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Transesterification of *Citrullus colocynthis* (Thumba) oil: Optimization for biodiesel production

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ABSTRACT

An increasing demand offossil fuels has being a critical problem for us. The natural resources of fossil fuel are dwindling day by day. Biodiesel that may called natural fuel may be a good source or substitute for fossil fuel in future. Biodiesel can be produced from non edible oil like Jatrophacurcus, pongamiapinnata, Madhucaindica, Gossypiumarboreum, Simaroubaglauca etc. and more. There is a best source as a raw material that is Citrullus Colocynthisschard (Thumba) oil for biodiesel production. As it is anclimber and grows wild in western part of Rajasthan. Our study is focused on the collection of seeds and oil extraction then proceed for biodiesel production with molar ratio 8:1, KOH were 0.75wt%, tempreture 65^{o}c, reaction time 90minutes were used and testing of parameters as per ASTM 6751 standards. The physical properties like acid value, density, Calorific value, Flash point, Fire point and Moisture, Viscosity of Thumba methyl ester (TME) were 0.42,0.870gm/cc, 37.00MJ/Kg, 164^{0}c, 172^{0}c and 0.02%, 4.78 Cst found. The process variables that influence the transesterification of triglycerides, such as catalyst concentration, molar ratio of methanol to raw oil, reaction time, reaction temperature, and free fatty acids content of raw oil in the reaction system were investigated and optimized. It was concluded that TME may works as a sustainable feedstock for biodiesel production that is equivalent to fissile fuel as per ASTM 6751.

Key words: *Citrullus colocynthisschard oil*, transesterification, triglyceride etc.

INTRODUCTION

The concept using vegetable oil as a fuel dates back to 1895 when Dr. Rudolf Diesel developed the first diesel engine to run on vegetable oil. Rudolf Diesel Sated: “the use of vegetable oil for engine fuels may seem insignificant today. But such oil may become in source of time as important as petroleum & the coal tar products of the present time Biodiesel is a non petroleum based fuel defined as fatty acid methyl ethyl esters derived from vegetable oil or animal fats & it is used in diesel engines & heating systems. Thus this fuel could be regarded as mineral diesel substitute with the advantage of reducing greenhouse emissions because it is renewable resource.[1]Mostly biodiesel is prepared from oils like soyabean, sunflower, rap seed etc. throughout the world. Depending on the climate and soil conditions, different nations looking into different vegetable oils for diesel fuel substitute; soyabean oil in USA, sunflower and rapseed oil in Europe, palm oil in Malaysis and coconut oil Philippines are being considered as a substitutes for diesel fuel seed oil.The extracted oil could not be used directly in diesel because of its higher viscosity. High viscosity of pure vegetable oil would reduce the fuel atomization and increase the fuel spray penetration, which would be responsible for high engine deposits and thickening of lubricating oil. The use of chemically altered vegetable oil called biodiesel does not require modification in engine or injection system or fuel lines and is directly possible in any diesel engine. Biodiesel can be produced from vegetable oils or animal fats via transesterification. The transesterification is the reaction between oil and fat, with a short chain alcohol (methanol, ethanol, and propanol) in the presence of suitable catalysts in the transesterification reaction, as they give high production yield .[2]Few researchers have worked feedstock having higher FFA levels using alternative processes. But there are certain exceptional cases wherein direct trans-esterification cannot be performed. Such cases appear in raw vegetables oils (non edible oils) like karanja[3]., Jatropha[4], mahua[5],castor[6], simaroubae[7], neem, cotton seed, and Thumba i.e. Citrulluscolocynthisschard.Because these non edible oils possesses high free fatty acids (FFA). For determining whether the raw vegetable oils can be trans-esterified directly, the acid value is the most important property that must be known. Oils of high free fatty acids content can be converted into biodiesel via dual step transesterification process. In the first step, the oil is treated by an acid dissolved in methanol to reduce FFA content, whereas in the second step the preheated oil is transesterified with methanol in the presence of base catalyst to form ester & glycerol.[8]

Alkali-catalysedtransesterification process is the most common process for production of biodiesel and need to be optimized for different process variables.[9] Sharma[3] et.al. were evaluated and optimized conversion of pongamiapinnata oil into its methyl ester and analyzed reaction variables like molar ratio, catalyst concentration, reaction time, reaction temperature and stirring speed for reaction. He found that 89.5% yield was obtained at 8:1 alcohol to oil molar ratio for acid esterification, 9:1 molar ration for alkaline esterification, 0.5 catalyst (NaOH/ KOH) using mechanical stirrer. Rashid[10] et.al.were found 97.1% yield of sunflower methyl ester at 6:1 molar ration of alcohol to oil, 1.00% catalyst (NaOH) concentration, 60^{o}c reaction temperature.Singh[11] et.al.found 97% yield of Jatropha methyl ester with molar ration 6:1, 07% catalyst, 60^{o}c reaction temprature, and at 2 hr. ratction time.Faizal[12]et. Al was found 95-97% yield of Madhucaindica methyl ester with 6:1 molar ratio, 0.75% KOH concentration, 55^{o}c-60^{o}c reaction temperature for 60min. reaction time.A lot of work have been done on biodiesel production with edible oils. In this paper, we have introduced a non edible and unutilized, wild palnt that is Thumba. In this research work, investigations were carried out to optimize highest yiled with major parameters like molar ratio of oil to methanol, catalyst concentration, reaction temperature and reaction time.

Why Citrulluscolocynthisschard

Citrulluscolocynthisschardis a species of family Cucurbitaceae, citrullus genus native to Turkey. Commonly it is called as 'Bitter apple'(in English), Thumba, (in Marathi), Indrayan(in Hindi), It is a creeper, short period crop grown naturally wild in Indian arid zone (Western Rajasthan). Thumba is planted/ grown naturally in rainy season and its fruits / seeds are available in winter. It has annular and rough stem, rough leaves that are 3-7 lobed, 5-10cm long in middle, flowers are monoleceios and have yellow rounded fruit. This plant leaf may be used as fodder in summer when there is a very high scarcity of regulr fodder crops. The average yield is about 2500-3500 kg of seeds/ ha. with minimum inputs. Seeds contains 12-20% of golden yellow- brown oil. Deoiled cake has a great importance in organic fertilizer industry. Currently all extracted oil is consumed by saponification industries.

A B C

Fig.- 1 shows A- Thumba Plant, B- Thumba seeds, C- Thumba Raw oil

MATERIALS AND METHODS

Seed Material

The fresh seeds are collected from wild region of Jodhapur and Jaipurof Rajasthan state, India. The seeds are selected according to their conditions where damaged seeds are discarded and the good conditioned seeds are cleaned. De-shelled and dried at higher temperature at 100-105^{o}C for 30min in oven. Then seeds are processed for oil extraction through mechanical expeller at room tempreture.

Pretreatment

Filtered Thumba oil is first taken to remove moisture. As water content of the feedstock is major parameter and should be kept below 0.06% w/w for better conversion of oil to esters.[13] Hence the raw oil is kept in an oven at 105^{o}c for 2-3hrs to remove the water content from the oil.

After demoisture, the oil was filtered to remove suspended particles. The parameters present in trace quantity like carbon residue, unsaponificable material and fiber etc. are removed. The oil was the processed for property testing are were shown in Table-1

The free fatty acid content of raw oil and products after reactions were determined by standard titrimetry methods (ASTM-664). To determine exact molecular weight of Thumba oil, it was analysed by Gas chromatography, that gives available fatty acid . The chrmatograph of oil was shown in Graph -1.The molecular weight and fatty acid composition was shown in table 2.

As the acid value of Thumba oil was found to be 2.30mg KOH/gm. So there was no need to go for esterification process. We directly carry out base catalysedtransesterification reaction.

Transesterification Reaction

Transesterification or alcoholysis is the displacement of alcohol from an ester by another in a process similar to hydrolysis, except an alcohol is used instead of water.[14]

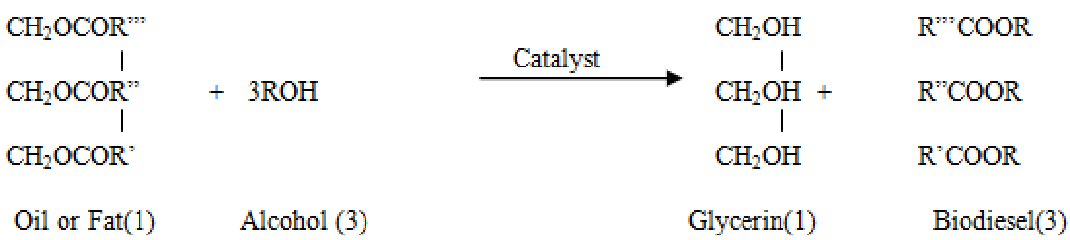
This process has been widely used to reduce the high viscosity of triglycerides. The transesterification reaction is represented by the general equation as below

$$RCOOR' + R''OH \leftrightarrow RCOOR'' + R'OH$$

Scheme-1: General equation of transesterification

Some feedstock must be pretreated before they can go through the transesterification process. Feedstock with less than 5 % Free Fatty Acid, may not require pretreatment. When an alkali catalyst is added to the feedstock's (With FFA > 5 %), the Free Fatty Acid react with the catalyst to form soap and water as shown in the reaction below:

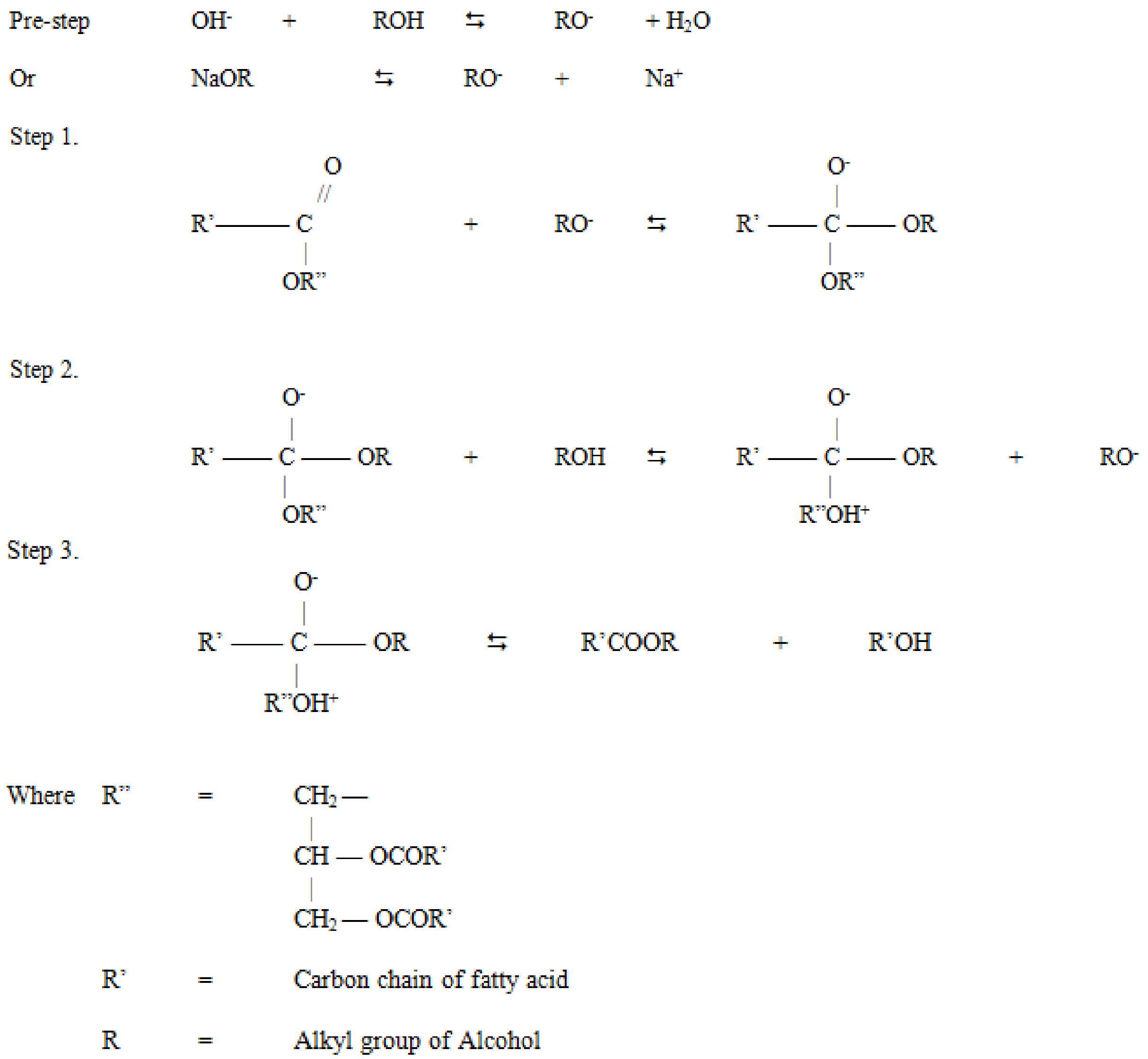
If methane is used in this process it is called methanolysis. Methanolysis of triglyceride is represented:



Scheme-2: General equation for methanolysis of triglycerides

Transesterification is one of the reversible reactions. However, the presence of a catalyst (a strong acid or base) accelerates the conversion. In the present work the reaction is conducted in the presence of base catalyst [15]. The mechanism of alkali-catalyzed transesterification is described below. The first step involves the attack of the alkoxide ion to the carbonyl carbon of the triglyceride molecule, which results in the formation of tetrahedral intermediate. The reaction of this intermediate with an alcohol produces the alkoxide ion in the second step. In the last step the rearrangement of the tetrahedral intermediate gives rise to an ester & a diglyceride. The same mechanism is applied to diglyceride and monoglyceride. The reaction mechanism of transesterification is shown in Scheme-3.

Reaction mechanism



Scheme-3: Mechanism of base catalyzed transesterification

Experimental set up

The experimental set up is shown in figure 2. A 2000 ml three necked round –bottom flask was used as a reactor. The flask was placed in heating mantle whose temperature could be controlled within $\pm 2\ ^0C$. One of the two side necks was equipped with a condenser and the other was used as a thermo well. A thermometer was placed in the thermo well containing little glycerol for temperature measurement inside the reactor. A blade stirrer was passed through the central neck, which was connected to a motor along with speed regulator for adjusting and controlling the stirrer speed.

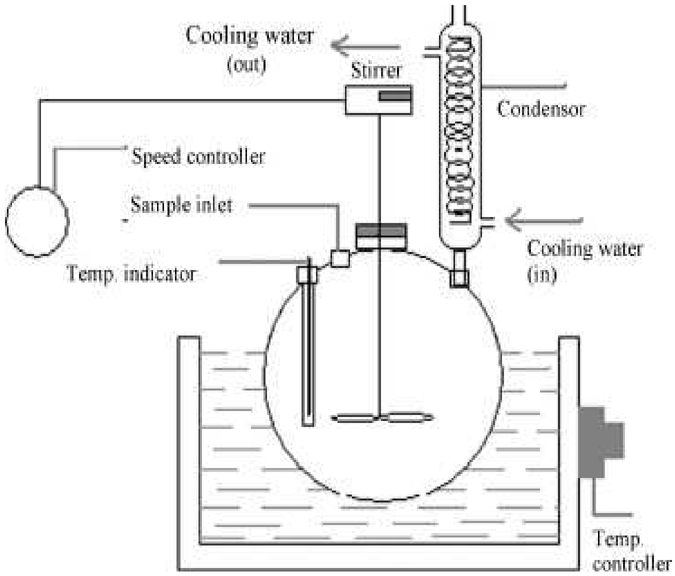


Figure 2- Experimental Set up For Transesterification of Thumba oil

1000ml of Thumbaoilwas measured and poured into a 2000 ml three necked round bottom flask. This oil was heated upto 60^0c. In 250ml beaker a solution of potassium methoxide was prepared using 0.5, 0.75 and 1.25 wt.% potassium hydroxide pellet with the molar ratio 1:6, 1:8 and 1:10 ofoil to methanol were studied. The solution was stirred until the potassium hydroxide pellet was completely dissolved(the mixture was called potassium methoxide solution). The solution was then heated upto 60 ^{o}c and slowly poured into preheated oil. The mixture was stirred (650rpm) vigorously for 10, 20, 30, 40, 50, 60, 70, 80 and 90 min.. Finally FFA was checked and mixture was allowed to settle for 24 hours in a separating funnel. Thereafter, upper layer biodiesel was decanted into a separate beaker while the lower layer which comprised glycerol and soap was collected from the bottom of separating funnel. To remove any excess glycerol and soap from the biodiesel, hot water was used to wash it then allowed it to remain in separating funnel until clear water was seen below the biodiesel in the separating funnel. The P^H of biodiesel was then tested. The washed biodiesel sample was then dried by placing it on a hot plate and excess water still in the biodiesel removed[16]. These batches were taken to achieve highest yield and to study the effect of these parameters on yield of methyl ester.

RESULTS AND DISCUSSION

1. Seed characterization-
Fresh seeds contains 8-10% of moisture.

2. Oil Percentage-
The available oil percentage in Thumba seeds is 12-20%. As per our practical trial, we recorded 14% of oil.

3. Physico- chemical Properties-
The fresh extracted crude oil is yellowish brown in color& it get darkened during the storage. The oil having slightly sweet odor & bitter taste. All properties are given in Table no- 2 &were carried out as per American Standards' For Testing & Material (ASTM)- 6751.
Physico-chemical properties of Thumba crude oil

The compressibility effect of the vegetable oil causes an earlier injection of fuel into the engine cylinder as compared to diesel fuel.[17]This earlier injection does not play an important role, as the injection advance difference is at maximim1^{o}CA even for the neat vegetable oil.[18]The major difference occurs in atomization process, i.e. the mean droplet size of vegetable oil is much higher than diesel fuel.[19]This is because high viscosity (38.17Cst) and low volatility of vegetable oils lead to difficulty in atomizing the fuel and in mixing it with air.

Table 1- Physico-chemical properties of Thumba oil

Sr.	Properties	unit	Test values
1	Color	-	Yellowish brown
2	Odor	-	Slightly sweet
3	Density	gm/cc	0.927
4	Kinematic Viscosity @ 40°C	mm^2/s	40.2
5	Acid value	mgKOH/gm	2.30
6	Pour point	°C	6
7	Cloud point	°C	3.5
8	Flash point	°C	225
9	Calorific value	MJ/Kg	8742
10	Saponification value		184
11	Carbon residue	wt%	1.51

The Fatty acid composition of Thumba oil

It was analyzed by GC and calculated molecular weight of Thumba oil was 872.61.Extracted oil consisted of pure triglyceride and rests were free fatty acids and lipid associates, which is the measure of Unsaponifiable matter.

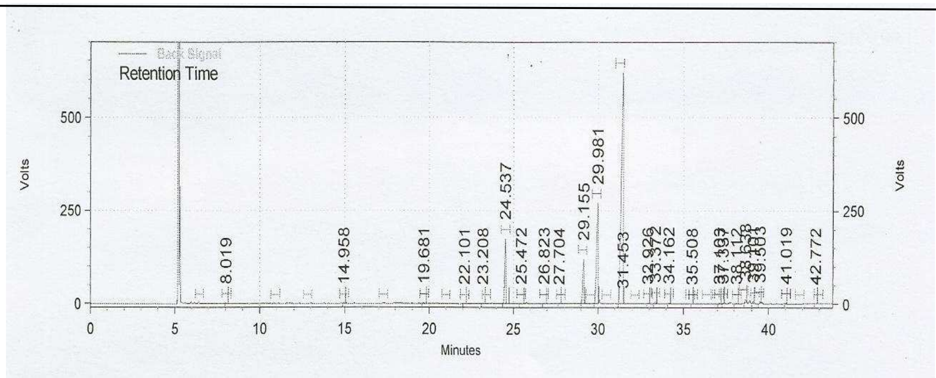


Figure 3.- Chromatograph Showing Fatty acid composition of Thumba oil

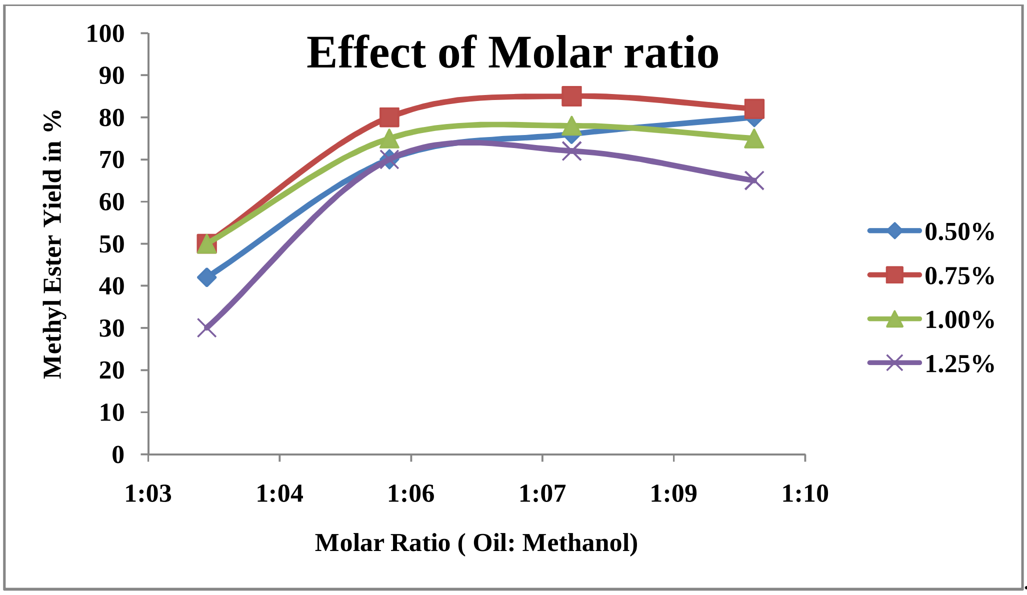
Table 2- Fatty acid composition of Thumba oil

Sr.	Fatty acid name	Formula	Composition(%)
1	Carprylic Acid	C6:0	**0.091**
2	Lauric Acid	C12:0	**0.018**
3	Myristic Acid	C14:0	**0.084**
4	Palmitic acid	C16:0	**10.070**
5	Stearic acid	C18:0	**7.890**
6	Tricosanoic acid	C23:0	**0.432**
7	Lignoceric Acid	C24:0	**0.189**
8	Cis-10 Pentadecenoic Acid	C15:1	**0.019**
9	Palmitoleic Acid	C16:1	**0.094**
10	Cis-10 Heptodeconic Acid	C17:1	**0.028**
11	Oleic acid	C18:1	**18.190**
12	Cis-11 Eicosenoic acid	C20:1	**0.277**
13	Erucic Acid	C22:1	**0.096**
14	Linoleic Acid	C18:2n6c	**56.890**
15	Alpha-Linolenic acid	C18:3n3	**0.114**
16	Gamma- Linolenic acid	C18:3n6	**0.095**
17	Eicosadienoic Acid	C20:2	**0.010**
18	Cis- Eicosapentaenoic Acid	C20:5n3	**0.114**
19	Cis- Docosadienoic Acid	C22:2	**0.211**

The Thumba oil was contains both saturated and unsaturated fatty acids. Amongst these, Linoleic acid were (56.890%) found in highest amount, Oleic acid (18.190%) were in the next quantity then palmitic acid (10.70%) and stearic acid (7.890%) were found.

Yield
To achieve highest yield of TME, we have out many trials on following parameters

1. Effect of Molar Ratio (to mol. wt of oil)

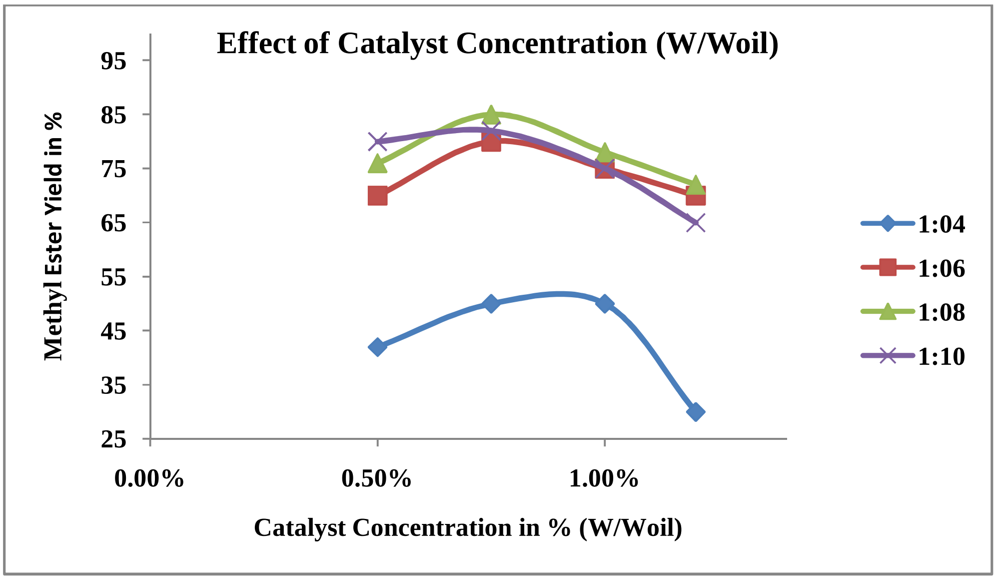


Graph:1- Effect of molar ratio on THE yield

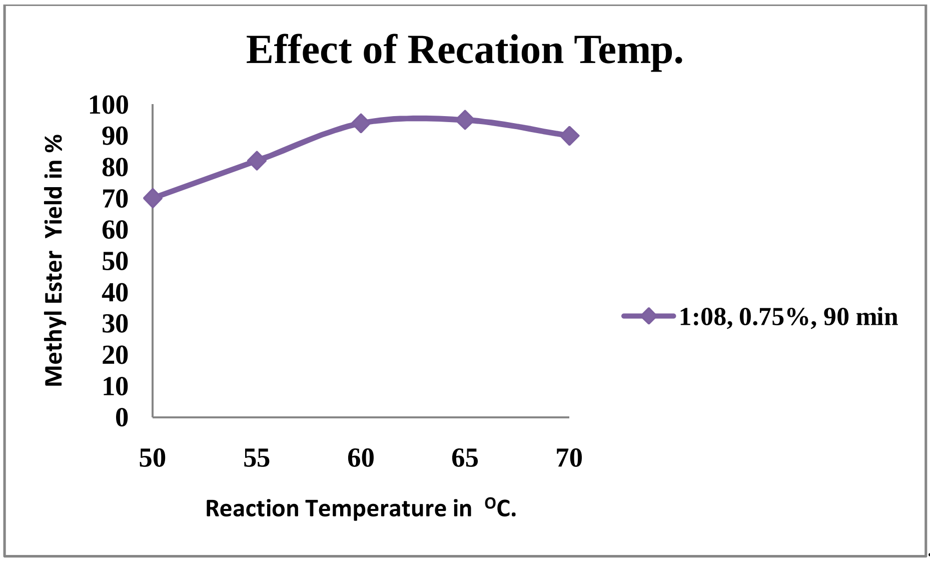
Stichometrically 3 moles of methanol should used to every mole of triglyceride that gives 3 moles of its methyl ester and 1 mole of glycerine. So that oil to alcohol molar ratio should be 1:3 (by molar mass of oil). To shift the transesterification reaction to right, it is neccessory to use excess alcohol. Higher molar ration of oil to alcohol interferes in the separation of glycerol. So to avoid this problem we carried some experiments with 1:4, 1:6, 1:8,1:10raio of oil to alcohol (considering molecular weight of oil) with different concentration of catalystloading. All experients were completed at constant temperature 60^{o}c and reaction time 90min. From the work we concluded that yield goes on increasing with increase on molar ratio. 1:8 molar ratio shows highest yield 85% with 0.75% catalyst KOH. Further increase in methanol ration does not affect on the yield of THE.

2. Effect of catalyst concentration (to the wt. of oil)
The effect of catalyst on yield of THE was studied with catalyst varring from 0.5% to 1.20% considering weight of oil. All reactions were carried out constant temperature 60^{o}c and reaction time 90min with variation in molar ratio. We concluded that yield of TME increased on increase in catalyst concentration. 0.75wt % KOH shows highest yield with 1:8 molar ratio of oil to methanol.

3. Effect of Reaction Temperature
The reaction temperature is an important parameter that affect the yield of methyl ester. It is well known chwmicalkineics that rate of reaction increase with increase in temperature of reaction. Its effect was studied with variation of temperature from 50^{O}c to 70^{o}c. with 1:8 molar ratio, 075wt% catalyst, 90 min. reaction time. It was concluded the yield of biodiesel was gradually increased with increase in temperature from 50^{O}c to 60^{o}c. Highest yield of THE was obtained at 60^{o}c reaction temperature But it goes on decreasing on further increase in reaction temperatureupto 70^{o}c. The boiling point of methanol is near to this temperature, so there may be a loss of methanol that affect on the yield. So finally reaction temperature 60^{o}c was concluded to give optimum yield of TME.



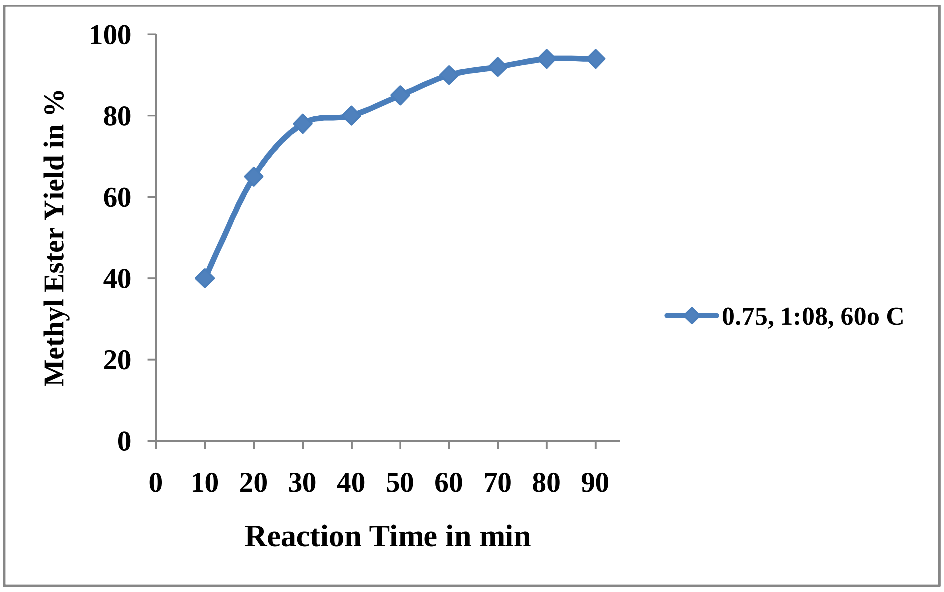
Graph:2- Effect of Ctalyst concentration in % on THE yield



Graph:3- Effect of Reaction Temperature on THE yield

4. Effect of Reaction time

Reaction time is one of the major parameter that influences yield of methyl ester. The conversion of triglyceride into ester with is increases with time as the reaction progress towards completion. This effect wse studied with variation of time from 10 min to 90 min. It is shown in the graph 4. When reaction gets completed then time dones not affect on the yield. It is because maximum triglyceride get converted into its ester. So that in the graph 4, 80-90 min. time shows result near to completion of reaction.



Graph:4- Effect of Reaction Time on THE yield

5. Effect of Stirring Speed-

The Thumba oil was immiscible with methanol. So to overcome the mass transfer limit, oil and methanol were brought into contact by agitation. According to researchers, stirring speed og 600-650rpm is sufficiedto carry out the reaction. So that in this case we have carried out all experiments on 650rpm speed and recovers best results with maximum experiments.

- **Physico- chemical properties of TME**

Comparison of Thumbabiodiesel(TME) with Diesel fuel

Table:3- Physico-chemical properties of THE

Sr.	Properties	Unit	Thumba Methyl Ester	Diesel
1	Density	gm/cc	0.870	0.830
2	Kinematic Viscosity @ 40°C	Cst	4.78	2.98
3	Acid value	mgKOH/gm	0.42	0.35
4.	Cloud point	°C	2	-16
	Pour Point	°C	-6	-
5	CFPP	°C	-8	-
6	Flash point	°C	164	67
7	Fire Point	°C	172	-
8	Cetane number	-	41.7	49.0
9	Calorific value	Kcal/KG	3700	4285
10	Moisture	%	0.02	0.02
11	Carbon residue	%	0.005	0.01
12	Ash content	wt %	0.01	0.02

Density is the mass per unit volume. Biodiesel is slightly heavier than conventional diesel fuel. As compared to density of raw thumba oil (0.927gm/cc) it was much reduced but denser than fossil fuel. To recover this problem we can use biodiesel with blending on the top of fossile fuel.

Viscosity is too an important parameter that affect atomization and fuel spray rate. Alcoholysis/ transesterification principally works to reduce viscosity of oil. As compared to raw thumba oil it was much reduced but higher than fossil fuel.

Acid value of raw oil was 2.30mg KOH/gm and it get reduced upto 0.42mg KOH/gm which was near to 0.35mgKOH/gm of fossil fuel. This property was important to calculate the percent yield of biodiesel According o Ramos [20]et. al. percent yeaster yield was calculated as below

$$\text{Yield of Ester in \%} = \frac{\text{(Initial FFA- Final FFA)}}{\text{Initial FFA}} * 100$$

The Cloud point is the temperature at which wax first becomes visible when the fuel is cooled. While pour is the lowest temperature at which the fuel can flow. Biodiesel has a higher colud and pour points compared to fossil fuel.. It can be recovered by the blending with fossil fuel.

Flash point of a fuel is the temperature at which it ignites when exposed to a flame or spark while fire point is the temperature at which fuel starts burning continuously. The flash point of Thumba oil was 235^{o}c while that of its methyl ester was 164^{o}c. The flash point of Thumba oil decreases after transesterification that shows improvement in its volatile characteristics.The flash as well as fire point of biodiesel is higher than the petro diesel, which makes it safer fuel in storage,transport and to handle.

Cetane number was an important property that shows the quality of fuel. Generally biodiesel has higher cetane number than fossil fuel. It was due to availability of long carbon chain of triglycerides and some saturated molecules.

Calorific value is an important property while selecting the fuel. As calorific vavue of TME is 3700 K calKG while that of fossl fuel is 4285Kcal/ KG. The heat content of biodiesel that synthesized from Thumba oil is nearly 90% that of diesel fuel.

CONCLUSION

Part- I-

1. The Thumbaoil exhibited good physico chemical properties & could be used as a biodiesel feedstock and as a industrial application.
2. The way of reducing the biodiesel production costs is to use less expensive feedstock containing free fatty acids, such as non edible oils. With no competing food uses, this characteristic turns attention to Citrulluscolocynthisschard which grows in wild area of western Rajasthan in our country.
3. The production of biodiesel from this oil may provide a valuable local, regional and national benefit.
4. Thumba can be planted as an inter crop with maincropn like with bajara or jawar,and it can aosl be planted in waste lands, on road sides, railway track. IBDC, Baramati is working for plantation of these non edible oil trees through their NGO.
5. To develop biodiesel into an economically important option in India,it is required to work on biological innovations to increase the yield.

Part_II

1. It was found that KOH can be used as a alkaline catalyst for transesterification of Thumba oil. As this catalyst were easy to remove and waste stream will be utilized as a fertilizer.
2. It was also found that the combination of process parameters to obtain highest yield of TMEachieved at 1:8 molar ratio, 0.75% catalyst (KOH) concentration with 65 ^{o}c reaction temperature for 90min. reaction time.
3. Physical Properties like Density, Viscosity, cloud point, pour point, etc. were slightly higher that fossil fuel. Flash point and fire point were too higher, that makes fuel safer in transport, storage and in handling. The calorific value of fuel is lower that fossil fuel. But all these properties matches with properties that mentioned in ASTM 6751 standards.
4. Compare to JME, KME and CME ester cloud point of THE is much lower.
5. Density, viscosity, cloud and pour can be further reduced with increase in blend ratio with fossil fuel.
6. Hence considering all these factors THE can be used directly or with the blends in C.I. engine.

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