Feasibility of Continuous Fatty Acid Methyl Esters (FAME) Production from Hydrolyzed Sea Mango (Cerbera odollam) Oil at Room Temperature Using Cationic Ion Exchange Resin

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Abstract. This research project demonstrated the feasibility of continuous fatty acid methyl esters (FAME) production from hydrolyzed sea mango (Cerbera odollam) oil at room temperature using cationic ion exchange resin, specifically Amberlyst 15. The experimental works of this research project were carried out in a fabricated glass tubular reactor. The effects of four variables; catalyst load (15 – 30 g), molar ratio of oil to methanol (1:6 – 1:12), feed flow rate (1.0 – 5.0 ml min⁻¹), and moisture content (0 – 5%) against the FAME yield were studied. The effects of two other supporting variables; temperature and the reusability of the ion exchange resin, against the FAME yield were also investigated for comparison purposes. The experimental results showed that it is highly possible to convert the hydrolyzed sea mango oil into FAME at room temperature using Amberlyst 15. High FAME yields (>90%) were achievable with higher catalyst load (30 g), smaller molar ratio of oil to methanol (1:6) and optimal feed flow rate (1.0 ml min⁻¹), and minimal (zero) moisture content. It is suggested that the high conversion of sea mango oil into FAME was due to the strong ion exchange (adsorption and desorption) between the reactant molecules and the sulfonic active sites to form more stable product (FAME) molecules that is independent of temperature. The free fatty acids (FFA) of the hydrolyzed sea mango oil disassociate into carboxylate ions (R-COO⁻) and hydrogen ions (H⁺) which enables it to exchange ions with the sulfonic active sites (strong proton donor) to produce FAME and water.

1. Introduction

In biodiesel production, energy usually in the form of heat is added to the process to convert vegetable oils into biodiesel, or technically known as fatty acid alkyl esters (FAAE). The chemical reactions to produce FAAE; transesterification or esterification processes, are endothermic; energy must be supplied to allow the reactions to occur, i.e. to overcome the activation energy [1]. The chemical reactions, especially transesterification process have very high activation energy, which translates to the requirement of high temperature (and pressure). The requirement is evident in the non-catalytic biodiesel production whereby it uses extremely high temperature and pressure (supercritical conditions) to
produce high yield of FFAE [1, 2]. For instance, the conversion of waste cooking oil into fatty acid methyl esters (FAME) using supercritical methanol is carried out at 250 ºC and 200 bar [3].

In most biodiesel production processes however, a catalyst is employed to reduce the activation energy and hence lower the required temperature and pressure. The reduction of the activation energy is heavily dependent on the reactivity of the catalyst itself. Different catalysts will have different reduction of activation energy.

In biodiesel production, there are many catalysts that can be used to reduce the activation energy, and thus produce high yield of FFAE. These catalysts are generally divided into three categories [2, 4, 5]; (1) homogenous types which include sodium hydroxide [2], potassium hydroxide [6], sulfuric acid [7], and hydrochloric acid [8], (2) heterogeneous types which include active metals [9], metal oxides [10], and zeolites [11], and (3) biological enzymes which include lipase enzymes [12].

Homogeneous catalysts, which are the most conventionally used catalysts in biodiesel industries, are comparatively more reactive than heterogeneous catalysts. This is evident by the use of moderate temperature (65 ºC to 75 ºC) at atmospheric pressure for homogeneous catalysis process [4], compared to (80 ºC to 200 ºC) for heterogeneous catalytic process [13, 14] to achieve similar yield of FFAE. On the other hand, enzymatic processes are able to produce high yield of FFAE at much lower temperature (30 ºC to 40 ºC) due to its specific reaction pathways [12, 15].

Despite the requirement of higher energy, heterogeneous catalytic process can still be advantageous over homogenous catalytic process due to its relatively simpler and easier downstream separation and purification process [14]. Heterogeneous catalysts can also be easily recovered and reused. Enzymatic processes on the other hand, despite its obvious advantage over homogenous and heterogeneous catalytic processes, it can be disadvantageous due to high cost of enzymes. Moreover, enzymes can be easily denatured or inhibited.

As energy is expensive in industry, it is therefore desirable to use a catalyst that is readily reactive at low temperature to produce high yield of FFAE, and not pricey to produce biodiesel at minimal cost. Ideally, the catalyst also has to be advantageous in many aspects; can be easily separated and reused without the risk of denaturation or inhibition.

Ion exchange resin is one of the candidates that meets most the specifications. It is in solid form, which can be easily separated from liquid mixtures as all heterogeneous catalysts can be. It is also has uniform size and good mechanical strength which are ideal to be used in packed bed reactor for continuous production of biodiesel. Ion exchange resins are also readily reactive at low temperature, unlike most heterogeneous catalysts.

In biodiesel production, ion exchange resins have been utilized as catalyst at moderately temperature (50 ºC to 80 ºC) which is comparable to those of homogenous catalytic process [16]. In water softening and purification process (common application for ion exchange resins) however, ion exchange resins are used at room temperature without the addition of any heat. It is therefore hypothesized that ion exchange resins are actually readily reactive at room temperature, regardless of application. However, as of today, there is yet a study that have been conducted on biodiesel production at room temperature specifically using ion exchange resins.

This research project is aimed to demonstrate the capability of an ion exchange resin, specifically cationic Amberlyst 15 in biodiesel production at room temperature. The outcome of this research project is expected to give new insight that is hopefully reduce the cost of biodiesel production and therefore, reduce the price of the biodiesel itself.

2. Materials and Methods

2.1. Materials
Sea mango oil which is currently not available commercially was extracted from sea mango kernels following a method from our previous study [17]. The extracted sea mango oil was then hydrolyzed according to another method from our previous study [18] – hydrolysis temperature of 200 ºC, oil to water volume ratio of 20:80, initial pressure of 0.1MPa – to achieve a minimum acid value of 200 mg
KOH g-1 or 90% FFA (palmitic acid) prior to use. This was carried out to ensure all of the triglycerides
and diglycerides in the sea mango oil converted to FFA.

Anhydrous methanol (purity of 99%) (feedstock for the esterification process) and solvent n-hexane
(98%) were purchased from Merck, Darmstadt, Germany. The ion exchange resins (Dowex DR-G8 and
Dowex DR-2030) and concentrated sulfuric acid (95-98%) were purchased from Sigma-Aldrich,
Malaysia whereas the standards for the FAME GC analysis (methyl laurate, methyl myristate, methyl
palmitate, methyl stearate, methyl oleate, methyl linoleate and methyl heptadecanoate (internal
standard)), all with purity of >99%) were purchased from Fluka Chemie, Germany.

2.2. Continuous Esterification Process

The experiments were carried out in a fabricated glass reactor system (inner tube diameter (ID) of 20
mm x length (L) 275 mm) equipped with a water jacket (ID 50 mm x L 255) as shown in Figure 1.

Anhydrous methanol (purity of 99%) (feedstock for the esterification process) and solvent n-hexane
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standard)), all with purity of >99%) were purchased from Fluka Chemie, Germany.

Prior to the experiments for the continuous esterification process, a pre-determined amount of dry
ion exchange resins (15 – 30 g) was initially soaked in anhydrous methanol in a separate container and
left for at least 2-3 h to allow the active sites of the ion exchange resins saturated with methanol and
also for the resin beads to expand adequately. The wet ion exchange resins were then carefully packed inside the tubular reactor (either glass or stainless-steel reactor) to avoid pockets of air bubbles.

In a normal operation of the continuous system, the feed (mixture of oil and methanol, with a predetermined molar ratio from 1:6-1:12 mol mol\textsuperscript{-1}) was pumped into the packed bed reactor using a digital peristaltic pump with a pre-determined flow rate (1-5 mL min\textsuperscript{-1}). These values were selected from trial and error runs. Collection of product samples began with the first drop of the product from the reactor outlet (0 min) and continued with a time interval of 0.5 h until total running time for at least 5 h. For the experiments to investigate the effect of moisture (water) to the esterification process, a certain amount of distilled/deionized water (1-5 %) was added into the feed tank prior to the operation.

The product samples consisted of two distinctive layers; oil layer (composed of FAME and unreacted oil) and aqueous layer (composed of byproduct water and excess methanol). Both layers were separated using a separating funnel. The oil layer was dried in a rotary evaporator to remove excess methanol before being subjected to gas chromatography analysis for its FAME yield.

3. Results and Discussions

3.1. Preliminary Continuous Esterification Process Using Selected Ion Exchange Resins

This preliminary study was conducted to compare the catalytic performances of Amberlyst 15 with two other selected ion exchange resins; Dowex DR-2030 and DR-G8 to convert the FFA into FAME in the continuous esterification of the hydrolyzed sea mango oil at room temperature. These two ion exchange resins were selected based on their comparable performances in terms of FAME yield to Amberlyst 15 as shown in our previous study [19].

Figure 2 shows the profile of FAME content of the product from the continuous system at room condition using the three selected ion exchange resins, each with 30 g of catalyst loading at feed flow rate of 2 mL min\textsuperscript{-1} and molar ratio of oil to methanol of 1:6. From Figure 2, it can be said that in general, all three cationic ion exchange resins were capable of producing FAME at room temperature whereby Amberlyst 15 produced the highest FAME contents followed by Dowex DR-2030 and finally Dowex DR-G8. The high contents of FAME (as high as 92.5 %) produced in this experiment, despite the absence of additional heat therefore proves that heat is not necessarily a sole driving force for the production of FAME using ion exchange resins. It is suggested in this study that the esterification reactions using ion exchange resins were driven largely by the strong cationic force of the active sites (sulfonic acids). It is also postulated in this study that the final products of the esterification process using ion exchange resins are in fact the most stable re-arrangement of the reactants molecules after a series of ion exchange with the active sites.
The rearrangement of the reactants molecules begins with the active sites itself, sulfonic acids, become negatively charged by losing or donating proton (H$^+$). This occurs spontaneously in the presence of methanol which acts as a proton acceptor. Sulfonic acids, being a proton donor similarly to sulfuric acid react rapidly with methanol to release heat (exo-thermic process).

The methanol then becomes positively charged (protonation) by accepting the proton from the sulfonic acids (1). This formation (protonated methanol on the active sites) is however yet to be stable as methanol is not a strong proton acceptor (compared to water), allowing another attack (reaction) from FFA to further stabilize the formation. This subsequently forces molecular rearrangement between the protonated methanol and FFA to produce more stable molecules; FAME and water (2). The resultant water, which is a stronger proton acceptor compared to methanol and FAME, then quickly displaces the FAME from the active sites (3).

Also seen on Figure 2, the rate of decrease of the FAME contents of the product using Amberlyst 15 was much smaller than those using Dowex DR-2030 and Dowex DR-G8. Their initial FAME contents at 0 h were also significantly different whereby the initial FAME content of Amberlyst 15 was measured at 92.5 % compared to only 86.6 % and 73.6 % by Dowex DR-2030 and Dowex DR-G8, respectively. This suggests the difference in their initial rates of reaction which are dependent on their number of active sites. It is suggested that in this study, Amberlyst 15 contains the highest number of active sites per weight of catalyst compared to Dowex DR-2030 and Dowex DR-G8 [20].

This is justified by their properties, particularly their total exchange capacity and surface area. The total exchange capacities of the ion exchange resins which indicate its acidity are; 4.7 meq g$^{-1}$ for Amberlyst 15 and Dowex DR-2030, and 4.5 meq g$^{-1}$ for Dowex DR-G8. The lower exchange capacity
of the Dowex DR-G8 thus contributed to its lower production of FAME. Dowex DR-2030 on the other hand, although it has total exchange capacity similar to Amberlyst 15, its surface area is however much smaller which is only 30 m² g⁻¹ compared to 53 m² g⁻¹ of the Amberlyst 15. The smaller surface area of the Dowex DR-2030 could have limited the number of reactions which subsequently reduces the production of FAME.

The decrease in FAME contents by all three ion exchange resins after certain period of reaction time is understandable as the active sites are becoming more saturated with water which prevents further esterification reactions.

3.2. Effect of Catalyst Loading

Figure 3 shows the FAME contents of the continuous esterification products at room condition using Amberlyst 15 with various catalyst loadings. As shown in Figure 3, the rate of decrease of the FAME content is more evident with the smaller catalyst loading. This behavior can be easily explained as the smaller catalyst loading contains lesser number of active sites. The lesser number of active sites effectively reduces the number of reactions which eventually caused the lower production of FAME.

The sharper decrease in the FAME contents with the smaller catalyst loading could also have been caused by the faster water saturation onto the active sites. For smaller catalyst loading, water saturation onto the active sites occurs more quickly since the number of active sites is much smaller. For larger catalyst loading, the water saturation takes longer time as there are a large number of active sites. Thus, with the availability of excess active sites that are yet to be saturated with water, more reactions could occur with which produces more FAME.

Figure 3. Profile of the FAME contents for the continuous esterification of hydrolyzed sea using Amberlyst 15 at room temperature and pressure with various catalyst loading (feed flow rate = 2 mL min⁻¹, molar ratio of oil to methanol = 1:6)

The identical initial FAME contents for all catalyst loading at time 0 h suggests that their initial rates of reactions are also similar. This is valid as all of these runs were carried out using the same catalyst with the same reaction condition. Their packing arrangements are also identical, which shares the same cross-sectional area (Figure 4). This packing arrangement produces the same flow rate which could
contribute to their identical rate of reactions. The only difference in their packing arrangement is the length of the bed which could have resulted in the different retention times and the rate of water saturation onto the active sites of the catalyst. The shorter retention time for those with smaller catalyst loading could have reduced its FAME production due to shorter contact with the active sites.

![Diagram of packed bed reactor with different catalyst bed heights](image)

**Figure 4.** Illustration of the catalyst packing arrangement inside the packed bed reactor using different catalyst loading (h1 and h2 indicate different catalyst bed height, h)

3.3. **Effect of Molar Ratio of Oil to Methanol**

**Figure 5** shows the profile of the FAME contents for the continuous esterification of hydrolyzed sea mango oil using Amberlyst 15 at room temperature with varying molar ratio of oil to methanol.
As shown in Figure 5, the initial FAME contents for all molar ratios of oil to methanol are significantly different from each other. The initial FAME content for smaller amount of methanol (molar ratio of oil to methanol of 1:6) was much higher than those with larger amount of methanol (molar ratio of 1:12). The overall FAME contents of the smaller amount of methanol were also seemed to be much higher than those for larger amount of methanol. This seems to be in contrast with the common conception in the biodiesel production which suggests larger amount of alcohol significantly increases the production of FAME.

The ‘contrasting’ finding can be explained however as the low FAME content of the larger amount of methanol (molar ratio of oil to methanol of 1:12) could have been caused by the dilution effect of the feed mixture [22]. The FFA in the larger amount of methanol (molar ratio of oil to methanol of 1:12) becomes sparsely dispersed in the bulk liquid, reducing their physical contact with the protonated methanol. Similarly, the FFA in the smaller amount of methanol (molar ratio of 1:6) becomes more concentrated, enabling them to have more physical contact with the protonated methanol and thus reactions to produce more FAME. This therefore suggests that a more concentrated FFA (lower molar ratio of oil to methanol) would be ideal to produce higher FAME content. However, in our case, a molar ratio of lesser than 1:6 would create another problem as the mixture (oil and methanol) would solidify at room temperature. This is disadvantageous as it would require additional heating to liquefy the mixture in order to make them easier to be pumped into the continuous system.

The gradual decrease in FAME contents for all molar ratio of oil to methanol is expected as water produced from the esterification could have gradually saturate the active sites which effectively reduces the esterification reactions.

3.4. Effect of Flow Rate

Figure 6 shows the FAME profile of the continuous esterification of hydrolyzed sea mango oil at room temperature using various feed flow rate. As shown in Figure 6, the FAME contents of the product
using larger feed flow rate decrease at greater rate compared to those using smaller feed flow rate despite their almost identical initial FAME contents.

**Figure 6.** Profile of the FAME contents for the continuous esterification of hydrolyzed sea using Amberlyst 15 at room temperature and pressure with various feed flow rate, mL min\(^{-1}\) (catalyst loading = 30 g, molar ratio of oil to methanol = 1:6)

This behavior can be explained easily as the larger feed flow rate resulted in shorter retention time. The shorter retention time thus limits the contact time for the reactants to undergo reactions with the active sites. The larger feed flow rate would also cause the products to be discharged at faster rate than those with smaller feed flow rate. Moreover, the larger feed flow rate would also induce faster water saturation onto the active sites which could effectively reduce the production of FAME.

As suggested earlier, the identical initial FAME contents signify similar rates of reactions. This is also valid in this case as all of the runs were carried out using the same type and amount of catalyst (catalyst loading) under the same reaction condition. The identical initial FAME contents for all feed flow rate could also suggest a very fast reactions i.e. ion exchange between the active sites and the reactants. This comes with the fact that despite the large feed flow rate which effectively reduces its retention time, it has still managed to produce high initial FAME content, closer to those with smaller feed flow rate (longer retention time).

### 3.5. Effect of Moisture (Water)

**Figure 7** shows the profile of the FAME contents of the product using Amberlyst 15 with different quality of hydrolyzed sea mango oil feedstock in term of moisture content. As shown in **Figure 7**, there is significant effect of the moisture towards the FAME contents of the product.

The FAME contents of those with the highest moisture contents seem to decrease drastically over time compared to those with lower moisture contents. Their initial FAME contents were also significantly different. This behavior can be explained as water could have been competing with the reactants especially methanol for the active sites. Water is a stronger proton acceptor compared to methanol and FFA. With the presence of water in the mixture, the protonation of methanol would have been disrupted. Therefore, instead of methanol occupying all of the active sites, most of them would be
replaced with water. The amount of methanol being protonated onto the active sites is dependent on the amount of water that is present in the mixture whereby the more water present, the less chances of methanol being protonated. The lesser amount of protonated methanol thus reduces the formation of FAME.

Figure 7. Profile of the FAME contents for the continuous esterification of hydrolyzed sea using Amberlyst 15 at room temperature and pressure with added various additional moisture (feed flow rate = 2 mL min⁻¹, catalyst loading = 30 g, molar ratio of oil to methanol = 1:6)

The stark difference in their initial FAME contents suggests that their rates of reactions are also varied. This is expected as water saturation onto the active sites could have already started at the beginning of the process. This thus resulted in the varying rates of reactions.

3.6. Effect of Moisture (Water)

Figure 8 shows the comparison of the FAME content profile from those carried out at room temperature and those with additional heat. From Figure 8, it can be seen that there is a slight difference between the FAME contents of those carried out at room temperature with those carried out with additional heat in terms of initial FAME contents and their rate of decrease. It is evident on Figure 8 that the initial FAME contents for those with higher reaction temperature are slightly higher than those with lower reaction temperature.
As different initial FAME contents indicate different rates of reactions as explained earlier, thus the higher initial FAME contents for those with higher reaction temperature would indicate higher rates of reactions. The higher rates of reactions could have been contributed by the more physical contact between the reactants (FFA) with the protonated methanol. As the esterification reactions are dependent on the physical contact between the protonated methanol and FFA, the presence of heat onto the system could have resulted in the more mobilized FFA, thus increasing its physical contact with the protonated methanol. The presence of heat could have also reduced the physical barrier (e.g. viscosity) of the mixture that increased their contact with the protonated methanol on the active sites, both on the internal and external surface of the catalyst. This is a theory constructed based on mass transfer theory where less viscosity increases the mass transfer rate. Viscosity is inversely proportional to temperature. Hence, at high temperature, the viscosity decreases, which lead to higher mass transfer rate [21].

The increased FAME contents in those that are carried at higher temperature could also come from additional reactions of the protonated methanol with other components in the oil apart from FFA, for example monoglycerides, diglycerides and triglycerides. With the presence of heat, these components could also have participated in the chemical reactions with the sulfonic acids through different mechanism (e.g. transesterification) that yielded in the more formation of FAME.

3.7. Reusability of Catalyst

Figure 9 and Figure 10 show the profiles of the FAME contents of the reused Amberlyst 15 catalyst from two different regeneration methods; (1) on-site regeneration and (2) with drying. The catalyst used in Figure 9 was regenerated with drying, i.e. the spent catalyst was removed from the packed bed reactor and dried in the oven to remove the excess water prior to regeneration with sulfuric acid solution whereas the catalyst used in Figure 10 was regenerated on site without drying in the oven. Both reused catalysts were subjected to six cycles of continuous esterification process.
As shown in these figures, the decrease in the FAME contents using those regenerated with drying on each cycle (Figure 9) seem to be much smaller than those regenerated on site (Figure 10). This can be easily explained as the regeneration method with drying could have reclaimed most of the active sites by removing most of the water. The regeneration on site on the other hand, could have not been able to remove most of the water from the active sites thus reducing the number of active sites for the next cycle of esterification reaction.

This therefore suggests that regeneration with drying is the best among the two methods to reuse the catalyst. This would still be imperfect however as indicated by the still reduction in the FAME contents with higher cycles in Figure 9. The still reduction in the FAME contents could have come from other factors apart from saturation by water, for example, poisoning of the active sites by other components (ions) in the oil, or incomplete regeneration by the regenerant sulfuric acid.

Figure 9. Profile of the FAME contents using regenerated ion exchange resin with drying (feed flow rate = 2 mL min⁻¹, catalyst loading = 25 g, molar ratio of oil to methanol = 1:6)
Figure 10. Profile of the FAME contents using regenerated ion exchange resin with in-situ regeneration (without drying) (feed flow rate = 2 mL min$^{-1}$, catalyst loading = 25 g, molar ratio of oil to methanol = 1:6)

4. Conclusions
This study has successfully demonstrated the actual operation of the continuous system (packed bed reactor) for the biodiesel production from non-edible (hydrolyzed) sea mango oil at room temperature. As shown in this study, Amberlyst 15, which is the best ion exchange resin studied in this research project, was capable of converting the FFA into FAME with high content which could be contributed to its total exchange capacity and better surface area compared to Dowex DR-2030 and Dowex DR-G8. It was also shown in this study that despite the absence of additional heat, high FAME contents are still achievable, suggesting that the esterification reactions using ion exchange resins are largely driven by the opposite ion attractions between the active sites and the reactants instead of heat.

From this study, it was shown that higher catalyst loading, smaller molar ratio of oil to methanol and smaller feed flow rate contributed to higher FAME content. The presence of water in the feed mixture was shown to have great impact on the FAME contents whereby larger amount of water significantly decreases the FAME content by water saturation onto the active sites. Additional heat was also shown to have slightly significant effect on the FAME contents whereby higher reaction temperature could improve the FAME contents. Regeneration study suggested the best way to regenerate the spent catalyst which is through additional drying to remove most of the moisture (water) from the active sites prior to regenerating it with the sulfuric acid.

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