

RESEARCH ARTICLE

Esterification of hydrolyzed sea mango (*Cerbera odollam*) oil using various cationic ion exchange resins

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Abstract

This study investigates the esterification of hydrolyzed sea mango (*Cerbera odollam*) oil using several cationic ion exchange resins. The best resins were selected based on their performance in a preliminary esterification process. The best resins were then subsequently used in the optimization of the process parameters. The esterification parameters studied were reaction temperature (40–160°C), reaction time (0–5 h), molar ratio of oil to methanol (0.5:1 to 1:14), and catalyst loading (1–14 wt%). Among the resins studied, Amberlyst 15 was found to be the most promising catalyst in the esterification of the hydrolyzed sea mango oil. Moderate reaction temperatures, 60–100°C, were found to be adequate in converting the hydrolyzed sea mango oil into esters. Further investigation revealed that the esterification reaction using the cationic ion exchange resins proceeds at a fast rate, whereby fatty acid methyl esters (FAME) yield of over 80% at moderate reaction temperature was achievable in less than 1 h of reaction time. Small amount of catalyst, which is less than 5 wt%, was also found to be sufficient in catalyzing the esterification process to an acceptable yield.

Introduction

The presence of free fatty acids (FFA) in conventional production of biodiesel – particularly in those that use sodium hydroxide (NaOH) or potassium hydroxide (KOH) as catalyst – is always deemed as nuisance due to its tendency to react with the catalyst itself to produce soap instead of esters [1]. Formation of soap in biodiesel production is unfavorable as it lowers the yield of esters (components of biodiesel) and creates emulsion especially when water is present. Emulsion causes the downstream separation and purification of the product (esters) to become more complicated. This adds unnecessary cost and is uneconomical for commercial production of biodiesel. Consequently, in conventional biodiesel production process, the oil feedstock used must not contain more

than 0.5% of FFA [2]. In cases where the oil feedstock inevitably contains more FFA, other methods apart from homogenous basic catalysts must be used.

However, recent development and advancement in biodiesel production process have shown that the presence of FFA in oil feedstock could be actually beneficial. Hence, instead of reducing the FFA content in the oil feedstock, many new studies have attempted to utilize FFA to produce esters via esterification process. New methods such as noncatalytic process which utilizes superheated alcohol (sub- or supercritical alcohol) [3] and heterogeneous process which utilizes solid acid catalysts [4] were reported to take advantage of the high amount of FFA in oil feedstock for biodiesel production.

FFA are beneficial in biodiesel production due to its tendency to react easily with alcohol to form esters. Its

relative easiness to react is due to its lower molecular stability compared to triglycerides (in which fatty acids bond strongly with glycerol). This lower molecular stability makes FFA to dissociate better in polar solvent to produce carboxylate ($R-COO^-$) and hydronium (H^+) ions compared to triglycerides molecules.

FFA are also advantageous in biodiesel production because of its similar polarity with alcohol by having a polar functional group ($-COOH$) on one of its molecular ends. Being partially polar makes FFA more soluble in alcohol compared to triglycerides. A high solubility of oil (FFA) in alcohol is important as it overcomes the mass transfer problem that has long been hindering the commercial production of biodiesel. A high solubility of oil (FFA) in alcohol is also necessary for a system where physical mixing to overcome the mass transfer problem is limited or cannot be implemented, for example, in a packed bed reactor.

Similar to transesterification process, the esterification process to convert FFA into esters can be carried out with or without catalyst [1, 2, 5]. Due to FFA's lower molecular stability, the activation energy of esterification process is generally much lower compared to transesterification process, making the former process more advantageous. This enables catalysts which are active at much lower temperature to be used in biodiesel production that can reduce the requirement of energy.

Ion exchange resin is an example of heterogeneous catalyst that can be used for esterification process. Ion exchange resins, particularly cationic ion exchange resins, are desirable due to their ability to catalyze the esterification process faster even at a lower temperature. The operating temperature by ion exchange resins normally range from 30°C to 150°C [6, 7], which is significantly lower than the requirement of 100–200°C [8, 9] by most other solid catalysts. By comparison, the operating temperature for conventional homogenous catalysts is around 60–70°C; however, homogenous catalysts in this case would not be suitable as they will react with the FFA to produce soap instead of fatty acid methyl esters (FAME).

Ion exchange resins, which are typically made of organic polymer substrate (e.g., cross-linked polystyrene), also have good mechanical strength, allowing them to be used in packed bed reactor for continuous production of biodiesel. Ion exchange resins are also easy to be regenerated and reused, making them more economical to be used as catalyst in biodiesel production.

With the intention of reaping the benefits of FFA in oil feedstock and its subsequent esterification process for biodiesel production, the objective of this project is to study and perform the esterification process of hydrolyzed sea mango (*Cerbera odollam*) oil using several cationic ion exchange resins. Several parameters – reaction temperature,

reaction time, molar ratio of oil to methanol, and catalyst loading – of the esterification process were investigated to determine the best condition to convert the hydrolyzed sea mango oil into esters using cationic ion exchange resins.

Material and Methods

Materials

Sea mango (*C. odollam*) oil was extracted from the kernels of mature/ripe sea mango fruits following a method by Kansedo and Lee [4, 10]. The fruits were collected around Penang Island, Malaysia (5°25'N 100°24'E). The composition and physical properties of the crude sea mango oil are shown in Table 1 [4]. Prior to use in the esterification process, the crude sea mango oil was hydrolyzed (without catalyst) using distilled water, at 200°C, volume ratio of oil to water of 20:80, and hydrolysis period of 10 h to increase its FFA content. The hydrolyzed sea mango oil was titrated using standard titration method and its acid value was measured to be 199.56 mg

Table 1. Composition and physical properties of crude sea mango oil [7].

Description	Method	Sea mango oil
Density ($kg\ m^{-3}$)	ASTM	919.80
Viscosity at 40°C ($mm^2\ sec^{-1}$)	ASTM	29.57
Free fatty acids (%)	MPOB P2.5	6.40
Acid value ($mg\ KOH\ g^{-1}$)	Standard titration	12.42
Water content (%)	Karl-Fisher	0.90
Fatty acid composition	GC	
C12: 0 (Lauric acid)		–
C14: 0 (Myristic acid)		–
C16: 0 (Palmitic acid)		24.86
C16: 1 (Palmitoleic acid)		0.75
C18: 0 (Stearic acid)		5.79
C18: 1 trans (Oleic acid)		0.24
C18: 1 cis (Oleic acid)		52.82
C18: 2 cis (Linoleic acid)		13.65
C18: 3n3 (Linolenic acid)		0.08
C20: 0 (Arachidic acid)		1.09
C20: 1 (Gadoleic acid)		0.19
C22: 0 (Behenic acid)		0.37
C24: 0 (Lignoceric acid)		0.16
Free fatty acids (FFA) ($g\ L^{-1}$)		2.27
Monoglycerides (MG) ($g\ L^{-1}$)		5.63
Diglycerides (DG) ($g\ L^{-1}$)		2.99
Triglycerides (TG) ($g\ L^{-1}$)		84.69
Average molecular weight (free fatty acids) ($g\ mol^{-1}$)		276.35
Average molecular weight (monoglycerides) ($g\ mol^{-1}$)		350.43
Average molecular weight (diglycerides) ($g\ mol^{-1}$)		608.77
Average molecular weight (triglycerides) ($g\ mol^{-1}$)		867.10

KOH g⁻¹, indicating a FFA composition of more than 90%.

The cationic ion exchange resins for the esterification process – Amberlyst 15, Dowex 50WX2, Dowex Marathon C, Dowex DR-G8, and Dowex DR-2030 – were all purchased from Sigma-Aldrich, Petaling Jaya Selangor, Malaysia. The cationic ion exchange resins were used in the esterification process without any pretreatment. The properties of the cationic ion exchange resins, obtained from their technical datasheets, are shown in Table 2. Sulfated zirconia catalyst, used for comparison purpose, was synthesized in the laboratory according to an optimized method by Kansedo and Lee [4]. Methanol (anhydrous grade), *n*-hexane (>99%), and FAME standard for gas chromatography analysis – methyl palmitate, methyl stearate, methyl oleate, methyl linoleate, and methyl heptadecanoate (internal standard) with purity above 99% – were all purchased from Fluka Chemie GmbH, Steinheim, Germany.

Esterification process

The esterification process (reaction) was carried out in a stainless steel tank reactor, equipped with magnetically driven stirrer with pressure and liquid-phase temperature indicators (Fig. 1). The reactor vessel has an internal volume of 220 mL and pressure rating of 5.5 MPa. The reactor temperature was controlled by an electrical heating device connected to a Proportional-integral-derivative (PID) controller.

In a typical reaction, 30 mL of preheated oil was pre-mixed with catalyst (1–14 wt%) and methanol (1:10 by molar ratio) before being discharged into the reactor ves-

sel. The initial pressure of the reactor vessel was raised to 2.0 MPa by an inlet nitrogen gas and sealed tightly before raising the reactor temperature to a predetermined setting (40–160°C). The reaction time was counted from the moment it reached the predetermined setting. After the specified reaction time, the heating device was switched off and the reactor vessel was immediately cooled with blowing air from a fan until it was cool enough to handle.

The reaction products consisted of two distinctive layers, oil layer (composed of methyl esters and unreacted oil) and aqueous layer (composed of byproduct water and excess methanol), which can be separated easily using a separating funnel. The separated oil layer was purified and dried using a rotary evaporator equipped with vacuum to remove excess methanol and moisture before being subjected to gas chromatography analysis for its methyl esters content.

Analysis of FAME

The analysis of sea mango esters was conducted using a Perkin Elmer Clarus 500 gas chromatography (PerkinElmer Inc., MA) using Nukol™ column (15 m × 0.53 mm, 0.5 μm film) with methyl heptadecanoate as internal standard. Helium gas was used as the carrier gas. Oven temperature at 110°C was initially held for 0.5 min and then increased to 220°C (held for 8 min) at a rate of 10°C per min. The temperature of the injector and detector was set at 220 and 250°C, respectively. The yield of sea mango oil into esters was calculated as the total mass (g) of methyl esters produced divided by the total mass (gram) of the fatty acids (hydrolyzed sea mango oil) in the feed [4, 10].

Table 2. Physicochemical properties of cationic ion exchange resins.

Properties	Amberlyst 15	Dowex DR-G8	Dowex DR-2030	Dowex 50WX2	Dowex Marathon C
Matrix	Styrene-divinylbenzene (macroporous)	Styrene-divinylbenzene (macroporous)	Styrene-divinylbenzene (macroporous)	Styrene-divinylbenzene (gel)	Styrene-divinylbenzene (gel)
Functional group	Sulfonics	Sulfonics	Sulfonics	Sulfonics	Sulfonics
Moisture content (%)	<3	<3	~3	74–82	53
Operating pH	0–14	0–14	0–14	0–14	0–14
Type	Strong cation (hydrogen form)	Strong cation (hydrogen form)	Strong cation (hydrogen form)	Strong cation (hydrogen form)	Strong cation (hydrogen form)
Particle size range/Particle average diameter	18–23 mesh 600–850 μm	16–50 mesh	16–40 mesh 425–525 μm	100–200 mesh	23–27 mesh 550–650 μm
Total exchange capacity					
By wetted volume (meq mL ⁻¹)	1.8	4.5	1.7	0.6	1.8
By dry weight (meq g ⁻¹)	4.7	5.1	4.7	–	2.6
Maximum operating temperature (°C)	120	150	150	150	149
Relative density (g cm ⁻³)	0.770	1.230	0.590	0.690	0.800

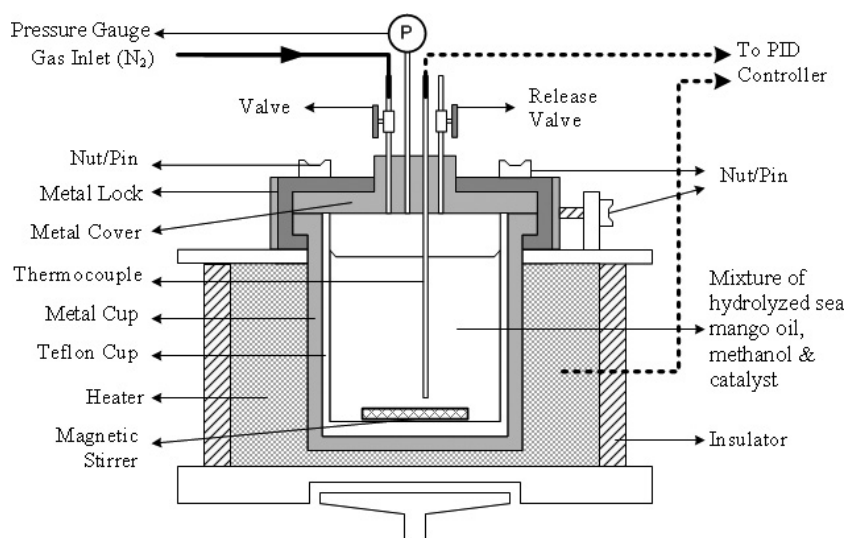


Figure 1. Experimental setup for the esterification process.

Results and Discussions

Selection of catalyst

Figure 2 shows the esterification of hydrolyzed sea mango oil using various cationic ion exchange resins and also sulfated zirconia catalyst. The catalytic performance of the cationic ion exchange resins and sulfated zirconia was measured by its yield of FAME. The catalytic performances of three cationic ion exchange resins, Amberlyst 15, Dowex DR-G8, and Dowex DR-2030, seem to be at

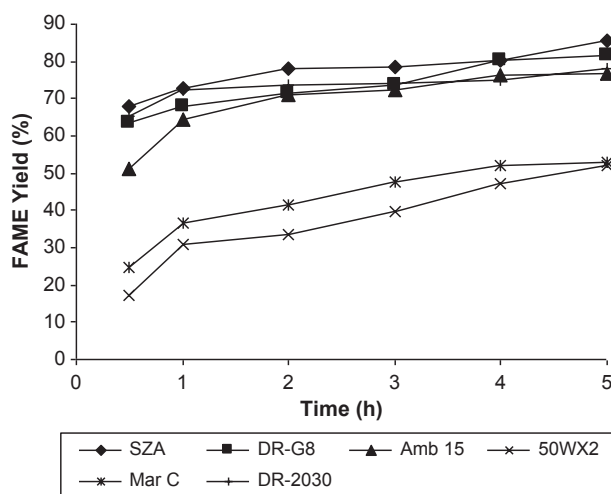


Figure 2. Esterification of hydrolyzed sea mango oil using various cationic ion exchange resins and sulfated zirconia catalyst (SZA). DR-G8, Dowex DR-G8; Amb 15, Amberlyst 15; 50WX2, Dowex 50WX2; Mar C, Dowex Marathon C; DR-2030, Dowex DR-2030 (reaction temperature = 100°C, molar ratio of oil to methanol = 1:3, catalyst loading = 5 wt%).

par with those by sulfated zirconia catalyst, whereas the catalytic performances of the rest of the ion exchange resins, Dowex 50WX2 and Dowex Marathon C, seem to be inferior.

The inferiority of Dowex 50WX2 and Dowex Marathon C compared to Amberlyst 15, Dowex DR-G8, and Dowex DR-2030 on the esterification process of the hydrolyzed sea mango oil could be due to their different physical and chemical properties. As shown in Table 2, Dowex 50WX2 and Dowex Marathon C were all in wet form (moisture content of 74–82% and 53% respectively), whereas the other three cationic ion exchange resins, Amberlyst 15, Dowex DR-G8, and Dowex DR-2030, were all in dry form (moisture content of about or less than 3%). The moisture in the cationic ion exchange resins could have inhibited the esterification process by creating a physical barrier between the reactants and the active sites (sulfonic group). The moisture (water) could also have attached to the active sites of the cationic ion exchange resins which prevented the reaction between fatty acids and methanol.

The good catalytic performance by Amberlyst 15, Dowex DR-G8, and Dowex DR-2030 compared to those by sulfated zirconia catalyst, a solid superacid catalyst, thereby confirmed their capability in converting fatty acids in the hydrolyzed sea mango oil into esters.

Optimization of parameters

Effect of temperature

Figure 3 shows the esterification of hydrolyzed sea mango oil by three of the best cationic ion exchange resins, Amberlyst 15, Dowex DR-G8, and Dowex DR-2030, at various reaction temperatures, ranging from 40°C to 160°C. Generally, the catalytic performances of the cationic ion

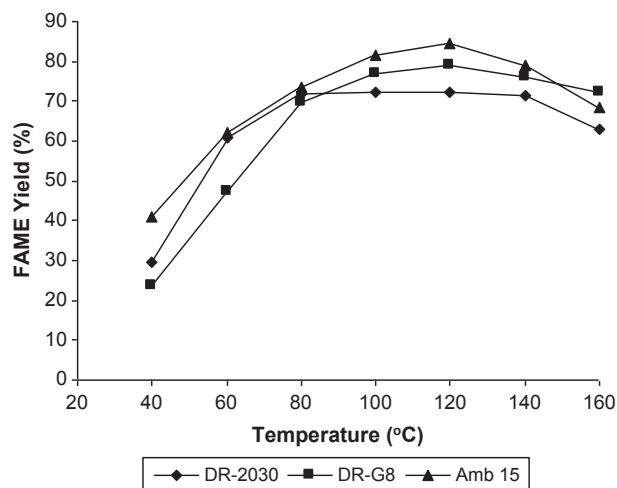


Figure 3. Effect of temperature on the esterification of hydrolyzed sea mango oil (molar ratio of oil to methanol = 1:3, catalyst loading = 5 wt%, reaction time = 1 h).

exchange resins were improved with increasing reaction temperature. This is expected as esterification process is an endothermic reaction, whereby energy is required in the process. The equilibrium of the reaction may have been shifted forward at higher temperature, resulting in more forward esterification reactions to produce more FAME.

According to Tesser et al. [11], esterification process using ion exchange resin as catalyst is assumed to proceed through a series of adsorption and desorption of reactants and products on the active sites of the catalyst. FFA are assumed to attach on the active sites (protonation) and react with methanol coming from the bulk liquid surrounding the catalyst particle to produce esters (surface reaction following Eley–Rideal mechanism). The whole adsorption and desorption process requires energy; therefore, the increase in reaction temperature could accelerate the adsorption and desorption process and also the surface reactions, and thereby increase the yield of FAME.

From Figure 3, among the three cationic ion exchange resins, Amberlyst 15 seems to have the upper hand in the esterification process compared to Dowex DR-G8 and Dowex DR-2030. Between Dowex DR-G8 and Dowex DR-2030, they seem to have a contrasting trend of FAME yield at different temperature. At lower temperature which is between 40°C and 80°C, Dowex DR-2030 produces higher FAME yield compared to Dowex DR-G8, but at higher temperature, which is more than 90°C, it was Dowex DR-G8 that produces the higher yield of FAME. This may suggest a distinctive optimum or suitable operating temperature for each type of cationic ion exchange resins for the esterification process. As indicated in Figure 3, the best operating temperature for Dowex

DR-G8 and Amberlyst 15 could be between 100°C and 120°C, whereas for Dowex DR-2030, the best operating temperature could be anywhere between 80°C and 140°C judged from their highest yield of FAME produced.

The performances (yield of FAME) of all three cationic ion exchange resins were found to significantly decrease at reaction temperature beyond 120°C. The decrease was particularly apparent for Amberlyst 15, whereby a steep decline in FAME yield was observed when the reaction temperature is raised above 120°C. On the other hand, the decrease in the catalytic activity of Dowex DR-G8 and Dowex DR-2030 becomes only apparent when the temperature is raised above 140°C, which is slightly higher than those for Amberlyst 15. This could be easily explained as each cationic ion exchange resin has its own maximum operating temperature. According to Table 2, the maximum operating temperature for Amberlyst 15 is 120°C, whereas for Dowex DR-G8 and Dowex DR-2030, the maximum operating temperature is 150°C. Beyond these temperatures, the cationic ion exchange resins (the matrix itself or its active sulfonic group) could be thermally destroyed or decomposed. The decomposition of the cationic ion exchange resin certainly reduces its ability to convert the fatty acids into esters, thereby lowers the yield of FAME.

Other possible explanation of the decrease in FAME yield at higher temperature as suggested by a reviewer is the excessive evaporation of methanol to the gas phase at higher temperature, especially above the boiling point of methanol (<65°C). This excessive evaporation of methanol at higher temperature caused decreased amount of methanol in the liquid phase that effectively reduces the reactions between oil and methanol.

The capability of Amberlyst 15 and Dowex DR-2030 to produce esters (although only achieving moderate yield) in the esterification process at lower temperature between 60°C and 80°C could be beneficial for operations which require reaction temperature below the boiling point of methanol. The operation below the boiling point of methanol, which is at 65°C under normal condition, is certainly advantageous as it could reduce the rapid loss of methanol by evaporation and therefore reduce the cost of biodiesel production.

Comparison with heterogeneous transesterification process that uses active metal oxides (which normally operates at much higher reaction temperature of 150–190°C), esterification process which operates at moderate low temperatures (as shown in this study) could be economical as it reduces energy consumption. In heterogeneous transesterification process, the triglycerides molecules are more structurally stable; therefore, more energy is required to break the triglycerides into fatty acids before it could react with alcohol in the transesterification

process. FFA in esterification process, on the other hand, are less structurally stable; therefore, they could react more easily with alcohol to produce esters. Oils rich in FFA, for example, palm fatty acid distillate, a byproduct from palm oil refining which comprise of more than 80% of FFA [12], could easily be used in the esterification process for biodiesel production at much lower energy requirement (lower reaction temperature).

Effect of molar ratio of oil to methanol

Figure 4 shows the esterification of hydrolyzed sea mango oil by Amberlyst 15, Dowex DR-G8, and Dowex DR-2030 at 100°C using various molar ratio of oil to methanol from 0.5:1 to 1:10. As it can be observed from Figure 4, the catalytic performance by Amberlyst 15 seems to be significantly higher than those by Dowex DR-G8 and Dowex DR-2030. It can also be observed that the catalytic performance of the three cationic ion exchange resins for molar ratio of oil to methanol of less than 1:1 is very low. This is expected, as according to the reaction stoichiometry, one mol of fatty acids requires one mol of alcohol to produce one mol of esters. Hence, when the amount of methanol used is less than the stoichiometric theoretical requirement, it will result to a very low yield of FAME.

Similar like any reversible process, the esterification process can be enhanced by shifting the equilibrium forward. This can be done by adding more methanol so that more esters could be formed. This is demonstrated in Figure 4, whereby significant increase in FAME yield is observed when the molar ratio of oil to methanol is increased from 1:1 to 1:3. However, beyond this point,

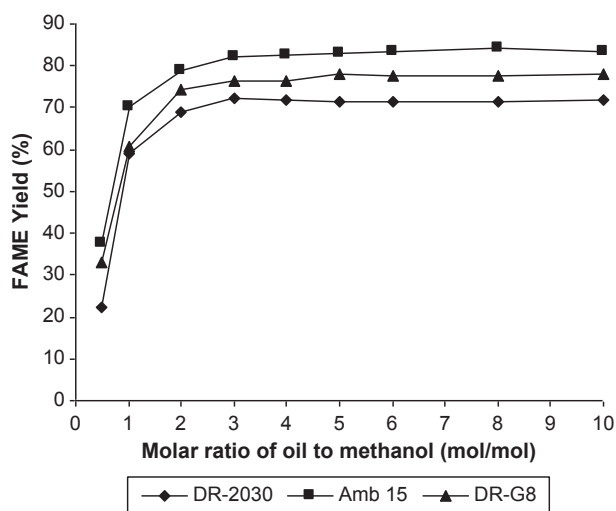


Figure 4. Effect of molar ratio of methanol to oil on the esterification of hydrolyzed sea mango oil (CATALYST loading = 5 wt %, reaction temperature = 100°C, reaction time = 1 h).

the FAME yield seems to reach a stagnant phase, whereby no significant increase in FAME could be observed albeit raising the molar ratio of oil to methanol beyond 1:3. This can be easily explained as at higher molar ratio, the catalyst becomes more diluted in the reaction media which reduces the reaction rate. This could also be caused by the disruption to the catalytic process that prevents further formation of esters. The disruption may come from water formed as byproduct in the esterification process whereby water attaches to the active sites of the cationic ion exchange resin. As water have better affinity toward the active sites of the cationic ion exchange resin with respect to fatty acids and methanol, thus it could displace the protonated fatty acids that are attached on the active sites. As ester formation is dependent on the surface reaction (exchange between protonated fatty acids attached on active sites and methanol coming from the bulk liquid), the displacement of protonated fatty acids by water therefore prevents formation of more esters.

Effect of catalyst loading

Figure 5 shows the esterification process by Amberlyst 15, Dowex DR-G8, and Dowex DR-2030 at 100°C with molar ratio of oil to methanol of 1:3, using different catalyst loading, from 1 wt% to 14 wt%. The best overall performance seems to be by Amberlyst 15, whereas the lowest seems to be by Dowex DR-2030. From Figure 5, it can be observed that addition of more catalyst (2–14 wt%) to the esterification process did not produce significant increase on the yield of FAME. This seems to be in contrast to what was expected as addition of more catalyst

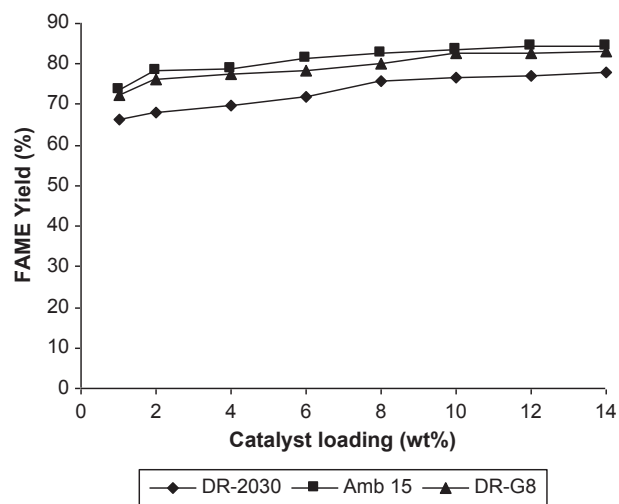


Figure 5. Effect of catalyst loading on the esterification of hydrolyzed sea mango oil (molar ratio of oil to methanol = 1:3, reaction temperature = 100°C, reaction time = 1 h).

should have enhanced the esterification process due to the availability of more active sites for the catalytic surface reactions.

The insignificant increase in FAME yield despite the addition of more catalyst could be explained by the constant amount of methanol supplied to the process. As mentioned in Figure 5, the molar ratio of methanol to oil for all catalyst loading is maintained at 1:3. With the same amount of methanol supplied to the process, it can be expected that the rate of reaction is also similar. This subsequently produces similar amount of FAME which is evident in Figure 5. On the other hand, the similar rate of reaction produces identical amount of water. This resulted in a nearly constant effect of catalyst poisoning by water on the active sites of the catalyst. However, with the addition of more catalyst, more active sites are still available for the reactions to occur. Significant increase of FAME, however, would not be expected due to the limitation of the methanol that is supplied to the process.

Figure 5 also indicates that small amount of catalyst could be adequate in converting the fatty acids into esters. As shown in Figure 5, Amberlyst 15 catalyst loading of 2 wt% is already sufficient to produce a modest 78% FAME yield. This is certainly promising as the requirement of less amount of catalyst can save the biodiesel production cost.

Effect of time

Figure 6 shows the effect of reaction time on the esterification of hydrolyzed sea mango oil using Amberlyst 15, Dowex DR-G8, and Dowex DR-2030, at 100°C, molar ratio of oil to methanol of 1:3, and catalyst loading of 5 wt%. As can be seen in Figure 6, increasing the reaction time from 1 to 5 h did not significantly improve the yield of FAME.

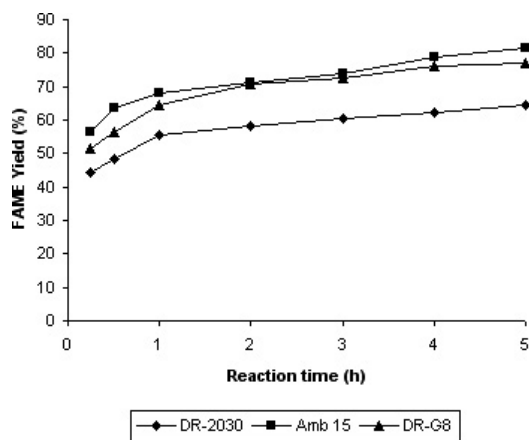


Figure 6. Effect of reaction time on the esterification of hydrolyzed sea mango oil (reaction temperature = 100°C, molar ratio of oil to methanol = 1:3, catalyst loading = 5 wt%).

Significant increase in FAME yield for all cationic ion exchange resins was only observed within the 1 h of reaction time. This may indicate that the esterification process is a fast process, whereby adsorption and desorption of reactants and products, to and from the active sites, could happen in a rapid manner. As the interaction between reactants is entirely driven by ions exchange, whereby positively charged molecules interact with negatively charged molecules, the esterification process could happen in rapidly manner, unlike those in transesterification process where reacting molecules such as triglycerides are in neutrally charged form. In heterogeneous transesterification process, the reaction time required for the conversion of oil into esters normally ranged from 1 to 5 h [13–15]. In some other cases, the reaction time required was reported to be as long as 8 h [16, 17], and even up to 18 h [18]. The long reaction time is definitely uneconomical as it is energy intensive. Therefore, the fast reaction rate by esterification process using cationic ion exchange resins, as shown in this study, could be economically more feasible for more economic biodiesel production.

Optimization

Based on the experimental results in this project, the esterification process is best carried out using Amberlyst 15. The best reaction condition is as follow: reaction temperature = 100°C, reaction time = 1 h, molar ratio of oil to methanol = 1:3, and catalyst loading = 2 wt%.

Conclusions

This study demonstrated that it is possible to produce esters (FAME) via esterification process at moderate temperature (60–100°C) using cationic ion exchange resins for biodiesel production. Amberlyst 15 was shown to have the best catalytic activity in the esterification process compared to other cationic ion exchange resins, namely, Dowex DR-G8, Dowex DR-2030, Dowex Marathon C, Dowex 50WX2, and Diaion PK228. The requirement of moderate temperature (60–100°C), much lesser amount of methanol (1:3), and also small amount of catalyst (less than 2 wt%) is advantageous to the esterification process over conventional transesterification process. Esterification process which requires a rather short reaction time (less than 1 h) compared to 3–5 h for conventional heterogeneous transesterification process could be a viable way to produce esters for utilization as biodiesel.

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Conflict of Interest

None declared.

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