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Production of Biodiesel from Cottonseed Oil over Aminated Flax Fibres Catalyst: Kinetic and Thermodynamic Behaviour and Biodiesel Properties

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Abstract

The transesterification of cottonseed oil in the presence of methanol to fatty acid methyl ester (FAME) using flax-based fibres catalyst modified with an alkaline moiety was studied. The catalyst was prepared by radiation induced grafting (RIG) of glycidyl methacrylate (GMA) onto dignified flax fibres followed by amination with diethylamine (DEA) and treatment with NaOH solution. A maximum FAME conversion of 88.6% was obtained at 60°C with a catalyst dosage of 2.5 wt%, an oil/methanol ratio of 1:33 and a time of 2 h. The biodiesel quality was verified by nuclear magnetic resonance (^{1}H NMR). Kinetic analysis showed a reaction activation energy of 69.33 kJ·mol^{-1} and a rate constant of 0.00349 min^{-1} indicating that the catalytic reaction was kinetically controlled. Thermodynamic analyses revealed that the reaction was reversible, non-spontaneous and endothermic with an enthalpy of 66.62 kJ·mol^{-1}. The obtained biodiesel showed physical and chemical characteristics complying with ASTM D6751. It can be concluded that the alkaline biopolymer catalyst prepared in the present study is a promising green candidate for biodiesel production.

Keywords

Biodiesel Production, Radiation Grafted Basic Flax Fibres Catalyst,

Cottonseed Oil, Transesterification Kinetics and Thermodynamics, Radiation Induced Grafting

1. Introduction

Biodiesel is an alternative fuel to petro-diesel derived from renewable resources including vegetable oils. The advantages of biodiesel such as biodegradability, sustainability, non-toxicity and low gas emissions (e.g. SO_x and NO_x emission) made it promising fuel for reduction of greenhouse gas emission and mitigation of climate change. This has led to a major surge in the biodiesel production in the past few decades [1].

Biodiesel is fatty alkyl esters that are commonly obtained by transesterification of triglycerides in vegetable oils with methanol yielding mixtures of fatty acid methyl esters (FAME). Transesterification is widely carried out using homogenous basic catalysts like alkaline metal alkoxides or hydroxides. However, this process has low production efficiency caused by complicated downstream processing involving high cost and energy consumption for the recovery of excess methanol and catalyst in addition to massive water discharge despite FAME high yield. Thus, the interest in the development of heterogeneous catalysts for improving biodiesel production gained an increasing interest because of their advantages pertaining to cost reduction and environmental protection compared to homogeneous catalysts [2] [3].

Various types of heterogeneous catalysts with established kinetics have been used for production of biodiesel through transesterification and esterification reactions. Majority of tested heterogeneous catalysts for biodiesel production are inorganic materials [3]. Many solid acidic and basic inorganic catalysts have been studied for the transesterification of various vegetables oils. Solid base catalysts (e.g. cheap alkaline earth metal oxides) have been found to be effective in transesterification of vegetable oils with low free fatty acids (FFA) content compared to most of the solid acid catalysts. However, these catalysts are very sensitive to water, CO_2 and FFA content, which eventually deactivates the catalyst by saponification [4].

Polymer catalysts with ionic groups have been proposed as alternatives to inorganic catalysts. Particularly, ionic materials such as ion exchange resins and their corresponding functionalized polymeric materials have been considered for replacing heterogeneous catalysts for transesterification and esterification reactions for biodiesel production [2]. The catalytic activity of such materials depends heavily on the number of functional groups (active sites) and their accessibility by the reaction mixtures [5]. Thus, the application of ion exchange resins for catalysis depends heavily on the resin morphology [6] [7] [8]. However, resins with their porous structures have slow kinetics and mass transfer limitations and thus, catalysts with fibrous substrates have potential to overcome such limi-

tations by providing better access to active sites.

The potential of application of fibrous basic catalyst prepared by radiation induced grafting (RIG) of vinylbenzyl chloride onto polyethylene (PE) nonwoven sheet followed by amination for transesterification of triolein with various types of alcohols was investigated [9] [10]. Similar radiation grafted and aminated catalyst based on PE/polypropylene (PE/PP) nonwoven sheet was evaluated for transesterification of triacetine [11]. The potential of replacing synthetic PE and PE/PP substrates with flax (*Linum usitatissimum*) [12] and kenaf [13] fibres for preparation of aminated radiation grafted polymer catalyst based on natural fibres was recently explored. The preparation process involved RIG of glycidyl methacrylate (GMA) and subsequent amination with diethylamine and the obtained catalyst was preliminarily tested for transesterification of cottonseed oil/methanol [14]. The use of such natural fibres having low cost and good tensile strength [15] is motivated by the environmental friendless of lignocellulosic biomass and the ability to functionalise natural fibres, ease of handling, recoverability and higher supporting capacities than of synthetic resins counterparts [16]. Despite the green preparation route, value added to flax fibres and promising performance of radiation grafted catalyst based on aminated flax fibres in biodiesel production, no kinetic and thermodynamic investigations were conducted to assist further development and scaling up of transesterification reaction in addition to absence of any investigation on the quality of biodiesel obtained with this type of catalysts.

The objective of this study is to investigate kinetics and thermodynamics of transesterification of cottonseed oil in presence of methanol over the new basic biopolymer catalyst containing diethylamine (DEA)/poly(GMA) grafted on flax fibres. Such kinetic investigations is highly important for designing a scaled production process and it involves determination of reaction rates, rate constants and activation energy. The enthalpy, entropy and Gibbs free energy were also calculated. The physico-chemical characteristics of the obtained biodiesel were evaluated. The selection of cottonseed oil as a source of triglyceride together and flax fibres as substrate for catalyst making was motived by their low cost and abundance in countries like Sudan and Egypt.

2. Experimental

2.1. Materials

Flax fibres were obtained from Tanta Flax Ltd. Co. (Egypt). GMA monomer with 97% purity, polyoxyethylene sorbitan monolaurate (Tween-20) and isopropanol were purchased from Sigma Aldrich. Sodium hydroxide (97%), sodium chlorite (80%) and nitric acid (≥65%) were obtained from Sigma Aldrich and used to prepare the needed solutions in deionized water (DI). DEA (99.5%), methanol (99.8%) were purchased from Sigma Aldrich. All chemicals were used without further purification. Cottonseed oil (low grade) was obtained from a commercial supplier in Sudan and used as a source of triglycerides for biodiesel production.

2.2. Characterizations of Cottonseed Oil

The cotton seed oil properties such as saponification value, acid number and FFA contents were determined according to the Standard Methods of the American Oil Chemists' Society, AOCS.

2.3. Preparation of Aminated Poly(GMA) Grafted Flax Fibres Catalyst

The catalyst obtained in this study was prepared in 3 steps involving: 1) irradiation of delignified flax fibres, 2) RIG of grafting of GMA onto irradiated flax fibres and 3) treatment of grafted fibres with DEA and NaOH. The flax fibres were placed in a PE bag, which was sealed after blowing with purified N_2 and irradiated with an electron beam accelerator (Nissin High Voltage, Model: EPS 3000, Japan) over dry ice to a dose of 20 kGy at 5 kGy/pass. The irradiated flax fibres were removed and stored under freezing conditions of −40°C overnight before it was reacted with deoxygenated emulsion solution comprising of 5% GMA containing 0.5% Tween 20 surfactant at 40°C for 1 h. The grafted fibres were removed, rinsed and washed few times with methanol to completely remove any homopolymer. The degree of grafting (DG) was determined from the weight increase after grafting and was found to be 148% under the present conditions. More details on the preparation procedure can be found elsewhere [12]. The poly(GMA) grafted flax fibres [Flax-*g*-poly(GMA)] were aminated to a maximum amine density of 3.66 mmol/g, which was achieved at 80% EDA concentration, 80°C reaction temperature and 3 h reaction time [14]. The obtained functionalised fibres denoted as Flax-*g*-poly(GMA)/DEA was rinsed in 1 M NaOH solution for 16 h to introduce OH⁻ as a counter ion [11].

The total specific surface areas of the aminated catalyst and its corresponding grafted and delignified flax fibres were determined with N_2 as an adsorbate using 1 g of the sample using the Brunauer-Emmett-Teller (BET) technique by a Micromeritics' Gemini VII 2390 surface area analyser.

2.4. Transesterification of Cottonseed Oil with Methanol

The performance of the new catalyst [Flax-*g*-poly(GMA)/DEA] was evaluated for transesterification of cottonseed oil and methanol in a batch mode according to the procedure described in the literature and the conversion of fatty acid methyl ester (FAME) was mentioned using ¹H NMR. The Flax-*g*-poly(GMA)/DEA was treated with 1 M NaOH aqueous solution followed by washing with DI water and drying prior to use [17]. The catalyst and methanol were placed in 3-neck-round flask and the mixture was shacked for 10 min to swell the catalyst. The cottonseed oil was then introduced and the mixture was vigorously stirred using a magnetic stirrer at 300 rpm. The mixture was heated to different temperatures in an oil bath for various periods of time. The kinetics and thermodynamic investigations were evaluated for transesterification of cottonseed oil/methanol mixture at an optimum catalyst loading of 2.5 wt% and oil/methanol ratio of 1:33. The reaction time and temperature were varied in the ranges of 30 - 120

mins and 45˚C - 65˚C, respectively. The sampling process involved taking 5 ml of FAME samples at the desired temperature and time before transferring to ice bath to stop the reaction. After cooling, the samples were centrifuged to obtain the biodiesel samples required for the kinetic and thermodynamic investigations.

2.5. Evidence of FAME Conversion

The obtained products of the transesterification reaction were analysed using the Bruker Advance II 400 MHz model, ^{1}H NMR. The analysis was carried out by dissolving 0.050 mL of FAME sample in 0.5 mL of 99% deuterated chloroform (CDCl$_3$) and placed in the sample tubes. The sample was shaken carefully and transferred to the NMR probe (with 5 mm internal diameter) before analysis. The resulting spectra were recorded at room temperature and the obtained data was processed using Topsin software (version 3.1). Subsequently, the ^{1}H NMR spectra were used to identify the biodiesel products. The percentage of conversion to FAME was calculated according to the following equation [18].

$$\%\text{Conversion to FAME} = \left[\left(A_1/3 \right) \big/ \left(A_2/2 \right) \times 100 \right] \tag{1}$$

where, the terms A_1 represents the area of methoxy protons from methyl esters at chemical shift of 3.68 (singlet peak) and A_2 is the area of methylene protons from the triglycerides at chemical shifts of 2.30 ppm (triplet peak). The factors 3 and 2 are derived from the number of attached protons at the methoxy and methylene carbons.

2.6. Characterisation of Biodiesel

The physico-chemical characteristics of FAME obtained from transesterification of cottonseed oil with methanol were evaluated according to ASTM standard tests presented in Table 1.

2.7. Reaction Kinetics

The pseudo-first order model was adopted for the transesterification reaction in this study because an excess methanol to oil ratio (33:1) was used compared to the stoichiometric molar ratio of 3:1 required for this reaction. Considering such methanol excess, the rate law equation used to express the reaction in this study is as follows:

Table 1. Lists of the specifications ASTM biodiesel standard test.

Quality test	Standard methods
Pour point (min)	D 97
Kinematic viscosity at 40˚C (mm^2/s)	D 445
Flash point (˚C)	D 93
Density at 30˚C (mg/cm^3)	D 6751
Cloud point (˚C)	D 2500
Cetane number	D 613

$$-\ln\left(1-x\right) = kt \tag{2}$$

where, k is the apparent rate constant, t is reaction time and x is cottonseed oil concentration converted to FAME [19] [20]. Consequently, the temperature dependent rate constant, k was deduced from the slope of the line obtained by plotting $-\ln\left(1-x\right)$ against time (t) [21]. Moreover, the activation energy was determined in the temperature range of 45°C - 65°C using the Arrhenius equation [22]:

$$\ln k = \ln A - \frac{E_a}{RT} \tag{3}$$

where, k represents the apparent reaction rate constant, A is pre-exponential factor, E_a is the activation energy (kJ/mol), R is the universal gas constant and T is the reaction temperature (K).

2.8. Thermodynamics of the Reaction

The thermodynamic parameters such as enthalpy ($\Delta H^\star$) of transesterification was obtained using *Eyring* equation [20]:

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^*}{R}\left(\frac{1}{T}\right) + \left[\left(\ln\frac{k_B}{h}\right) + \frac{\Delta S^*}{R}\right] \tag{4}$$

where, k is the apparent rate constant, T is the temperature, R is universal gas constant (8.314 J·mol^{-1}·K^{-1}), k_B is Boltzman's constant (1.38×10^{-23}), h is Plank's constant (6.63×10^{-34}) and $\Delta S^\star$ is the entropy of transesterification. The entropy ($\Delta S^\star$) was determined from the intercept of the *Eyring* equation plot as expressed in Equation (5):

$$\text{Intercept} = \left[\left(\ln\frac{k_B}{h}\right) + \frac{\Delta S^*}{R}\right] \tag{5}$$

The Gibbs' free energy (ΔG^*) was calculated using Equation (6):

$$\Delta G^* = \Delta H^* - T\Delta S^* \tag{6}$$

2.9. Catalyst Deactivation Studies

The deactivation of prepared alkaline catalyst was observed for 4 cycles using a mixture of cottonseed oil/methanol solution at optimum conditions of oil-methanol molar ratio of 1:33, catalyst concentration of 2.5 wt% (catalyst/oil), reaction temperature of 60°C and time of 2 h. After each reaction, the catalyst was recovered by filtration followed by washing with methanol and 5% (v/v) citric acid and thereafter by treatment with 1 M NaOH according to the procedure reported by elsewhere [9].

3. Results and Discussion

3.1. Properties of Cottonseed Oil

The content of FFA and water are well known to affect the selection of the catalyst of biodiesel production [2]. Particularly, it is well established that the high

FFA and water contents lead to the production of large amounts of soap, which in turn lower the yield of FAME and makes its separation from glycerol difficult. The results of the analysis of cottonseed oil presented in Table 2 shows a negligible moister content (0.05%), a low FFA value (0.35%) and a low acid value (0.36 mg KOH/g). Such low FFA content confirms that transesterification with alkaline polymer catalyst is suitable for producing biodiesel from cottonseed oil in this study. Similar low FFA values were reported in literature for refined cottonseed oil [23] and its raw counterparts [24] [25].

The ^{1}H NMR spectrum for cottonseed oil is presented in Figure 1. A number of characteristic peaks resembling the triglycerides in cottonseed oil can be observed. Particularly, the peaks at δ 0.80 - 1.01 ppm correspond to the protons of the terminal methyl group whereas, the peaks in the range of δ 1.20 - 1.41 ppm represent the protons of all the internal CH_2 groups available in the fatty acid backbone [26]. The peaks shown at δ 1.53 - 1.70 ppm stand for the protons of CH_2 group neighbouring the terminal methyl group. The peaks at δ 1.94 - 2.11 ppm are assigned for allylic protons of $-CH_2$, whereas the peaks at δ 2.28 - 2.35 and 2.74 - 2.78 ppm represent the α-protons of the ester groups and CH_2 of double allylic protons, respectively. The doublet peaks at δ 4.09 - 4.34 ppm are assigned for protons in $-CH_2$ (C_1 and C_3) of glyceride moiety [27]. The peak at 5.25 is assigned for methinine protons present at C_2 of glyceride. The peaks appears at δ 5.28 - 5.43 ppm for protons of the olefinic (-CH=CH) moiety. It can be concluded that the characteristic peaks of the triacylglycerol chains in cottonseed oil are in a complete agreement with the literature [28].
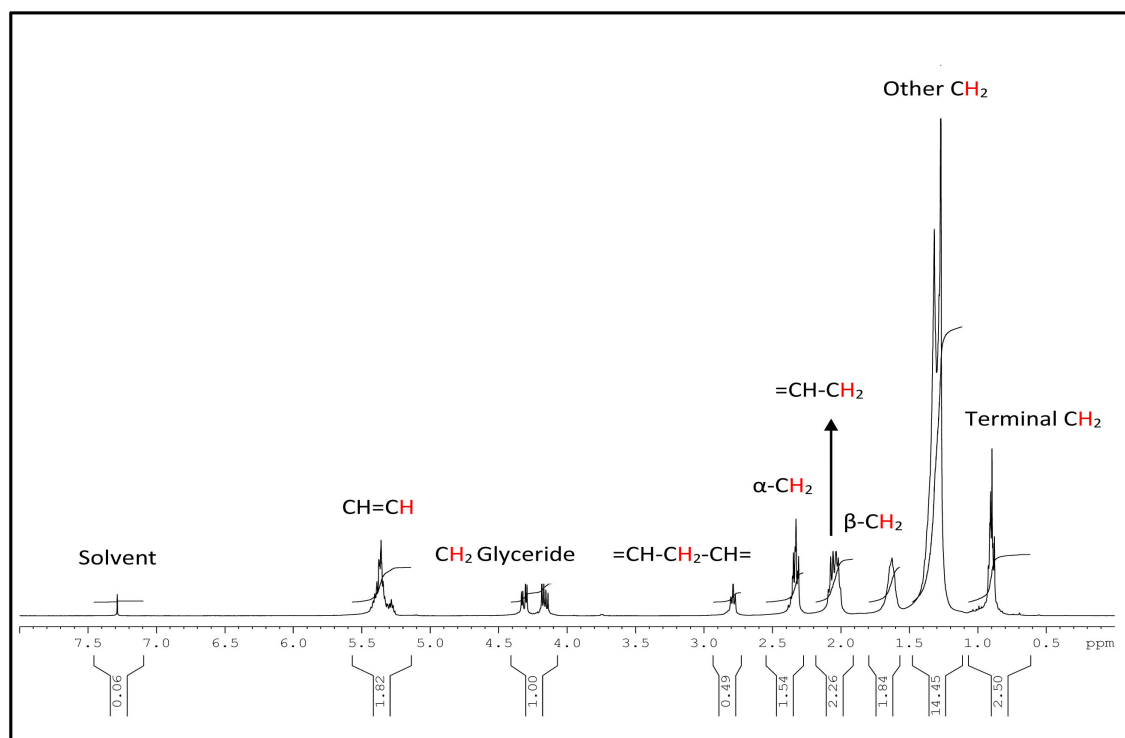
Figure 1. ^{1}H NMR Spectra of cottonseed oil.

Table 2. Physico-chemical properties of cottonseed oil.

Quantity	Units	Feedstock
Moisture (hot plate)	%	0.05
Saponification value	mg KOH/g	199.7
Free fatty acid	%	0.35
Iodine value	-	98.4
Acid value	mg KOH/g	0.36
Density (30˚C)	(mg/cm^3)	0.8752
Kinematic viscosity (40˚C)	mm^2/s	33.1

3.2. Properties of the Alkaline Biopolymer Catalyst

A new alkaline catalyst containing aminated poly(GMA) grafts covalently bonded to flax fibres and complexed with OH$^-$ counter ion was prepared by RIG of GMA onto delignified flax fibres followed by functionalisation with EDA and treatment with NaOH solution. The evidence of chemical changes accompanied incorporation of poly(GMA) and subsequent immobilization of EDA was in forms of two levels of feature changes as reported in our latest study [29]. Grafting was reported to impart chemical changes represented by the appearance of acrylate and epoxy related peaks in the grafted fibres. The introduction of DEA imparted amine (-NH$_2$) peaks overlapping with hydroxide (-OH) that was coupled with a substantial reduction in the epoxy rings peaks. The amine density in the obtained catalyst was found to be 3.65 mmol·g^{-1} and a degree of amination close to 100% was achieved using the adopted procedure [29].

The SEM images of raw, bleached, poly(GMA) grafted and aminated flaxfibres imported morphological changes in the flax fibres as reported elsewhere [12]. The raw flax fibre displayed a rough surface with a network structure comprising tight bundles of microfibrils bound together by hemicellulose. This was changed to cleaner and smooth surface in bundles of continuous cellulose microfibrils aligned along the fibres' direction. The introduction of poly(GMA) grafts imparted thick layers to the delignified flax microfibrils causing an increase in fibre diameters compared to the raw and bleached fibres. Additional increase in the diameter after amination of the grafted fibres with swelling causing some microfibrils structure to purse [29]. The published FTIR and SEM results provided strong evidence for grafting and amination of the fibres investigated.

A summary of the BET-adsorption properties of Flax-*g*-poly(GMA)/DEA catalyst together with the corresponding grafted and original flax fibres is presented in **Table 3**. The total specific surface area was 5.9 cm^3·g^{-1} with pore volume of 55 (mm^3·g^{-1}). Apparently, such values were increased starting from the untreated flax, delignified flax and grafted flax fibres and this trend is caused by incorporation of poly(GMA) and DEA in the flax fibres after each treatment.

Table 3. BET data for flax-*g*-poly(GMA)/DEA catalyst.

| Samples	Specific surface area (cm³·g⁻¹)	Pore volume (mm³·g⁻¹)
Untreated flax	0.33	32
Delginfied flax	0.63	40
Flax-*g*-poly(GMA)	1.3	35
Flax-*g*-poly(GMA)/DEA	5.9	55

3.3. Effect of Temperature on Conversion to FAME

The variation of conversion to FAME with the reaction time at different temperatures is shown in Figure 2. As can be observed, from one hand, there is a gradual increase in the conversion as the time prolonged at all temperatures. On the other hand the rise in the temperature from 45°C to 60°C led to an increase in the FAME conversion beyond which it started to decline. The former trend was due to the increase in the access of the reactants to the active groups available on catalyst with longer reaction times whereas the conversion-temperature dependence is most likely caused by the higher energy state of the molecules resulting in a reduction in the viscosity of reaction mixture that prompted more effective interactions accelerating conversion to FAME. When the temperature increased to 65°C, methanol started to evaporate and thus the reaction rate started to decline [30] [31]. The results of this study is at par with the transesterification of cottonseed oil using a liquid alkaline catalyst (NaOH) of 1 wt% concentration at 1:6 oil/methanol molar ratio, 60°C temperature and 90 min reaction time that yielded 93% maximum FAME conversion [24]. A close yield of 92% biodiesel was also reported when cottonseed oil was transesterified with methanol using CaO catalyst at reaction temperature, time, methanol/oil ratio and catalyst loading rate of 60°C, 50 min, 12:1 and 3% (wt%), respectively [32].

3.4. Evidence of Biodiesel Formation

The analysis of biodiesel considered in this study is based on the fact that the amplitude of a proton nuclear magnetic resonance (^{1}H NMR) signal is proportional to the number of hydrogen nuclei contained in the molecule. The presence of FAME *i.e.*, biodiesel could be observed when standard biodiesel spectrum depicted in Figure 3 is compared with that of cottonseed oil shown in Figure 1. A summary of the assignments of the peaks of 1 NMR spectrum of FAME and that of cottonseed oil is presented in Table 4. The -CH$_2$ protons related to the glyceride of cottonseed oil, which appeared at the range of δ 4.09 - 4.34 ppm in Figure 1 is completely disappeared. This was accompanied by the appearance of a strong peak at δ = 3.68 ppm representing -OCH$_3$ related to FAME [33]. The conversion (%) of triglyceride to FAME was calculated by taking the ratio of peak area of methoxy protons from methyl esters which appears at δ = 3.68 ppm whereas the methylene proton was at δ = 2.3 ppm as given in Equation (1) [18]. These results confirm the formation of FAME as a result of transesterification of cottonseed oil and methanol under the investigated conditions.
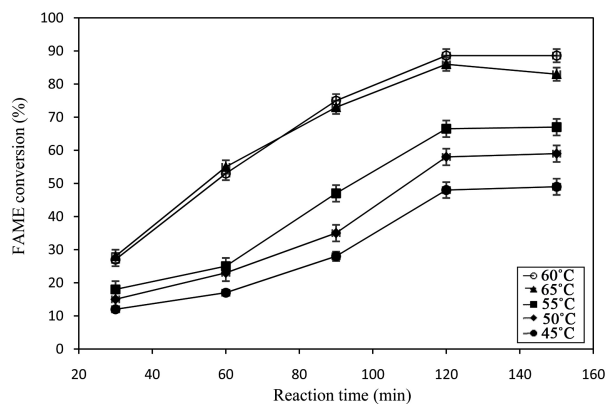
Figure 2. Variation of conversion to FAME with time at different temperatures (2.5 wt%, 33:1 methanol/oil molar ratio, 2 h).
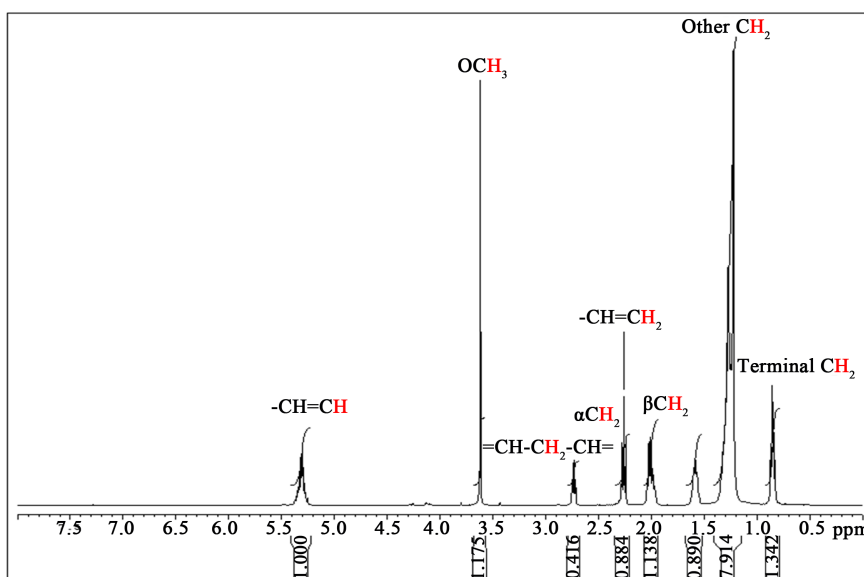

Figure 3. ^{1}H NMR spectra of FAME (biodiesel).

Table 4. ^{1}H NMR characteristic peaks of FAME and corresponding cottonseed oil.

| Proton (s)	Functional group	Chemical shift, δ (ppm)	
		Oil	Biodiesel
CH$_3$-C	Terminal methyl group	0.80 - 1.01	0.8 - 1.0
-(CH$_2$)$_n$-	Backbone CH$_2$	1.20 - 1.41	1.22 - 1.42
-CH$_2$CH$_2$-COOH	β-methylene proton	1.53 - 1.70	1.55 - 1.69
=CH-CH$_2$-	α-methylene group to one double bond	1.94 - 2.11	1.93 - 2.10
CH$_2$COOR	α-methylene group to ester	2.31	2.31
=CH-CH$_2$-CH=	α-methylene group to two double bonds	2.76	2.77
-COOCH$_3$	Methyl group of ester	-	3.67
-CH$_2$OCOR	Methylene group (C$_1$ and C$_3$) of glyceride	4.09 - 4.34	-
-CHOCOR	Methinine proton at C$_2$ of glyceride	5.25	-
-CH=CH-	Olefeinic protons	5.28 - 5.43	5.27 - 5.41

3.5. Kinetics of Reaction

The relationship between $-\ln(1 - X)$ and time for transesterification of cotton-seed oil in methanol over the aminated poly(GMA) grafted flax fibres at various temperatures (45°C - 60°C) and 1:33 oil-methanol ratio, 2.5 wt% catalyst dosage are shown in Figure 4. The linear fitting of the data showed the suitability of the pseudo first order model especially at 60°C. The apparent rate constants from the plots following this pseudo first order model at different temperatures are given in Figure 5. The reaction rate increased with the increase in the temperature and reached a value of 0.00345 (3.45×10^{-3}) min^{-1} at a temperature of 60°C beyond which it slightly declined to 0.00305 (3.05×10^{-3}) min^{-1} with rise of temperature 65°C. This is online with the effect of temperature on conversion cotton seed oil to FAME presented in Figure 2. Similar reaction rate constant increasing trend was reported for transesterification of soybean oil and methanol using calcium methoxide at different reaction temperatures (55°C - 65°C) [34]. It note worth mentioning that the low values of apparent reaction rate constants in the present study suggests that the mass transfer limitations are minimal in the present transesterification reaction and confirms that the kinetics of biodiesel production is controlled by the adsorption of methanol onto the active sites of the catalyst. Similar observation was reported in literature for transesterification of cotton seed oil with methanol over calcined clam shell catalyst [35].
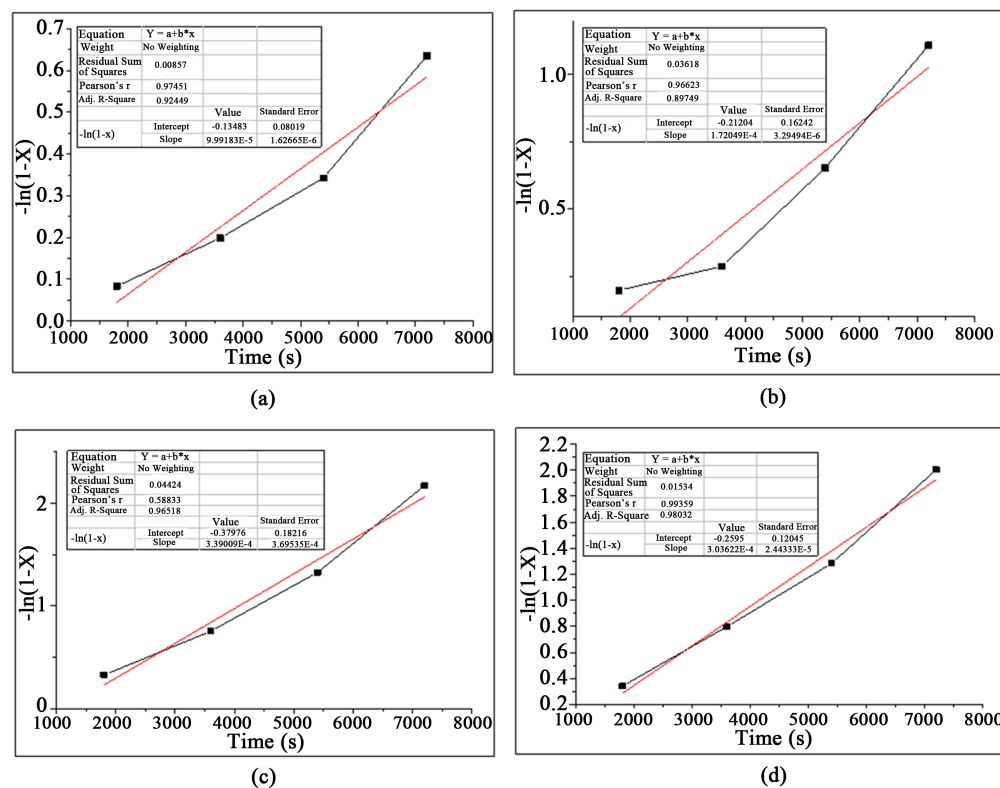
Figure 4. Plots of $-\ln(1 - X)$ vs. time for transesterification of cottonseed oil in methanol over aminated poly(GMA) grafted flax fibres: (a) 45°C; (b) 50°C; (c) 55°C and (d) 60°C (reaction conditions: 1:33 oil-methanol ratio, 2.5 wt% catalyst dosage).
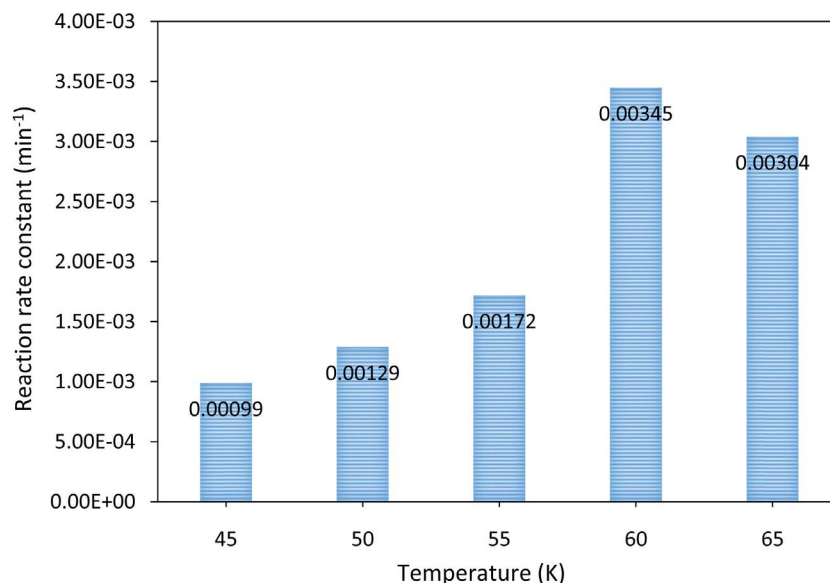
Figure 5. Variation of apparent reaction rate constant with temperature for transesterification of cottonseed oil with alkaline biopolymer catalyst.

The values of E_a was obtained from the Arrhenius plot showing ln k versus 1/T as depicted in **Figure 6**. The E_a was found to be 69.33 kJ·mol^{-1}. It is well established that the E_a values can also be used to determine whether a reaction is controlled by kinetics or mass transfer. When E_a values are within the range 26 - 82 kJ·mol^{-1}, the reaction is controlled by kinetics, otherwise it is controlled by mass transfer effect [20]. Therefore, it can be concluded that the transesterification of cottonseed oil with methanol using the aminated flax fibres in the present study is kinetically controlled and is free of mass transfer limitation.
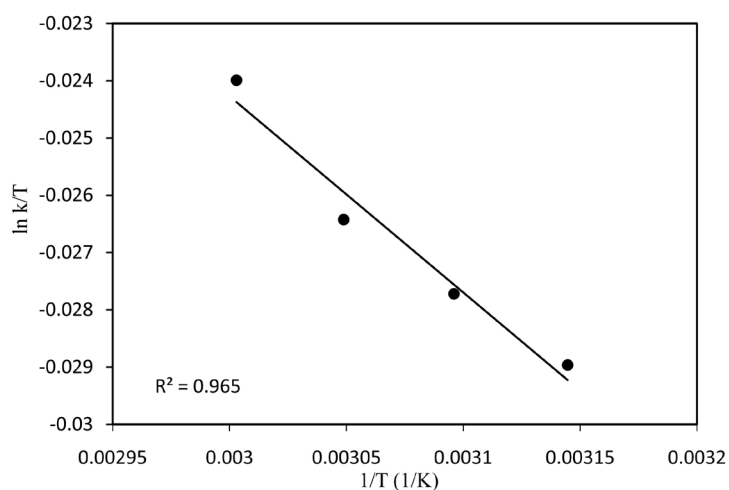
3.6. Thermodynamics

Figure 7 shows the Eyring plot for transesterification of cottonseed oil in methanol over aminated poly(GMA) grafted flax fibres, which was used to obtain the $\Delta H^{\star}$ of the reaction according to Equation (4). The $\Delta H^{\star}$ was found to be 66.62 kJ·mol^{-1}. The positive value of $\Delta H^{\star}$ indicates that the reaction is endothermic and the aminated catalyst with highest active site has the lowest energy requirement for the reaction. This leads to the highest conversion rate, which is in a close agreement with kinetics study.

The $\Delta S^{\star}$ was obtained from the intercept of *Eyring* equation plot expressed in Equation (5) and was found to be -113.269 kJ·mol^{-1}. The negative value of $\Delta S^{\star}$ confirms that the transesterification reaction with the present catalyst is reversible in nature. It can be suggested that there is an associative reaction mechanism in which reactant species might have joined together over the present catalyst surface to form a more ordered transition state species and is going along with the kinetic study [20]. The negative value of $\Delta S^{\star}$ also reveals there is a better degree of ordered geometry/alignment of the transition state compared to the ground state and this consistent with the literature [36].
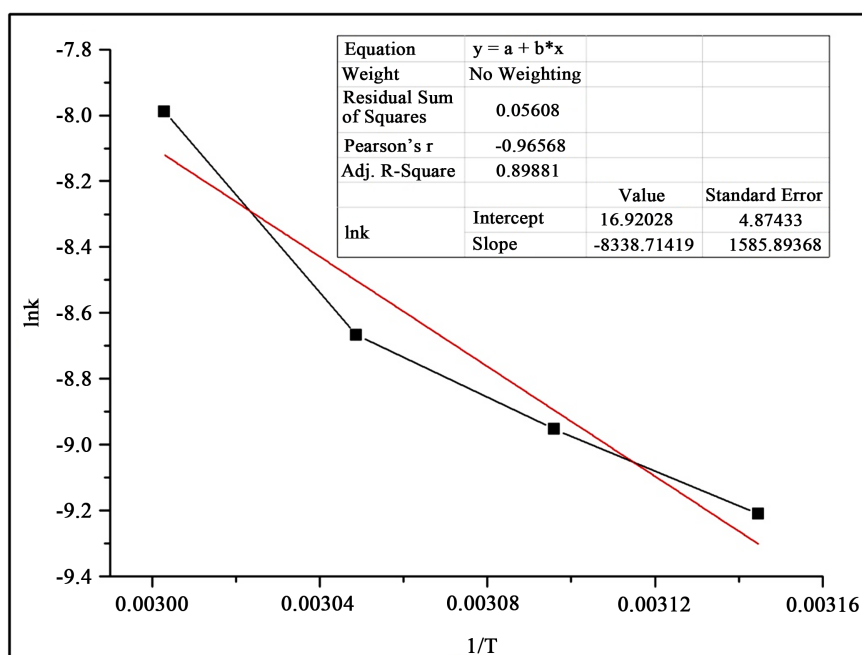
Figure 6. Arrhenius plot of ln k vs. 1/T for transesterification of cottonseed oil in methanol over aminated poly(GMA) grafted flax fibres (reaction conditions are as in **Figure 3**).

Figure 7. Eyring plot for transesterification of cottonseed oil in methanol over aminated poly(GMA) grafted flax fibres.

The ΔG^* at 60°C was calculated from Equation (6) and found to be 104 J·mol⁻¹·K⁻¹. The positive values of ΔG^* confirms that the reaction is endothermic, reversible and non-spontaneous. Accordingly, the reactants need a heat input in order to transfer reactants to the transition state so as to give products [36]. **Table 5** summarizes the values of the thermodynamic parameters.

3.7. Physico-Chemical Properties of Biodiesel

The key fuel quality parameters of FAME were determined and the obtained data is presented in **Table 6**. The density and kinematic viscosity of FAME was

Table 5. Thermodynamic parameters for biodiesel conversion by alkaline catalyst.

ΔH^* (kJ·mol^{-1})	ΔS^* (J·mol·K^{-1})	ΔG^* (J·mol·K^{-1}).
66.62	−113.269	104

Table 6. List of the specifications ASTM biodiesel standard test.

Quality test	Values
Pour point (min)	0
Kinematic viscosity at 40˚C (mm^2·s^{-1})	4.2
Flash point (˚C)	130
Density at 30˚C (mg·cm^{-3})	0.8127
Cloud point (˚C)	7
Cetane number	54

found to be 0.8127 mg·cm^{-3} and 2.4 mm^2·s^{-1}, respectively. The latter was reduced from 33.1 in the cottonseed oil to 4.2 thereby improving the FAME atomisation properties. The pour point is found to be zero, which is going along with literature [37]. The flash point equals 130˚C, which is lower than that of cottonseed oil and far higher than that of petroleum diesel (55˚C - 66˚C) suggesting its suitability for use as a fuel [25]. It can be concluded that the biodiesel obtained from the transesterification cottonseed oil/methanol mixtures using the present aminated grafted flax fibres catalyst has good characteristics in terms of its physiochemical properties and this further confirms the potential of the biopolymer catalyst for such application.

3.8. Catalyst Deactivation

The deactivation of the obtained catalyst used in this study was examined in relation with the loss in both conversion to FAME and catalyst weight and the data is presented in **Figure 8**. As can be seen, the conversion to FAME remained stable in the first two cycles then decreased by about 17% and 49% in the third and fourth cycles, respectively. This was accompanied by a negligible loss in the catalyst weight in 2nd cycle and such weight loss was increased in the 3rd and 4th cycles. This trend indicates that the catalytic activity was maintained in the first two cycles beyond, which it started to decline gradually with the increase in the number of cycles of transesterification reactions. Thus, the decrease in the catalytic activity is suggested to be mainly due to the detachment (degradation) of some of the amine groups represented by catalyst weight loss and this most likely took place during the process of regeneration with NaOH and citric acid. It can be suggested that the Flax-*g*-poly(GMA)/DEA catalyst has a reasonable stability taking into account its natural polymer substrate.
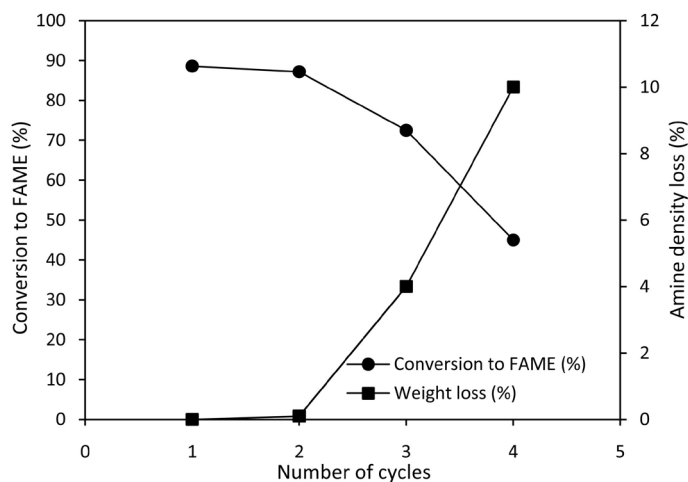
Figure 8. Variation of: (●) conversion to FAME and (■ weight loss in the catalyst with the number of cycles.

4. Conclusion

A new alkaline biopolymer catalyst based on delignified flax fibres grafted with poly(GMA) and loaded with alkalised DEA was successfully prepared and tested for transesterification of cottonseed oil in the presence of excess methanol to FAME. The kinetic and thermodynamic parameters of the reaction were established. The results showed a temperature-dependent transestification reaction and a maximum biodiesel conversion of 88.6% under the optimised conditions. Kinetic analysis revealed that the reaction followed the pseudo first order model and has a low activation energy of 69.33 kJ·mol^{-1} and an apparent rate constant of 0.00349 min^{-1} at 60°C. This clearly indicates that the catalytic process was kinetically controlled and independent of mass transfer limitation. The thermodynamic parameters such as $\Delta H^{\star}$, $\Delta S^{\star}$ and $\Delta G^{\star}$ were found to be 66.62 kJ·mol^{-1}, 113.269 and 104 J·mol^{-1}·K^{-1}, respectively. This suggests that the transesterification process is reversible, non-spontaneous and endothermic. The activity of the catalyst was reasonably maintained for the first 2 cycles before it was undermined by the loss of some of the grafted aminated groups. It can be concluded that the biopolymer based alkaline catalyst produced high biodiesel conversion comparable to other heterogeneous catalysts despite its degradable nature and it offers greater advantages based on production costs, environmental friendliness and sustainable materials development.

Acknowledgements

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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