

Kinetic study of the esterification of free fatty acids in non-edible *Pongamia pinnata* oil using acid catalyst

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Abstract: Pre treatment of high free fatty acid containing *Pongamia pinnata* oil using sulfuric acid catalyst has been optimized. The kinetics of the pre treatment esterification process was studied. The experimental results were found to fit a Pseudo first-order kinetics. The influence of temperature on the rate constants was determined by fitting the results to the Arrhenius equation. The activation energy and frequency factor were favorable for the forward reaction. Based on the experimental results, a methanol to oil ratio of 9:1, one percentage catalyst by weight, and a temperature of 60°C, were selected as the optimum settings for the esterification process.

Keywords: *Pongamia pinnata* oil, free fatty acid, esterification, acid catalyst, kinetics

Introduction

The use of vegetable oil for biodiesel processing is a promising technology because it is less polluting and it is a renewable resource compared to petroleum based diesels, which are facing potential depletion. Oils like soybean, rapeseed, sunflower and safflower (Lang *et al.*, 2001) which are edible in nature, have been used for biodiesel production. Attempts have been made for producing biodiesel from non-edible sources like used frying oil, greases, tallow and lard (Mittelbach *et al.*, 1992; Alcantara *et al.*, 2000; Canakci & Gerpen, 2001; Dorado *et al.*, 2002).

In India, there is a high annual production of a variety of non-edible oils that can be potential sources for biodiesel production to supplement other conventional energy sources (Kaul *et al.*, 2003). Karanja (*Pongamia pinnata*), *Jatropha* and *Madhuca* (Pramanik, 2003; Senthil Kumar *et al.*, 2003; Raheman & Phadatare, 2004; Ghadge & Raheman, 2006; Pugazhvadivu & Rajagopan, 2009) have been successfully used for biodiesel production.

Biodiesel produced from non-edible oils in our country will help reduce the cost of import on petroleum based fuels. Also, India being an agriculture based country, development of such non-edible oil crops is more feasible (Naga Prasad *et al.*, 2009).

The conventional method for vegetable oil

conversion into biodiesel is transesterification (Ma & Hanna, 1999; Srivastava & Prasad, 2000). Transesterification refers to a catalyzed (generally an alkaline catalyst) chemical reaction involving oil or fat, and an alcohol to yield fatty acid methyl esters and glycerol. The factors that affect transesterification are: alcohol to oil ratio, catalyst quantity, reaction temperature, pressure, time, and the free fatty acids (FFA) content in oils. Conversion of oil into biodiesel by transesterification is complicated if it contains higher amounts of FFA (> 4 mg KOH/g). Free fatty acids form soap with alkaline catalyst and prevent the separation of biodiesel. Crude *Pongamia Pinnata* (Pongamia) contains high FFA content and cannot be directly used with an alkaline catalyst. Earlier biodiesel have been prepared from low FFA containing Pongamia (Sanjib Kumar Karme & Anju Chadha, 2005) by direct transesterification using KOH and solid acid catalysts. Process optimization of direct transesterification of low FFA Pongamia has also been studied using a base catalyst (Avinash Kumar Agarwal & Tanu Priya Bajaj, 2009). Biodiesel production from high FFA Pongamia has been carried out using sulfuric acid and KOH catalysts (Sharma & Singh, 2008; Malaya Naik *et al.*, 2008).

This paper discusses the findings of the experiment carried out to optimize the pretreatment process for reducing the FFA content of Pongamia below 4 mg KOH/g for biodiesel production. The focus of our work is on the reaction parameters that affect the esterification of FFA in Pongamia. The need to reduce FFA and the interest in characterizing the kinetics of esterification reaction lead us to undertake kinetic and thermodynamic studies. Kinetic studies have been performed earlier on esterification of free fatty acids in sunflower oil and oleic acid (Berrios *et al.*, 2007; Kraai *et al.*, 2008). Transesterification kinetics of soybean oil with five different catalysts have also been studied (Singh & Fernando, 2007). However,

there has not been significant contribution to the study of FFA esterification kinetics in Pongamia. Moreover, a study of the kinetics with homogenous catalysts would provide us with a better understanding of the catalytic activity of several heterogeneous catalysts that have come into

Table 1. Fatty acid profile of *Pongamia pinnata*

Fatty acid	Chemical name	Formula	Structure	Wt %
Palmitic	Hexadecanoic	C ₁₆ H ₃₂ O ₂	16:0	10.6
Stearic	Octadecanoic	C ₁₈ H ₃₆ O ₂	18:0	6.8
Oleic	cis-9-Octadecenoic	C ₁₈ H ₃₄ O ₂	18:1	49.4
Linoleic	Cis-9,cis-12-Octadecenoic	C ₁₈ H ₃₂ O ₂	18:2	19.0
Arachidic	Eicosanoic	C ₂₀ H ₄₀ O ₂	20:0	4.1
Behenic	Docosanoic	C ₂₂ H ₄₄ O ₂	22:0	5.3
Lignoceric	Tetracosanoic	C ₂₄ H ₄₈ O ₂	24:0	2.4

use.

Materials and methods

Pongamia was purchased from the local market and used as such for our study. Methanol, ethanol, sulfuric acid and all other reagents were purchased from Qualigens Fine Chemicals Limited. The reagents were of 99% purity and used without any purification.

The initial acid value which is a measure of the FFA content of the oil was found to be 15.96 mg KOH/g. The fatty acid profile of the oil was determined by gas chromatography, given in Table 1. Esterification of FFA was carried out with methanol and concentrated sulfuric acid as the catalyst. The reactions were performed in a batch process with a constant rate of stirring using a mechanical stirrer. Different methanol to oil ratios were employed between 6:1 to 12:1, catalyst amount was varied between 0.5 to 2% by weight. Studies were carried out at five different temperatures between 30 to 70°C.

Transesterification of the oil was carried out using KOH as catalyst under optimum conditions of catalyst 1% by weight at 60°C with a methanol to oil ratio of 6:1.

The acid value during the esterification reaction was determined by the standard titrimetry procedure. The fuel properties were determined by standard American Society for Testing and Materials (ASTM) methods.

Results and discussion

Optimization of reaction parameters

Classical optimization technique was used to optimize the reaction parameters such as catalyst quantity, methanol to oil ratio and temperature. One percent catalyst by weight was taken as the optimum amount as further increase in catalyst concentration did not cause significant improvement in the reaction. Esterification reaction was carried out at various methanol to oil ratios between 6:1 to 12:1. An increase in esterification was observed till a ratio of 9:1, beyond which no substantial increase in esterification rate was observed. Hence molar ratio of methanol to oil was fixed as optimum at 9:1, which is in accordance with the results obtained by Sharma and Singh (2008). Temperature studies were done in the range of 30 to 70°C. The optimum was found to be 60°C, because at a temperature greater than 60°C, methanol is lost from the reaction medium in spite of using a condenser.

Kinetics of esterification reaction

The model suggested by Berrios *et al.* (2007) was employed to study the kinetics of the esterification of free

Fig. 1. Determination of rate constants at methanol to oil ratio of 9:1, catalyst 0.5% by weight at a temperature of 60°C

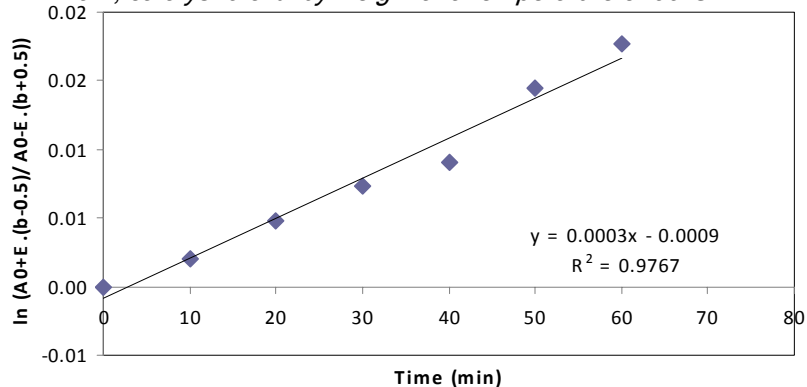


Fig. 2. Determination of rate constants at methanol to oil ratio of 9:1, catalyst 1.5% by weight at a temperature of 60°C

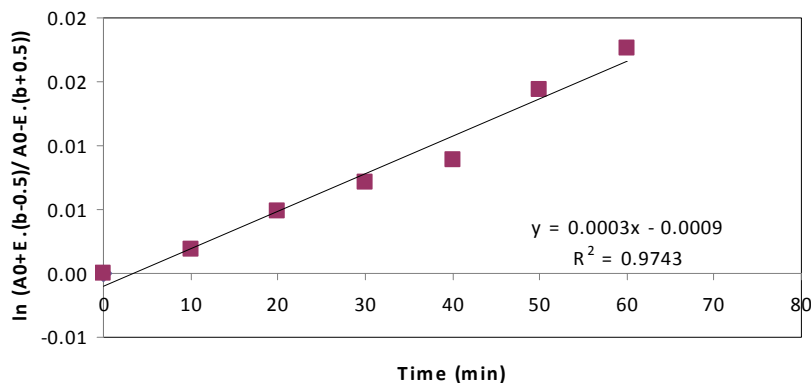
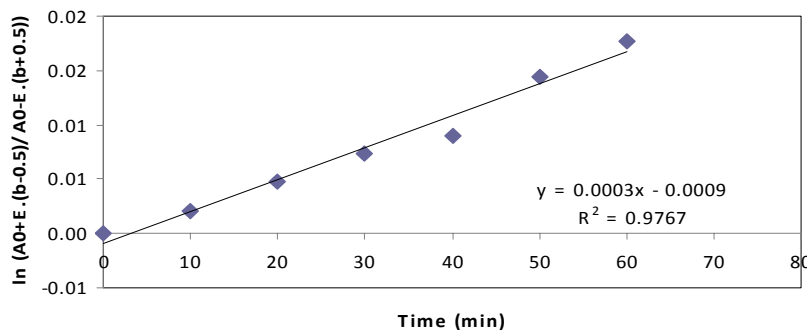


Fig. 3. Determination of rate constants at methanol to oil ratio of 9:1, catalyst 2.0% by weight at a temperature of 60°C



fatty acids in Pongamia. The assumptions made to fit the experimental data to the model were:

- (i) The esterification reaction was a reversible and heterogeneous process; the rate of which under the operating conditions used, was controlled by that of chemical reaction.
- (ii) Quantity of methanol maintained was high so as to remain constant throughout the reaction.
- (iii) The esterification reaction does not proceed in the absence of a catalyst.
- (iv) The chemical reaction occurred in the oil phase.

The kinetic equations for the esterification reaction based on the above are

$$2K_2 \cdot \alpha \cdot t = \ln \left[\frac{A_0 + E \cdot (\beta - \frac{1}{2})}{A_0 - E \cdot (\beta + \frac{1}{2})} \right] \quad (1)$$

$$\alpha = \sqrt{\left(\frac{K_1^2}{4}\right) + K_2 \cdot A_0} \quad (2)$$

$$\beta = \frac{\alpha}{K_1} \quad (3)$$

$$K = \frac{K_1}{K_2} \quad (4)$$

where K_1 and K_2 are the rate constants for the forward and backward reactions respectively. A_0 is the initial acid value of the oil; where A is the acid value of the oil at time t and E the amount of free fatty acid removed by the esterification process. K_1 and K_2 were calculated based on the above equations and the graphs were obtained by a fit of the experimental data.

Graphs obtained by fitting the experimental data were obtained with different quantity of catalysts, methanol to oil ratio are shown in Fig.1 to 7. It is evident from the rate constant values for the forward and backward reactions that the rate of the forward reaction is higher than the rate of the backward reaction. The values of rate constants obtained are shown in Table 2. It is also observed that the rate constant for the forward reaction increases with an increase in methanol to oil ratio and catalyst quantity which substantiates that the esterification reaction follows Pseudo first order kinetics.

Thermodynamic studies

The feasibility of a reaction is determined from the thermodynamic parameters. Arrhenius equation was used to study the influence of temperature on specific reaction rate. Arrhenius equation is written as

$$K_1 = A_1 \cdot \exp \left[\frac{-Ea_1}{R.T} \right] \quad (5)$$

$$K_2 = A_2 \cdot \exp \left[\frac{-Ea_2}{R.T} \right] \quad (6)$$

for the forward and backward reactions respectively. Rate constants obtained at various temperatures were fitted with equations (5) and (6).

Based on the above, the frequency factor and the activation energy were calculated for the forward and

Fig.4. Determination of rate constants at methanol to oil ratio of 3:1, catalyst 1.0% by weight at a temperature of 60°C

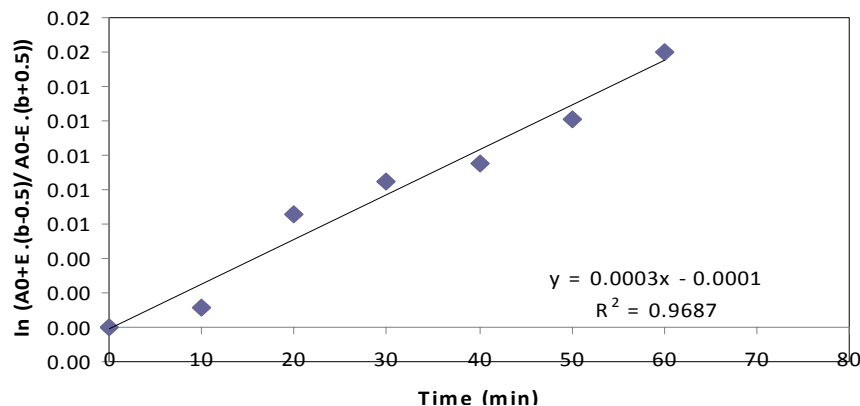


Fig.5. Determination of rate constants at methanol to oil ratio of 6:1, catalyst 1.0% by weight at a temperature of 60°C

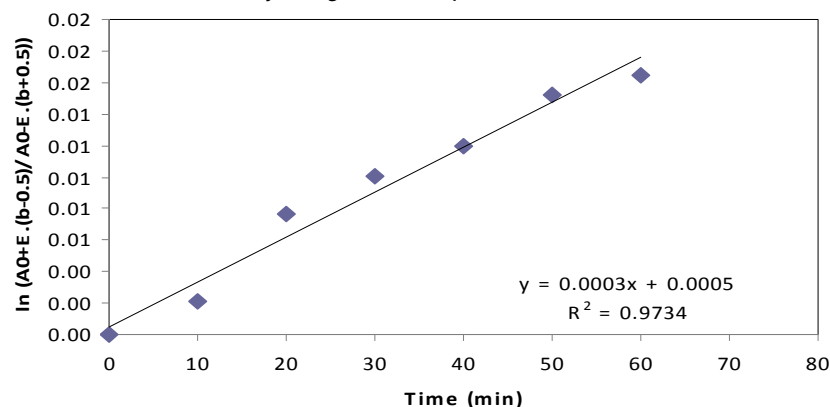
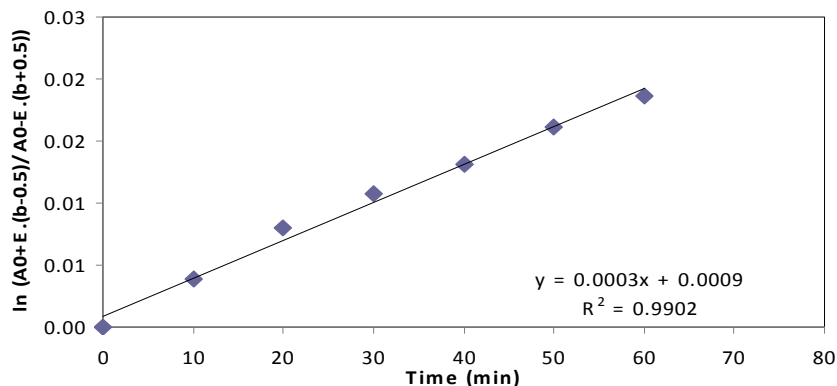


Fig.6. Determination of rate constants at methanol to oil ratio of 9:1, catalyst 1.0% by weight at a temperature of 60°C



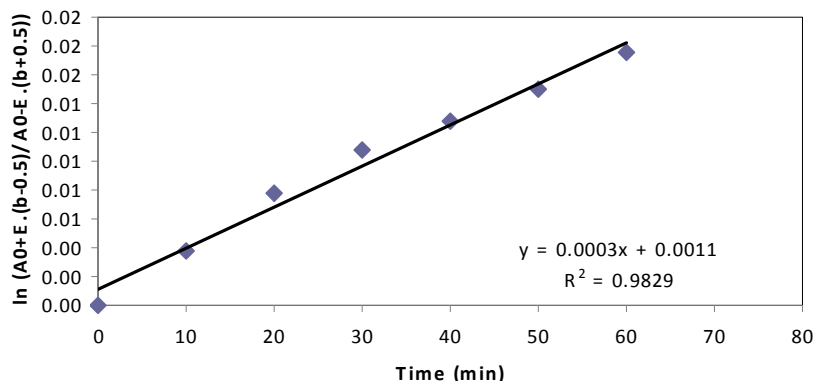
backward reactions and are given in Table 3. Frequency factor, which is a measure of collisions between reactants, is high for the forward reaction; this indicates that the reverse reaction is the less favored one. Activation energy for the reverse reaction is higher than that for the forward reaction, which again confirms the low possibility of reverse reaction.

Transesterification was carried out with the pre treated oil and the biodiesel obtained was tested for fuel properties. Table 4 summarizes the fuel properties of the

Table 2. Rate constant values

S.No	Catalyst loading(wt %)	Methanol to Oil ratio	K_1 (min^{-1})	K_2 (g/mg.min)	R^2
1	0.5	9	2.32×10^{-2}	-3.64×10^{-4}	0.9348
2	1	9	2.54×10^{-2}	-3.97×10^{-4}	0.9902
3	1.5	9	2.33×10^{-2}	-3.81×10^{-4}	0.9743
4	2.0	9	2.44×10^{-2}	-3.82×10^{-4}	0.9767
5	1	3	2.16×10^{-2}	-3.39×10^{-4}	0.9687
6	1	6	2.33×10^{-2}	-3.64×10^{-4}	0.9734
7	1	12	2.38×10^{-2}	-3.73×10^{-4}	0.9829

Fig. 7. Determination of rate constants at methanol to oil ratio of 12:1, catalyst 1.0% by weight at a temperature of 60°C



prepared biodiesel, it is found that the biodiesel properties were confirming to the ASTM standards.

Conclusions

Non-edible Pongamia oil which is available in abundance in India was chosen for production of biodiesel. In order to reduce the FFA content of Pongamia, esterification reaction was carried out using sulfuric acid catalyst at different methanol to oil ratios. The FFA content was reduced from 15.96 mg KOH/g to 2.42 mg KOH/g. Kinetic and thermodynamic studies were performed to calculate the rate constants and energy of activation. Energy of activation was found to be less for the forward reaction in comparison to the backward reaction. Transesterification was carried out with the pretreated oil by the conventional base catalyzed reaction. The properties of the biodiesel obtained by transesterification were in good agreement with ASTM standards.

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Table 3. Activation energy & frequency factor for forward and reverse reaction

Rate constant	A	E_a (J/mol)
K_1	25701.8	280.1
K_2	25764.1	4.33

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Table 4. Fuel properties of Pongamia biodiesel

Properties	Limits	Test methods	Biodiesel quality
Flash point °C	>130	ASTM D93	170
Water and sediments % vol., max	0.050	ASTM D2709	0.005
Kin. Viscosity at 40°C (cSt)	1.9 - 6.0	ASTM D445	4.33
Sulfated ash % mass, max	0.020	ASTM D874	0.005
Sulphur % mass, max	0.0015/0.5	ASTM D5453	19 ppm
Cetane number	47	ASTM D613	57
Free glycerin % mass	0.020	ASTM D6584	101 ppm
Total glycerin % mass	0.240	ASTM D6584	1860 ppm
Phosphorus content % mass, max	0.001	ASTM D4951	<10 ppm
Distillation temperature °C	360 max	ASTM D1160	360



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