

## Production of Biodiesel from Thumba Oil: Optimization of Process Parameters

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(Received: October 21, 2010; Accepted: December 29, 2010)

**Abstract:** Fast depletion of world's petroleum reserves and increasing ecological concerns has created a great demand for environmentally benign renewable energy resources. Biodiesel has emerged as a sustainable alternative to petroleum origin diesel and its usage have been encouraged by many countries. Transesterification reaction is the most common process to produce biodiesel from variety of vegetable oils and animal fat. Transesterification process depends upon a number of process parameters which are required to be optimized in order to maximize the biodiesel yield. Thumba oil is an underutilized non-edible vegetable oil, available in large quantities in Rajasthan, India and its potential suitability as a biodiesel feedstock is still not evaluated comprehensively. In this research paper, the transesterification process for production of Thumba oil methyl ester has been analyzed and the various process variables like temperature, catalyst concentration, amount of methanol and reaction time have been optimized with the objective to maximize yield. The optimum conditions for transesterification of Thumba oil with methanol and KOH as catalyst were found to be 60°C reaction temperature, 6:1 molar ratio of Thumba oil to methanol, 0.75% catalyst (w/w<sub>oil</sub>) and 1 hour reaction time.

**Key words:** Thumba oil % Transesterification % Process optimization % Maximum yield

### INTRODUCTION

Diesel fuel is extensively used in heavy trucks, city transport buses, locomotives, electric generators, farm equipments, underground mine equipments and plays an important role in the economy of India [1]. Various forms of gaseous, liquid and solid pollutants from diesel engine can endanger human health and damage the ecological environment [2-4]. Diminishing petroleum reserves and environmental consequences of exhaust gases from diesel fuelled engines are some of the major reasons for using biodiesel as an alternative fuel for diesel engines [5]. Biodiesel is mono-alkyl-esters of long chain fatty acids derived from vegetable oils or animal fats produced by process of transesterification in which, oil is reacted with a monohydric alcohol in presence of a catalyst [6]. It is an oxygenated, renewable, biodegradable and environmentally friendly fuel with similar flow and combustion properties and low emission profile [7, 8].

The raw material being exploited commercially by the developed countries constitutes the edible fatty oils derived from rapeseed, soybean, palm, sunflower, coconut, linseed, etc. [9]. However, in India, it is not viable to produce biodiesel using such edible oil to produce biodiesel because of a big difference in demand and supply of edible oils [10]. In this context, crops that can produce non-edible oils such as Jatropha, Karanja, Mahua, Cotton seed, Polanga, Rice bran oil, Palm oil etc. in substantial quantities, can be grown in large scale on non-cropped waste lands.

Alkali-catalyzed transesterification process is the most common process for production of biodiesel and need to be optimized for different process variables [11]. Ghassan *et al* evaluated and optimized conversion of waste animal fat into ethyl and methyl ester and analysed reaction temperature, molar ratio of alcohol/oil, type of alcohol type and type of catalyst as major variables. They found that ethanol was better than methanol and 50°C was found as optimum temperature with two hours of

reaction time [12]. Leung et. al found the optimal reaction variables for the transesterification of used frying oil as reaction temperature of 60°C, reaction time of 20 min, 1.1 wt.% NaOH and 7:1 molar ratio [13]. Ghadge et. al used a central composite rotatable design to study the effect of methanol quantity, acid concentration and reaction time on the reduction of free fatty acids content of mahua oil during its pretreatment for making biodiesel using response surface methodology and found optimum combination for reducing the acid level of mahua oil to less than 1% after pretreatment out of 23 designed experiments [14]. Meher *et al.* carried optimization of transesterification of Karanja oil and found optimum reaction conditions as 1% KOH as catalyst, MeOH/oil molar ratio 6:1, reaction temperature 65°C, rate of mixing 360 rpm for a period of 3h and reported 97-98% yield of methyl esters from Karanja oil under the optimal conditions [15]. Yuan *et al* studied optimization of conversion process parameters of waste rapeseed oil with high free fatty acids (FFA) into biodiesel by response surface methodology and found maximum conversion at methanol/oil molar ratio of 6.5:1, catalyst concentration of 1% (by the weight of the oil), reaction time of 65.4 min and temperature of 48.2°C [16]. Sinha et. al optimized the various transesterification process variables like temperature, catalyst concentration, amount of methanol and reaction time to get maximum yield of high quality rice bran oil biodiesel and concluded with optimum conditions 55 °C reaction temperature, 1 h reaction time, 9:1 molar ratio of rice bran oil to methanol and 0.75% catalyst NaOH (w/w<sub>oil</sub>) [17]. Several researchers also optimized biodiesel production process variables like catalyst concentration, amount of methanol, reaction time and reaction temperature for different other oils [11, 18-20]. Jeong *et al.* found that response surface methodology can be applied effectively to the optimization of the process parameters in biodiesel production from lard oil [21].

A lot of work has been done on biodiesel process optimization incorporating edible oils. However, there are plenty of oilseeds which remain un-utilized or underutilized for biodiesel production. Thumba (*Citrullus colocynthis* Schrad), is an unexploited perennial creeper growing wild in hot Indian arid zone. Being a perennial creeper with luxuriant growth, its soil binding capacity is of considerable significance and it has a potential to yield around one million tones of the oil rich seeds from the arid districts of Rajasthan [22]. In this study, investigations have been carried out to assess the potential suitability of Thumba oil as biodiesel feedstock and optimization of process parameters such as molar ratio, catalyst concentration, reaction time and reaction temperature.

## MATERIALS AND METHODS

**Biodiesel Production Method:** Transesterification is a catalyzed (KOH/NaOH) chemical reaction involving oil/fat (triglyceride) and an alcohol (methanol/ethanol) to yield fatty acid alkyl esters (biodiesel) and glycerol as a byproduct. All the chemicals and reagents used in the study were purchased from local market in Delhi and Thumba oil was procured from Udaipur, Rajasthan. Acid number of Thumba oil was determined as per ASTM D664 and was found to be 0.8. Since FFA content was less than 1%, base catalyzed reaction was selected for biodiesel production.

The experimental setup included 250 ml glass three-necked batch reactor equipped with a reflux condenser, a mechanical stirrer and a thermometer, immersed in a constant-temperature bath. 100 g Thumba oil was taken in the reactor and placed in the water bath at the desired temperature. Different weight percentage of Methanol and Potassium Hydroxide (KOH) were mixed and added to oil in the reactor at the prefixed temperature. After the required time, mixture was transferred to a separating funnel, allowing glycerol to separate by gravity for overnight. After removing the glycerol layer, washing of methyl ester was done with lukewarm water to remove catalyst, methanol and glycerol residuals. The raw biodiesel after successive washing was heated to 100°C in an open vessel to remove any water particles.

**Procedure for Evaluation of Biodiesel Conversion:** The conversion of Thumba oil into its methyl ester was evaluated using Gas Chromatograph (Make-Netel India Ltd.) using EN14103 test method. The basic instrumentation for Gas Chromatograph included a carrier gas cylinder with regulator, a flow controller for the gas, an injection port for introducing the sample, the column, the detector and the recorder. The injection port, column and detector were heated to a pre-specified temperature of 140 °C to 240 °C in 20 minutes and then they remained at 240°C for 10 minutes. Since the mobile phase is a carrier gas, the components present in the analytical mixture should be vaporized, so that it can be effectively carried through the column. The methyl esters sample was prepared by diluting 250 mg methyl esters with 5 ml methyl hepta deconate standard solution (500 mg per 50 ml hexane) in a small vial. 1 micro-liter of the diluted sample was injected into Flame Ionization Detector (FID) for ester conversion analysis. The percentages of each peaks/methyl esters were calculated and based on these values, ester conversion was calculated.

**Experimental Plan:** The stirring speed was kept constant at 250 rpm throughout the experiments. The reaction temperature was varied from 50°C to 65°C in steps of 5°C. The molar ratio of alcohol was varied from 3:1 to 15:1 in steps of 3:1, the catalyst amount was varied from 0.5% to 1.5% (w/w<sub>oil</sub>) in steps of 0.25% and the process time was varied from 10 min to 90 min in steps of 10 min.

Initial 25 sets of experiments were performed with different combination of molar ratio and catalyst quantity by keeping reaction temperature and reaction time constant as 60°C and 60 minute. The effect of molar ratio and catalyst quantity on ester yield was evaluated during these experiments. Experiments of each set of variables were repeated twice to reduce experimental errors. After the exhaustive experiments, combination of optimum values of molar ratio and catalyst concentration was evaluated on the basis of maximum percentage yield. Subsequently, transesterification reaction was carried using optimum value of molar ratio and catalyst concentration keeping temperature constant at 60°C and samples were drawn at every 10 minutes till the reaction was completed in 90 minutes. Thereafter, four transesterification reactions were carried using optimum values of molar ratio, catalyst concentration and reaction time at different temperatures ranging from 50°C to 65°C with an increment of 5°C.

## RESULT AND DISCUSSION

**Effect of Molar Ratio:** Molar ratio of alcohol to vegetable oil is one of the most important parameters affecting the yield of ester. The stoichiometry of the transesterification

reaction requires 3:1 molar ratio to yield 3 mol of ester and 1 mol of glycerol, however, excess alcohol is required to drive the reaction close to completion. In this work, the effect of methanol was investigated in the range of 3:1 to 15:1 (molar ratio), keeping other process parameters constant. The reaction was performed with different concentrations of KOH. The results are shown in Fig. 1. It was found that the ester yield increases with increase in molar ratio of methanol to vegetable oil. Experimental results revealed that molar ratio 6:1 and catalyst concentration of 0.75 % KOH showed maximum ester conversion of 97.8 %. The results are similar to the results obtained by other researchers using variety of vegetable oils [11, 13, 19].

**Effect of Catalyst Concentration:** The effect of KOH concentration was studied in the range of 0.5-1.5% (weight of KOH/weight of oil). The reaction temperature and time were kept constant as 60°C and 1 hour respectively. The results for different molar ratios of methanol to oil are shown in Fig. 2. It was found that the ester yield initially increases and then decreases as the amount of catalyst increased from 0.5% to 1.5%. High concentration of KOH reduces the yield because of high soap formation and also leads to undesirable extra processing cost because it is necessary to remove it from the reaction products at the end. Similar results were reported by Dorado *et al.* [23] for brassica carinata oil with KOH catalyst and Sinha *et al.* [19] using rice bran oil and NaOH as catalyst. 6:1 and 0.75% KOH were found to be optimum values of molar ratio and catalyst concentration.

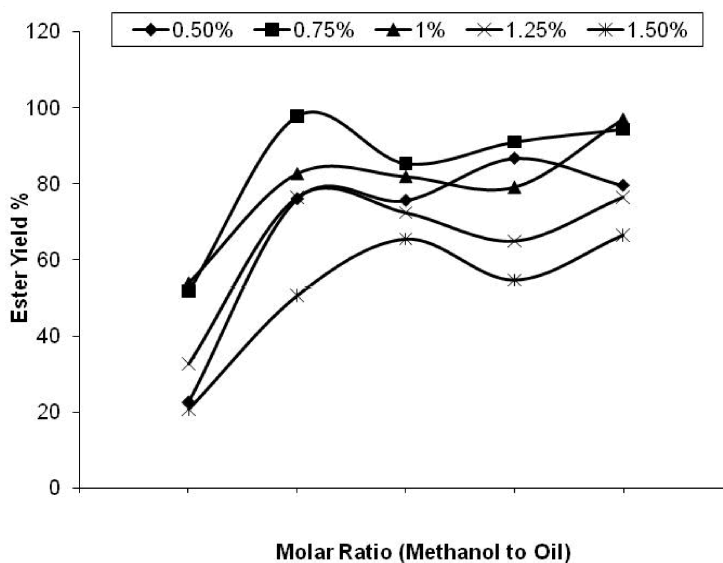


Fig. 1: Effect of molar ratio (methanol to oil) on ester yield at different KOH concentration.

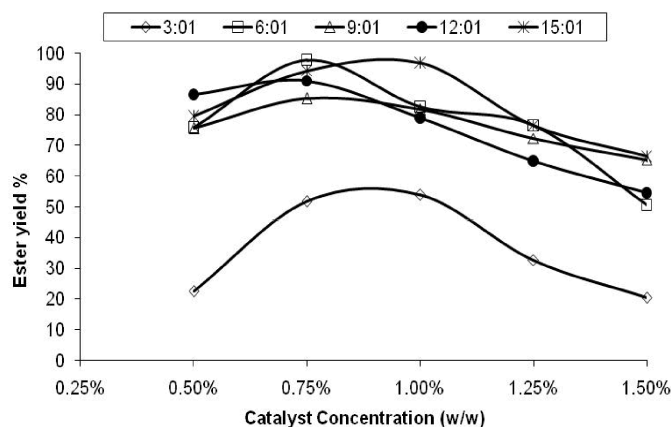


Fig. 2: Effect of KOH concentration on ester yield at different molar ratio of alcohol to oil.

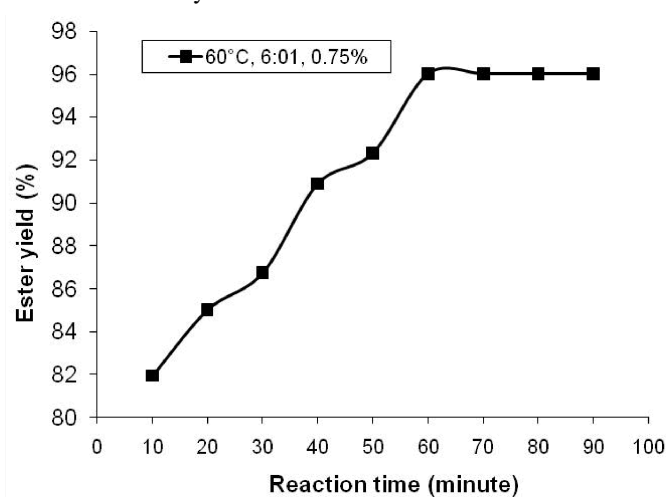


Fig. 3: Effect of Reaction time on ester yield

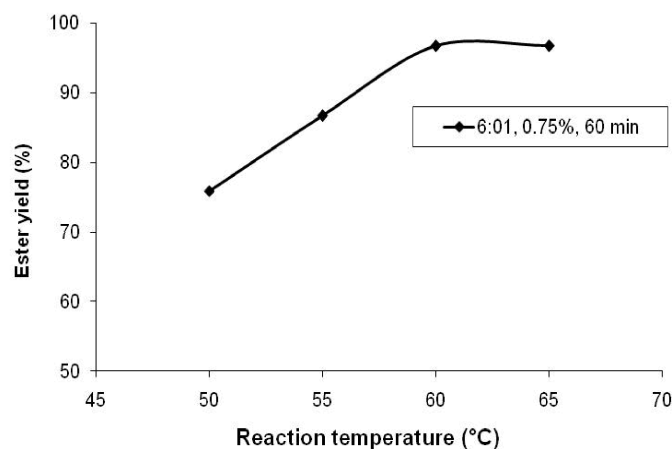


Fig. 4: Effect of Reaction temperature on ester yield.

**Effect of Reaction Time:** Effect of reaction time was studied from 10 minutes to 90 minutes in the interval of 10 minutes while all other parameters e.g. molar ratio, catalyst concentration and reaction temperature were kept constant as 6:01, 0.75 % and as 60°C respectively. The

reaction starts very fast and almost 80% of the conversion takes place in first 5 min and after 1 hour, almost 93-98% conversion of the triglycerides into ester takes place [17]. The effect of reaction time on ester yield is shown in Fig. 3. After 10 minutes of reaction, conversion was found

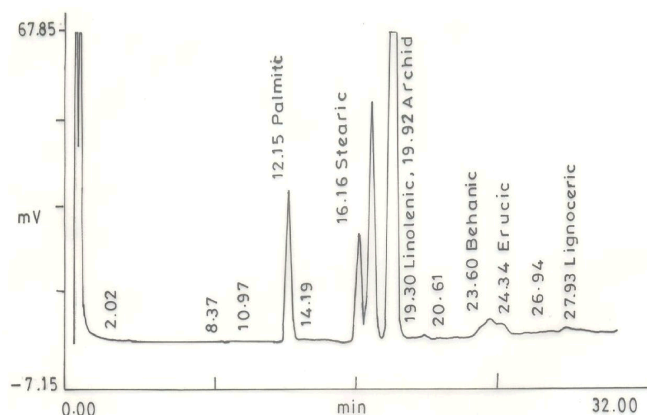


Fig. 5: Chromatograph Showing Fatty Acid Composition of TME.

Table 1: Physico-chemical properties of mineral diesel and TME.

Property	Test Procedures	Diesel	Thumba methyl ester
Specific gravity @ 15 °C	ASTM D1298	0.8329	0.88
Kinematic Viscosity @ 40 °C (cSt)	ASTM D445	2.6	5.3
Cloud Point	ASTM D2500	-5	-1
Pour Point		-12	-8
CFPP	ASTM D6371	-11	-6
Flash Point °C	ASTM D93	65.5	187.5
Fire Point		70.5	195.5
Carbon residue (Micro Method)%	ASTM D4530	0.05	0.01
Calorific Value (MJ/kg)	ASTM D240	46.05	39.798
Elemental analysis (% w/w)	C	81	71.6
	H	14	11.8
	N	1.97	1.13
	O	0.38	12.9
	S	0.61	----

Table 2: Fatty acid profile of Thumba oil.

S. No.	Fatty acids	wt %
1.	Palmitic (C <sub>16</sub> H <sub>34</sub> )	9.38
2.	Stearic (C <sub>18</sub> H <sub>38</sub> )	7.34
3.	Oleic (C <sub>18</sub> H <sub>36</sub> )	17.04
4.	Linoleic (C <sub>18</sub> H <sub>34</sub> )	61.05
5.	Behenic (C <sub>21</sub> H <sub>43</sub> )	4.05

to be 82 % and after one hour maximum conversion was observed as 96 %. After one hour, the ester yield decreased slightly.

**Effect of Reaction Temperature:** For studying the effect of temperature on the transesterification reaction, the reaction temperature was varied as 50, 55, 60 and 65°C, while the other parameters such as molar ratio of methanol to oil (6:1), reaction time (1 h) and KOH as 0.75% (w/w<sub>oil</sub>) were kept constant. The effect of reaction temperature on the ester yield is shown in Fig. 4. It was found that ester yield decreases as the reaction temperature increases above 60°C. Several researchers found that the increase in temperature influences the reaction in a positive manner [17, 19, 24].

### Physico-Chemical Characterization of Thumba Methyl Ester:

The physico-chemical properties of the Thumba Methyl Ester (TME) and Mineral Diesel were determined as per standard test procedures given in Table 1. The properties were evaluated at Biodiesel Production and Testing Center, Delhi Technological University, Delhi. Calorific Value is an important property measuring the energy content of the fuel, suggests its suitability as an alternative to Mineral Diesel. The calorific value of TME was measured using Parr 6100 Calorimeter and found to be 39.78 MJ/kg, which is around 86% of the calorific value of diesel (46.05 MJ/kg). The lower calorific value of TME is attributed to the presence of oxygen in the ester. The flash point and fire point were determined with the help of a closed cup Pensky Marten's apparatus. The flash point represents the tendency of a fuel to form flammable mixtures when exposed to air. This parameter is considered very vital in the handling, storage and safety of the fuels. The high flash point in the case of TME makes it safer fuel to handle. Specific gravity was measured with Anton paarr DMA 4500 density meter and found comparable to diesel. Kinematic Viscosity was

measured by Petrotest viscobath and CHNS was measured by Euro EA 3000-single. It can be seen from physio-chemical characterizations that TME has comparable properties to diesel.

The fatty acid composition of TME was also determined with the help of Gas Chromatograph and results are shown in Fig. 5 and also represented in Table 2. The Molecular weight of Thumba oil was calculated using fatty acid composition and was found 914.63.

### CONCLUSION

In this study, biodiesel production from Thumba oil using KOH as catalyst was carried out and it was found that KOH can be utilized as a catalyst for biodiesel production without any difficulty. The catalyst removal and purification of biodiesel using wet method, was studied in detail. It was also found that excessive catalyst concentration results in formation of soap and can also cause emulsion formation during purification of biodiesel. The optimization of major process parameters such as molar ratio (oil to alcohol), catalyst concentration ( $w/w_{oil}$ ), reaction temperature and reaction time was also carried out. The combination of process parameters giving optimum biodiesel yield was found to be 6:1 molar ratio of methanol to oil, 0.75% KOH ( $w/w_{oil}$ ), 60°C reaction temperature and 1 hour reaction time.

The density, flash point, cloud and pour points were higher for TME than those of mineral Diesel. The higher flash point of TME makes it a safer fuel to handle. The calorific value of TME was lower than that of Diesel. From the result of elemental analysis, it was found that TME has no sulphur and around 12 % oxygen content which would help in better combustion. It can be concluded after physio-chemical characterization that TME has comparable fuel properties to diesel and this makes it a potential substitute for Diesel fuel in compression ignition engines.

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