

RACE 2014 [12th – 13th July 2014]
Recent Advances in Chemical Engineering

Comparative Study on Kinetic Parameters for Tranesterification of Pongamia and Cotton Seed Oil

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Abstract: Tranesterification of pongamia and cotton seed oil were performed at various experimental conditions such as temperature, molar ratio, catalyst concentration, reaction time and stirring speed. Maximum yield of around 85 % was obtained for pongamia and cotton seed oil at optimum conditions of temperature (338 K), molar ratio of methanol to oil (6:1), cation exchange resin catalyst (1.5 wt. %), stirring speed (10 Hz) and reaction time of 3 h. Kinetics of tranesterified pongamia and cotton seed oil were studied using Arrhenius plot. In excess of methanol, the tranesterification reaction follows pseudo-first order reaction. The activation energies of pongamia and cotton seed oil were found to be 41570 and 23694.9 J/mol respectively. Kinetic study revealed that cotton seed oil is best suited for the maximum yield of biodiesel production.

Key words: Tranesterification; Pongamia oil; Cotton Seed oil; Biodiesel; Activation energy.

1 Introduction

In recent decades, the biodiesel has bloomed as a greener and new renewable substitute to the petroleum diesel, which is nontoxic, neutral carbon, sulfur and aromatics free fuel^{1,2}. Fatty Acid Methyl Ester (FAME) (biodiesel) has almost the same physico-chemical properties and engine performance as petroleum diesel fuel³. It was normally produced via transesterification of naturally occurring triglycerides. FAMEs were blend with conventional diesel up to 20 % which could be substituted in diesel engines⁴. More than 80 % of India's fuel demand is met by importing crude oil from other countries⁵. Oil yielding crop are the sources for economic, energy and agricultural sectors growth. The oil yielding crop seeds contain polyunsaturated fatty acids (PUFA) which are the source of raw material for biodiesel production^{6,7}. Organic seed oils have the better physico-chemical properties and biodegradability than diesel fuels⁸. Cotton seed oil contains an average of 28–34% oil with higher percentage of PUFA⁶. Karanja oil was also the one of the potential oils with yearly production of 200 T (metric ton), out of which 6 % is being presently utilized⁹. Biodiesel production with potential and low emission characteristics are considered in India which are derived locally from the available nonedible oils. It doesn't need any further modification in any compression ignition engines¹⁰.

The present work reports on the study of influence of various factors affecting FAME yield such as molar ratio, amount of catalyst, temperature, stirring speed and reaction time. The kinetic studies were performed to determine the activation energy of the reaction.

2 Experimental Methodology

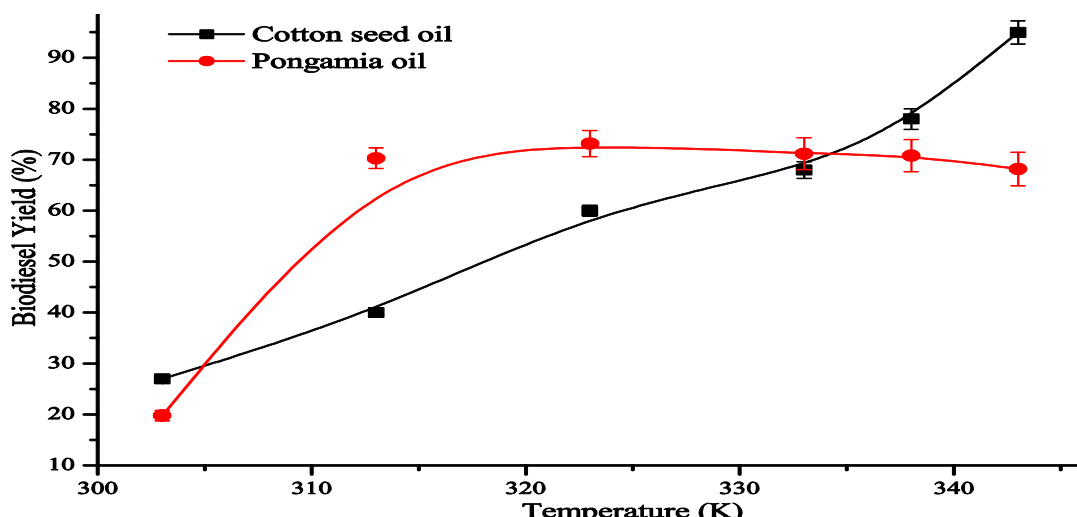
The cation resins are obtained from Ion-Exchange resin India Ltd. It has the moisture holding capacity of 52-56 %, particle size distribution was in the range from 350-1195 microns, Effective size was 0.5-0.6 mm, pH ranges from 0-15 and operating temperature of 394-424 K. Pretreatment of the resins were done by mixing the resin with 1 M HCl solution and washed with distilled water. Then the resins were dried under vacuum at 378 K and soaked with methanol for 12 h before transesterification. Oil was pre-heated and calculated stoichiometric amount of methanol to oil were injected into the flask. The mixture was stirred and heated to the reaction temperature of 303-343 K. The ion-exchange resin catalyst of 0.5-2.5 wt % was introduced to the reaction system. The transesterification was conducted in three necked round bottom flask equipped with mechanical stirrer, stirring at a rate of 2 to 10 Hz for 6 h. A sample of 3 cm³ was collected by drip tube at time interval of 1 h. The spent catalysts are separated from reaction mixture by filtration¹¹.

3. Results and Discussion

3.1 Influence of Reaction Temperature on Biodiesel Yield

The impacts of reaction temperature on transesterification reaction of pongamia and cotton seed were in the range of 303-343 K on the yield of biodiesel (Fig. 1). The rate of reaction increases with increase in temperature. This increased energy state of the molecules results in more active collisions and solubility of reactants also increases at elevated temperature. In cationic environment, at 338 K reaction temperature, the yield of biodiesel was observed to be high within 3 h. At elevated reaction temperatures, there is a chance of loss of solvent methanol and decrease in the visibility of the product. Ilgen *et al*¹² discussed the transesterification of canola oil using dolomite catalyst with methanol to biodiesel in a heterogeneous system. On transesterification at 850 °C, molar ratio (6:1) of methanol to canola oil, 3 wt. % of dolomite catalyst, FAME yield was found to be 91.78 % for reaction time of 3 h.

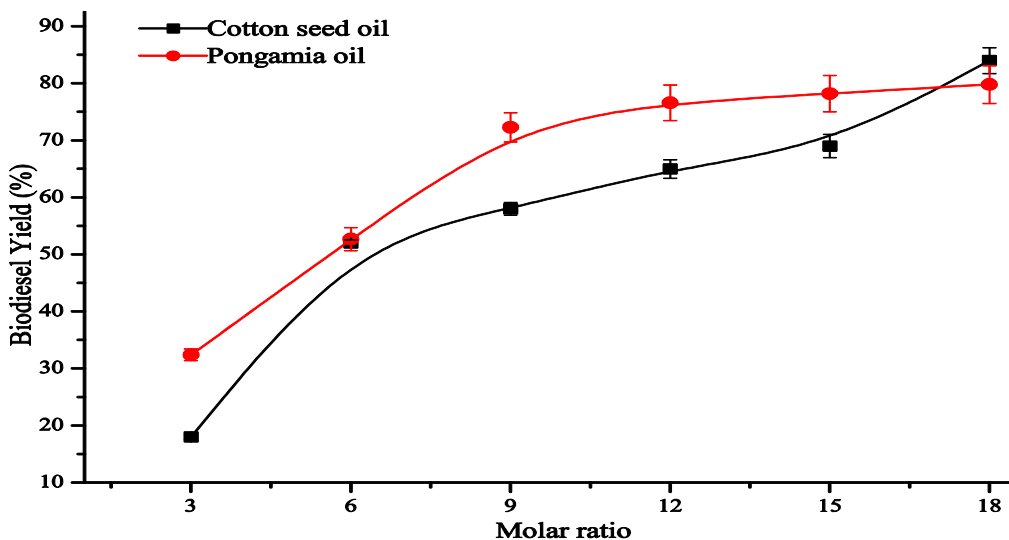
Fig. 1 Effect of reaction temperature on the yield of biodiesel with 1.5 wt % of cation catalyst, 6:1 molar ratio, 3 h reaction time and 10 Hz



3.2 Influence of Molar ratio of methanol to cottonseed oil.

Adsorption of methanol occurs by the active methoxide species on the catalyst surface and the transesterification reaction becomes mass transfer-controlled. The driving force for methanol adsorption increases as methanol/cottonseed oil ratio increases. The influence of the molar ratio of methanol to pongamia and cottonseed oil in the range of 3:1–12:1 showed more than 80 % conversion at 6:1 molar ratio for reaction time of 3 h (Fig. 2). Higher molar ratio (12:1) of methanol to cottonseed oil hinders the separation of glycerol because of its high solubility. The glycerol in the esters drives the equilibrium and favors the backward transesterification reaction¹³. Wan and Hameed¹⁴ achieved maximum of 80.98 % of conversion with 5.5 wt. % activated carbon supported calcium oxide as a solid base catalyst at 190 °C temperature, 15:1 methanol to palm oil molar ratio and reaction time of 1 h and 21 min.

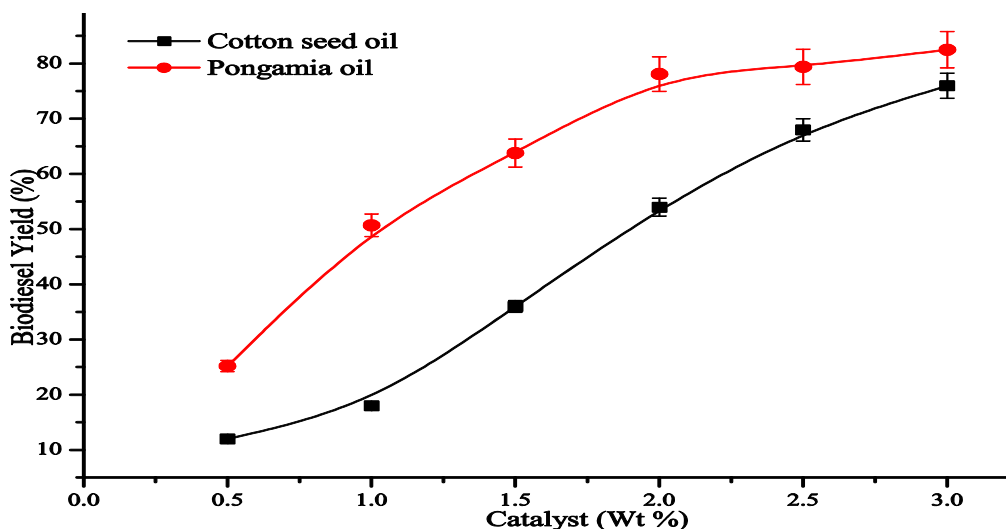
Fig. 2 Effect of molar ratio of methanol on biodiesel yield at 338 K with 1.5 wt % of cation resin catalyst, 3 h reaction time and 10 Hz stirring rate.



3.3 Influence of weight of cation-resin catalyst

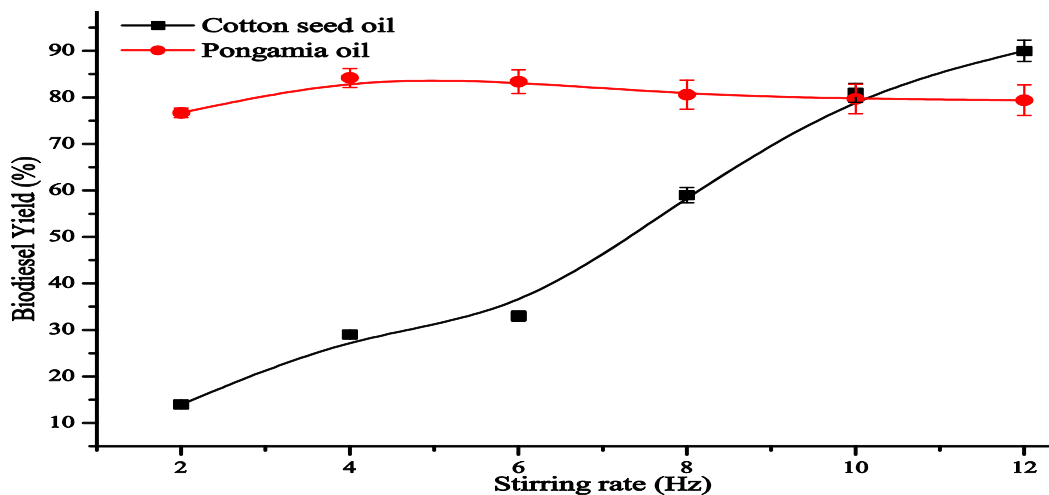
The number of acidic sites of the catalyst and their contacting chances increases, by gradually increasing the weight of cation-resin catalyst. This showed an increased yield of biodiesel. It was observed that, when the weight of cation-resin catalyst reaches 1.5 wt %, the yield of biodiesel reaches higher value in 3 h for pongamia and cotton seed oil (Fig. 3). Verziu et al [15] prepared various alumina supported alkaline fluoride compounds as catalysts with different loadings from 1 to 20 wt. % using aqueous solutions of the alkaline fluoride compounds by wet impregnation of basic mesoporous alumina. Recycling experiments showed that these catalysts are stable for a limited number of cycles.

Fig. 3 Effect of amount of cation catalyst on the biodiesel yield at 338 K with 6:1 molar Ratio, 3 h reaction time and 10 Hz stirring rate



3.4 Influence of Stirring Rate

Transesterification reaction is diffusion controlled three phase heterogeneous reaction. Mass transfer resistance can be lowered with the increasing the stirring rate and this may result in increased contact area. The higher yield of greater than 80 % of biodiesel were obtained at 10 Hz at reaction time of 3 h for pongamia and cotton seed oil (Fig. 4).

Fig. 4 Arrhenius plot for the transesterification of pongamia and cotton seed oil

3.5 Kinetic studies on transesterification of pongamia oil and cotton seed oil

The reaction time and temperature dependencies allow the determination of the kinetic parameters of transesterification of pongamia oil and cotton seed oil to the corresponding fatty acid methyl esters. However, for simplicity, a reasonable mathematical model may be based only on the overall reaction and ignoring the intermediate reactions. In excess of methanol, the transesterification is a pseudo- first order reaction. The rate of pseudo-first order kinetic law can be considered as follows,

$$r = kC_G \quad (1)$$

Where C_G is the concentration of glyceride group, Equation (1) can also be written by introducing the glyceride group's conversion (X_G),

$$r = kC_G^0 X_G \quad (2)$$

As for non-acid oil, the yield (η) corresponds to the glyceride group conversion (X_G); relation (2) can also be written as,

$$r = kC_G^0 \eta \quad (3)$$

The kinetic constant (k) can then be calculated at each temperature by integration of relation (3).

$$k = -\ln(1-\eta)/t \quad (4)$$

Where, t is the time. The average overall reaction rate constant at different temperature can be calculated according to the experimental data. According to Arrhenius theory, the overall reaction rate constant has relationship with temperature as follows:

$$\ln k = \frac{-E_a}{RT} + C \quad (5)$$

Where E_a is the activation energy (J/mol), R is the gas constant ($J\ mol^{-1}K^{-1}$), T is the absolute temperature (K) and C is constant. The plot of $\ln k$ versus $1/T$ gives the slope of $(-E_a/R)$ as shown in Fig. 5. Thus, values for E_a of pongamia and cotton seed oil are calculated to be 41570 and 23694.9 J/mol respectively.

4 Conclusion

The biodiesel as high as 80 % were obtained for pongamia and cotton seed oil with the molar ratio of methanol to oil of 6:1, a catalyst amount of 1.5 wt %, a reaction temperature of 338 K, a stirring rate of 10 Hz and a reaction time of 3 h. Activation energy for cotton seed oil was higher than pongamia oil. This reveals that cotton seed oil is best suited for higher yield of biodiesel production. Further analysis should be done to strengthen the stability and increase the lifetime of the catalyst.

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