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A new heterogeneous acid catalyst system for esterification of free fatty acids into methyl esters

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ABSTRACT

A new heterogeneous acid catalyst system for production of environmentally friendly fuel, biodiesel was created from ferric sulfate and non-toxic, inexpensive source of biopolymer, sodium alginate. The catalyst, in the form of ferric-alginate beads produced from the reaction of 2 wt.% sodium alginate gel with 0.1 M ferric sulfate solution gave excellent methyl ester conversion of 98% with mild reaction conditions. The esterification of 0.5 g lauric acid was carried out at optimum conditions; 16 wt.% of ferric-alginate beads (2.8 wt.% Fe) methanol refluxing temperature, 15:1 methanol to lauric acid molar ratio for 3 h. The ferric-alginate beads were reusable up to 7 times without any pre-treatment. Characterization of the ferric-alginate beads showed the formation of FeOOH that held the alginate chain in place. Thermal analysis showed that the beads are able to withstand the refluxing temperature without degradation. Iron content was found to be 0.175 g Fe/g beads as determined by AAS and 0.189 g Fe/g beads as determined by TGA. Easy catalyst separation, reusability and ability of the ferric-alginate beads to esterify lauric acid to give high conversion of methyl laurate makes this catalyst desirable for biodiesel production from high free fatty acid oils.

1. Introduction

Biodiesel, the environmentally friendly, carbon neutral fuel with low exhaust emissions [1] is the nature's answer to mankind for the depletion of the petroleum (fossil) fuel reserve. Biodiesel (monoalkyl esters) is commonly produced through the transesterification of triglycerides with low molecular alcohol (ethanol or methanol) in the presence of homogeneous basic catalysts such as sodium or potassium hydroxides, carbonates, sodium and potassium alkoxides such as sodium methoxides, sodium ethoxide, sodium propoxide and sodium butoxide [2,3]. These catalysts are basic in nature, therefore can only be used for transesterifying low free fatty acid (FFA) oil [2]. However, the production cost to synthesize biodiesel through this way is higher compared to petroleum-based diesel fuel due to the use of high quality refined oils as the feedstock [4].

These problems prompted further research toward biodiesel production using waste oils and fats of higher FFA and moisture content [5–7]. The use of such low quality feedstock for biodiesel production comes with additional concerns on the choice of catalyst. Conventional homogeneous base catalysts are no longer feasible for transesterification as the base catalyst reacts with FFA to form soap that eventually leads to difficulty in product separation and decrease in biodiesel yield. The main advantages of heterogeneous basic catalysts in transesterification are lower production cost due to catalyst reusability [8–10] and the higher tolerance toward moisture and FFA [6,9].

Another option to overcome the problem of catalyst poisoning by FFA and moisture is the usage of homogeneous or heterogeneous acid catalysts. Homogeneous acid catalysts are not preferred because of the long reaction time and difficult catalyst separation due to their corrosive nature [11]. Therefore, extensive research had been done over the years to find the most suitable heterogeneous acid catalyst to convert low quality waste oils and fats into biodiesel [5,12,13]. Russbueldt and Hoelderich [14] in their work proposed the use of sulfonic acid ion-exchange resins to pre-esterify free fatty acids into methyl esters. They achieved good methyl esters conversion with 1 wt.% catalyst and FFA to methanol ratio of 1:12.

In this work, the authors investigated esterification of lauric acid to methyl laurate using a new heterogeneous acid catalyst prepared from sodium alginate and ferric sulfate. Although the discovery of sodium alginate can be traced to more than 100 years ago [15], the usage in biodiesel production is practically unheard of except for the use of a similar biopolymer, κ-carrageenan in immobilizing lipases for enzymatic catalysis [16]. However, sodium alginate has a myriad of other uses in agricultural, biomedical [17] and waste water treatment [18]. Alginate was vehemently investigated due to its inexpensive and non-toxic nature. Ferric sulfate on the contrary,

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has been proved to work excellently as a Lewis acid catalyst for esterification [19,20]. This paper looks at the possibility of making use of the gelling property of alginate to trap ferric ions that will eventually esterify lauric acid into methyl laurate.

1.1. Materials

Lauric acid (99%) was obtained from Fluka, iron(III) sulfate hydrate was supplied by Riedel-de Haen (Switzerland) whereas sodium alginate, methanol, *n*-hexane were of QREC brand supplied by Brightchem Sdn. Bhd. (Penang). Anhydrous sodium sulfate was from BDH Chemical Ltd. (Poole, England). All the chemicals were of analytical grade. The chromatographic methyl ester standard, methyl heptadecanoate was supplied by Sigma (Deisenhofen, Germany).

1.2. Preparation of ferric-alginate beads

Approximately, 2 g of sodium alginate was added to 100 mL of distilled water (heated to 60 °C), stirred until a clear viscous solution was obtained and allowed to cool to 45 °C. Then, the viscous solution was added drop-wise using a Pasteur pipette into 100 mL of 0.1 M $Fe_2(SO_4)_3$ solution at room temperature (28–30 °C). The ferric-alginate (FA) beads formed were left to equilibrate in the ferric sulfate solution for 2 h, washed and dried in oven at 60 °C for two days.

1.3. Characterization of the catalyst

The Fe content of the FA beads was determined by whole stripping 5 beads (×5 replicates) with 36% H_2SO_4. Sodium alginate, iron(III) sulfate and FA beads were subjected to X-ray diffraction (XRD) analysis on Siemens Diffractometer D5000 using Cu Kα, 2θ range from 25° to 125° with step sizes of 0.1°, at a scanning speed of $1^\circ\,\text{min}^{-1}$. Transmission electron microscopy (TEM) measurements were performed using Philips CM12 equipped with analySIS Docu ver 3.2 image analysis system; where the 0.1 M ferric sulfate solution was dropped on to the copper-grid followed by dropping sodium alginate gel onto the grid and washing with distilled water after 2 h. The grid is then heated in oven at 60 °C for two days prior to analysis. Sample for TEM analysis was carefully prepared to emulate the preparation of the beads. Functional group analysis of sodium alginate and FA beads were done on PerkinElmer System 2000 using potassium bromide (KBr) as standard pellet technique where the spectra were recorded with a resolution of $4\,\text{cm}^{-1}$ and in the scan range of $400–4000\,\text{cm}^{-1}$. Thermogravimetric analysis (TGA) was done on the FA beads to understand the thermostability of the catalyst using Mettler Toledo TGA/SDTA 851e instrument, from 30 °C to 900 °C with $10\,^\circ\text{C}\,\text{min}^{-1}$ heating rate, under air.

1.4. Esterification of lauric acid with ferric-alginate (FA) beads as a catalyst

Lauric acid (0.5 g) was esterified with the FA beads at methanol refluxing temperature using a stirred reflux system consisting of a 50 ml round bottom flask fixed to a condenser. The esterified product was pipetted out from the reaction vessel and allowed to air dry. Once the methanol was evaporated off, the methyl laurate was clearly separated from the water produced during the esterification reaction. The methyl laurate was carefully pipetted out and added with a small amount of sodium bicarbonate (to absorb water produced during esterification) and left overnight. Then, the methyl laurate was filtered to remove the solids and kept in a vial in the refrigerator for further analysis. Firstly, the reaction time was optimized from 0 h to 4 h for maximum reaction conditions of 24 wt.% FA beads and 20:1 methanol to lauric acid molar ratio. Then, small aliquots of reaction mixture were taken out hourly for methyl esters yield determination using GC analysis. Optimization of catalyst amount and methanol to oil molar ratio were carried out at the best reaction time determined at maximum reaction conditions. The amount of beads used was varied from 4 wt.% to 24 wt.%. Methanol to lauric acid molar ratio was varied from 6:1 to 20:1. The methyl laurate produced was analyzed using gas chromatography apparatus (Agilent Technologies, 7890A GC System) fitted with a flame ionization detector (FID) and the conversion was calculated according to EN 14103 procedure with methyl heptadecanoate as the internal standard. The esterification of lauric acid catalyzed by sodium alginate was carried out as a control experiment using the optimized reaction conditions.

1.5. Reusability of ferric-alginate beads

Catalyst reusability was determined by collecting the beads after each reaction and repeating the esterification reaction with the used beads (without any further washing or treatment to the used beads) until very little or no conversion was observed (end product forms solid after drying).

2. Results and discussion

2.1. Characterization of the catalyst

When sodium alginate gel is dropped into the ferric sulfate solution, FA bead is formed immediately. The gelling property of alginate in the presence of multivalent cation is due to the ionic crosslinking that produces alginate gels with well-defined forms [21]. The amount of Fe in the beads produced was determined to be 0.175 ± 0.009 g Fe per g of beads as determined by AAS. Sreeram et al. [22] in their study on the nature of interaction of iron(III) with alginates, concluded that the interaction is better explained by assuming a site binding model. In this model, they explained that iron(III) ions are bound to the binding sites on the alginate forming spatially separated iron(III) centers on the alginate backbone. The number of binding sites per molecule of alginate of this type (brown algae) has been estimated to be 66 [22]. They also reported that iron(III) are stabilized against hydrolysis in the presence of alginate, therefore opening a myriad of industrial applications. This stabilization property of iron(III)-alginate complexes (as depicted in Fig. 1) has been utilized in the formation of the FA beads for esterification.

Based on Fig. 2, it can be seen that sodium alginate does not have any distinguished peaks for the polymers as expected of polysaccharides [23]. The XRD of the FA beads does not show any sharp defined peaks; only broad, weak XRD signals were obtained which are similar to iron oxyhydroxide–polysaccharide complexes reported [23–25]. The line broadening could be attributed to internal strain as observed by Finotelli et al. [26]. Jones et al. [27] and Coe et al. [25] also reported the possibility of the iron oxyhydroxide phase to be in the form of ‘cell contracted akaganeite’ or two-line ferrihydrite. The peaks at 2θ angles of approximately 12°, 18°, 27°, 35°, 38°, 47°, 52° and 58° are similar to the pure akaganeite (β-FeOOH) peaks as reported by Glotch and Kraft [28]. The XRD pattern of FA beads observed in Fig. 2 can be matched with typical iron oxyhydroxides but the bonding with alginate makes the peaks less defined as they are linked via the carboxylate groups of alginate (Fig. 1). Finotelli et al. [26] reported that the iron is attached to alginate as Fe(III) based on the MS and EPR spectroscopy. As expected, the EPR suggested that isolated Fe(III) ion substituted the sodium in the alginate polymeric structure, inducing the linkage of alginate units forming alginate microspheres. They also observed that

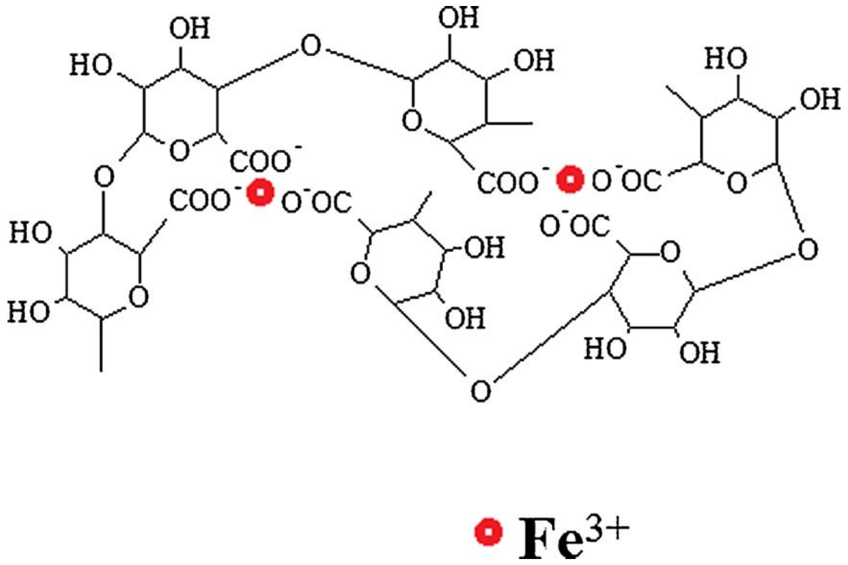

Fig. 1. Plausible structure of the beads based on the bonding scheme as suggested by Zaafarany [34].

during the formation of the microsphere, iron hydroxide particles are precipitated inside the polymer network.

A TEM picture of FA in Fig. 3 clearly shows the formation of iron oxyhydroxide particles on the grid. The poly-dispersed, dark spherical electron dense particles are the iron core (5–15 nm) that gels the alginate chains together [23,29]. As the FA sample was prepared directly on the grid using the exact same methods for FA beads preparation, the tendency for aggregation shown by the complexes on the grid is similar to the structure of the beads. The TEM shows completely separated nanoparticles as reported previously by Jones et al. [23] and Sipos et al. [29]. During the preparation of the FA beads, the alginate gel droplet comes into contact with ferric sulfate solution and forms beads immediately, similar to the aggregation of the complex on the grid. This is one of the well-known properties of alginate gels in the presence of divalent or polyvalent cations. The resultant is an ionotropic metal alginate gel where the polyvalent metal ion is chelated by the macromolecular chain [30].

The binding model of Fe(III) to alginate molecules were confirmed by FTIR analysis. Iron(III) forms metal carboxylate bonds with alginate molecules during the ion exchange interaction. Fe(III) ion in the ferric sulfate solution is exchanged with Na ion from the sodium alginate solution. The Fe(III) ion forms bonds with the carboxylate groups of alginate molecules. The sulfate ion will form bonds with sodium ions and are then washed off. Table 1 lists the functional groups identified in FTIR analysis of sodium alginate and FA beads found in this study and compared to functional groups of sodium alginate molecule reported in previous studies [31]. Filipiuk et al. [31] in their study found that the broad absorption peak at 3429 cm^{-1} is due to –OH; similar to the 3450 cm^{-1} and 3393 cm^{-1} vibrations found in this study (Fig. 4) for FA beads and sodium alginate, respectively. Two bands are exhibited by complexed carboxylate group; strong asymmetrical stretching band (1618 cm^{-1} for sodium alginate and 1636 cm^{-1} for FA beads) and a weaker symmetrical stretching band (1419 cm^{-1} for sodium alginate and 1403 cm^{-1} for FA beads). An obvious peak around

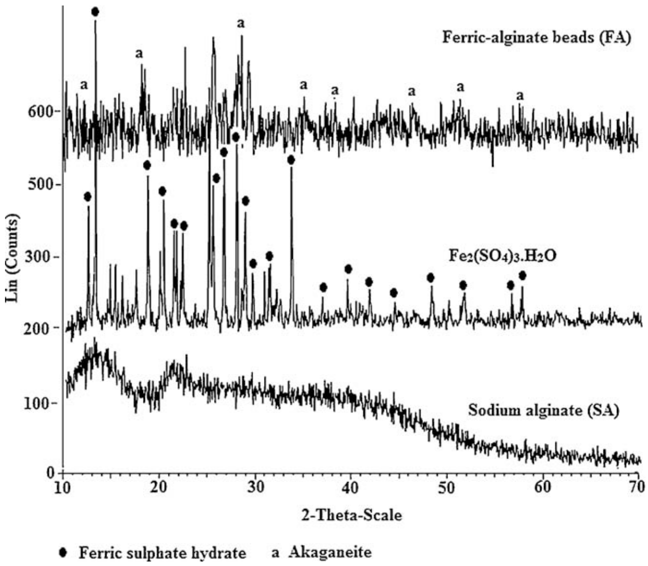

Fig. 2. XRD patterns of ferric-alginate (FA) beads, ferric sulfate and sodium alginate.

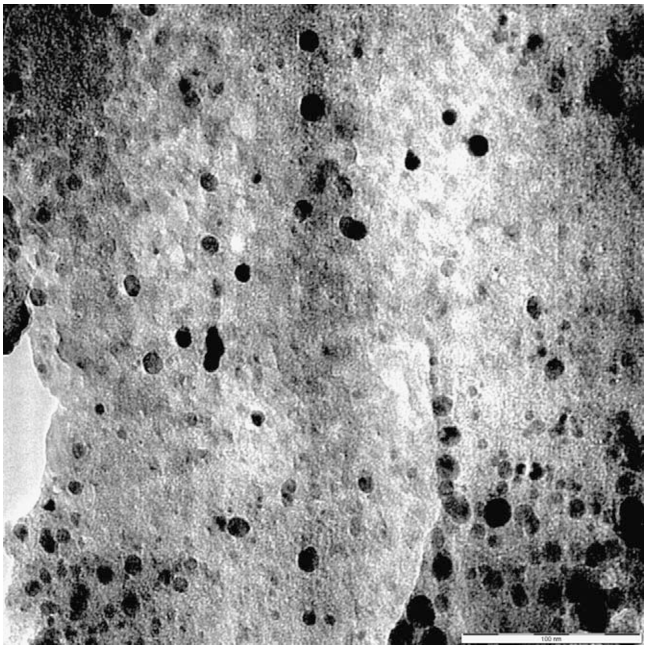

Fig. 3. TEM image of poly-dispersed iron particles in ferric-alginate.

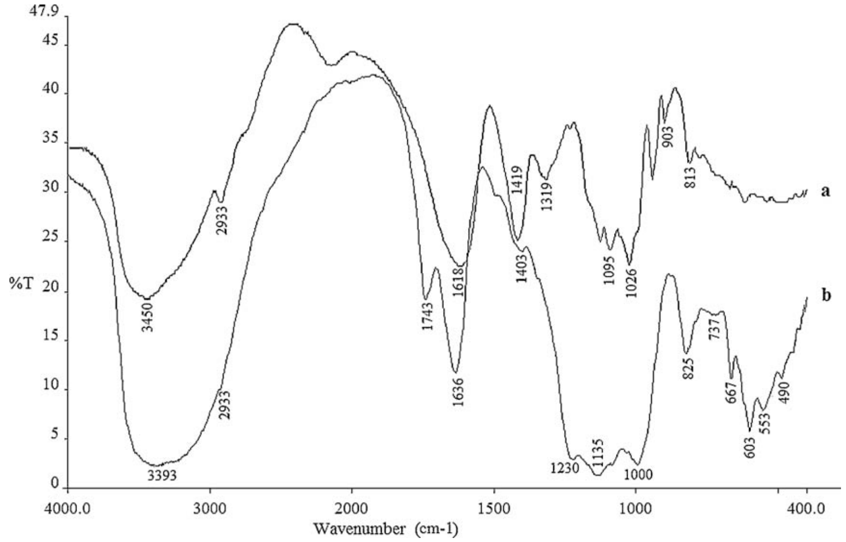

Fig. 4. FTIR spectra of (a) sodium alginate and (b) ferric-alginate (FA) beads.

1743 cm^{-1}, found only in the FA beads corresponds to C═O stretching vibration of free carboxylate anions. However, this band was not observed in the spectrum of sodium alginate. The C═O stretching bonds of alcoholic and ether groups produces broad absorption bands around 1095 cm^{-1} for sodium alginate and 1135 cm^{-1} for FA beads. The large absorption bands around 500–700 cm^{-1} in FA beads are attributed to the stretching vibrations of Fe—O bond in iron oxide as reported by Wu et al. [32]. Absorption bands around 667 cm^{-1} and 490 cm^{-1} are characteristics peaks of Fe—O stretch of akaganeite [33]. These strong broad bands are clearly absent in sodium alginate. This corresponds well with compound identification of XRD where the peaks are similar to cell contracted akaganiete. Zaafarany [34] explained in his work that a stable coordination geometry is achieved by the polyvalent metal ion by inter- or intramolecular bonding with the carboxylate and hydroxyl functional groups of alginate, respectively. Iron(III) is restricted to cross-linking via intermolecular association in their alginate complexes. This tendency toward intermolecular bonding explains the more elongated metal–oxygen bonds that decreased the bond stretching as observed in Fig. 4.

The TG–DTG curves given in Fig. 5 is similar to the typical TG–DTG curves of Fe(III)-alginate [34] and calcium alginate curves [32]. The first weight loss in the range of 30–149 °C can be attributed to evaporation of water in the sample. Weight loss ranging from 149 to 380 °C is due to the preliminary degradation of alginate and the subsequent two weight loss around 380–560 °C and 560–895 °C are due to further degradation of alginate [32,35]. This shows that at methanol refluxing temperature during esterification reaction, the beads remains intact without any degradation. Approximately 4.50 mg of beads was used for TGA analysis and the total residue at the end of the forth step is 1.22 mg. Assuming the thermal decomposition is complete and the residue is only made up Fe_2O_3; 0.189 g Fe per g of beads was obtained by stoichiometric calculations. This value is similar to the Fe content determined using AAS analysis method mentioned above.

Table 1
The main vibrational modes for sodium alginate and ferric-alginate.

Vibration	Sodium alginate[a]	Sodium alginate	Ferric-alginate
ν(OH)	3429	3450	3393
ν(CH)-anomer	2921	2933	2933
$\nu(COO^-)_{sym}$	1743	–	1743
$\nu(COO)_{sym}$	1629.3	1618	1636
$\nu(COO)_{asym}$	1419	1419	1403
δ(CCH) + δ(COH)	1320.7	1319	1230
ν(CO) + ν(CCC)	1102	1095	1135
ν(CO) + δ(CCO) + δ(CC)	1026.9	1026	1000
Mannuronic acid residues	889.7	903	825
Guluronic acid residues	821.5	813	737

[a] Literature data [31].

2.2. Optimization of ferric-alginate beads catalyzed esterification of lauric acid

Optimization of reaction time for esterification of lauric acid was carried out at maximum conditions of 24 wt.% (4.2 wt.% of Fe) FA beads and 20:1 methanol to lauric acid molar ratio. Fig. 6a shows that as the reaction progresses above 3 h, the reaction reached a plateau as there are no significant differences in the yield of methyl esters. Using this as an indicator for the completion of the esterification reaction, all other optimization reactions were carried out for 3 h. As depicted in Fig. 6b, low methanol to lauric acid molar ratio does not give satisfactory methyl ester conversion. Although theoretically, for esterification of 1 mol of lauric acid requires 1 mol of methanol to produce 1 mol of methyl laurate and 1 mol of water, the reaction will not reach completion as it is reversible. Therefore, excess methanol is required to drive the reaction forward and toward completion.

Catalyst amount more than 16 wt.% (2.8 wt.% Fe) did not make much difference to the methyl laurate conversion as almost 100% yield had been obtained. The ferric ion in the beads that holds the alginate structure together is postulated to act as a Lewis acid site for attachment of fatty acids for formation of methyl esters [36]. Carbonyl oxygen of lauric acid molecule attaches to the ferric ion making the carbonyl carbon susceptible for nucleophilic attack by methanol. Comparing the results of this experiment to esterification of waste cooking oil using ferric sulfate by Gan et al. [20], the authors reported 59% free fatty acids conversion in a 1 h reaction with methanol to oil molar ratio of 15:1 and catalyst concentration of 2 wt.% at 60 °C. Wang et al. [19] in their two-step catalyzed process for biodiesel production from waste cooking oil obtained 97% free fatty acid conversion in 4 h at methanol to oil molar ratio of 10:1 and 2 wt.% ferric sulfate concentration at 95 °C. Based on the optimization results of this study, the best conditions for esterification of lauric acid (0.5 g) using ferric-alginate beads was found to be 16 wt.% beads (2.8 wt.% Fe, catalyst amount to lauric acid mass ratio

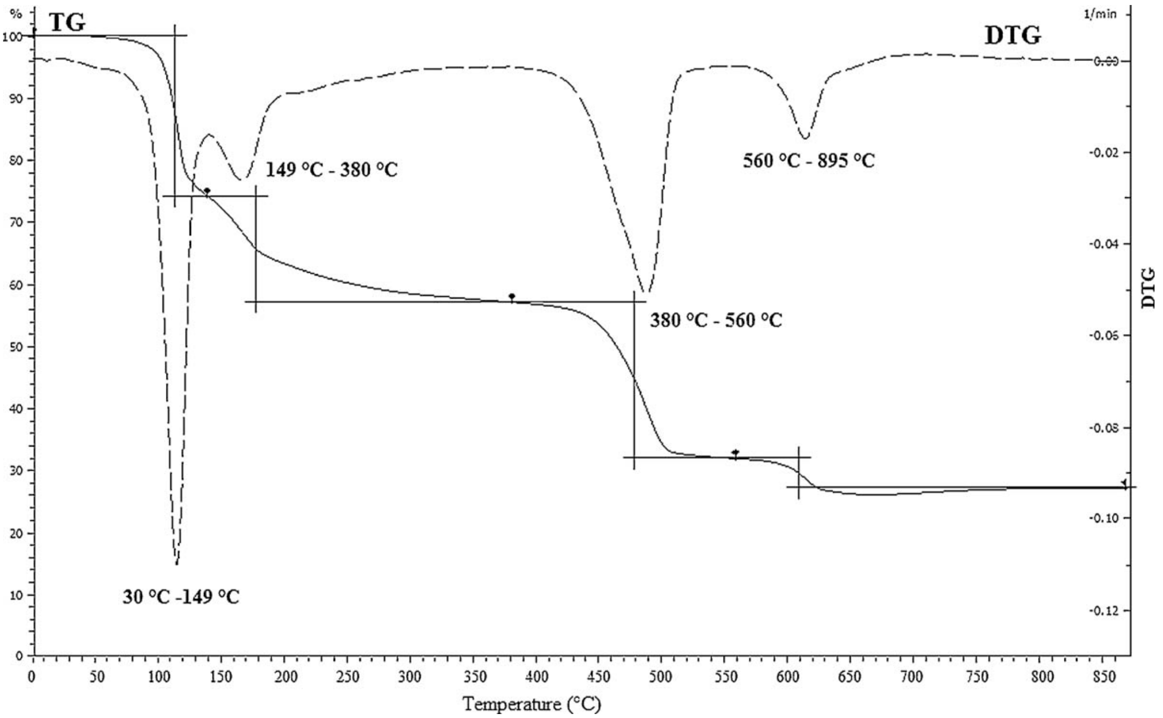

Fig. 5. Typical TGA curve of ferric-alginate (FA) beads.

of 0.16:1) and 15:1 methanol to lauric acid molar ratio refluxed at methanol refluxing temperature for 3 h with methyl ester yield of 98 ± 0.7%. Esterification of lauric acid catalyzed by sodium alginate did not show any catalytic activity proving that the esterification reaction was catalyzed by FA beads. The presence of an obvious peak at 1748 cm^{-1} for free carboxylate anions in FTIR spectrum (attached as supplementary data) of reused FA beads clearly shows that the anion did not take part in the esterification reaction.

2.3. Catalyst reusability

The reusability test showed that the FA beads can be used up to 8 times with more than 90% conversion of methyl esters (Fig. 6c). After 7 times reuse, the beads were found to start disintegrating. This could be due to the repeated heating and agitation of the beads during the esterification reaction. Gan et al. [20] reported that at 2 wt.% ferric sulfate concentration, the catalyst is

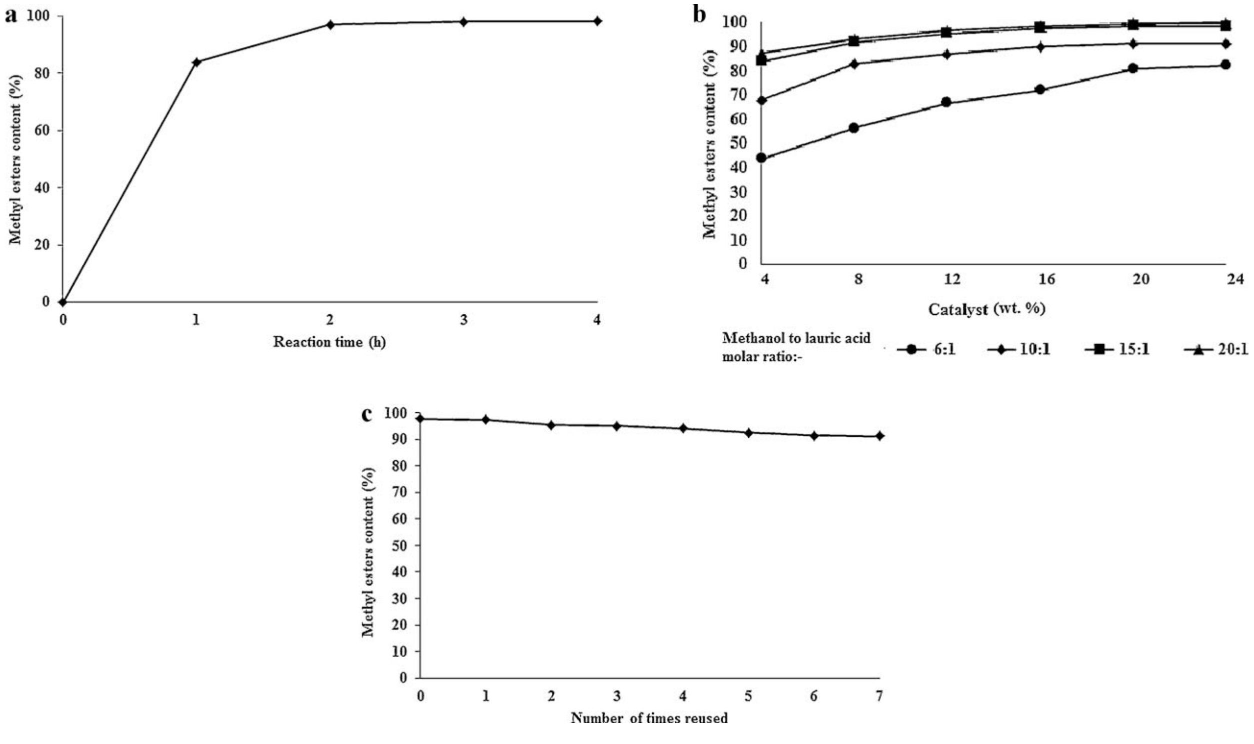

Fig. 6. Optimization graphs of (a) esterification reaction time (0.5 g lauric acid, 0.12 g beads, 20:1 methanol to lauric acid molar ratio, 60 °C), (b) methanol to lauric acid molar ratio and catalyst amount (0.5 g lauric acid, 3 h, 60 °C) and (c) catalyst reusability (0.5 g lauric acid, 0.08 g beads, 15:1 methanol to lauric acid molar ratio, 60 °C, 3 h).

fully dissolved in the reaction mixture. The reaction was reported to follow the pseudo-homogeneous pathway where H^+ ions are produced through hydrolysis of metal complex $[Fe(H_2O)_6]^{3+}$ (aq). No recovery or reuse of the catalyst was reported. Comparing this to FA beads, easy catalyst removal and reuse without any further treatment adds appeal to FA beads to be used as a catalyst for esterification. Crosslinking agents (multivalent cations), as in this case Fe (III), increases the water resistance of alginate [37]. Therefore, catalyst removal and reuse is done with ease. AAS analysis of the reused beads shows that the beads contain 0.168 ± 0.0025 g Fe/g beads.

3. Conclusion

FA beads prepared from reaction of sodium alginate and ferric sulfate showed great potential as a heterogeneous acid catalyst for esterification of free fatty acids. Thermal analysis showed that the prepared catalyst is able to withstand refluxing temperature enabling esterification reaction without catalyst destruction. The prepared ferric-alginate beads as catalyst for esterification of lauric acid gave 98% methyl esters yield in a 3 h reaction, with catalyst amount to lauric acid mass ratio of 0.16 (2.8 wt.% Fe) and methanol to lauric acid molar ratio of 15:1. Catalyst separation was done easily and reused without any treatment up to 7 times with more than 90% methyl ester yield. Iron content determined by AAS and TGA was 0.175 g Fe per g of beads and 0.189 g Fe per g of beads, respectively. This new catalyst system paves way for biodiesel production from high free fatty acids oils.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2012.04.036.

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