

Kinetic study of preparation of biodiesel from crude rubber seed oil over a modified heterogeneous catalyst

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A detailed study of kinetics in transesterification of non edible crude rubber seed oil using calcium oxide, CaO prepared from waste eggshells as catalyst has been carried out. Egg shells are generally waste materials which several researches had reported to contain high content of calcium oxide. Utilization of these waste materials as catalysts reduces catalyst cost, promotes environment friendly process and also serves as a source of income if the biodiesel is to be commercialized. Transesterification reactions are carried out and the yield and conversion of the product are optimized by varying the methanol to oil molar ratio, catalyst amount, reaction temperature, and time. A biodiesel conversion of 98.58% is obtained with a yield of 89.12%. The reaction follows pseudo-first order kinetics. The activation energy (E_a) is 79 kJ/mol and the frequency factor (A) is $2.98 \times 10^{10} \text{ min}^{-1}$.

Keywords: Biodiesel, rubber seed oil, heterogeneous catalyst, reaction kinetics, activation energy

Due to ecological, geo-political and economical reasons, orientation to biodiesel usage is becoming an inevitable part of sustainable economy. Biodiesel is the most valuable form of renewable energy that can be used directly in any existing, unmodified diesel engine. Energy independence and smaller trade deficit can be achieved by development of biofuels i.e. we would be using our own living resources to power our development and enhance our economies. Biofuels create new markets for agricultural products and stimulate rural development because biofuels are generated from crops; they hold enormous potential for farmers. Biofuels burn more cleanly than gasoline and diesel. Using biofuels means producing fewer emissions of carbon monoxide, particulates, and toxic chemicals that cause smog, aggravate respiratory and heart disease, and contribute to thousands of premature deaths each year. Biofuels contain carbon that is taken out of the atmosphere by plants and trees as they grow and leads to less global warming.

Studies show that biodiesel reduces CO₂ emissions to a considerable extent and in some cases all most nearly to zero¹⁻⁵.

Biodiesel can be prepared by transesterification reaction using homogeneous and heterogeneous catalysts. However, numerous advantages of heterogeneous over homogeneous catalysis are generally known. In this particular case these advantages can be classified as: (a) ecological – elimination of the washing section and huge amounts of waste water; easier disposal of spent solid catalyst; (b) economical – cheaper reusable catalyst, production of glycerol and the end product of high purity; and (c) investment-type – process simplification and elimination of entire sections from the process schemes. Among various heterogeneous catalysts, CaO is widely used in research. Its properties regarding leaching of the catalyst could be improved by several methods such as mixing with other oxides or by calcinations etc. In this work the ability of CaO as a potential heterogeneous catalyst for biodiesel synthesis from crude rubber seed oil was investigated in a broad range of reaction temperatures and pressures. Kinetic parameters including the activation energies were calculated. A correlation of ester yields to the physicochemical properties of differently activated catalyst samples was ascertained in order to determine those characteristics that make CaO, a suitable catalyst for biodiesel production⁶⁻¹⁰.

Experimental Section

Rubber seed oil used is non-edible and is commercially obtained after extraction from rubber seeds. As far as the availability of the feed stock is concerned Kerala is the leader in rubber production among the states of India. More than 90 percent of the rubber produced in India is from Kerala. Rubber seeds are being a byproduct in this plantation which is not being utilized properly at present. For reducing the overall production cost of biodiesel, feed stock has been selected as rubber seed oil extracted from rubber seeds which are being unutilized. The physical and chemical properties of the feedstock as well as of the obtained biodiesel – density, iodine and saponification values, kinematic viscosity, acid value, cetane number etc were determined according to the appropriate standards. Methanol with a purity of 99.5% is

commercially obtained. Catalyst used is prepared from waste eggshells and calcined at 950°C.

Catalyst preparation and characterization

The eggshells were washed with tap water to remove impurities adhering to the shells. The clean and dry shells were crushed in an agate mortar, rinsed with distilled water, and dried in an oven at 120°C for 24 h. The dried crushed shells were calcined in a muffle furnace for 5 h at 950°C. Characterization of catalyst includes SEM (Scanning Electron Microscope), BET (Brunauer–Emmett–Teller) etc. BET was carried out to determine properties like surface area, mean pore diameter and pore volume¹¹⁻¹⁶.

Reaction procedure

The transesterification batch reaction was carried out in a three-necked 500 mL round bottom flask fitted with a condenser, a thermometer, and a mechanical stirrer whose speed was monitored by a digital tachometer. Measured quantity of crude rubber seed oil was placed into the reaction flask with a catalyst (0.2-2.0 wt. % of oil) and methanol (methanol to oil molar ratio varying from 3.5 to 10). The reaction temperature was varied from 50 to 65°C and reaction time was varied from 0.5 to 3 h. The experiment was carried out in a constant temperature water bath. After completion of the reaction, the catalyst was separated from the reaction mixture by filtration. The filtrate was poured into a separating funnel, the glycerol layer was drained from the bottom and the biodiesel was washed with hot distilled water containing a few drops of orthophosphoric acid to neutralize the pH and remove traces of glycerol and catalyst particles¹⁷⁻²¹.

The yield of biodiesel was calculated using the following equation:

$$\text{Yield (\%)} = \frac{\text{Weight of biodiesel}}{\text{Weight of oil}} * 100 \quad \dots (1)$$

Determination of kinetics of the process

To determine the kinetics of the reaction, the effect of reaction temperature and time were measured. It was assumed that the catalyst was used in sufficient amount with respect to oil to shift the reaction equilibrium towards the formation of fatty acid methyl esters. Thus, the reverse reaction could be ignored and change in concentration of the catalyst during the course of reaction can be assumed to be negligible^{9,10}. Assuming the reaction to be a single step transesterification, the rate law of the

transesterification reaction for forward reaction can be expressed by Eq. 2:

$$-r_A = \frac{-d[TG]}{dt} = k_1 * [TG] * [ROH]^2 \quad \dots (2)$$

where [TG] is the concentration of triglycerides and [ROH] that of methanol and k_1 is the equilibrium rate constant. This overall reaction follows a second order reaction rate law. However, due to the high molar ratio of methanol to oil, the change in methanol concentration can be considered as constant during reaction. This means that by taking methanol in excess, its concentration does not change the reaction order and it behaves as a first order chemical reaction²²⁻²⁵. Hence, the reaction obeys pseudo-first order kinetics. Finally, the rate expression can be written as:

$$-r_A = \frac{-d[TG]}{dt} = k * [TG] \quad \dots (3)$$

where k is modified rate constant and $k = k_1 * [ROH]^2$. Assuming the initial triglyceride concentration was $[TG_0]$ at time $t = 0$, and at time t it falls down $[TG_t]$. The integration of above Eq. (3) with the assumptions gives the following equation:

$$\ln[TG_0] - \ln[TG_t] = k * t \quad \dots (4)$$

From mass balance:

$$X_{FAME} = 1 - \frac{[TG]}{[TG_0]} \quad \dots (5)$$

Or

$$[TG] = [[TG_0](1 - X_{FAME})] \quad \dots (6)$$

where X_{FAME} is the conversion of methyl ester. In addition, in terms of conversion the rate expression can be written as

$$\frac{dX_{FAME}}{dt} = k (1 - X_{FAME}) \quad \dots (7)$$

which on integration and rearrangement gives,

$$-\ln(1 - [X_{FAME}]) = k * t \quad \dots (8)$$

Results and Discussion

Characterization of oil

The physical and chemical characteristics of the crude rubber seed oil were determined according to international standards and are shown in Table 1.

Catalyst characterization

Brunauer–Emmett–Teller (BET) surface area and pore volume, specific surface area and active sites play important roles in catalyst activity. The specific surface area was 22.5m²/g. The average adsorption pore diameter was 810nm and the average desorption pore diameter was 670nm. The high pore size is found to be desirable for better diffusion of reactants and product molecules. Scanning Electron Microscopy (SEM –EDS) analysis is being done for the prepared catalyst and results are shown in Fig. 1.

Transesterification of rubber seed oil over CaO heterogeneous catalyst

Methanolysis of rubber seed oil at 65°C – working conditions are shown in Table 2.

Table 1 — Property analysis of rubber seed oil

Density	857 kg/m ³
Viscosity	6 cSt.
Flash Point	208°C
Fire Point: 212°C	210°C
Cloud Point: -5°C	-5°C
Pour Point: -2°C	-2°C
Calorific value: 36.1 MJ/kg	37.5 MJ/kg
Acid value: 1.68 mg KOH/g	1.68 mg KOH/g
Iodine value: 134.5	134.5
Saponification value: 193.6 mg KOH/g	193.6 mg KOH/g

Property analysis of the prepared biodiesel

The Table 3 shows the property analysis of the prepared biodiesel.

Kinetics of conversion of crude rubber seed oil to methyl ester

The thermal transesterification reaction is divided into three steps. With increase in reaction time, it is found that in each reaction step one molecule of methyl ester is formed by consuming one mole of methanol. By ignoring the intermediate reactions of diglyceride and monoglyceride, the three steps have

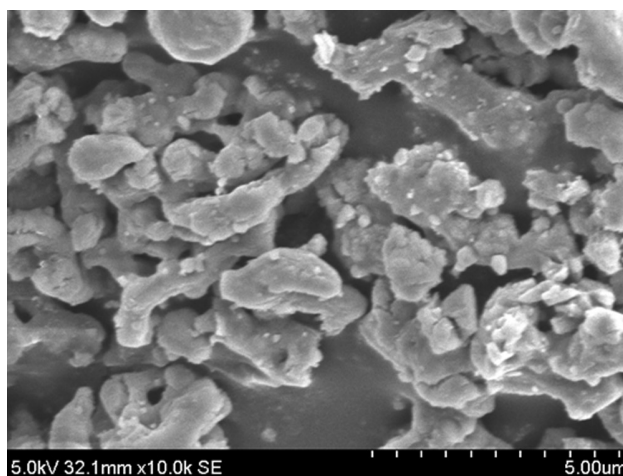


Fig. 1 — SEM-EDS analysis of the prepared catalyst

Table 2 — Methanolysis of rubber seed oil at 60°C – working conditions

Expt	Methanol: oil mole ratio	Mass of used catalyst, wt%	Stirring intensity, rpm	DG, max time, min	MG, max time, min	Maximal yield of FAME Time, min
1	4:1	0.6	1000	12.1/45	1.55/80	97.2/105
2	6:1	0.8	800	10.5/90	0.97/160	98.2/270
3	8:1	1	600	8.2/180	0.76/240	97.1/300
4	10:1	1.2	600	6.3/270	3.11/300	97.3/400
5	12:1	2	300	11.1/150	1.7/150	95.6/240

Table 3 — Property analysis of the prepared biodiesel

Property	ASTM Method	Unit	Biodiesel B100	Petro-diesel
Flash point	D93	°C	110	54
Fire point		°C	115	60
Viscosity	D445	cSt	3.7	2.0-5.5
Cloud Point	D2500	°C	-6	2 max
Pour Point	D97	°C	-4	-3 max
Calorific value	D240	MJ/kg	39.78	43.73
Cetane number			50	45
Density	D1298	Kg/m ³	892	835
Acid value	D974	mg KOH/g	0.22	0.835

been combined in a single step. Upon optimization, it was found that maximum conversion was obtained at the optimum conditions of catalyst amount of 0.8 wt. % relative to oil and methanol/ oil molar ratio of 6:1. The fractional conversion of methyl ester was obtained by the study of temperature and time on % conversion of biodiesel as shown in Fig. 2. Since the alcohol concentration is high, reaction is assumed to follow pseudo first-order kinetics. By fitting the data between $\ln(1 - X_{FAME})$ and t , a linear relationship was obtained which supports the hypothesis that the reaction is of pseudo-first order. From Fig. 3, the value of reaction rate constant k was determined at different temperature. The activation energy of transesterification reaction was calculated using the Arrhenius equation. The slope and intercept of the graph between $\ln k$ and $1/T * 10^3$ (Fig. 4) gives the values of activation energy and frequency factor. The activation energy (E_A) determined from graph was 75.8 kJ/mol and the frequency factor (A) was $2.76 * 10^{10} \text{ min}^{-1}$. The activation energy for the transesterification of rubber seed oil was in the range

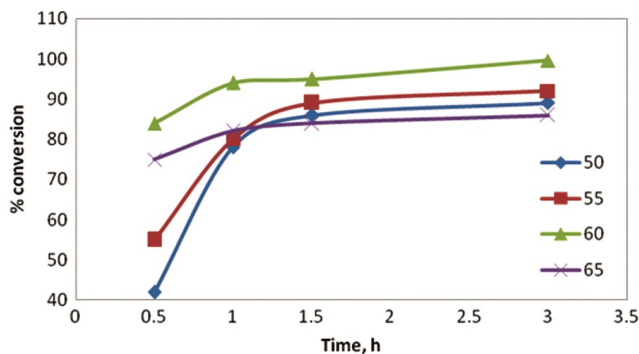


Fig. 2 — Effect of reaction temperature and time on % conversion of biodiesel at a reaction condition catalyst loading 0.8 wt. %

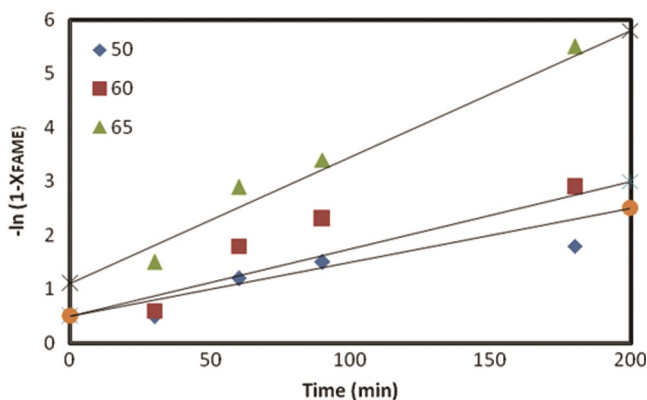


Fig. 3 — $-\ln(1 - X_{FAME})$ versus reaction time plot at different temperatures (methanol/ oil molar ratio = 6:1, catalyst loading = 0.8 wt. % relative to oil)

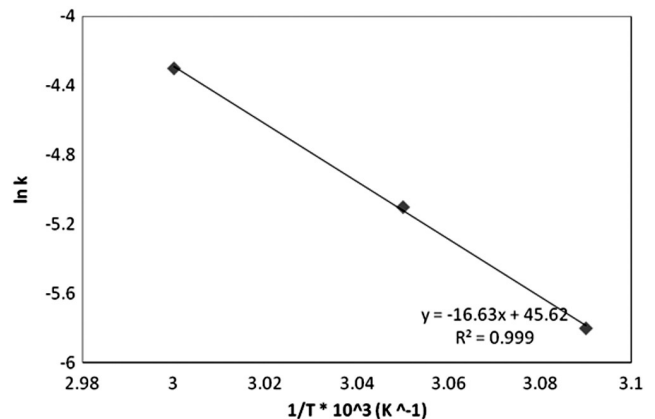


Fig. 4 — Arrhenius plot $\ln k$ versus $1/T * 10^3$ for transesterification of rubber seed oil by CaO derived from eggshells

of activation energy obtained for transesterification of soybean oil i.e. 31.6-80 kJ/mol. Arrhenius plot gives an R^2 value of 0.99 (R^2 should be in the range of <1) fits with the experimental data.

Conclusion

CaO obtained after calcination of waste egg shells has shown excellent activity for the transesterification of rubber seed oil with biodiesel conversion and yield obtained under optimal conditions of 99.32% and 98.2%, respectively. The present study addresses environmental as well as economic aspects of biodiesel production by using rubber seed oil as feedstock and CaO as catalyst. The kinetics study shows that for the transesterification reaction, the activation energy is obtained as 75.8 KJ/mol and follows pseudo first-order kinetics.

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