

Effective Conversion of Kapok Seed (Ceiba Pentandra) Oil into Biodiesel and Investigation of Effects of Catalyst concentrations and Chromatographic Characterization

M.A. Asokan^{1*} and R.Vijayan²

School of Mechanical and Building Sciences, VIT University,
Vellore, Tamilnadu, India.

Department of Mechanical Engineering, Government College Of Engineering,
Salem, Tamilnadu, India.

*Corres.author: asokan.ma@vit.ac.in, +919952664776

Abstract: In this study the biodiesel produced from Kapok (Ceiba Pentandra) seed Oil with methanol(CH₃OH) has been considered in the presence of catalyst i.e., sodium hydroxide (NaOH), Optimum yield conditions were determined experimentally by changing the parameters of temperature, reaction duration, quantity of methanol and weight of catalyst is investigated, at the end of the experiments, the maximum yield of 95% was obtained in with the use of 21 percent methanol at 60°C reaction temperature for 2 h reaction period by catalyzing with 12g NaOH. The changes in physical property of viscosity, density, calorific value (CV) and flash point of kapok seed oil biodiesel were determined by ASTM procedures and were found to be comparable to ASTM standards for diesel fuel. GC-MS (Gas chromatography – mass spectrometry) demonstrated the presence of hydrocarbons.

Key words : Biodiesel, kapok oil, catalyst, methanol, maximum yield, reaction period, Gas chroma-tography–Mass spectrometry, diesel.

1. Introduction

Rapid increase in energy requirements, industrial development and inadequacy of petroleum diesel fuels to meet the increased demand requires increased research and enhancement of studies for new and renewable energy sources. The availability of sulphur in the diesel causes corrosion of engine parts and environmental pollution. Large number of researchers has concluded that vegetable oils having potential to used as alternative fuels (1, 2). On the other hand, using raw vegetable oils for diesel engines can cause various engine-related problems like poor fuel atomization, higher viscosities, higher flash points, low volatility, incomplete combustion, engine deposits, injector chocking and piston ring sticking (3,4). The results have shown that the crude vegetable oils are not suitable for direct alternate for diesel fuel. Many methods are used to reduce viscosity of vegetable oil. These are pyrolysis, dilution, micro emulsion and trans-esterification. Currently, trans-esterification is one of the foremost methods due to its conversion efficiency. Alkali catalyst such as Potassium Hydroxide (KOH) is easily getting dissolved in methanol. In methanolysis, formations of emulsion were quick and easily break down to form glycerol rich bottom layer and Methyl ester rich upper layer (5). Biodiesel can be produced from both vegetable oil and animal fat and its chief advantage is it is clean fuel than fossil fuel, the typical biodiesel prepared through transesterification of crude oil over homogeneous catalysts such as NaOH and KOH (6). Catalyst is used to enhance the transesterification reaction rate and yield. Methanol is preferred alcohol when compared to other alcohols, because of its low-cost and its physical and chemical advantages it can quickly react with Triglycerides. Excess presence of alcohol makes to complete the reversible reaction (7). Transesterification also called alcoholysis which is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis except that an alcohol is used instead of water (8).

This has been generally used to decrease the viscosity of the vegetable oil. Transesterification of vegetable oils are influenced by various factors such as vegetable oil/methanol molar ratio, catalyst concentration, Nature of catalysts, and temperature. Also, reaction time plays an important role in obtaining biodiesel of the required purity. Therefore, we considered above parameters for producing biodiesel. Biodiesel can be derived from edible oil seed crops like sunflower, palm, rapeseed, soybean, coconut, etc. these are first generation biodiesel feedstocks. The various types of vegetable edible oils and biodiesels are used in the many countries as an alternate fuel for petro-diesel it is mainly depending on the environment conditions. For example, soybean oil in the USA, rapeseed in Canada and sun flower oils in Europe, palm oil in Malaysia, Indonesia and Thailand, coconut oil in the Philippines and cottonseed oil in Turkey and Greece are being produced (9). But their production is not sustainable because of its perceived competition with food therefore the price of edible oils and biodiesel cost increases. The elevated price of bio-diesel, the researchers made to find the new non edible bio-diesel to solve these issues. Non-edible vegetable oils have lower price than edible vegetable oil(10). Moreover the use of non-edible oil does not compete with food harvest. Some of non edible oils like *Jatropha curcas*, *Calophyllum inophyllum*, *karanja*, *jojoba*, *mahua*, and waste cooking oil, animal fats, tobacco seed oil, rubber seed oil etc. have focused in the last few years as feedstock's for biodiesel production and it shows that use of non-edible oil is one of the solutions for energy demand.

The present work is on bio-diesel produced from Kapok seed (*Ceiba Pentandra*) oil and is one of the new alternative feed stocks for petroleum diesel. Use of pure biodiesel, or biodiesel blends i.e., mixture of biodiesel and diesel can be used as a fuel in any Diesel engine without any modification.

2. Experimental work

2.1. Materials

The biodiesel conversion equipment and chemicals i.e., magnetic stirrer with heating plate, Pyrex make glass beakers, Fuel measuring jar, separating funnel, burette stand, electronic weighing scale and methanol and sodium hydroxide were purchased.

2.2 Oil Extraction

Required amount of Kapok seeds were collected from Erode region, Tamilnadu, India. The collected seeds were dried in the sun light for two to three days for removing moisture. The moisture free seeds feed to the steam assisted mechanical oil expeller, the oil is extracted an average of 4–5 turns of the kapok seed cake, at the end oil was fully extracted from seeds. The obtained oil was filtered to remove the suspended particles and stored in an air tight glass container.

2.3 Transesterification

The transesterification process begins with 1 liter of kapok oil was poured in to the 2 Litre single-necked round bottom flask which was kept on the magnetic stirrer supported with 1.5 kW heating plate. The oil was heated at 40°C the thermometer reads the temperature at regular interval of time. In order to achieve uniform temperature of the oil, they must be stirred well at constant rate of 750 rpm to ensure homogeneous mixing.

Sodium methoxide solution was prepared simultaneously by dissolving 12g of NaOH with 225mL methanol in separate beaker and stirred for half an hour. The resultant methoxide solution was added into one liter of kapok oil which is already heated in the separate magnetic stirrer, the mixture was heated at 60°C with stirring at 750 rpm for 120 min. The reaction mixture was kept to room temperature and allowed to one day to settle down, resulting in the separation of two phases. The upper phase contained biodiesel and the lower phase contained glycerin as byproduct. Finally bio-diesel separated from glycerol and washed three times with ordinary tap water by aqua air pump. In order to optimize the biodiesel process, a number of parameters and operating conditions were investigated. The transesterification reactions were conducted at various quantity of methanol starting from 15%, 18%, 21%, and 24% ,The catalyst concentrations were varied from 8g, 9g,10g,11g,12g,13g and 14g whereas the temperatures range from 45 to 70°C at an interval of 5°C and reaction duration varied from 45 minutes to 150 minutes.

The biodiesel yield was calculated by using the expression:

$$\% \text{ yield} = \frac{\text{grams of methyl ester produced}}{\text{grams of oil used for reaction}} \times 100$$

3. Results and Discussion:

3.1 Fuel properties:

3.1.1 Viscosity

Viscosity is a very important property for the fuels used in the diesel engine for fuel atomization, as well as fuel distribution. Viscosity is a measure of a fluid's resistance to flow. A fluid with high viscosity resists motion due to its high molecular cohesiveness gives a lot of internal friction. A fluid with low viscosity flows easily because its low molecular cohesiveness results in very small friction when it is in motion. The high viscosity of kapok oil is the major reason to carry out the transesterification processes. High viscosity of Fuels affects the injector lubrication and atomization (11). Fuels with low viscosity lead to increase leakages, wear and tear of moving parts of the injection system. And also the leakages is one of the reason for power loss in the engine. Fuels with large viscosity have a tendency to form larger droplets on injection which cause poor combustion, increased exhaust smoke and emissions. The high viscosity and low volatility of kapok oil are the major problem for the direct use of vegetable oil as fuel. The measured kinematic viscosity of the kapok oil methyl ester at 40°C is 5.96 mm²/sec. This value is within the ASTM specification range.

3.1.2 Density

Fuel density is very important property of fuel with low energy content per liter will cause the engine to produce less peak power; however this high density of Biodiesel compensates the lower energy content. The mean density value of kapok oil Biodiesel is 878 kg/m³, which lies in the specified range of ASTM specification. Ash is a measure of the amount of inorganic matter (non-combustible matter) contained in the fuel. High concentrations of these materials can cause injector tip plugging, combustion deposits and injection system wear. The average ash content of the prepared Biodiesel was 0.007% by mass which is lower than that of ASTM specification range. This is due to the fact that during the transesterification of kapok seed oil, most of inorganic content materials are removed with the glycerin layer.

3.1.3. Calorific Value

Calorific value is another important parameter. It is defined as the number of heat evolved by the complete combustion per unit weight of fuel. Bomb calorimeter was used to measure the calorific value of fuel. The measured Calorific value of produced kapok oil biodiesel is 30978kJ/kg.

3.1.4. Flash Point

Flash point is the property of the fuel and is a measure of flammability of a fuel. Higher flash point indicates safe storage and transportation of the fuel. The measured value of flash point of kapok oil biodiesel is 140°C this value lies in the ASTM specification ranges.

Table- 1 Physical and fuel properties of Kapok seed Oil Biodiesel and Diesel

Physical and fuel properties	ASTM Method	ASTM D6751/Biodiesel	ASTM D975/Diesel	Biodiesel
Kinematic viscosity (40°C in mm ² /s)	D445	1.9 – 6.0	1.9 – 4.1	5.96
Pour point °C		-15 to 16	-35 to -15	Less than -5
Flash point °C	D93	130 min	60 - 80	140
Copper strip corrosion	D130	No. 3 max	--	2b
Ash (% by mass)	D874	0.020 max	--	0.007
Distillation percent v/v recovered at 350°C	D1160	360 °C max	--	35
Density at 15°C, kg/m ³	D4052	860-900	820 – 845	878
Acid number, mg KOH/g	EN14104	0.80 max	0.50	0.96

The synthesized kapok seed oil biodiesel was characterized for its physical and chemical properties employing the methods of ASTM and the results are given in (Table -1) along with the recommended values for biodiesel (ASTM-D6751) and diesel (ASTM-D975). The determined density at 15°C was 878 kg/m³ and Kinematic viscosity at 40°C is 5.96 mm²/sec, which are comparable to ASTM values for diesel (Table -1). Viscosity is the most important property of biodiesel since it affects the operation of fuel injection equipment at low temperature while increasing viscosity affects the fluidity of the fuel (12). The produced Fatty Acid Methyl Ester (FAME) has acid values higher than the ASTM recommended value due to leaching of the sulphonic acid group (13). The acid number can be achieved to meet ASTM specifications through water stripping, a common processing step for the industrial production of biodiesel or with the use of adsorbents, liquid-liquid extraction, membrane or ion exchange.

3.1.5 GC-MS Analysis

GC-MS analyses were performed by using a GC make Perkin Elmer clarus 680 coupled to Mass Spectrometer clarus 600 (EI) 1 µL biodiesel in hexane was injected in Elite Column-5MS(30.0m, 0.25mmID, 250µm df). The carrier gas was helium. The injection was performed in split mode (10:1). The parameters of the oven temperature program are: start at 60 °C for 2 min with 10 °C/min intervals up to 300 °C. The temperatures of the injector and detector were set at 250°C. The mass spectrometer was set to scan in the range of m/z 50–600. The GC-MS information, Acquisition parameters and Mass condition (EI) are given in table-2, Table-3 and Table-4 respectively.

Table -2 GC-MS Information

Make	Perkin Elmer
GC model	Clarus 680
Mass Spectrometer	Clarus 600 (EI)
Software	Turbo Mass version 5.4.2
Library version	NIST-2008

Table -3 Acquisition parameters

Oven	Initial temp 60°C for 2 min, ramp 10°C/min to 300°C, hold 6 min
Total Run Time	32.00 minutes
Injection	250°C, Volume=1 µL, Split=10:1, Flow Rate: 1 mL/minutes
Carrier Gas	Helium
Column	Elite-5MS (30.0m, 0.25mmID, 250µm df)

Table -4 Mass Condition (EI)

Solvent Delay	2.00 min
Transfer Temp	240°C
Source Temp	240°C
Scan	50 to 600Da

3.1.6 Analysis of Fatty Acid Methyl Esters with GC-MS

Gas Chromatography and Mass Spectrometry GC-MS was used to study the chemical composition of the kapok oil biodiesel product. Fatty acid methyl esters are suitable for separation, identification, quantification and analysis by GC. Different fatty acid methyl esters were detected at different retention times. The GC-MS confirmed the presence of 13 major components, The gas chromatograms of kapok oil biodiesel are shown in figure-1, the identified FAMES were 10-methyl-undecanoate (C13:0) Mwt214(Molecular weight), 12-methyl-tridecanoate (C15:0)Mwt242, tetradecanoic acid (C16:0) Mwt270, 16-methyl-heptadecanoate (C18:0)Mwt298, 9,10-methylenehexadecanoate (C18:1) Mwt282, octadecenoate (C18:1) Mwt296, methylene- heptadec (C18:2) Mwt294, 9,12-octadecadienoate Mwt322, methylene-octadec Mwt308, methylene-octadecanoate Mwt310, naphthalenone,octahydro Mwt194, heptacosanoic acid Mwt438, and nitrocyclohexane Mwt213. The identified FAMES were verified by retention time data and mass fragmentation pattern. Surprisingly we found four FAME are saturated

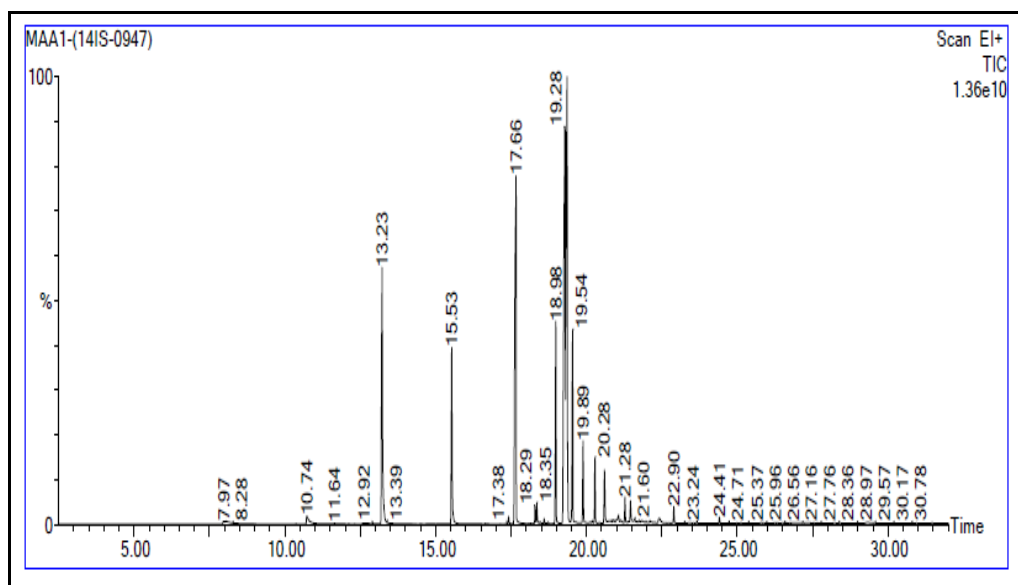


Figure -1 The GC-MS graph of kapok oil methyl ester

3.2. Biodiesel Yield

The synthesis of biodiesel from kapok oil was investigated by transesterification of oil with methanol. The maximum yield of biodiesel obtained by, optimizing different parameters. The detailed discussion of the optimization is as given below.

3.2.1 Effect of Methanol Percentage on Biodiesel Reaction (NaOH=12g):

The reaction temperature of the kapok oil methyl ester is very significant due to the high melting point of kapok oil. While the reaction temperatures range between 45– 70 °C, at the interval of 5°C and by changing the methanol quantity from 15 %, 18 %, 21 % and 24%, remaining parameters like concentration of catalyst and reaction time were fixed throughout the experiments, the experiment starts with 15% methanol, it is found that no reaction till temperature reached 45°C for all above cases. No trace of glycerine during this temperature range.

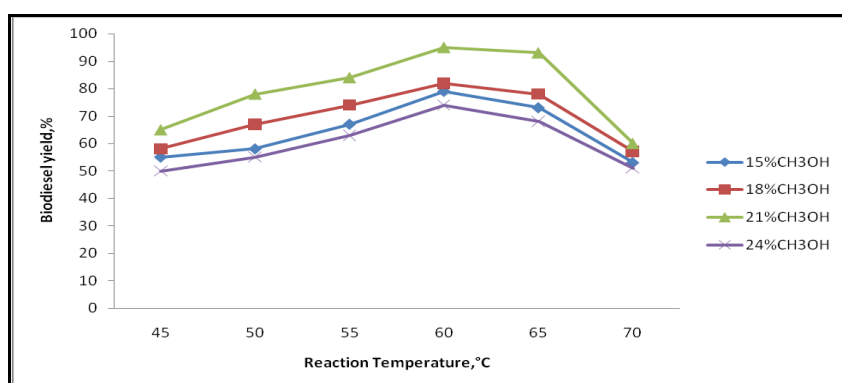


Figure- 2 Biodiesel yield vs Temperature (12 g NaOH and variation of methanol quantity)

The figure-2 shows the temperature from 45 to 70° C, the reaction starts slowly, at 50°C a small amount of the glycerine phase was observed at the bottom of the flask during 1hr reaction time. After one hour the mixture was kept in a room about one day and biodiesel yield was measured. The next batch of bio diesel production maintains the same temperature but the reaction time extended to 2 hours. Then this mixture kept in a room for 24 hours for settling. Finally it is found that the bio diesel yield increases considerably with temperature and time, which are important parameters in the reaction. Yield Increases in the temperature range from 45°C to 60°C. Further increasing the temperature to 70°C, it is seen that the yield decreased (14). This is due to higher temperature, methanol starts to vaporize and deactivation of lipase. The processes repeated by changing the methanol volume by 18%, 21% and 24%. It is found that out of the four categories, the optimum

temperature for the reaction is found to be in the range of 60°C at 21% of methanol and the reaction duration 2 hour which gives the maximum yield of 95%. The biodiesel yield increased considerably with increasing reaction temperature, however higher amount of methanol leads to decrease in biodiesel yield due to presence of more methanol glycerol mixture, which is difficult to separate.

3.2.2 Effects of Catalyst Concentration on Biodiesel Reaction.

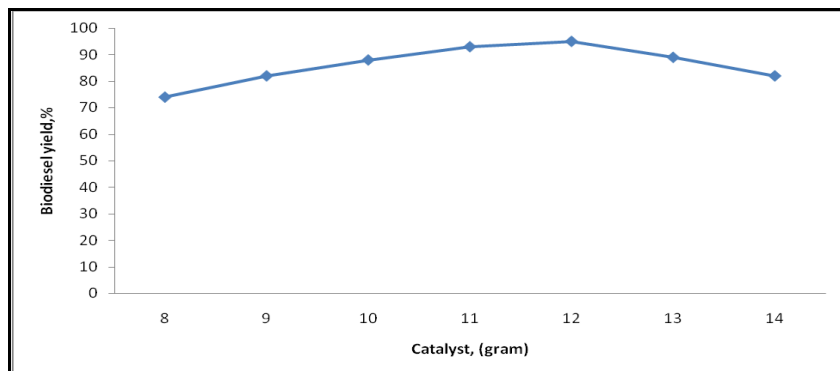


Figure-3 Variation of Catalyst (NaOH) vs Bio diesel yield (methanol 21%, reaction temperature 60 °C and reaction duration 2 hour)

Based on the results obtained from methanol optimization followed to examine the effect of the catalyst concentration on Biodiesel yield, the reaction was carried out at different catalyst concentrations. While keeping other parameters constant like methanol 21%, reaction temperature 60°C and reaction duration 2 hour. By increasing the catalyst concentration increased the transesterification rate, the catalyst concentration increased from (8 to 14 gram) at an interval of one gram (1 g) using half an hour of shaking at 60 °C and the results are given in figure-3, which shows that maximum conversion of 70 to 95 % was obtained at 12 grams concentration of catalyst, with 2 hr reaction period. The reason may be increase of catalyst amount could improve the contact between catalyst and reactants. Therefore, in this study the optimum catalyst concentration was 12 grams. With further increase in catalyst's concentration the percentage conversion gradually decreased (12).

3.2.3 Effect of Reaction Time on the Reaction

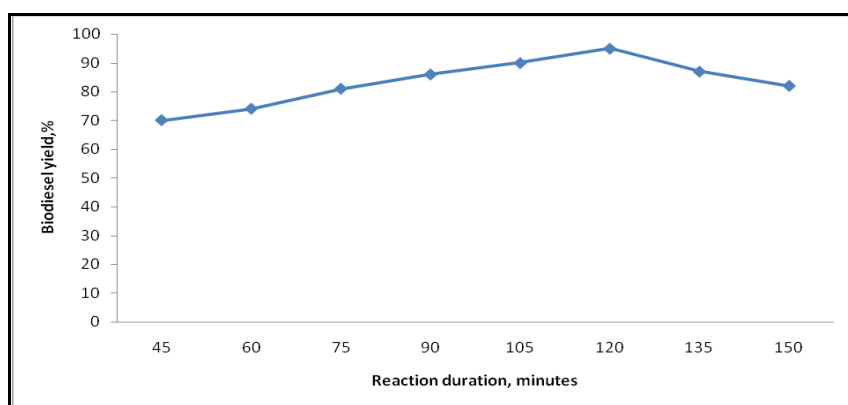


Figure -4 Bio diesel yield vs Reaction duration (temperature 60°C, NaOH = 12g, methanol 21 %)

Based on the catalyst concentration optimization the effect of reaction time on percentage of conversion of kapok oil into biodiesel was also investigated under the optimized conditions of 21% of methanol, NaOH concentration of 12 g and temperature of 60 °C. The reaction time was varied from 45 to 150 minutes and the results are shown in figure -4, which depicts that the percentage conversion of oil into biodiesel increases gradually with the increase in reaction time and was maximum at 120 minutes. Biodiesel conversion rate increased significantly with increasing the reaction time (15). The percentage yield for the production of kapok seed oil biodiesel by using the optimized parameters was found to be 95%. Biodiesel yield decreased with time, such decrease may be due to the combination reaction of the biodiesel product and by-product (glycerol) into mono-glycerides and the formation of gels.

4. Conclusions

The study was focused on the effect of temperatures, methanol percentage, catalyst concentrations and reaction duration on the production of Biodiesel from kapok seed oil. Besides, the physic-chemical properties of the produced biodiesel were determined. The results showed that the produced biodiesel satisfied the requirements specified by EN and ASTM standards for biodiesel. In addition, the highest yield of biodiesel approximately 95% was achieved with a methanol of 21%, catalyst (NaOH) concentration of 12 grams, 60°C reaction temperature when the reaction time is 2 hours. Increasing the catalyst concentration reduced the biodiesel yield due to the formation of soap and gels which hindered the separation of the biodiesel. The reaction temperature was observed to enhance Biodiesel formation. However, operating at temperature near the boiling point of methanol resulted in reduced Biodiesel yield. By increasing the reaction temperature beyond 60°C results in reduction of biodiesel yield, this is due to the formation of a large number of bubbles which slow down the reaction. The physical and chemical properties of the Kapok oil biodiesel (viscosity, density, flash point and heating values) was verified and these values are equivalent to ASTM standards for diesel. Fatty acid methyl esters (FAMES) of kapok seed oil biodiesel was determined by GC–MS analyses.

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