Studies of base catalyzed transesterification of karanja oil

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Abstract
Karanja oil methyl ester was synthesized by the transesterification of karanja oil with methanol using potassium hydroxide as catalyst. The reaction was carried out at 55°C for 1 hour. The reactants were continuously stirred with speed ranging from 250-650 rpm. The acid value of oil was found to be 18.62 mg KOH/g of oil. Influence of parameters like water content (%), oil flow rate (ml/min) and effect of stirring speed (rpm) were investigated by varying these parameters in 5 levels and a design for performing the experiments was developed using Minitab and Design-Expert. An approach has been made to study the pressure and velocity changes when the reactants flow through the inlet and outlet pipes. Glycerol being insoluble remained in the reactor and the conversion was found by testing the ester using Gas Chromatography and also by analyzing the acidity of the samples.
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Keywords: Transesterification, Methyl ester, Karanja oil, Chromatography.

1. Introduction
The interest in the use of renewable raw materials for fuel production started during the early 1990's and one significant research has been the utilization of fatty acids esters derived from vegetable oils for biofuel production [1, 2].Fatty acids and glycerol have wide range of applications and fatty acids are used as a feedstock for the production of oleo chemicals such as fatty alcohols, fatty amines and fatty esters. These oleo chemicals are used as lubricant greases, anti-block agents, plasticizers, emulsifiers and as ingredients in the manufacture of soaps, detergents and animal feed. Generally, biodiesel is produced by alkali-catalyzed (e.g. NaOH, KOH) transesterification with methanol which requires a relatively short reaction time than enzyme catalyzed reaction. Transesterification of vegetable oil was performed as early as 1853 by scientists E. Duffy and J. Patrick, many years before the first diesel engine became functional [3]. Biodiesel is being used in public transportation system of Europe, Japan and North America. In the recent years, biodiesel has gained importance as a renewable fuel. The environmental issues concerned with the exhaust gases emission by the usage of fossil fuels also encourage the usage of biodiesel which has proven to be eco-friendly than fossil fuels [4, 5]. Biodiesel offers enhanced safety characteristics when compared to diesel fuel. The higher price of biodiesel compared to petroleum diesel is partly compensated by legislation due to lower emissions and biodegradability of biodiesel. Low cost feedstock, such as non-edible oils, waste frying oils and animal fats could be used as raw materials to reduce production costs associated with biodiesel and make it competitive with petroleum diesel. However, the relatively higher amounts of free fatty acids (FFA) and water in this feedstock results in the production of soap in the presence of alkali catalyst. Thus, additional steps are required to remove water from the reaction mixture. In fact, base-catalyzed processes often employ an acid-catalyzed pre-

esterification reactor to remove excess FFAs [6]. For the alkali-catalyzed reaction, the effect of alcohol to oil ratio was found to be the most important variable affecting the yield, while temperature had a significant effect on the initial reaction rate. Acid catalysts would be more effective when the degree of refinement of oil was low, and for oils that had a high FFA content. Studies have also been done on enzyme-catalyzed transesterification and trend is towards the ecologically acceptable processes. An optimized chemical synthesis of biodiesel improves the conversion yield and reduces the cost of production in most favorable conditions. In this paper, we report on the biodiesel production using alkali catalyzed transesterification with optimization of some parameters like inlet flow rate of oil, reactor agitation speed and water content in the reaction system.

2. Materials and methods

Methanol (99.5% pure) was provided by SRL (Sisco research laboratories, Chennai).Distilled Water and karanja oil were supplied by local agents. Fatty acid methyl ester (FAME) was produced by the alkali catalyzed transesterification of karanja oil. Air-dry kernels of karanja have 19.0% moisture, 27.5% fatty oil, 17.4% protein, 6.6% starch, 7.3% crude fiber, and 2.4% ash. Fatty acid composition: palmitic 3.7-7.9%, stearic 2.4-8.9%, arachidic 2.2-4.7%, behenic 4.2-5.3%, lignoseric 1.1-3.5%, oleic 44.5-71.3%, linoleic 10.8-18.3% and eicosenoic 9.5-12.4%. Schematic system of the reactor is shown in Figure 1. The temperature was controlled by the usage of a water bath. The temperature was maintained at 55°C. Without dehydration, the oil was pumped into the reactor (2000ml) steadily and the reaction started when a quantitative amount of methanol liquor dissolved in NaOH was pumped by another way into the reactor. Many studies of alkali-catalyzed transesterification were conducted, and a temperature near the boiling point of the methanol and a 6:1 mole ratio of methanol to triglyceride was maintained. A separating funnel separated by-product glycerol after reaction.
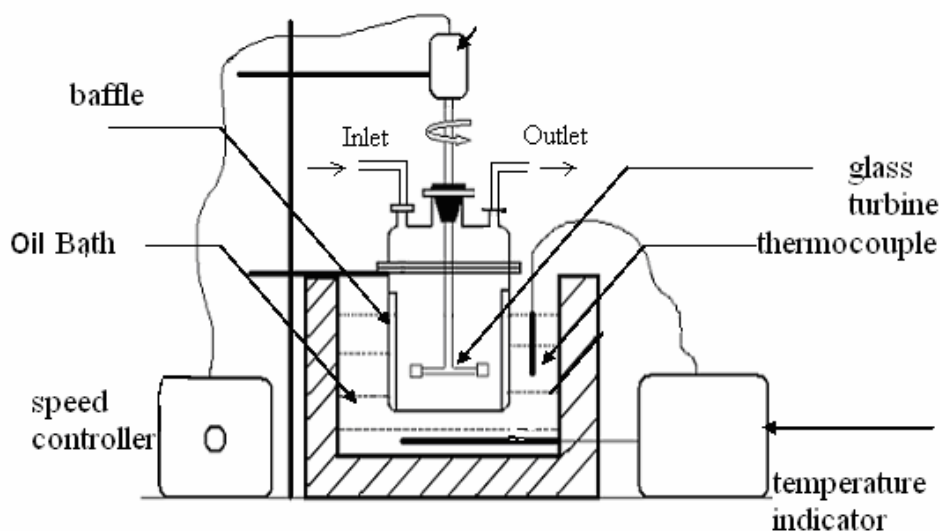

Figure 1. Reactor setup

A gas chromatograph is used to determine the fatty acid composition of the ester sample. The esterification of fatty acid is done according to the BIS standards. After esterification a sample of 1μl of fatty acid methyl ester was withdrawn using a 10ml syringe and injected into the gas chromatography. Flame ionization mode was selected and area of each peak was detected. The oven temperature was maintained at 200°C. The injector and the detector temperatures were at 240°C.for comparison, initially standards of stearic, palmitic and oleic acid were prepared using heptane and analyzed [7].

3. Results and discussion

Flow rate of oil, rpm (stirring speed) were considered as the parameters for investigation (Table 1), since other parameters like temperature, pH, reaction time for alkali catalyzed reaction were extensively investigated by many researchers. Using Minitab and Design-Expert, the numbers of runs were reduced and yield obtained for the different levels of parameters are presented in Table 2.

Table 1. Experimental variables and their levels

Parameters	-2	-1	0	1	2
% Water content	2	5	8	11	14
Flow rate	10	15	20	25	30
RPM	250	350	450	550	650

Table 2. Variation in parameters and their corresponding yield (%).

Experiment no	% Water content	Oil flow rate	Rpm	% Ester yield
1	-2	-2	-1	23.41
2	-2	-2	-2	17.92
3	-1	-1	2	24.21
4	-1	-1	-1	26.12
5	-1	-1	-2	19.21
6	-2	-2	1	10.21
7	2	2	2	12.32
8	0	0	-2	27.45
9	1	1	-2	32.21
10	-1	-1	0	17.98
11	-2	-2	-2	9.34
12	1	1	1	49.87
13	0	0	-1	31.43
14	1	1	-1	33.89
15	1	1	0	41.65
16	0	0	1	36.12
17	-2	-2	-2	23.12
18	0	0	2	31.19
19	-2	-2	0	21.67

3.1 Effect of water content
Methyl ester production decreased with increasing amounts of water in the reaction mixture (Figure 2). In the case of enzyme catalyzed transesterification, with water content of 10–15%, a plateau conversion reached and after which the conversion ratio of methyl ester began to decrease with increasing water content [8]. It has been reported that water greatly reduces the amount of esters formed when refined vegetables are esterified with methanol. The inhibition of methanolysis by a small amount of water content present in the oil can be eliminated by performing the reaction in cycles and by heating the oil to remove moisture [9].
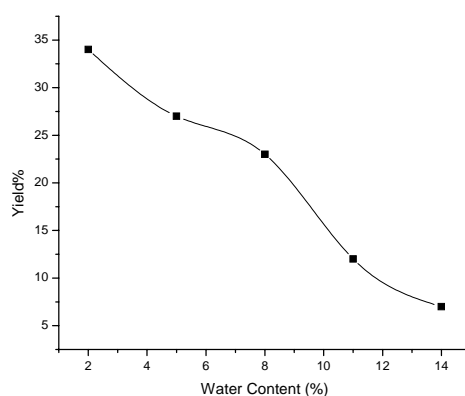

Figure 2. Effect of water content on the yield of ester

3.2 Influence of flow rate of oil
If the velocity is too high, the contact time of substrate with catalyst will be too short and the reaction will be incomplete (Figure 3). If the velocity is too low, the throughput of the reactor will be little [8].

3.3 Effect of stirring speed

The 250 ml conical flask (reactor system) is continuously agitated with a magnetic stirrer, with other optimized conditions remaining constant (Figure 4). A maximum yield of 48% (approx) was achieved when the temperature is maintained at 55ºC with flow rate of substrate maintained at 25ml/min. The water content is the reaction mixture was 11%.
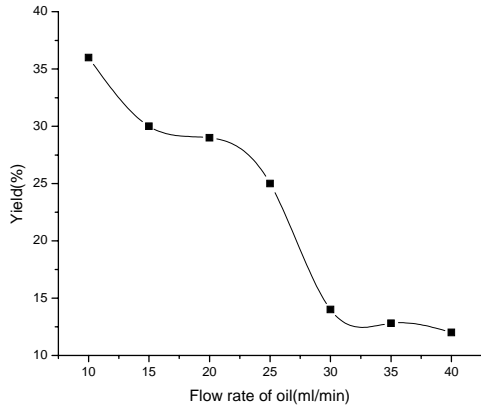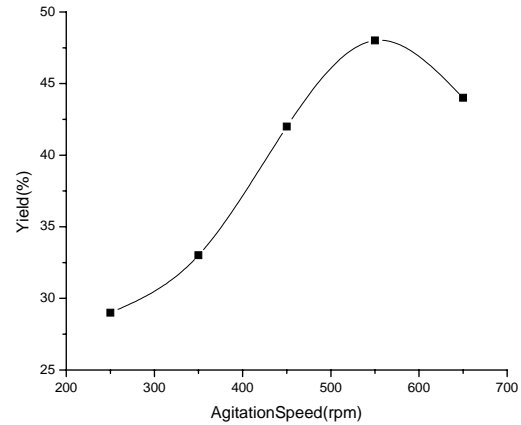
Figure 3. Effect of oil flow rate on the yield of ester

Figure 4. Effect of stirring speed on the yield of ester

4. Simulation using fluent

The velocity and the pressure profile at both the inlet and the outlet of the pipe section were plotted as a function of position. The pipe section was modeled using Gambit and the simulation was done using Fluent 6.0. The pip is of 1 meter length and 0.005m diameter. The meshing was done with an interval count of 12 and the solver used is fluent 5/6. The continuum is selected suitably were the fluid 1 (karanja oil) flows in the first pipe and the fluid 2(methyl alcohol) flows in the second pipe. The laminar flow regime is selected, as the optimum velocity of the fluid is 0.0053 m/s. The velocity and pressure profile both at the inlet and the outlet are simulated the velocity at the outlet pipe was found to be 0.0086 m/s. The velocity distribution and the pressure profile at the inlet and outlet are shown in Figures 5-7.
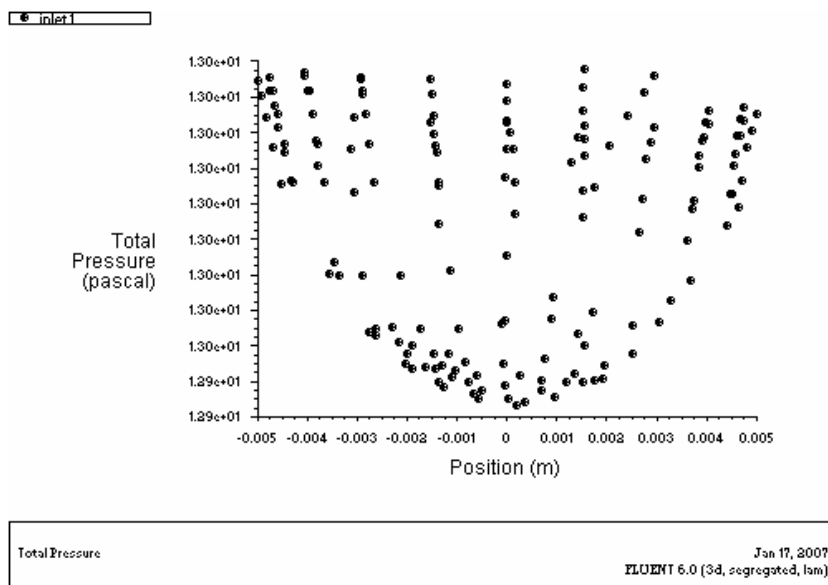
Figure 5. Total pressure at inlet 1 as a function of length of pipe
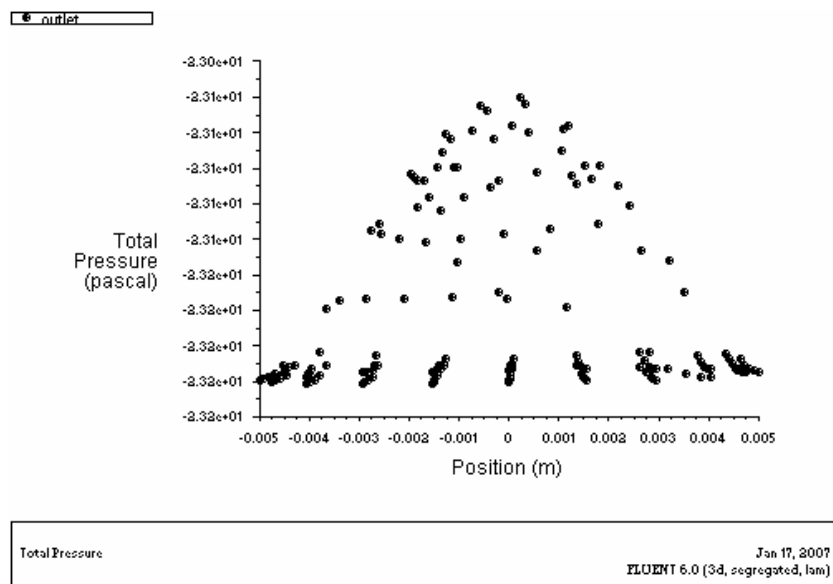
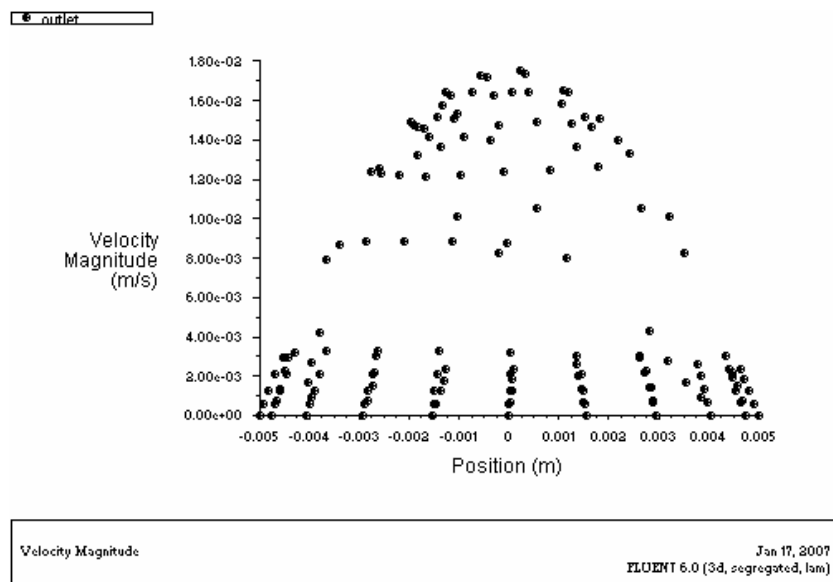Figure 6. Total pressure at the outlet as a function of length of pipe

Figure 7. Velocity change at the outlet as a function of length of pipe

5. Conclusions

Karanja oil was tested for its potential use as substrate for biofuel production. The high conversion of oil with methanol was sensitive to the presence of water content, reducing the amount of ester formed. However, water in lower percentage also inhibited the effective transesterification and yielding high glycerol content. Maximum conversion of 49.87% was obtained when the water content in the reactor was 11% with substrate flow rate at 24 ml/min and agitation speed maintained at 550 rpm. In conclusion, alkali esterification is a viable method for the production of alkyl esters from karanja oil, vegetable oil and greases. Extensive research works are being carried out in the enzyme catalyzed transesterification to enhance the cold-temperature properties, emissions and engine performance of methyl esters produced.

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