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Esterification of free fatty acids present in Jatropha oil: A kinetic study

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Methanesulfonic acid has been used as a catalyst for the esterification of free fatty acids (FFA) present in jatropha oil with methanol. The reaction kinetics are estimated for 1 to 2.5 wt% catalyst concentrations, temperature from 45-60°C and methanol-FFA mole ratios ranging from 10:1 to 25:1. The optimum conditions are found to be 20:1 methanol-FFA mole ratio and 1 wt% catalyst at 60°C and 400 rpm for 270 min which give a maximum conversion of 97.9%. A second-order kinetic model for both the forward and backward reactions is proposed to study the reaction. The effect of temperature on the reaction rate constants and equilibrium constant has been determined using Arrhenius and von't Hoff equations respectively. The heat of reaction is found to be 25.936 kcal/mol.

Keywords: Biodiesel, Esterification, Free fatty acids, Jatropha, Kinetics, Methanesulfonic acid.

In recent years, biodiesel has gained a lot of momentum because of its properties such as low carbon monoxide emissions, particulate matter, high flash point and unburned hydrocarbons[1]. Biodiesel consists of long-chain fatty acid methyl esters (FAME) and are derived from renewable sources such as vegetable oils or animal fats. Oils like rapeseed, sunflower, soybean, palm and peanut oil, as well as animal fat are being used for the preparation of biodiesel[2-4]. However usage of these oils for biodiesel is limited because of their high cost and non availability, this forced some researchers to take up work using non-edible oils, animal fats and waste cooking oils[5]. Non-edible oils like Jatropha curcas L oil are attractive as potential raw material for the preparation of biodiesel. Jatropha curcas L belongs to the family of Euphorbiaceae and can grow in arid, semi-arid and waste lands[6].

Methanesulfonic acid was used to reduce the acidity of crude palm oil prior to the alkaline transesterification reaction by Hayyan ***et al.***[7]. The authors also used ultrasonic energy for the reduction of FFA in crude palm oil Hayyan ***et al.***[8]. Aranda ***et al.***[9] studied esterification of palm fatty acids using methanesulfonic acid. The authors showed that the presence of water in the reaction medium gave a negative effect in the reaction velocity. Protonation of the carboxylic moiety of the fatty acid were defined as rate determinant step for the reaction. Tran ***et al.***[10] also used methanesulfonic acid for the production of biodiesel. Fassbender ***et al.***[11] reports a process for preparing fatty acid esters and/or fatty acid ester mixtures of monohydric alcohols having 1 to 5 carbon using methanesulfonic acid for preparing fatty acid esters. Biodiesel was produced from the oil of ***Raphia taedigera Mart*** commonly known as jupati, by Leyvison Rafael V. da Conceicao ***et al.***[12] using methanesulfonic acid.

Gernon ***et al.***[13] reviewed chemical and physical characteristics of methane sulphonic acid and the short-chain alkane sulfonic acids in general. The article emphasis that the conductivity, low solubility and aqueous solubility of metal methane sulfonates make methane sulfonic acid (aq) an ideal electrolyte for many electrochemical processes, especially those involving tin and lead. Different aspects of aqueous process effluent treatment, acid recovery and metal alkane sulfonate salt preparation are discussed. Economic aspects of methanesulfonic acid are also considered.

Though literature reports little work using methane sulphonic acid as catalyst for esterification of free fatty acids in oil there is no detailed kinetic study available, hence this work was taken up with an aim to study the effect of process variables esterification of FFA in ***Jatropha curcas L*** oil using methane sulphonic acid as catalyst and also interpret the kinetic parameters.

Experimental Section

Materials

Jatropha curcas L oil with acid value 55.1 was procured from the local industry (Local Industry, A.P). All chemicals used in the experiments such as methanol (99.5%) and methane sulphonic acid (99%) were of analytical grade and were procured from M/s. Sd. Fine Chem. Pvt. Ltd., Mumbai and used as such.

Analytical methods

Acid value of the oil was determined using AOCS method[14]. The extent of reaction conversion was based on the titrimetric analysis of the FFA in the samples and in the final product.

Experimental procedure

A 250 mL jacketed glass stirred vessel equipped with mechanical stirrer (propeller type impeller of 5.4 cm diameter), thermocouple, provision for sampling and a condenser was used for the esterification of free fatty acids present in jatropha oil. The system was heated by circulating water through the jacket of the reactor from a thermostat Model No FP 50. For a typical experiment, jatropha oil (125 g) was charged into the reactor and (0.307825 g) methane sulfonic acid and methanol (69.85 g) were added after the reaction temperature reached 60°C. The speed of the agitator was maintained constant at 400 rpm. Samples were drawn at regular time intervals of 15 min and 30 min. The withdrawn samples were analyzed by titration for the evaluation of free residual acidity. The sample was washed with water in order to arrest the reaction and separate the catalyst and alcohol from the oil phase, thoroughly dried and then analyzed for FFA.

The first set of experiments was carried out at different speeds of agitation ranging from 300-450 rpm at a fixed methanol-FFA molar ratio of 20:1, catalyst concentration of 1% (relative to FFA) and temperature of 60°C. The second set of experiments was carried varying catalyst concentration from 0.5% to 2.5% at fixed methanol-FFA molar ratio of 20:1 and temperature of 60°C. The third set of experiments was carried out at different methanol-FFA molar ratios of 10:1, 15:1, 20:1 and 25:1 at a temperature of 60°C and catalyst concentrations of 1%. The fourth set of experiments were carried out at different temperatures ranging from 45 to 60°C with methanol-FFA mole ratio of 20:1 using 1% catalyst.

Statistical analysis

The data, presented was analyzed by ANOVA to evaluate the level of statistical significance

Kinetic model

A second order kinetic model in both forward and reverse directions was proposed[15] to describe the esterification kinetics of FFAs in jatropha oil using methane sulfonic acid as catalyst for the present system.

The acid catalyzed esterification reaction by which the conversion of FFA takes place is,

$$R_1 - COOH + R_2 - OH \Leftrightarrow R_1 - COO - R_2 + H_2O \qquad \ldots (1)$$

The following assumptions were made in the development of the kinetic model for the studied esterification reaction.

(i) The rate of non-catalyzed reaction is negligible compared to the catalyzed reaction

(ii) The esterification reaction is a reversible heterogeneous process and the rate is kinetically controlled,

(iii) The chemical reaction is taking place in the oil phase

and

(iv) The reaction is second-order in both the forward and backward directions

Therefore the kinetic equation can be expressed as,

$$\frac{-dC_P}{dt} = k_1 C_P C_Q - k_2 C_R C_S \qquad \ldots (2)$$

where, C_P denotes the concentration of FFA, C_Q denotes the concentration of methanol, C_R and C_S are the concentrations of FAME and water, respectively, formed during the reaction, and k_1 and k_2 are the kinetic rate constants for the forward and reverse reactions, respectively.

As $C_P = C_{P_0} - C_E$ (where C_E is the concentration of acid removed and C_{P_0} is the initial concentration of FFA), $C_Q = C_{Q_0} - C_E$ (where C_{Q_0} is the initial concentration of methanol) and $M = C_{Q_0}/C_{P_0}$, the Eq. (2) becomes,

$$\frac{dC_E}{dt} = k_1 (C_{P_0} - C_E)(MC_{P_0} - C_E) - k_2 C_E^2 \qquad \ldots (3)$$

The conversion, $X_P = \frac{C_{P_0} - C_P}{C_{P_0}}$ and

$X_P C_{P_0} = C_{P_0} - C_P = C_E$,

then $C_{P_0} dX_P = -dC_P = dC_E$

By substituting these in Eq. (3), we get

$$C_{P_0} \frac{dX_P}{dt} = k_1 C_{P_0}^2 (1 - X_P)(M - X_P) - k_2 C_{P_0}^2 X_P^2 \qquad \ldots (4)$$

Integration of Eq. (4) yields,

$$2\boldsymbol{k}_2(\boldsymbol{K}-1)\boldsymbol{C}_{\boldsymbol{P}_0}\quad \boldsymbol{t} = \ln\left[\frac{[\boldsymbol{X}_{\boldsymbol{P}}-(\quad+\quad)](\quad-\quad)}{[\boldsymbol{X}_{\boldsymbol{P}}-(\quad-\quad)](\quad+\quad)}\right] \quad \ldots(5)$$

where

$$= \frac{\boldsymbol{K}(\boldsymbol{M}+1)}{2(\boldsymbol{K}-1)} \quad \ldots(6)$$

$$= \frac{\sqrt{(\boldsymbol{K}(\boldsymbol{M}+1))^2-4(\boldsymbol{K}-1)\boldsymbol{KM}}}{2(\boldsymbol{K}-1)} \quad \ldots(7)$$

and

equilibrium constant, $\boldsymbol{K} = \frac{\boldsymbol{k}_1}{\boldsymbol{k}_2}$ …(8)

The conversion as a function of time can be deduced from Eq. (5) as follows,

$$\boldsymbol{X}_{\boldsymbol{P}} = \frac{(\quad^2-\quad^2)(1-\boldsymbol{e}^{2\quad\boldsymbol{k}_2(\boldsymbol{K}-1)\boldsymbol{C}_{\boldsymbol{P}_0}\boldsymbol{t}})}{(\quad-\quad)-(\quad+\quad)\boldsymbol{e}^{2\quad\boldsymbol{k}_2(\boldsymbol{K}-1)\boldsymbol{C}_{\boldsymbol{P}_0}\boldsymbol{t}}} \quad \ldots(9)$$

Results and Discussion

Jatropha oil used for the present study contains 24.52% of FFA. The fatty acid composition of the oil was found to be 15.7% palmitic, 10.5% stearic, 38.9% oleic and 33.4% linoleic acids as determined by Gas Chromatography.

Effect of speed of agitation

The effect of agitation on the reduction of acid value, was studied at a fixed methanol-FFA molar ratio of 20:1, catalyst concentration of 1% and 60°C. Increase in speed of agitation from 300 to 400 rpm increased the conversion of FFA from 74.23% to 97.47% in 270 min. Further increase in agitation speed to 450 rpm, showed negligible increase in the reduction of FFA. It was therefore concluded that a speed of agitation of 400 rpm was above the critical speed required for the given system. All the experiments were conducted with the speed of agitation fixed at 400 rpm.

Effect of catalyst concentration

The effect of catalyst concentration on the conversion of FFA present in jatropha oil with methanol was studied. Catalyst used in the reaction ranged from 0.5 to 2.5% based on FFA in jatropha oil. It was observed from Fig. 1 that with an increase in the catalyst concentration from 0.5 to 1.0%; the conversion reached up to 97.87 from 75.86%. There was no prominent change by further increase in catalyst from 1.0 to 2.5%, so all the experiments were conducted using 1.0% catalyst, 20:1 methanol/FFA mole ratio for 270 min.

Effect of methanol to FFA mole ratio

Effect of methanol-FFA mole ratio on the esterification of free fatty acids present in jatropha oil was studied using constant 1% methane sulphonic acid concentration at 60°C for 270 min by varying methanol-FFA mole ratios from 10:1 to 25:1. It is evident from Fig. 2 that with 10:1 ratio a conversion of 84.18% was obtained, increasing the ratio to 15:1 resulted an increase in conversion of 93.6% and increasing the methanol-FFA mole ratio to 20:1 increased the conversion to 97.87%, further increasing the ratio to 25:1 did not provide any significant increase in conversion, therefore 20:1 methanol-FFA mole ratio was considered for all experiments.

Effect of temperature

The reaction temperature plays an important role on reaction rate. The effect of temperature on

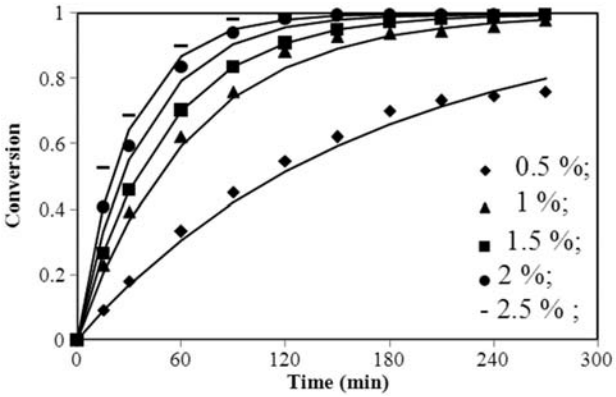

Fig. 1 — Effect of the catalyst concentration on the esterification of FFA in jatropha oil at 20:1 methanol-FFA mole ratio, 400 rpm and 60°C.

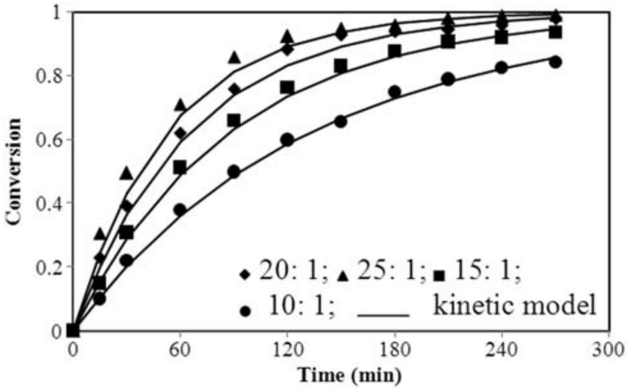

Fig. 2 — Effect of methanol - FFA mole ratio on the esterification of FFA in jatropha oil at 60°C and 1 wt% methane sulphonic acid concentration

esterification of free fatty acids present in jatropha oil using methane sulphonic acid was studied at temperature from 45 to 60°C by maintaining other reaction parameters constant. It can observed from Fig. 3 that at 45°C a conversion of 56% was achieved, increasing the temperature to 50°C resulted a conversion of 66.5% and at 55°C a value of 80.2% was observed and further increasing temperature to 60°C the conversion was increased to 97.87%.

Applying the kinetic model

Reaction rate constants

The forward reaction rate constant, $\boldsymbol{k_1}$, can be calculated from the initial rates as follows:

At t=0, the initial concentrations of products, $\boldsymbol{C_R}$ and $\boldsymbol{C_S}$, are zero i.e. $\boldsymbol{C_E=0}$, and Eq. (3) becomes,

$$r_0 = \left.\frac{-dC_P}{dt}\right|_{t=0} = k_1 C_{P_0} MC_{P_0} = k_1 MC_{P_0}^2 \qquad \ldots(10)$$

$$\left.\frac{C_{P_0}\,dX_P}{dt}\right|_{t=0} = k_1 MC_{P_0}^2 \qquad \ldots(11)$$

$$r_o = k_1 MC_{P_0} \qquad \ldots(12)$$

The initial rates have been calculated using Eq. (12), and the effect of mole ratio on initial rate has been plotted in Fig. 4a for 1% catalyst concentration at 60°C, and the values of $\boldsymbol{k_1}$ have been obtained from the slopes of this plot. By substituting $\boldsymbol{k_1}$ in Eq. (5), $\boldsymbol{k_2}$ was determined by trial and error until the slope of the plot of Eq. (5) matches the assumed value, as shown in Fig. 4b for 20:1 methanol-FFA mole ratio, 1% catalyst concentration at 60°C.

The kinetic rate constants were obtained similarly for 45, 50, 55 and 60°C temperatures. The forward and backward reaction rate constants, $\boldsymbol{k_1}$ and $\boldsymbol{k_2}$, for 1% catalyst concentration at 60°C were 9.535×10^{-4} and 2.59×10^{-5} lit/(mol min) respectively.

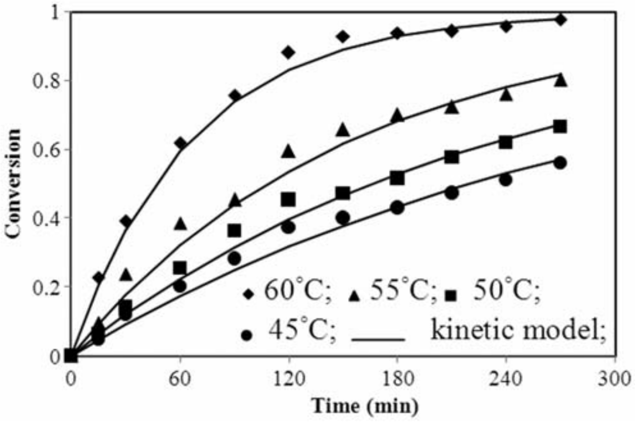

Fig. 3 — Effect of temperature on the esterification of FFA in jatropha oil at 20:1 methanol-FFA mole ratio and 1% methane sulphonic acid

Activation energies and frequency factors

The effect of temperature on the reaction rate constants was obtained by fitting $\boldsymbol{k_1}$ and $\boldsymbol{k_2}$ to the Arrhenius equation.

$$k = Ae^{\left[\frac{-\Delta E}{RT}\right]} \qquad \ldots(13)$$

and

$$\ln k = \frac{-\Delta E}{RT} + \ln A \qquad \ldots(14)$$

From the plots of ***ln k*** as a function of the reciprocal temperature, both forward and backward reactions rate constants were obtained, and the results are presented in Table 1. The energy of activation for the forward reaction as well as backward reaction was found to be 21.427 kcal/mol respectively for forward reaction and -4.509 kcal/mol respectively for backward reaction.

Equilibrium constant and heat of reaction

The effect of temperature on equilibrium constant, ***K***, has also been obtained by fitting the data to van’t Hoff equation.

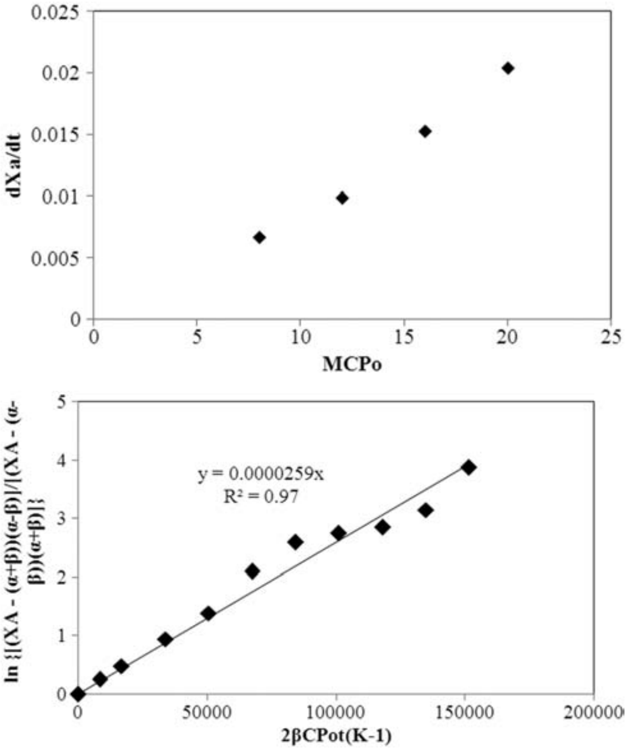

Fig. 4 — (a) Intial rate ***vs*** methanol-FFA mole ratio; 4 — (b) Determination of the kinetic constant ($\boldsymbol{k_2}$) using Eq. (5) at 20:1 methanol-FFA mole ratio, 1% catalyst concentration and 60°C.

Table 1 — Kinetic rate constants and equilibrium constant for esterification of FFA in jatropha oil at different reaction conditions.

Reaction Conditions		k_1	k_2	K	R^2
Temperature[a] (°C)	45	0.0002001	0.00003642	5.494646	0.97
	50	0.0002652	0.00003162	8.387097	0.99
	55	0.000406	0.0000301	13.48837	0.98
	60	0.0009535	0.0000259	36.81467	0.97
Catalyst concentration[b] (wt%)	0.5	0.0003806	9.89E-06	38.48089	0.97
	1	0.0009535	2.59E-05	36.81467	0.97
	1.5	0.0012866	4.11E-05	31.30491	0.95
	2	0.001690526	6.16E-05	27.4347	0.89
	2.5	0.002190188	8.34E-05	26.25495	0.89

[a] At 20:1 methanol-FFA mole ratio and 1% methane sulphonic acid

[b] At 20:1 methanol-FFA mole ratio and 60°C

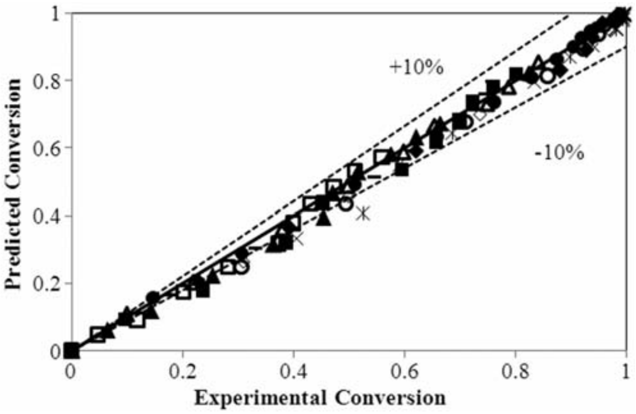

Fig. 5 — Comparison of the experimental and predicted conversions

$$\ln K = \frac{-\Delta H}{RT} + const \qquad \ldots(15)$$

The values of equilibrium constant are given Table 1. From the plot of **ln*K*** and the reciprocal temperature, the heat of reaction has been obtained and was found to be 25.936 kcal/mol with R^2 of 0.95.

Comparison of experimental and predicted values

The fitting of the experimental data to the proposed model was also assessed by comparing the experimental conversion values with the theoretically predicted values using Eq. (9) and is presented in Fig. 5. A p-value of 0.003563 was obtained by regressing the values using ANOVA which was considered significant. It can be concluded from the plot that the developed kinetic model explained the kinetics of the esterification of free fatty acids (FFA) in jatropha oil satisfactorily.

Conclusion

Acid value was brought to below 1 mg KOH/g oil within 270 min using 1% methane sulfonic acid catalyst and 20:1 methanol-FFA mole ratio at 60°C and 400 rpm as speed of agitation. A kinetic model was proposed with second-order kinetics for both forward and backward reactions and it represented the present system of esterification satisfactorily. The forward and backward reaction rate constants, k_1 and k_2, for 1% catalyst concentration at 60°C were 9.535×10^{-4} and 2.59×10^{-5} lit/(mol min) respectively.

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