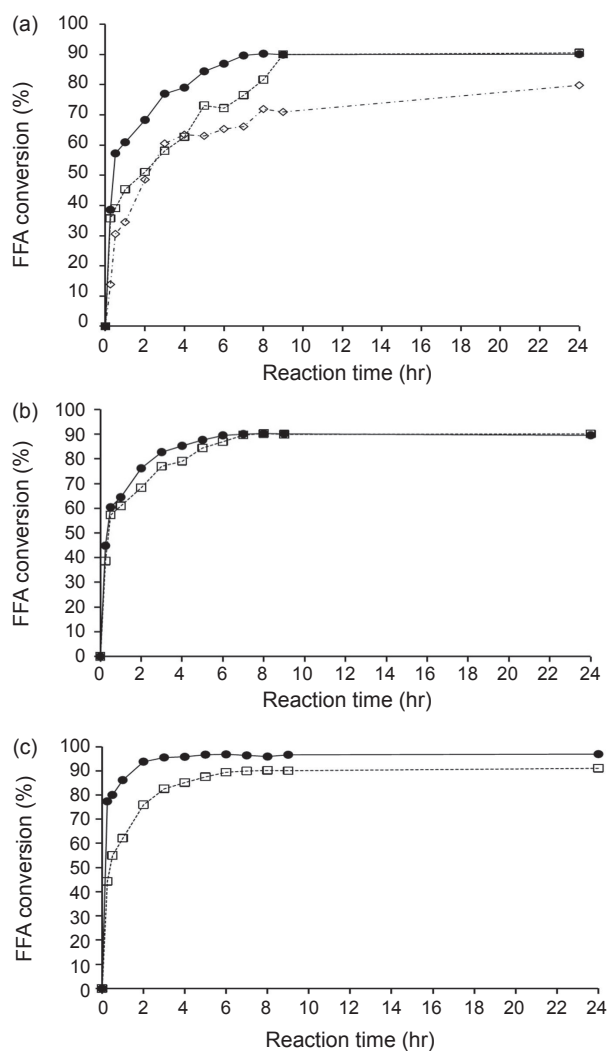


Figure 4. (a) Effect of flow rate on free fatty acid (FFA) conversion in a packed bed reactor: recycling flow rate of 4 (\diamond), 5 (\bullet) and 6 (\square) ml min⁻¹; (b) effect of volumetric ratio of bed to catalyst on FFA conversion in the circulated batch process: volumetric ratio of bed to catalyst of 1:1 (packed bed, \square) and 2:1 (expanded bed, \bullet); (c) effect of enzyme loading on FFA conversion in the circulated batch process using an expanded bed reactor at enzyme loading of 5% (\square) and 10% (\bullet) (w/w of FFA).

Reusability of Novozym 435 in the circulated batch process using an expanded bed reactor. For long-term operation and scale-up purposes, the reusability and stability of Novozym 435 in the single expanded bed reactor were investigated. Figure 5a shows the reusability of Novozym 435 as a catalyst for the esterification reaction in the expanded bed reactor under the following conditions: 45°C, FFA-to-methanol molar ratio of 1:2, enzyme loading at 10% w/w of FFA, bed-to-catalyst volumetric ratio of 2:1 and feed flow rate of 5 ml min⁻¹. For the total reaction time in each batch of 5 hr, the FFA conversion could be maintained at greater than 90% for 22 cycles (110 hr). This result demonstrates the higher efficiency and reusability of Novozym 435 as a biocatalyst in the circulated batch process using an expanded bed

reactor compared with those of circulated batch processes in packed bed reactors (Hajar *et al.*, 2009; Veny *et al.*, 2014) and a repeated batch process in a shaking flask (Mulalee *et al.*, 2015).

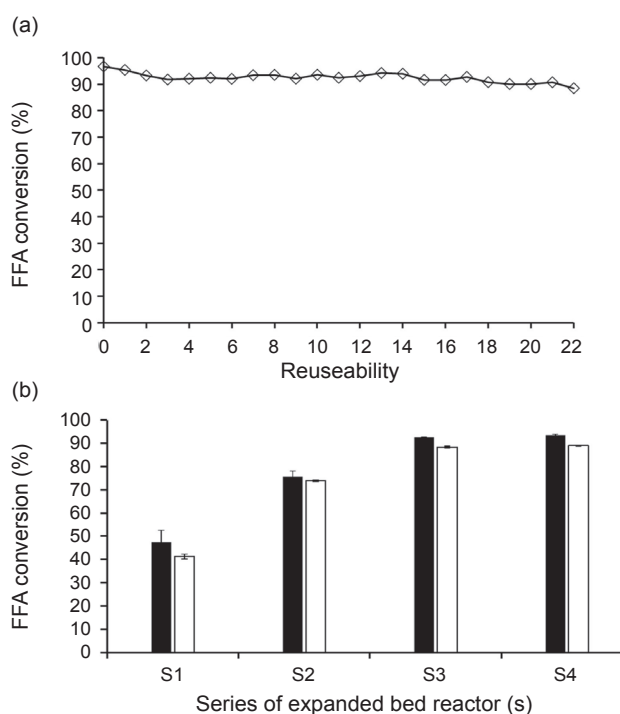


Figure 5. (a) Reusability of Novozym 435 on the esterification of oleic acid and methanol in the circulated batch process using an expanded bed reactor; (b) free fatty acid (FFA) conversion of oleic acid (■) and palm fatty acid distillate (PFAD) (□) in the continuous process using four expanded bed reactors connected in series (values were expressed as mean \pm SD, $n=6$).

Continuous Esterification of Oleic Acid and PFAD Catalysed by Novozym 435 Using Expanded Bed Reactors Connected in Series

The continuous esterification process using four expanded bed reactors connected in series was developed to improve productivity and reduce operating time. The optimal operating conditions described in the previous section were used. The mean residence time in each reactor was 20 min. The result from the continuous esterification of oleic acid with methanol catalysed by Novozym 435 in the four expanded bed reactors connected in series is shown in Figure 5b. The FFA conversions from the first, second, third and fourth reactors were 47.4%, 75.6%, 92.6% and 93.5%, respectively. Therefore, the number of expanded bed reactors required to reach equilibrium conversion was approximately four. Previously, an FFA conversion over 88% was maintained for 192 hr in biodiesel production using a mixture of soyabean oil, distilled water, methanol and n-hexane, using four packed bed reactors connected in series that contained lipase- Fe_3O_4 nanoparticle biocomposites as the catalyst (Wang *et al.*, 2011).

However, the residence time used in the packed bed reactors was about 10 hr, which is much longer than that in the expanded bed reactors used in this study (80 min). The overall productivity of biodiesel from the esterification of oleic acid was approximately 1000 g (FAME) litre⁻¹ hr⁻¹. The productivity of this process was considerably higher than those of the continuous processes using packed bed reactors previously reported (Chen *et al.*, 2009; Wang *et al.*, 2011; Chattopadhyay and Sen, 2012; 2013). However, other parameters such as differences in substrates, biocatalysts and operating conditions can also affect reaction performance (Silva *et al.*, 2014). Compared with the systems using the same substrates catalysed by Novozym 435, the average productivity of the continuous process in four expanded bed reactors connected in series was about four times that of the circulated batch process in the expanded bed reactor and about six times that of the batch process in shake flasks (Mulalee *et al.*, 2015). The comparison of transesterification and esterification studies was summarised as shown in Table 1.

Previously, the important parameters that affected the reusability of Novozyme 435 were temperature, type of alcohol, and water content (Mulalee *et al.*, 2015). Therefore, it can be expected that the stability of Novozyme 435 in the expanded bed reactors connected in series operated under continuous mode should not be much difference from that of the expanded bed reactor under circulated batch operation. Nevertheless, for commercial exploitation, it is suggested that the stability of the expanded bed reactors connected in series operated under continuous mode should be further examined in detail before process scale-up.

The low cost feedstock PFAD was then applied for biodiesel production. The esterification of PFAD and methanol was catalysed by Novozym 435 in the continuous process of four expanded bed reactors connected in series under the previous optimal conditions. PFAD is a by-product obtained from the palm oil refining process in the edible oil industry. PFAD is an alternative low cost feedstock for next generation palm biodiesel in South-east Asia, with an emphasis on Indonesia, Malaysia and Thailand. PFAD contains FFA (~93%) with palmitic acid (50.7%) and oleic acid (41.0%) as major components (Mulalee *et al.*, 2015). As shown in Figure 5b, the FFA conversion using PFAD as a feedstock was relatively lower than that using oleic acid. The FFA conversions from the first, second, third and fourth reactors were 41.2%, 73.9%, 88.3% and 88.9%, respectively. The final FFA conversion was about 5% lower than that using oleic acid as the FFA. The overall productivity of biodiesel from the esterification of PFAD was approximately 940 g FAME litre⁻¹ hr⁻¹. PFAD contains FFA and a small amount of unsaponifiable components and neutral oil. The process by-products include glycerol from the transesterification (Chongkhong *et al.*, 2007;

TABLE 1. COMPARISON OF TRANSESTERIFICATION AND ESTERIFICATION STUDIES

Process	System information	Free fatty acids conversion	Reaction time	Effective reactor volume	Reference
Packed-bed reactor	Transesterification of canola oil and methanol at 45°C catalysed by Novozym 435	97% (reusability for 6 batches)	72 hr	≈ 40 cm ³	Hajar <i>et al.</i> (2009)
Circulated batch packed bed	Transesterification of jatropha oil and methanol at 45°C catalysed by <i>Lipozyme</i> [®] IM	≈ 85%	8 hr	≈ 20 cm ³	Veny <i>et al.</i> (2014)
Batch in shake flasks		90.6%-94.8% (reusability for 13 batches)	8 hr	150 cm ³	Mulalee <i>et al.</i> (2015)
Circulated batch expanded bed	Esterification of oleic acid and methanol at 45°C catalysed by Novozym 435	90.1%-96.7% (reusability for 22 batches)	5 hr	100 cm ³	This study
Continuous operation in expanded bed		93.5%	80 min (for 4 in series)	200 cm ³ (50 cm ³ /reactor)	This study

Royon *et al.*, 2007). Glycerol and other impurities from PFAD could absorb and coat the surface of Novozym 435. It was noticed that by using PFAD as a feedstock, the colour of the outer surface of Novozym 435 became darker with longer operating times. The coatings on the surface of Novozym 435 might lower the enzyme's activity (Royon *et al.*, 2007). This problem might be avoided by the addition of a solvent such as acetone without significantly affecting enzyme activity (Chen *et al.*, 2009).

CONCLUSION

Esterification of FFA by Novozym 435 with methanol in expanded bed reactor gave better conversion as compared to packed bed reactor. The optimal operating conditions for expanded bed reactors are as follows: FFA-to-methanol molar ratio of 1:2, 45°C, feed flow rate of 5 ml min⁻¹, bed-to-catalyst volumetric ratio of 2:1, enzyme loading of 10% (w/w of FFA). In circulated batch expanded bed, FFA conversion greater than 90% could be achieved at a reaction time of 5 hr with 22 cycles of reuse of Novozym 435. Under continuous operation using four expanded bed reactors connected in series with a total residence time of 80 min, FFA conversions from the esterification of oleic acid and PFAD were 93.5% and 88.5%, respectively. The overall productivities of biodiesel from the continuous esterification of oleic acid and PFAD were approximately four to six times those of batch processes. Therefore, the continuous operation in expanded bed represents a more cost-effective method. Nevertheless, for commercial exploitation, it is suggested that the stability of the

expanded bed reactors under continuous mode should be further examined in detail before process scale-up.

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