

Production of Bio-Diesel from Non-Edible Thumba (Citrullus Colocyntis) Seed Oil Using Mechanical Stirring Methodology and Analysis of Fuel Properties

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Abstract

The depletion of fossils fuels are going on very rapidly. After few decades fossils fuels will be exhausted. So to fulfil the demand of the fossils fuel there is a big need to find out the alternative fuel of the fossils fuel. The fuels which are based on petroleum play a very significant role in the development and growth of the industries, transportation, agriculture field and many other human requirements sector. Though these petroleum base fuels are limited and lessening day by day as the demand and consumption is increasing very rapidly. In addition, petroleum fuels are also polluting the environment and creating problem to human being as well as society also. Therefore, there is a need of research for alternative fuels and Biodiesel is a very good alternative fuel. In India, there is a various type of trees, shrubs, seeds and herbs are copiously available, which can be subjugated for the production of biodiesel.

Citrullus colocyntis (Thumba) is a type of non edible fruit which is widely found in western Rajasthan region and Gujarat state. It can be well used for production of biodiesel. In the present work, biodiesel has been obtained from Thumba seed oil (Citrullus colocyntis) using transesterification process with methanol & potassium hydroxide as catalyst by Mechanical stirring production technique. The properties of this Bio-diesel have been evaluated and it is found that the properties of Thumba Bio-diesel are comparable to conventional diesel fuel and can be acceptably used as alternative fuel with better performance compared with diesel and it may play a very vital role for the overall economic development.

Keywords: Thumba Seed Oil (Citrullus colocyntis), Transesterification, Bio- Diesel, Mechanical stirring production technique.

I. Introduction

The scarcity of conventional fossils fuels and the emissions produced by these fuels are serious concern in front of us. The world wide use of fossils fuels are continuously increasing as well as price of crude oil is also rising day by day. The economical growth of any developing country is based on agriculture and industrial sector. The basic power source of industrial sector as well as agriculture sector is diesel fuel. The expansion of economics is always come with increase in the transport ^[1]. India will be the third largest consumer of transportation fuel by 2020 after USA and China. In year 2009-10 India imported 159.26 million tons of crude oil ^[2]. About 90% of the total imported oil is consumed in transportation, many of the alternates of fossils fuels are available but the most efficient alternate is the biodiesel ^[3]. It is proposed by biodiesel mission Government of India, that by 2017, 20% of energy needs of India should be met by biodiesel. To meet this expectation it would require 12 to 13 million hectare of land for biodiesel feed stock plantation ^[4]. Bio-diesel is safe, renewable, non-toxic, and biodegradable in water (98% biodegrades in just a few

weeks), contains less sulfur compounds and has a high flash point (>130 °C). Biodiesel can be produced from edible or non edible vegetables oils, paper wastes, cooking wastes animals fats etc. Biodiesel is considered renewable because its primary feed stocks are vegetable oil and animal fat^[5]. Diesel engines operated on biodiesel have lower emissions of carbon monoxide, unburned hydrocarbons, particulate matter, and air toxics than when operated on petroleum-based diesel fuel. At present biodiesel mostly produced by the transesterification process of vegetables seeds (edible or non-edible) using methanol and consistent catalyst ^[6]. The most common method is transesterification and its leads to mono alkyl esters of vegetable oils and fats, now called Bio-diesel when used for fuel purposes. The methyl ester produced by transesterification of vegetable oil has a high cetane number, low viscosity and improved heating value compared to those of pure vegetable oil which results in shorter ignition delay and longer combustion duration and hence low particulate emissions ^[7]. Bio-diesel can be used in pure form (B100) or may be blended with petroleum diesel at any concentration in most injection pump diesel engines.

II. Potential Feedstock in India

India is the sixth largest consumer of crude oil in the world with about 70% of its local requirement met through imports. It produced 70,000 barrel/day of crude oil in 2007, while the consumption of petroleum products was at 2.5 million barrel/day. The oil import bill surged to US\$77 billion in 2007-08 from US\$6 billion in 1990-91. Consequently, the share of crude oil imports in the total import bill increased to 32.7% in 2007 from 25% in 1990^[9]. In India 70% of the population live in 638,596 villages and to a large extent thrive on farming^[10]. With growing population, farming community is under pressure to grow more food.

Jatropha, Pongamia pinnata or Karanj, Calophyllum inophyllum or Nagchampa, Hevea brasiliensis or Rubber seeds, Calotropis gigantea or Ark, Euphorbia tirucalli or Sher, Boswellia ovalifololata, Citrullus colocynthis or Thumba, Sunflower, Soybean, Corn, Rapeseed, Palm, Coconut,

Peanut, Mahua seed, Waste vegetables oil, Canola, Olive, Mustered. Non-edible oil feedstock's are: Daturastramonium, Opium poppy oil, Cottonseed, Sunflower, Castor, Karanja seed.

In this work, biodiesel has been prepared from Thumba oil by homogeneous catalyst e.g. KOH. Citrullus colocynthis (Thumba) seeds are rich in oil and protein and can be utilized on an industrial scale. Considering Citrullus colocynthis's potential as an oilseed feedstock for biodiesel Centre for Jatropha Promotion & Biodiesel (CJP) has honour to establish this untapped resource as alternative source for Biodiesel industry of future. The Citrullus colocynthis Plant must be regarded as a sure source of 2nd Generation Biodiesel and the foundation around which a profitable business plan can be built with combination of other non food biodiesel crops for its ability to provide large amount of oil and its pure hardiness and stress handling ability. Fig 1 shows the Thumba plant



Figure 1: Thumba Creeper Plant and Seeds

It is found wild in the warm, dry and sandy parts throughout India. It is most abundant in north-western plains of India, especially in the Barmer, Bikaner, Jaisalmer and Jodhpur districts of Rajasthan, and in Gujarat^[8].

III. Transesterification of vegetable oil:

Vegetable oil and animal fats were investigated well before the energy crisis of the 1970s. The early 1980s sparked renewed interest in alternative fuels. It is also known that Rudolf Diesel (1858-1913), the inventor of the diesel engine that bears his name, had used peanut oil as fuel in his invention. High fuel viscosity in compression ignition is the major problem associated with the use of vegetable oils; viscosities of vegetable oil are ranging 10 to 20 times higher than diesel fuel.

Bio-diesel is the product of the process of vegetable oil's transesterification^[13]. Bio-diesel is biodegradable, non-toxic and essentially free from sulphur; it is renewable and can be produced from agriculture and plant resources. Bio-diesel is an alternative fuel, which has a correlation with sustainable development, energy conservation, management, efficiency and environmental preservation. Transesterification is the reaction of a fat or oil with an alcohol to form esters and glycerol.

Alcohol combines with the triglycerides to form glycerol and esters. Among the alcohols that can be used in the transesterification process are methanol, ethanol, propanol, butanol and amyl alcohol. A catalyst is usually used to improve their action rate and yield. The process of transesterification brings about extreme change in viscosity of vegetable oil^[14]. Transesterification is the process of separating the fatty acids from their glycerol backbone to form fatty acid esters (FAE) and free glycerol. Fatty acid esters commonly known as Bio-diesel can be produced in batches or continuously by transesterifying triglycerides such as animal fat or vegetable oil with lower molecular weight alcohols in the presence of a base or an acid catalyst. This reaction occurs stepwise, with monoglycerides and diglycerides as intermediate products. The "R" groups are the fatty acids, which are usually 12 to 22 carbons in length. The large vegetable oil molecule is reduced to about 1/3 its original size, lowering the viscosity making it similar to diesel fuel. The resulting fuel operates similar to diesel fuel in an engine. The reaction produces three molecules of an ester fuel from one molecule of vegetable oil. In such reaction known as transesterification, a triglyceride is allowed to react with a threefold excess of an alcohol such as ethanol or methanol, and this alcohol takes the place of the

ester linkage to glycerol, yielding three fatty acid esters of the new alcohol and glycerol. Above the process using methanol is shown in figure 2.

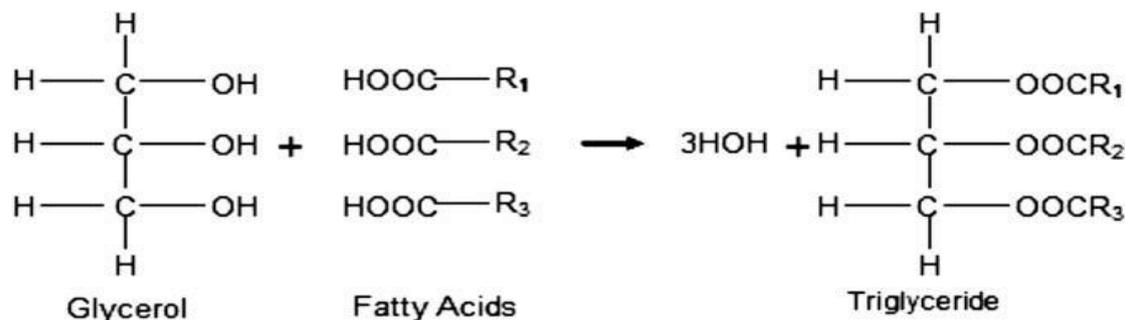


Figure 2: Transesterification Chemical Reaction

The Bio-diesel thus produced by this process is totally miscible with mineral diesel in any proportion. Bio-diesel viscosity comes very close to that of mineral diesel hence no problems in the existing fuel handling system. Flash point of the Bio-diesel gets lowered after etherification and the cetane number gets improved. Even lower concentrations of Bio-diesel act as cetane number improver for Bio-diesel blend. Calorific value of Bio-diesel is also found to be very close to mineral diesel. The overall process is normally a sequence of three consecutive steps, which are reversible reactions. In the 1st step from triglycerides, Diglycerides are obtained, in 2nd step from Diglycerides, monoglyceride is produced and in last step from mono glycerides, glycerin is obtained. In all these reactions esters are produced. The stoichiometric relation between alcohol and the oil is 3:1. However, an excess of alcohol is usually more appropriate to improve the reaction towards the desired product.

IV. Experimental work of Bio-diesel Production by Mechanical Stirrer Technique

In the present work Bio- diesel has been produced from Thumba oil using Mechanical Stirrer Technique which is purchased at local market of New Delhi.

Determination of FFA (Free Fatty Acid)

[Titration]:

For the determining the percent of FFA (free fatty acid) in the oil, a process called titration is used.

Here three molecules of one alcohol are replacing glycerol, another alcohol, in the triglyceride. Where, term R' represents different alkyl groups.

Three samples have been taken for find out of FFA% and data as follows:

Table 1: FFA content in Thumba seed oil

Sample No.	MI titration	% FFA
1	3	2.14
2	3.3	2.32
3	2.9	2.08

In the present work, the %FFA is determined of Thumba oil which is about 2.18 (average of three samples as mentioned in table 1) so only transesterification process is performed for production of biodiesel with alkali catalyst.

V. Mechanical Stirrer Technique Principle

Conventional mechanical stirring machine consist of temperature controller to control temp within the range of 0-100°C and speed controller is for controlling speed of stirrer in terms of revolution per minute (rpm). In this machine hot plate functions as a heating source to maintain the temperature of the solution. The beaker is placed on the hot plate then vegetable oil as per the requirement was poured into it at the beginning. The reaction started when a quantitative amount of methanol liquor dissolved in catalyst was poured into the beaker and then immediately drops the magnetic stirrer so that through its stirring action at a particular rpm, dilution of mixture can take place by switching the button on.

Experimental Set-up

The transesterification reactions were carried by conventional mechanical stirring method, which is shown in Figure 3.

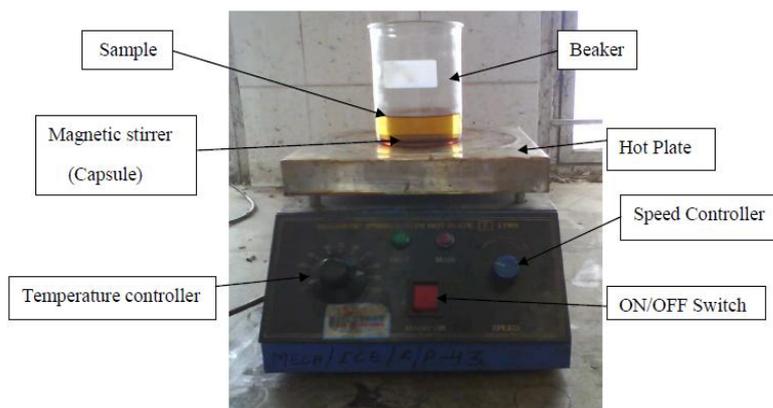


Figure 3: Mechanical Stirrer Equipment

Conventional mechanical stirring equipment consist of temperature controller to control temperature within the range of 0-100°C and speed controller is for controlling speed of stirrer. In this machine hot plate functions as a heating source to maintain the temperature of the solution. The beaker (500 ml) is placed on the hot plate and Thumba oil (400 g) was poured into it at the beginning. The reaction started when a quantitative amount of methanol as per molar ratio is dissolved with KOH was poured into the beaker. The magnetic stirrer due to its stirring action enhances the transesterification reaction.

VI. Reagents and Material used

1. Thumba oil, 400g/sample for preparing experimental biodiesel sample.
2. Methyl alcohol (CH₃OH) (99% pure) as per molar ratio.
3. Base catalyst (KOH) (85% pure) for accelerating the reaction mixture.

Experimental Procedure

This experiment has been performed to evaluate performance of mechanical stirring method of biodiesel production in terms of yield (%) and time.

Experiment has been performed with the following steps:

1. Thumba oil (400g) is taken in a beaker and filtered it to remove impurities. The raw oil is heated up to 110°C in order to remove water content of oil to avoid soap formation. This oil is allowed to cool up to 55°C temperature for the reaction to take place.
2. Now methyl alcohol (CH₃OH) is taken with a molar ratio of (1:4.5 & 1:6) and Catalyst (KOH) is taken as (0.5%, 0.75% and 1% by weight of oil).The mixer of methyl alcohol and KOH stirred until KOH dissolve in methyl alcohol.
3. This mixture is mixed with Thumba oil. The methanol is immiscible with the oil.
4. A magnetic capsule is dipped in the mixture of oil, methanol and catalyst and rotated with the help of magnetic stirrer.
5. During the reaction the temperature of mixture is kept between 55-60degC.
6. When reaction is completed the beaker is kept for the separation. Fatty acid has higher specific weight therefore it will settle at bottom. Separation of methyl ester and glycerol will take 2 to 3 hr duration.



Figure 4: Washing process of biodiesel.

7. After complete separation bio-diesel (methyl Ester) is visible in the upper layer and glycerol at the bottom.

8. Bio-diesel is separated from beaker for purification process. The catalyst present in the methyl ester is impurity.

9. Excess methanol present in biodiesel has been removed by vaporization process.

10. To remove the catalyst, water at around 60°C is mixed with the methyl ester and left for settling down. Water due to its higher specific gravity collected at bottom, this is shown in Figure

11. Excess water is removed by heating the biodiesel.

Experimental Data

The experiments are performed with alcohol to oil for the molar ratio as 6:1 and 4.5:1. The amount of oil, alcohol and catalyst taken is shown in Table 2. The main aim of this experiment is to calculate the maximum yield% (methyl ester for Thumba oil) of biodiesel production with time, catalyst percentage and molar ratio (alcohol/oil). The results (Experimental Data) obtained from Mechanical Stirrer Technique are shown in table 3.

Table 2: Oil, alcohol and catalyst during the experimentation

Molar ratio (alcohol/oil)	Quantity of non-edible oil (g)	Quantity methanol(g)	Catalyst(KOH)		
			0.5%	0.75%	1.0%
6:1	400g	88g	2.0g	3.0g	4.0g
4.5:1	400g	66.24g	2.0g	3.0g	4.0g

Table 3: Time and yield (%) of Thumba oil for different molar ratio and catalyst percentage

Percentage of catalyst (KOH)	Molar ratio 6:1		Molar ratio 4.5:1	
	Time (min)	Yield (%)	Time (min)	Yield (%)
0.5	20	85.65	20	82.26
	30	86.95	30	84.81
	40	89.28	40	87.06
	50	91.11	50	88.06
	60	91.70	60	87.61
0.75	20	89.38	20	86.27
	30	93.48	30	90.32
	40	94.67	40	93.50
	50	95.74	50	94.83
	60	96.93	60	94.39
1	20	90.76	20	88.62
	30	93.56	30	92.94
	40	94.61	40	94.53
	50	95.36	50	95.98
	60	97.82	60	95.76

VII. Results & Discussion

Figure 5.1 and 5.2 shows the graphical representation of Biodiesel yield with respect to time for 6:1 and 4.5:1 molar ratio respectively at different percentage of catalyst (KOH). It has been observed that there is higher yield in case of 6:1 molar ratio as compared to 4.5:1 molar ratio. It may be because of

alcohol using for 6:1 molar ratio is more than that of 4.5:1 molar ratio. The yield for 0.5% KOH is less as compare to 0.75% and 1% KOH in both the cases. It may be because of 0.5% KOH is not sufficient to enhance the reaction. The maximum yield obtained is 97.82 at 1% KOH for 6:1 molar ratio.

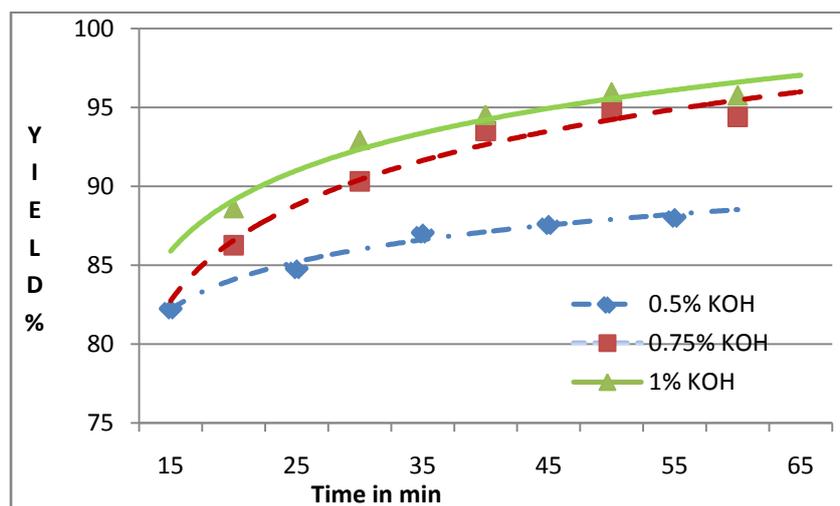


Figure 5.1: Time Vs Yield graph at 4.5:1 molar ratio for different KOH percentage

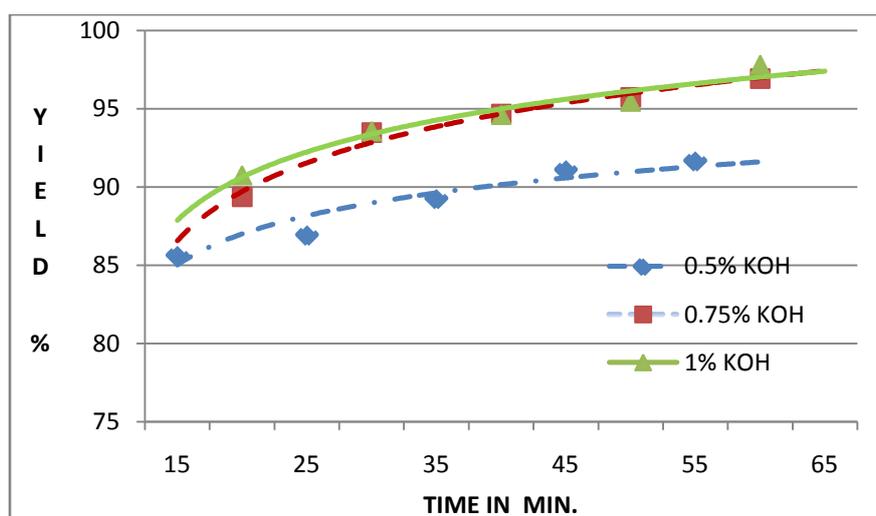


Figure.5.2: Time Vs Yield graph at 6:1 molar ratio for different percentage of KOH

VIII. Experimental data for physical and chemical properties

The experimental values of properties of fuels are specified below:

Table 4: Experimental data of physical and chemical properties

S. No.	Properties of fuel with data	Diesel Fuel	Bio-diesel
1	Viscosity@40°CcSt	1.25to 1.40	4.32
2	Density@15°C Kg/L	0.821	0.870
3	Cloud point(°C)	-23to12.5	4.5
4	Pour point(°C)	6to7	7.2
5	Flash point(°C)	47to70	91
6	Fire point (°C)	75	110
7	Calorific Value KJ/Kg	42000	37000
8	Boiling point (°C)	180-340	321

IX. Conclusion

Thumba (*Citrullus colocynthis*) has huge capability for biodiesel production. The most important feature of this Thumba is that it grows in the form of climbing plant in sandy soil with in a six month crop cycle. As we know that availability of the raw material controls the economics of the product. So, there should be a proper management for the plantation of neglecting trees and their usage to investigate the benefits from this Thumba Oil Plant. Bio-diesel is found better substitute for petroleum diesel and also most advantageous over petro-diesel for its environmental friendliness. The quality of biodiesel fuel was found to be considerable for its doing well use on compression ignition engines and ensuing replacement of non-renewable fossil fuels. Biodiesel produce from Thumba seed oil also yield comparable results with petroleum diesel. The important conclusions are as follows:

- It is found that in mechanical stirring the yield obtained at 1% KOH is higher.
- Maximum yield up to 97.82% is obtained from Thumba oil by mechanical stirrer technique.
- From results of experimental investigation of Thumba Biodiesel, it is found that it is having the properties similar to diesel. So blends are having the potential to reduce the over burden of the imports of diesel fuel.

Finally, it is concluded that Thumba Biodiesel can be made successfully by mechanical stirring method and can be suitably used in vehicles as Alternative of diesel fuel.

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