CANDIDATE'S DECLARATION

I hereby declare that the work which is being presented in this dissertation report entitled **"TRANSESTERIFICATION OF VEGETABLE OIL"**, in the partial fulfillment of the requirements for the award of the degree of Master of Technology in Chemical Engineering with specialization in "Industrial Safety & Hazards Management" and submitted to the Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, is an authentic record of my own work carried out during the period from June 2012 to June 2013 under the supervision of Dr. Prakash Biswas, Assistant Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee.

I have not submitted the work embodied in this report for the award of any other degree.

Date: June 15, 2013

Place: Roorkee   (**Kantilal Chouhan**)

CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge and belief.

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ACKNOWLEDGEMENT

ABSTRACT

Diminishing petroleum reserves, increasing demand, soaring crude oil price and environment degradation; have increased the interest in alternative fuels which are renewable, sustainable, biodegradable, non-toxic and environment friendly, such as Biodiesel. Biodiesel production by transesterification of non edible oils is getting tremendous attentions from researchers worldwide. It is mainly synthesized by homogeneous transesterification of vegetable oils. But many problems associated with homogeneous transesterification; increases production cost of biodiesel due various separation steps, waste water generation and saponification. Therefore, focus is being shifted to heterogeneous transesterification.

 To get insight into synthesis of biodiesel, results of a recently published paper on homogeneous transesterification of soybean oil have been reproduced. Jatropha and Karanja oil; both being non edible; are potential feedstocks from Indian prospective. Karanja is an underutilized tree. Karanja oil has been selected for biodiesel synthesis. A solid base catalyst was prepared by solid solid mixing of K_2CO_3 on MgO and characterized by X-ray diffraction (XRD) and Field emission scanning electron microscope (FESEM). Loading ratio was kept 0.6 m/m of K_2CO_3/MgO. Experiments were conducted to understand effect of reaction time, temperature and reactant molar ratio. Effect of different supports for K_2CO_3 was also investigated. Optimization of reaction parameters (reaction time, temperature, molar ratio and catalyst amount) have been done. Biodiesel yield of 91.5% was obtained at the optimum reaction conditions of temperature at 70°C, reaction time of 2 h, oil to methanol molar ratio 1:9 using 2 wt% catalyst amount. The fuel properties of biodiesel prepared from Karanja oil were determined using ASTM standards to check compliance with B100 standards.

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Worldwide petroleum consumption is increasing because of exponentially rising human population, fast industrialization and motorization resulting into exhausting petroleum reserves and rising price of petroleum products. Apart from this, excessive use of petroleum based fuels contributes to greenhouse gases emissions which lead to environment degradation and climate change and global warming. Diesel fuels play a crucial role for economy of developing country. For example, its consumption is five times higher than gasoline as compare to the rest of the world. The consumption of diesel fuels in India was 28.30 million tonnes in 1994–1995, and 66.78 million tonnes in 2010–2011, which was around 39% of the total consumption of petroleum products [1]. Use of alternative and renewable fuels even in small amount; will have a significant impact on environmental stability as well as the overall economy and rural economy of the country. Transportation sector is totally dependent on fossil fuels in India. Increasing number of vehicles for transportation would adversely affect the environmental stability and climate of earth [2]. As a result, there is a tremendous awareness for substitution of diesel fuels all over the world with a clean, renewable and sustainable fuel.

Dr. Rudolf Christian Karl Diesel proposed the concept of utilizing vegetable oils as a fuel for transportation on August 10, 1893. It was the demonstration of the first diesel engine capable to run on different vegetable oils. Peanut oil was tested as a substitute to petrodiesel for engine and found successful. The utilization of vegetable oils in diesel engines was reported during 1930–1940 and Second World, usually only in emergency. Since then vegetable oils were in focus. However, higher availability and cheaper price of petroleum shifted focus to petroleum products. In 1970, there was severe shortage of crude oil, which shifted the focus to vegetable oils again. Vegetable oils are biodegradable, environmental friendly, non-toxic, renewable and locally available. Furthermore, Vegetable oils are promising alternative to petrodiesel for CI engines. However, their high viscosity, lower volatility and higher pour point make them unsuitable to be used in CI engines. There are four methods to improve properties of vegetable oils as a fuel, namely blending, micro emulsification, transesterification and thermal cracking. Trasesterificarion is most widely used to reduce viscosity of vegetable oil among these four methods. Transesterification is a chemical reaction between triglyceride and alcohol in the presence of a catalyst to produce fatty acid methyl esters (biodiesel). Biodiesel was first utilized as a fuel for heavy duty vehicles before Second World War in South Africa.

Biodiesel is the most promising alternative to diesel fuels, which has gained acceptance and popularity because of its environmental friendly properties. It is a liquid fuel which has physical, chemical and combustion properties similar to petrodiesel. As compare to petrodiesel, it is a cleaner burning fuel. Biodiesel is a renewable fuel because of its production from renewable sources like vegetable oils, waste cooking oil and animal fats. It has many advantages as compare to diesel like biodegradability, lower engine emission and toxicity, negligible sulphur content, better flash point and greater combustion efficiency. It can be used as pure fuel directly or after blending with petrodiesel. Blend of biodiesel with petrodiesel shows stability in all proportions. Across the globe, it is getting tremendous attention from many governments and scientists. Extensive research on biodiesel production is going on worldwide. Although biodiesel has numerous advantages as compared to fossil diesel, the higher production cost is the main hurdle to its commercial utilization. Zhang et al. [3] reported that the price of biodiesel is about 0.5 US$/L and 0.35 US$/L for petrodiesel. Many researchers have investigated the performance of biodiesel in diesel engines to evaluate its environment friendly properties and its exhaust emissions. They have reported dramatic improvements on diesel engine exhaust emissions on the basis of engine life cycle. Carbon dioxide emissions reduce by 77.9% [4] as compared to conventional diesel fuel. It was also investigated that use of biodiesel reduces emission of carbon monoxide by nearly 47%, unburned hydrocarbons by 46% and particulate matter by 67%, respectively [5].

Chemically, biodiesel is the mixture of fatty acid alkyl esters (FAAEs), most often methyl or ethyl esters (FAMEs and FAEEs, respectively). It is obtained by the transesterification/alcoholysis of vegetable oils and/or by the esterification of fatty acids. It is mainly produced from vegetable oils. At present, edible oils are the main feedstock for production of biodiesel. Nearly 95% of the global biodiesel production is being carried out using edible oils [6]. Nevertheless, there are various reasons for not utilizing edible oils as feedstocks in production of biodiesel. Utilization of edible oils in biodiesel production can lead to big gap between global market demand and supply of edible oils for human consumption and biodiesel production. This consequently, results into rising prices of edible oils and raise fuel versus food debate. Thus, focus is being shifted to non edible oil sources which are not utilized in human nutrition. These could grow on the waste lands. Because of the presence of some compounds which make oils from these resources, toxic and unsuitable for human consumption. Hence, it eliminates food versus fuel conflict. The transesterification of vegetable oils to the methyl ester is one of the most important and well established chemical reactions for

the production of biodiesel that is recognized as the replacement for the conventional petrodiesel fuel [7]. Biodiesel is characterized by superb fuel properties as petrodiesel. It can be used in CI engines with small or no modification. Because of its simplicity, Transesterification is the most common method for production of biodiesel. It has been extensively studied and industrially utilized for conversion of vegetable oils to biodiesel [8].

The transesterification of vegetable oil involves the conversion of the triglycerides (TG) of the oil or fat to its alkyl esters when they are reacted with low molecular weight primary alcohols such as methanol, ethanol, or butanol. The transesterification reaction requires three moles of alcohol and one mole of triglyceride to give three moles of fatty acid alkyl esters and one mole of glycerol. Being a reversible reaction, it requires excess alcohol and catalyst for faster reaction rate. Transesterification process improves the fuel properties of the oil namely viscosity, density, calorific value, cloud point, flash point and pour point [9].

1.1.   Feedstocks for biodiesel production

Feedstocks for biodiesel production are conventionally classified into four categories namely, First, Vegetable oils are again classified into two groups namely edible and non edible; Second, animal fats; Third, used/waste cooking oils and Fourth, algal oils. Traditionally, different edible oils are being used as main feedstocks for production. For example, sunflower oil in European Union countries, rapeseed oil in Canada, soybean oil in USA, palm oil in Malaysia and Indonesia. Because of increasing human population and extensive demand of edible oil for human consumption are causing serious problems like shortage of edible oils for human consumption and increase of edible oil price for both domestic and industrial purpose. Use of edible oil for biodiesel production causes food versus fuel conflict. Their production also required agricultural land for growing edible oil crops. Hence, edible oil feedstocks are not feasible for large scale production for a long period. Therefore, non edible vegetable oils have emerged as promising feedstocks for biodiesel production. Non edible oil plants have lower cultivation cost as compare to edible oil plants and these can be cultivated on waste and non agricultural lands. There are total 26 plant species which can be potential source of non edible oils for production of biodiesel [10]. On the other hand, animal fats such as beef tallow, white lard have very low price as compare to vegetable oil but their limited availability can never meet demand for large scale production. Presence of higher amount of saturated fatty acids it becomes solid at room temperature which creates big problems during biodiesel production. Waste cooking oils (WCO) are 2-3 times cheaper than virgin oils; therefore, they could be a

good choice as biodiesel feedstocks. WCOs contain very high amount of free fatty acids and impurities (polymers, solid particles, etc.) which make biodiesel production complicated. Inconsistent supply chain, lower availability and complicated process make biodiesel cost high and unsustainable. In recent years, Algae has received high attention of scientific community for biodiesel feedstocks. Microalgae has many advantages such as it gives higher oil yield, can be grown on non agricultural land, needs sunlight for growth. But, it requires large water bodies for its growth which makes its use as biodiesel feedstocks infeasible for country like India.

For country like India which has huge non agricultural lands and barren lands and favourable climate condition, Non edible oil crops can be grown on large scale. Non edible oil plants are very promising and potential feedstocks for biodiesel production to meet the biofuel demand in India.

1.2   *Vegetable oils*

Vegetable oils are lipid materials obtained from plants. It exists in liquid form at room temperature. Most of the vegetable oils contain triglycerides which are the basic component of most lipids. Common vegetable oils are esters of saturated and unsaturated monocarboxylic acids with the tri-hydric alcohol glycerine. These oils are extracted from parts of the constituent plant using traditional mechanical pressing method or solvent extraction method. Extracted crude vegetable oil is further refined to remove solid particles, sterols and free fatty acids by filtration, chemical methods. Sometimes, it is purified by fractional distillation.

Most of the oils are extracted from the seeds of the plant, while a marginal amount of oils are extracted from other parts like the roots or stem also. It is obtained from a wide range of oil-seed plants such as peanut, soybean, rapeseed, sunflower, linseed. It can also be extracted from the seeds of different plants which are grown for fibres for textiles, like flax and cotton. Moreover, there are variety of oil bearing fruits from which it can be extracted namely, coconut palms, walnut trees, palm fruits and its kernels. Jatropha curcas, Pongamia pinnata (Karanja), Mahua trees are source of non-edible vegetable oils [11]. Oils and fats are esters of the tri-alcohol and glycerol. Therefore, oils and fats are generally called triglycerides. Triacylglycerols is a more accurate name for oils and fats.

1.2.1 Classification of vegetable oils

Vegetable oils are generally classified into two groups.

1. Edible vegetable oils

2. Non edible vegetable oils

1.2.1.1.   Edible vegetable oils

This class of vegetable oil includes sunflower oil, rapeseed oil, rice bran oil, soybean oil, coconut oil, corn oil, palm oil, olive oil, pistachio oil, sesame seed oil, peanut oil, and safflower oil, respectively.

1.2.1.2.   Non edible vegetable oils

These include jatropha curcas oil, karanja or pongamia pinnata oil, castor oil, neem oil, jojoba oil, linseed oil, mahua oil, deccan hemp oil, kusum oil, orange oil, rubber seed oil, tobacco seed oil etc.

1.2.2. Composition of vegetable oils

Chemically the oils consist of triglyceride molecules of three long chain fatty acids that are ester bonded to a single glycerol molecule. These fatty acids differ by carbon chain length, number of double bonds in these chains and their orientation. There are five types of chains that are common in vegetable oil and animal fats (others are present in small amounts). These include Palmitic, Stearic, Oleic, Linoleic, Linolenic chains.

Palmitic: $R = -(CH_2)_{14}-CH_3$ 16 carbons, 0 double bonds(16:0)

Stearic: $R = -(CH_2)_{16}-CH_3$ 18 carbons, 0 double bonds(18:0)

Oleic: $R = -(CH_2)_7-CH=CH(CH_2)_7-CH_3$ 18 carbons, 1 double bond (18:1)

Linoleic: $R = -(CH_2)_7-CH=CH-CH_2-CH=CH(CH_2)_4-CH_3$

                                                18 carbons, 2 double bonds (18:2)

Linolenic $R = -(CH_2)_7-CH=CH-CH_2-CH=CH-CH_2-CH=CH-CH_2-CH_3$

                                                18 carbons, 3 double bonds (18:3)

Table 1.1. Fatty acid composition (wt %) of different vegetable oils [12]

Vegetable oil source	Typical fatty acid composition (wt %)				
	Palmitic 16:0	Stearic 18:0	Oleic 18:1	Linoleic 18:2	Linolenic 18:3
Edibile oils					
Corn oil	13.0	3.0	31.0	52.0	1.0
Peanut	13.0	3.0	38.0	41.0	Trace
Rapeseed(Canola)	4.0	2.0	56.0	26.0	10.0
Sesame	9.0	6.0	41.0	43.0	-
Sunflower	6.0	5.0	20.0	60.0	Trace
Sunflower(Sunola)	4.0	5.0	81.0	8.0	Trace
Sunflower(NuSun)	4.0	5.0	65.0	26.0	-
Soybean	11.0	4.0	22.0	53.0	8.0
Safflower	7.0	3.0	14.0	75.0	-
Palm	44.0	4.0	39.0	11.0	Trace
Olive	10.0	2.0	78.0	7.0	1.0
Rice bran	20.0	2.0	42.0	32.0	-

Table 1.1. (Continued.)

Vegetable oil source	Typical fatty acid composition (wt %)				
	Palmitic 16:0	Stearic 18:0	Oleic 18:1	Linoleic 18:2	Linolenic 18:3
Non-edible oils Linseed oil	6	3	17	14	60
Jatropha	14.2	7	44.7	32.8	Trace
Karanja	3.7 - 7.9	2.4 - 8.9	44.5 - 71.3	10.8 - 18.3	-
Mahua	20 - 25	20 - 25	41 - 51	10 - 14	-
Neem	13.6 - 16.2	14.4 - 24	49 - 62	2.3 - 15.8	-
Tobacco	9.6	6.3	21.7	55.6	
Rubber seed oil	8.7 - 10.6	8 - 12	17 - 20	33 - 39	21 - 26

1.3.   Importance of vegetable oil as CI engine fuel

Vegetable oils are a potential alternative to petrodiesel fuels due to the similar physical and chemical attributes. They have the numerous advantages such as they are biodegradable, carbon dioxide neutral, non-toxic and renewable as they are originated from plants. Blends of vegetable oil with petrodiesel oils can be also considered. They are similar to fossil fuels from thermal efficiency point of view. As compared to diesel, Vegetable oils have higher density and lower energy content around 10%.

They have Cetane number 10 to 20% lower than that of petrodiesel which results in ignition delay and engine knocking. They have higher viscosity than petrodiesel which leads to higher pumping power requirement, poor atomisation and higher wear of components of pumps and injectors.

Table 1.2. Comparative properties of fossil diesel and vegetable oils [14]

CI engine fuel	Properties						
Commom name	Calorific Value[MJ/kg]	Density [kg/m^3]	Flash point [^{o}C]	Pour Point [^{o}C]	Kinematic viscosity [cStoke]	Carbon residues [% w/w]	Cetane number
Diesel	43.35	815	45-60	-6.70	4.30	0.03-1	47.00
Sunflower oil	39.52	918	73	-15.00	58.50	0.23	37.10
Cottonseed oil	39.64	912	234	-15.00	50.10	0.42	48.10
Soybean oil	39.62	914	254	-12.20	65.40	0.27	38.00
Peanut oil	39.80	903	271	-6.70	39.60	0.24	41.80
Corn oil	37.82	915	277	-40.00	46.30	0.24	37.60
Rapeseed oil	37.62	914	246	-31.70	39.20	0.30	37.60
Sesame seed oil	39.30	913	260	-9.40	35.50	0.25	40.20
Palm oil	36.51	918	267	-31.70	39.60	-	42.00
Coconut oil	35.80	915	-	-	31.59	-	-
Mahua oil	38.86	900	238	15.00	37.18	0.42	-
Rice bran oil	39.50	916	-	-	44.52	-	-
Karanja oil	34.10	914	263	-	37.12	-	-
Jatropha oil	39.77	918	240	-	49.90	0.22	45.00
Rubber seed oil	37.50	922	198	-	39.91	-	37.0

They have much higher flash point than petrodiesel which causes difficulty in ignition, coke deposition in engines. Prolonged use of vegetable oil in diesel engine may cause damage to engine parts. But it can be used as a substitute of traditionally used diesel after modification. Transesterification of vegetable oil is most common method for biodiesel production due to its simplicity.

Transesterification is the reaction process in which alkoxy group of ester compound exchanges by another alcohol in the presence of a catalyst. Transesterification reaction is reversible. Different types of alcohols such as methanol, ethanol, propanol and butanol can be used. Transesterification is also known as alcoholysis.

$$RCOOR^1 + R^2OH \xrightleftharpoons{\text{Catalyst}} RCOOR^2 + R^1OH$$

Ester   Alcohol   Ester   Alcohol
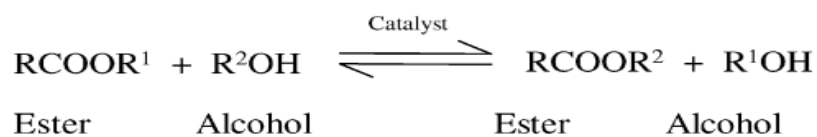
Figure 1.1. Transesterification process

"Transesterification is the reaction process in which triglyceride molecules present in animal fats or vegetable oils react with an alcohol in the presence of a catalyst to form esters (main product) and glycerol as by product"[8].

1.4.   Transesterification of vegetable oil

The transesterification of vegetable oil involves the conversion of the triglycerides (TG) of the oil into its corresponding alkyl esters and glycerol when they are reacted with short chain alcohols such as methanol, ethanol, or butanol. Generally, vegetable oil and alcohol are not miscible to make a single phase mixture. Due to this poor contact between reactants causes transesterification to proceed at very slow reaction rate. This leads to low biodiesel yield and long reaction time. But, Introduction of catalysts into reacting mixture improves surface contact. This results into faster reaction rates and higher biodiesel yield.

$$
\begin{array}{l}
CH_2-OCOR^1 \\
| \\
CH-OCOR^2 \\
| \\
CH_2-OCOR^3
\end{array}
+ 3CH_3OH
\xrightleftharpoons{\text{Catalyst}}
\begin{array}{l}
CH_2OH \\
| \\
CHOH \\
| \\
CH_2OH
\end{array}
+
\begin{array}{l}
R^1COOCH_3 \\
R^2COOCH_3 \\
R^3COOCH_3
\end{array}
$$

Triglyceride   Methanol   Glycerol   Methyl esters
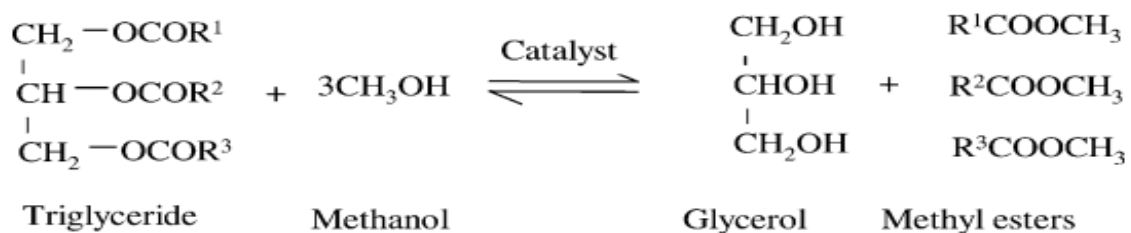
Figure 1.2. Transesterification of triglycerides.

It is reversible; therefore, excess alcohol is used to shift the equilibrium to the products side. Figure 1.2 shows the overall scheme for the transesterification of triglycerides.

Methanol and ethanol are used most frequently in the transesterification process. Methanol is preferred because of its lower cost and its physical and chemical advantages (polar and shortest chain alcohol) over ethanol.

The transesterification reaction requires three moles of alcohol and one mole of triglyceride to give three moles of alkyl esters and one mole of glycerol. Transesterification of vegetable oils proceeds in three consecutive reversible reactions. In the first step, triglycerides get converted into diglycerides, followed by conversion of diglycerides into monoglycerides in second step and finally conversion of monoglycerides into glycerol. Each step yields one fatty acid methyl ester molecule from each glyceride.

$$CH_2-O-CO-R_1$$
$$CH-O-CO-R_2 \ + \ CH_3-OH \ \underset{}{\overset{Catalyst}{\rightleftharpoons}} \ CH_3-O-CO-R_1 \ + CH-O-CO-R_2$$
$$CH_2-O-CO-R_3 \qquad\qquad\qquad\qquad\qquad\qquad\qquad CH_2-O-CO-R_3$$

Triglycerides   Methanol   Methyl ester   Diglyceride

$$CH_2-OH$$
$$CH-O-CO-R_2 \ + \ CH_3-OH \ \underset{}{\overset{Catalyst}{\rightleftharpoons}} \ CH_3-O-CO-R_2 \ + CH-OH$$
$$CH_2-O-CO-R_3 \qquad\qquad\qquad\qquad\qquad\qquad\qquad CH_2-O-CO-R_3$$

Diglyceride   Methanol   Methyl ester   Monoglyceride

$$CH_2-OH$$
$$CH-OH \qquad\qquad + \ CH_3-OH \ \underset{}{\overset{Catalyst}{\rightleftharpoons}} \ CH_3-O-CO-R_3 \ + \ CH-OH$$
$$CH_2-O-CO-R_3 \qquad\qquad\qquad\qquad\qquad\qquad\qquad CH_2-OH$$

Monoglyceride   Methanol   Methyl ester   Glycerol
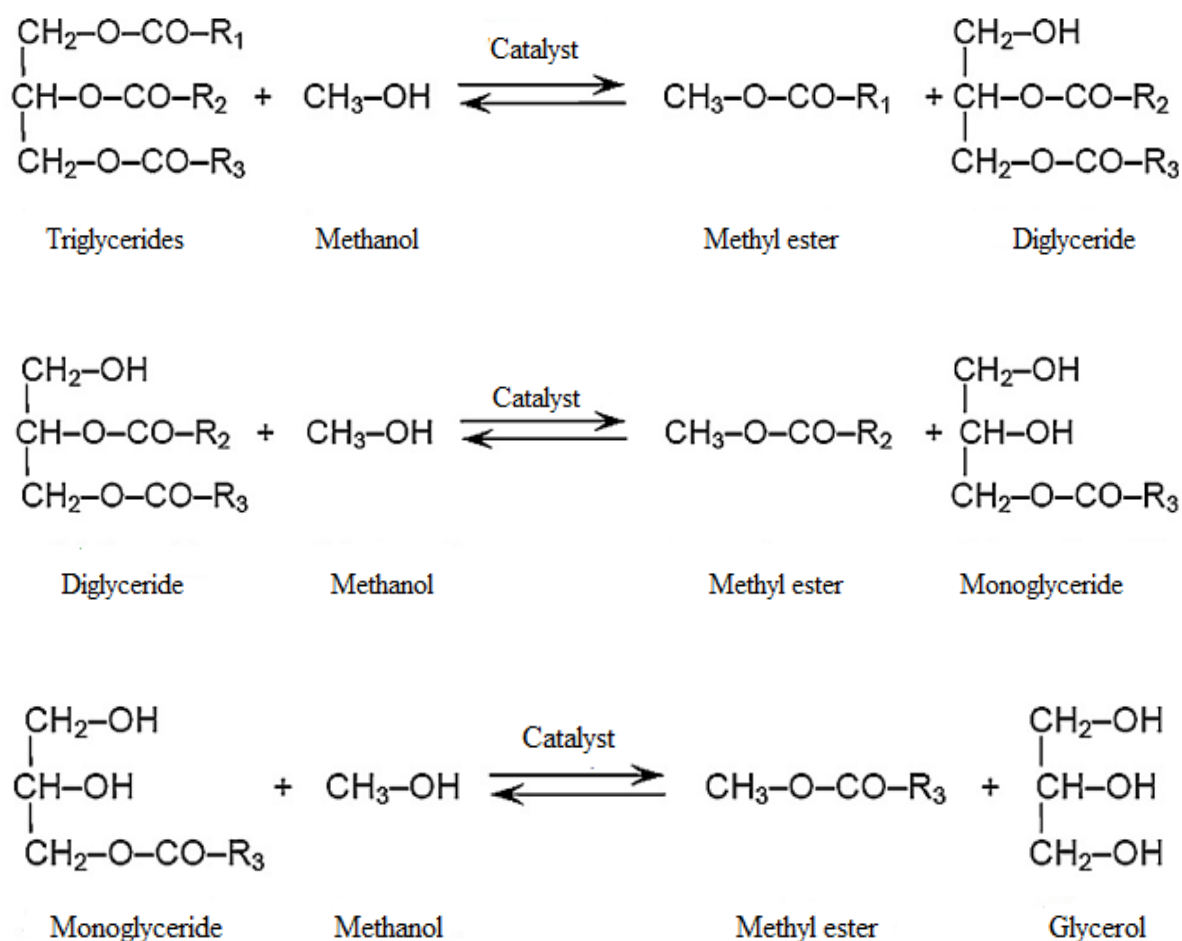
Figure 1.3. Transesterification reaction steps.

Transesterification of vegetable oil can be chemically or enzyme catalyzed. Chemical catalysts can be basic or acidic in nature. It can be catalyzed by homogeneous or heterogeneous catalysts depending on their solubility in reacting mixture. In presence of excess alcohol, the forward reaction is pseudo first order and the reverse reaction is found to be second order. It was also observed that transesterification is faster when catalyzed by alkali [15].

1.4.1. Mechanism of transesterification reaction

The mechanism of alkali catalyzed transesterification is described in Figure 4. In the first step alkoxide ion attacks to the carbonyl carbon of the triglyceride molecule, this results in the formation of a tetrahedral intermediate which reacts with alcohol to form the alkoxide ion in the second step. In the third step the rearrangement of the tetrahedral intermediate gives rise to fatty acid alkyl ester (FAAE) and a diglyceride molecule.
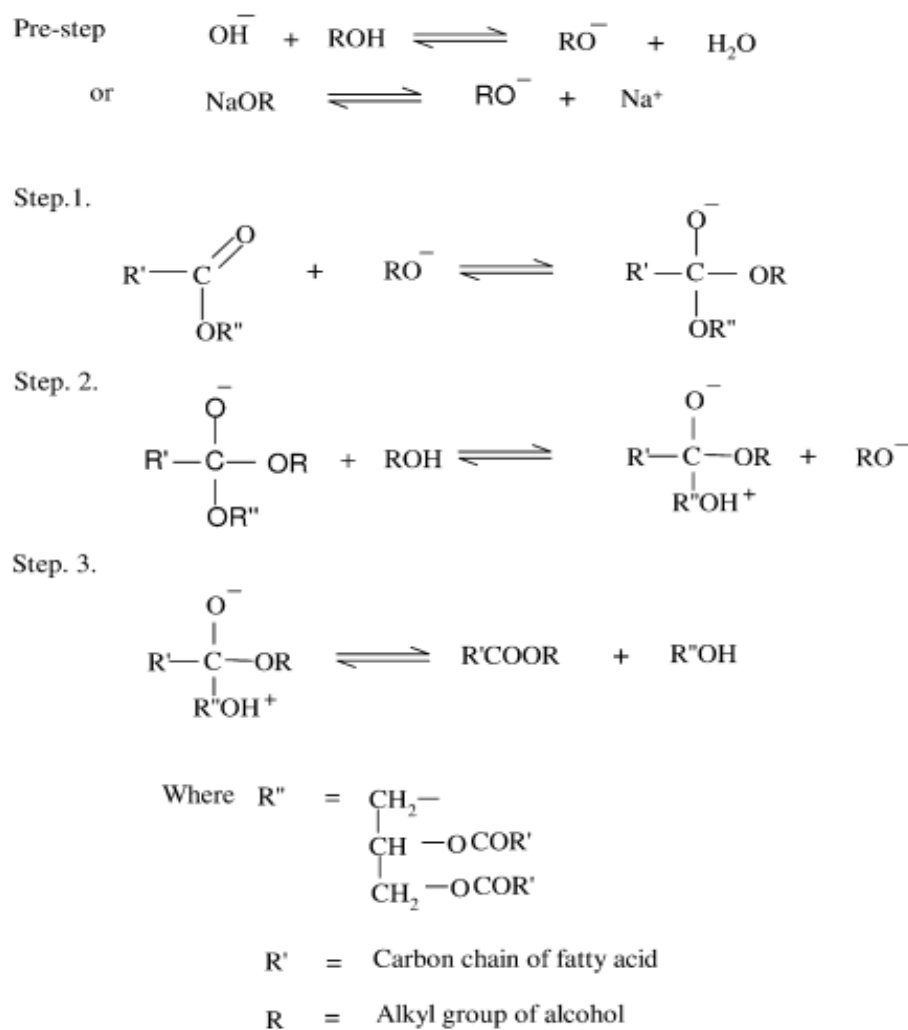
Figure 1.4. Mechanism of base catalyzed transesterification [15].

In the same manner this diglyceride gets converted into monoglyceride and fatty acid alkyl ester, and conversion of monoglyceride into glycerol and fatty acid alkyl ester [15].

1.4.2. Biodiesel

Biodiesel is the mixture of fatty acid alkyl esters (FAAEs), mostly methyl or ethyl esters (FAMEs and FAEEs, respectively). It is obtained by the transesterification of triacylglycerols (TAGs) from vegetable oil and animal fats in three consecutive reversible reactions. The transesterification reaction requires three moles of alcohol and one mole of triglyceride to give three moles of fatty acid alkyl esters and one mole of glycerol. Because of a reversible reaction, it requires excess alcohol and catalyst for faster reaction rate. Biodiesel is a liquid fuel having physical, chemical and combustion attributes similar to petrodiesel. Table 1.3 shows ASTM standards for petrodiesel and biodiesel.

Table 1.3. Comparison of the standards for diesel and biodiesel based on ASTM [12]

Property	Diesel	Biodiesel
Satandard number	ASTM D975	ASTM D6751
Composition	Hydrocarbon (C10-C21)	Fatty acid methyl ester (C12-C22)
Specific gravity (gm/ml)	0.85	0.88
Flash point (K)	333-353	373-443
Cloud point (K)	258-279	270-285
Pour point (K)	243-258	258-289
Water (vol%)	0.05	0.05
Carbon (wt%)	87	77
Hydrogen (wt%)	13	12
Oxygen (wt%)	0	11
Sulphur (wt%)	0.05	0.05
Cetane number	40-55	48-60

1.4.2.1. Advantages of biodiesel

Being a renewable and cleaner fuel, biodiesel has a numerous technical advantages over fossil fuels which include:

➢ Biodegradability
➢ superior flash point
➢ higher combustion efficiency
➢ derivation from domestic feedstock
➢ Lower overall exhaust emission and toxicity
➢ negligible sulphur, nitrogen and metals content
➢ CO_2 neutral (reduction of greenhouse gas emissions)

Biodiesel is commonly obtained by transesterification of refined vegetable oils with methanol in the presence of homogeneous base catalysts such as sodium or potassium hydroxides or alkoxides.

This reaction is affected by various reaction parameters such as oil to alcohol molar ratio, reaction temperature, reaction time, catalyst amount, stirring speed (rpm), purity of alcohol, free fatty acid (FFA) content of oil and moisture content of oil and alcohol. Transesterification can be catalyzed by homogeneous or heterogeneous catalyst and basic or acidic catalysts may be used for this reaction.

2.1 *Homogeneous transesterification*

Homogeneous catalysts are generally used for transesterification of vegetable oils for biodiesel production. These are of two types alkali homogeneous catalysts and acid homogeneous catalysts. Alkali homogeneous transesterification is more appropriate for refined vegetable oils containing low free fatty acids (FFA) contents, generally less than 3%. High FFA content in presence of base catalyst cause saponification leading to soap formation, which results in low FAME yield, loss of catalyst and complication in separation of FAME and glycerol phase. Acid catalysts are more suitable for oils containing high FFA content. Acid catalysts are not susceptible to FFA content because, they can simultaneously catalyze esterification of FFA and transesterification of triglycerides.

Alkali homogeneous transesterification is well established and most widely used method for biodiesel production. It utilizes NaOH, KOH, CH_3ONa and CH_3OK as alkali catalysts. This is very economical process. It requires low reaction temperature (50-70° C), short reaction time (40-60 min) under atmospheric pressure. However, alkali catalysts are highly hygroscopic in nature and absorb water from air which leads to water formation when dissolved in methanol/ethanol and lowers biodiesel yield.

Acid homogeneous transesterification is preferred for high FFA vegetable oils. H_2SO_4, HCl, H_3PO_4 and organic sulfonic acids are mostly used as acid catalyst [6]. Acid catalyzed transesterification has many disadvantages such as requirement of high reaction temperature and time, high oil to alcohol molar ratio, slower reaction rate and low catalyst activity.

Freedman et al. [16] conducted very significant work in alkali catalyzed homogeneous transesterification. They studied variables affecting transesterification and optimized reaction conditions for maximum conversion of vegetable oils into fatty acid methyl esters. The reaction was carried out at 60° C, and oil to methanol molar ratio of 1:6 was used. 97% yield of soybean and sunflower esters have been reported after 1h of reaction time in presence of 1% NaOH or 0.5% CH_3ONa catalyst. Authors also found that acid catalysed transesterification proceeded much slower rate as compared to alkali catalysed reaction.

Georgogianni et al. [17] investigated the effect of catalyst (NaOH) amount on biodiesel yield at reaction the conditions (1:6 oil to methanol molar ratio, 60° C, 1 h and 600 rpm stirrer speed). Authors reported yield of 90%, 92% and 96% for catalyst amount of 1%, 1.5% and 2%, respectively for sunflower oil. Keera et al. [18] compared transesterification of soybean oil and cottonseed oil and studied effect of different reaction parameters. They optimized reaction conditions with 1:6 molar ratio, at 60° C, reaction time 1 hour and 1 wt% NaOH. Authors reported yield of 90% and 98% for soybean and cottonseed oil respectively Authors also observed that increasing catalyst amount beyond 1 wt% reduced yield because of soap formation and increasing molar ratio beyond 1:12 caused difficulty in separation of ester and glycerol phase.

Meher et al. [19] optimized transesterification reaction conditions for Karanja oil using KOH as basic catalyst. Authors observed optimum yield of 97% with oil to methanol ratio 1:6, reaction temperature 65° C, 1% catalyst amount using mechanical stirrer at 360 rpm for a period of 3 h. Naik et al. [20] studied transesterification of high FFA Karanja oil. Authors carried out esterification of oil using 0.5% H_2SO_4 to convert FFA into their methyl esters, followed by transesterification with 1% KOH. Both reactions were conducted at 65° C with oil to methanol molar ratio of 1:6. They observed high yield of 97% in 2 hours of reaction time.

Sharma and Singh [21] achieved optimum yield of 89.5% at 1:8 molar ratio for acid esterification (0.5 % H_2SO_4) and 1:9 molar ratio for alkaline transesterification (0.5% NaOH/KOH) with mechanical stirring. Patil and Deng [22] optimized reaction conditions for dual step biodiesel production using acid esterification followed by alkali transesterification of non edible oils. They obtained maximum ester conversions 95% and 80% for jatropha and karanja oil respectively. Table 2.1 summarizes optimum reaction conditions for homogeneous transesterification.

Table 2.1. The literature review of different catalysts and reaction conditions applied in homogeneous transesterification of different vegetable oils.

Vegetable oil	Catalyst	Reaction conditions				FAME yield	Ref.
		Oil to Methanol ratio	Catalyst amount (wt%)	Tempe-rature (^{o}C)	Reaction time (h)		
Jatropha oil	NaOH	1:5.6	1	60	1	98	[23]
Neem	KOH	1:6	2	60	1	83.4	[23]
Tobacco	NaOH	1:6	<1.5	55	1.5	86	[24]
Tobacco	KOH	1:10	1	50	5 min	98	[25]
Castor seed oil	NaOC$_2$H$_5$	1:16 (oil: ethanol)	1	30	30 min	93	[26]
Cottonseed	KOH	1:6	1.5	60	30 min	91.4	[27]
Karanja oil	KOH	1:6	1	65	3	89	[28]
Karanja	KOH	1:6	1	65	3	97	[19]
Soybean oil	NaOH	1:6	1	60	1	93	[18]

Kinetics of transesterification of soybean oil was investigated by Freedman et al. [15]. Forward reactions were found to be pseudo first order for 1:30 oil to alcohol molar ratio and second order for 1:6 molar ratio. However, reverse reactions were observed to be second order for both molar ratios.

Homogeneous transesterification is a well established and simple industrial process for production of biodiesel. Homogeneous alkaline catalysts such as NaOH and KOH are more efficient than equivalent acid catalysts as their use results in a much higher rate of reaction [29].There are many problems associated with the use of homogeneous catalyst namely difficulty in the removal of the catalysts after the reaction, generation of great amount of wastewater and formation of emulsion. In this process, it is essential to use feedstocks (vegetable oils or animal fats) having low free fatty acids content. When feedstocks contain high percentage of free fatty acids or water, the alkali catalyst reacts with the free fatty acids to produce soaps and the water. This water can hydrolyze the triglycerides to give diglycerides and more free fatty acids [30]. Homogeneous alkaline catalysts speedup the reaction at moderate temperatures (between 60° and 70° C) [31] and atmospheric pressure. There are still many disadvantages for industrial applications of homogeneous catalyst. For example, they require a high quality feedstock i.e. of low water and free fatty acid content to get rid of unwanted saponification reaction because it is very difficult to separate soap from biodiesel. It is required to do multiple washing of biodiesel product to remove the catalyst leads to huge amount of waste water generation.

2.2. Heterogeneous transesterification

Transesterification of vegetable oil by using heterogeneous catalysts are an attractive alternative. Use of solid catalysts can tolerate high amount of free fatty acid and water in the oil. This leads to removal of saponification side reaction and simpler raw glycerol purification. In order to overcome the problems associated with homogeneous catalytic process, recently attention has shifted to heterogeneous catalysts development and applications for production of biodiesel.

Several metal oxides such as magnesium oxide, calcium oxide, strontium oxide, barium oxide mixed oxides and hydrotalcites are used as a solid base catalyst. Solid base catalyst has numerous advantages such as high activity, long catalyst life, and requirement of moderate reaction conditions.

Yoosuk et al. [32] utilized a natural calcite source to produce CaO. Authors suggested an efficient method to increase the activity of natural calcite. They performed hydration and successive thermal decomposition to enhance activity of calcined calcite. This method produces calcium oxide with excellent textural properties and a large number of basic sites. Encian et al. [33] investigated transesterification over commercial CaO, CaO from thermal decomposition of calcium nitrate, calcium carbonate, calcium oxalate and calcium acetate. High FAME yields were obtained at relatively low reaction temperatures (50-80° C). However, CaO adsorbs CO_2 and moisture from atmosphere; it requires thermal treatment for activation to facilitate the removal of carbon dioxide and moisture. Leaching of CaO in methanol and biodiesel layer has been reported as major disadvantage.

Kumar and Ali [34] studied the activity of Li ion on CaO. They prepared catalysts by impregnating Li_2CO_3 on CaO having highest surface area of 6.5 m^2/g and performed at the highest activity in the transesterification reaction. Li-CaO was found excellent for transesterification of vegetable oils containing high moisture content (5-20%). Reaction completed in 2.5 hours for 15% moisture containing oil.

Kaur and Ali [35] investigated the activity of Li ion on CaO as nano catalyst for transesterification and found that reaction completed in 1 hour and 2 h for karanja and jatropha oils, respectively at 65° C. 99% conversion to methyl esters has been reported in presence of 5% catalyst with oil to methanol molar ratio of 1:12.

Taufiq et al. [36] reported mixed oxides catalyst containing CaO and MgO prepared by co-precipitation method and used for transesterification of jatropha oil. Oil to methanol molar ratio of 1:25 and 3% catalysts was used. They obtained nearly 90% yield of biodiesel at 120° C, after a reaction time of 3 h. Li et al. [37] prepared a new catalyst by impregnation of KOH on Nd_2O_3 and carried out transesterification of soybean oil and reported 92% yield after a reaction time of 1.5h for a oil to methanol molar ratio of 1:14 at 60° C. In their study, 6% catalyst was used. Authors reported that catalyst maintained its activity even after being used for 5 cycles.

Tang et al. [38] investigated activity of modified CaO with bromo-octane and noted nearly 99.5% yield from soybean with oil to alcohol molar ratio of 1:15at at 65° C after 3 h. He also studied reusability of modified CaO up to 15 cycles and found negligible loss in activity of catalyst. Table 2.2 summarizes different solid catalysts and optimum reaction conditions for heterogeneously catalyzed transesterification reported in the literature.

Table 2.2. The literature review of different solid catalysts and reaction conditions used in heterogeneous transesterification of different vegetable oils

Vegetable oil (Edible)	Catalyst	Reaction conditions				Biodiesel FAME Yield	Ref.
		Oil to alcohol ratio	Catalyst amount (wt%)	Tempe-rature (^{o}C)	Reaction time (h)		
Palm olein oil	CaO from natural calcites	1:15	7	60	45 min	95.7	[32]
Palm olein oil	CaO from egg shells	1:18	10	60	2	>90	[39]
Palm oil	CaO from egg shells	1:12	1.5	65	2	98	[40]
Sunflower oil	CaO	1:6	1	80	5.5	91	[41]
Sunflower oil	CaO	1:4	1.2	75	45 min	80	[42]
Rapeseed oil	KNO$_3$/CaO	1:6	1	65	3	98	[43]
Soybean oil	Li/ Mgo	1:12	9	60	2	93.9	[44]
Sunflower oil	Mg-Al hydrotlcites commercial	1:12	2	60	24	50	[45]
Soybean oil	Mg-Al hydrotlcites	1:13	5	230	1	90	[46]
Soybean oil	CaO/ Mesoporous Silica	1:16	5	60	8	95.2	[47]
Soybean oil	Sodium silicate	1:7.5	3	60	1	≈100	[48]

Table 2.2 (continued)

Vegetable oil	Catalyst	Reaction conditions				Biodiesel FAME Yield	Ref.
		Oil to alcohol ratio	Catalyst amount (wt%)	Tempe -rature (^{o}C)	Reaction time (h)		
Soybean oil	SrO	1:12	3	65	30 min	95	[49]
Soybean oil	CaO	1:12	8	65	3	95	[50]
Soybean oil	KI/ mesoporous Silica	1:16	5	70	8	95	[51]
Soybean oil	Sr(NO$_3$)$_2$/ ZnO	1:12	5	70	5	94.7	[52]
Palm kernel oil	LiNO$_3$/ γ-Al$_2$O$_3$	1:65	10	60	3	93.4	[53]
Palm kernel oil	NaNO$_3$/ γ-Al$_2$O$_3$	1:65	10	60	3	95.1	[53]
Palm kernel oil	KNO$_3$/ γ-Al$_2$O$_3$	1:65	10	60	3	94.7	[53]
Palm kernel oil	Ca(NO$_3$)$_2$/ γ-Al$_2$O$_3$	1:65	10	60	3	94.3	[53]
Jatropha curcas oil	CaO/Fe$_3$O$_4$	1:15	2	70	80min	95	[54]
Jatropha curcas oil	CaMgO and CaZn	1:15	4	65	6	>80	[55]
Jatropha oil	Mg-Al hydrotalcite	1:4	1	45	1.5	95.2	[56]
Karanja	Li/CaO with Li ion	1:12	5	65	1	99	[35]

Olutoye and Hameed [57] prepared heterogeneous catalyst Al_2O_3 modified MgZnO (MgZnAlO by co precipitation method and investigated its versatility for transesterification of different vegetable oils. They obtained highest yield of 98% with coconut oil and 80-85% for palm oil and waste cooking oil. They reported that the recovery of used catalyst was much easy from product mixture and reused for five cycles without deactivation of catalyst.

Kumar and Ali [58] prepared nono crystalline K-Cao catalyst using CaO and aqueous solution of KOH by wet impregnation method. They conducted tansesterification of different feedstocks like soybean oil, castor oil, cotton seed oil, karanja and jatropha. It was found that the maximum yield was nearly 98%.

Lee et al. [59] reported nearly 94% yield using jatropha oil with mixed oxide (CaO-MgO) prepared by co-precipitation method. Reaction conditions were optimized at 116° C, reaction time of 3.5 h, 3.7% catalyst and molar ratio of 1:38. Catalyst can be reused up to 4 times with very less activity loss.

Guo et al. [48] examined the use of calcined sodium silicate as novel base catalyst. For preparation of catalyst, first dehydration of sodium silicate was carried out at 200° C for 20 min in hot air oven and then calcined at 400° C for 2 h. They reported maximum yield 99% at 60^0 C with 3% catalyst amount and mechanical mixing at 250 rpm. Oil to methanol molar ratio was taken as 1:7.5. Reusability of catalyst was found up to 5 cycles with almost constant activity.

Vyas et al.[60] used KNO_3 supported on Al_2O_3 for transesterification of jatropha oil preparation of catalyst was done by impregnation method using alumina and aqueous solution of KNO_3 which was followed by atmospheric drying and calcinations in muffle furnace at 500^0C. For the process of transesterification molar ratio of 1:12, temperature 70° C, reaction time 6 hour, 6% catalyst amount and mixing at 600 rpm were used and they achieved over 54% conversion to methyl ester. This catalyst had poor reusability because higher activity loss in subsequent runs.

Liang et al. [61] reported a very highly efficient catalyst for biodiesel production, authors prepared different catalyst using K_2CO_3 supported on carrier like MgO, ZnO, CaO, SiO_2, TiO_2, SnO_2, ZrO_2. They found that K_2CO_3 supported on MgO highly efficient for transesterification with 99% yield. It was also concluded that basic carriers showed higher activities than acidic carriers. Catalyst prepared by the solid state method followed by dehydration at 80^0C and

calcinations at 600^0C. Reusability was found to be very good with no loss in activity in 6 cycles.

Sree et al. [62] prepared composite catalyst Mg-Zr by co precipitation method and studied its catalytic activity for transesterification edible and non edible oils. They achieved nearly complete conversion at room temperature in 4.5 hour for soybean oil and reaction completed in 40 minutes at reaction temperature at 65^0C. This composite catalyst showed excellent activity for transesterification to complete reaction within 45 minutes at 65^0C. Authors reported reusability up to four cycles without any loss in activity.

Liu et al. [63] investigated cinder waste catalyst prepared by impregnation method. For preparation of catalyst, Cinder and CaO powder were mixed and after water evaporation CaO/ cinder was immersed in KF solution for impregnation and then calcined. This catalyst showed very high activity giving 99.5% conversion in 20 minutes using 2.1% catalyst with molar ratio of 1:12 slight loss in activity was observed when reused.

Zeng et al. [64] studied activated Mg-Al hydrotalcite catalysts. Catalyst was prepared by co-precipitation using nitrates of magnesium and aluminium followed by filtration, dehydration and calcinations. Authors achieved 90.5% yield under reaction conditions of molar ratio 1:6, temperature 65^0C, time 4 hours, 1.5% catalyst amount and mechanical stirring at 300 rpm.

It is clear from literature review that heterogeneous catalysts are much better than homogeneous catalysts for transesterification of vegetable oils. They have several advantages like easy separation of biodiesel and glycerol, removal of saponification side reaction, simpler purification of raw glycerol, easy recovery and reusability of catalyst. Various solid catalysts have been reported for synthesis of biodiesel in the literature. These include acidic and basic catalysts. According to the literature, solid basic catalysts have much higher catalytic activity than solid acidic catalysts for transesterification reaction. Alkaline earth metal oxides catalysts CaO, SrO, BaO, MgO have high activity. Different supports like Al_2O_3, SiO_2, ZnO, ZrO_2, TiO_2, SnO_2; are also modified by loading different ions (potassium and sodium) using different catalysts preparation method such as solid-solid mixing, impregnation, co-precipitation etc. Use of solid catalyst can reduce overall cost of biodiesel because of removal of several steps in purification of biodiesel and glycerol. Therefore, the objectives were:

- ❖ To reproduce results of a recently published paper on homogeneous transesterification of edible oil.

- ❖ Selection of potential feedstocks (non edible) for biodiesel production.

- ❖ Preparation of highly active solid base catalyst.

- ❖ To know insight of the catalysts, characterization of catalysts by X-ray diffraction (XRD) and Field emission scanning electron microscopy (FESEM).

- ❖ To check activity of catalyst for transesterification of non edible oil.

- ❖ To investigate the effect of process parameters like reaction time, temperature, reactant molar ratio and catalyst amount.

- ❖ Optimization of process parameters for maximum yield of biodiesel.

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4.1   *Materials*

Refined soybean oil (Nutrela make) for experiments was purchased from local grocery market of Roorkee. Sodium hydroxide (>97%), potassium hydroxide (>85%), methanol (99.5%) and n-heptane (>99%) and anhydrous sodium sulphate were purchased from Merck specialities, India. Karanja oil for experiments was purchased from Jatropha Vikas Sansthan, New Delhi. Potassium carbonate (>98%), magnesium oxide (>98% purity) were procured from Thomas Baker, India. Methyl heptadecanoate used as internal standard, was obtained from Sigma Aldrich, India.

4.2.   *Homogeneous transesterification of soybean oil*

Transesterification of soybean oil is most extensively studied with homogeneous alkaline catalyst like KOH, NaOH and alkoxides (CH_3ONa). In this work it has been tried to reproduce result of a latest research paper available on soybean oil transesterification.

4.2.1.   *Experimental procedures*

Experiments were carried out in 250 ml two-necked round-bottomed reaction flask. It was equipped with reflux condenser, magnetic stirrer and thermometer. The transesterification process was studied at three catalyst loadings (0.5%, 1.0% and 1.5% NaOH or KOH wt/wt). Reactions were carried at reaction temperature of 60^oC with oil to methanol molar ratios 1:6 and 1:7 for a reaction time of 1 and 1.5 hour. Catalyst (NaOH or KOH) was dissolved into methanol before its addition into reaction flask. 50 grams of the oil along with calculated amount of catalyst and methanol were introduced into the reaction flask. After the appropriate temperature was reached, the mixture was rigorously stirred by means of a magnetic stirrer. After the pre established time, the mixture was carefully transferred to a separating funnel and allowed to stand there overnight [18].

4.2.2.   *Purification*

After settlement, there were two layers. The upper layer contains biodiesel (methyl esters) with some methanol and traces of the catalyst. The lower layer contains glycerol along with excess methanol and most of the catalyst. The lower layer was drained out. The biodiesel layer was then cleaned thoroughly by washing with warm (50^oC) distilled water in order to remove the

impurities like methanol, unreacted oil and traces of catalyst. The process of washing was repeated until the water layer had a pH similar to the pH of distilled water, indicating that the biodiesel is free of catalyst [18]. Biodiesel (methyl esters) was heated to 110°C then dried with anhydrous Na_2SO_4 to remove traces of water. Methyl ester was filtered to remove Na_2SO_4 particles. This purified biodiesel was used to prepare samples analysis by GC.

Figure 4.1. Experimental setup

Figure 4.2. Biodiesel(top) and glycerol(bottom layer) **Figure 4.3.** Biodiesel after removal of glycerol
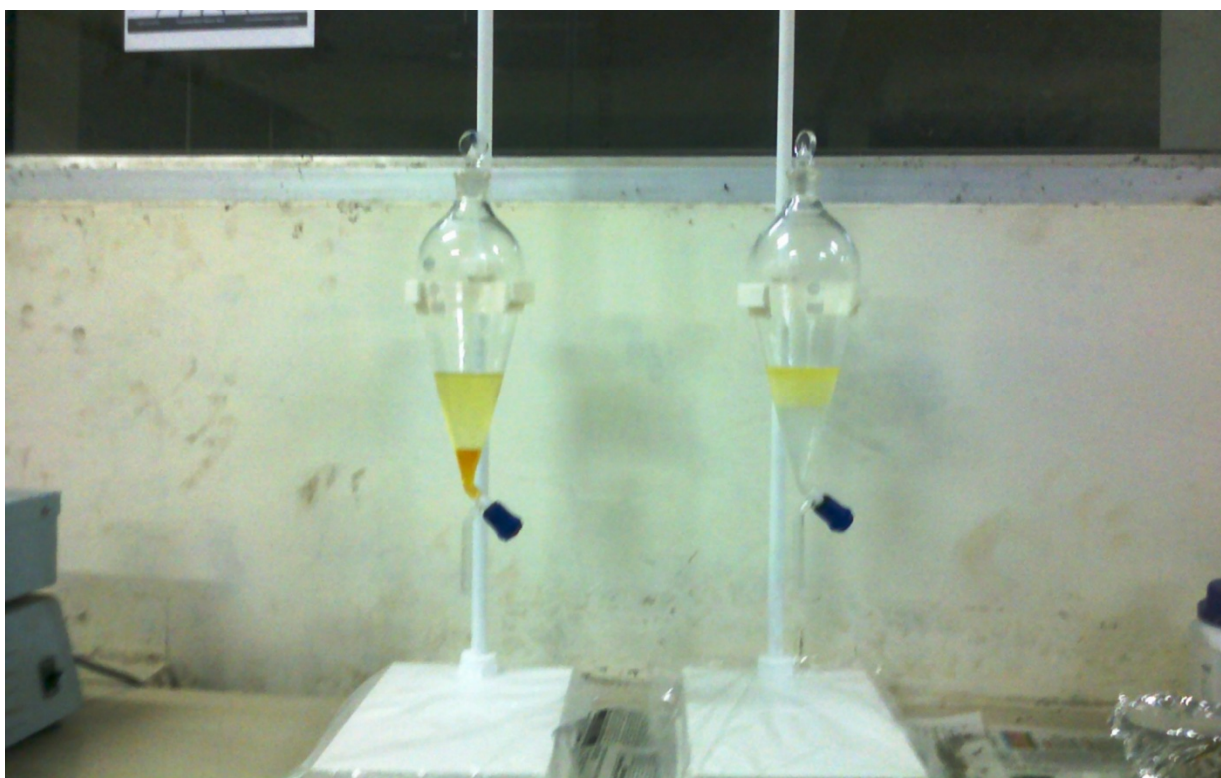

Figure 4.4. Biodiesel and glycerol layer (left) and biodiesel layer after multiple washing with distilled water (right)

4.3. Heterogeneous transesterification of Karanja oil

Heterogeneous catalysts are an attractive alternative because of several reasons. They have greater tolerance of free fatty acid and water in feedstocks. Also, saponification side reaction is removed, purification of the raw glycerol product is simpler and reusability when heterogeneous catalysts are used. In order to overcome the drawbacks of homogeneous catalytic process, recently attention has shifted for the development and application of heterogeneous catalysts for biodiesel production.

4.3.1. Catalyst preparation

The catalyst K_2CO_3 supported on MgO was prepared by solid state method. Certain amount of K_2CO_3 and carrier MgO were mixed together in a mortar. This mixture was skived for 20-30 minutes. Then the mixture was dried in the oven at 80^oC for 4 hours. After drying; catalyst was calcined at 650^oC for 3 hour in muffle furnace. Loading ratio of K_2CO_3/MgO was taken as 0.6 mass/mass for all the reactions [61].

4.3.2 Catalyst characterization

X-ray diffractometer (D8 ADVANCE, Bruker-AXS, Germany) was employed to carry out XRD analysis of pure MgO and K_2CO_3/MgO catalysts. XRD patterns were recorded by scanning diffractions of Cu-Kα radiation source while 2Θ kept between 10 and 80°.

Field emission scanning electrode microscope (FE-SEM QUANTA 200 FEG, FEI Neitherlands) was employed to obtain structural morphology of samples. Sputter coater was used to coat sample with gold.

4.3.3. Experimental procedures for transesterification

The transesterification was carried out in 250 ml two-necked round-bottomed reaction flask equipped with reflux condenser, magnetic stirrer and thermometer. 10 gm of karanja oil, calculated amount of methanol and catalyst were introduced into reaction flask. After the appropriate temperature was reached, vigorous stirring was started. Effect of reaction time, temperature, molar ratio of oil to methanol and carriers on transesterification of karanja oil was studied to optimize reaction condition for biodiesel production from karanja oil.

After certain reaction time product mixture was centrifugated for 25 minutes. It formed three phases. The top layer was Methyl esters (Biodiesel) and middle layer glycerol and bottom layer

was of catalyst. The upper layer was then separated and heated at 80°C for 20 minutes to remove excess methanol. This purified biodiesel was used for quantitative analysis by Gas Chromatograph.

4.4. Sampling and analysis

Methyl heptadecanoate was used as internal standard for GC analysis. Stock solution of concentration of 5 mg/ml is prepared using methyl heptadecanoate and n-heptane. 250 mg of purified biodiesel sample was diluted with 5 ml of stock solution. The samples were analyzed for Methyl Esters formation by Gas Chromatograph (Nucon make) equipped with a flame ionization detector and a packed column for injecting the sample. Nitrogen was used as carrier gas. Oven temperature was varied from 70°C to 240°C at fixed rate of 10°C/min. Injector and detector temperature was kept at 230° and 240°C respectively. 1 µl of prepared samples were injected into GC. The European standard EN 14103:2003; was used for quantitative analysis of biodiesel and FAME content was determined by using following formula.

$$FAME\ content\ = \frac{\sum A - A_{IS}}{A_{IS}} \times \frac{C_{IS} \times V_{IS}}{m} \times 100\%$$

Where,

FAME = Fatty acid methyl esters

$\sum A$ = Total signal area of all methyl esters (mV×sec)

A_{IS} = Signal area of the internal standard methyl heptadecanoate (mV×sec)

C_{IS} = Concentration of methyl heptadecanoate in stock solution (5 mg/ml)

V_{IS} = Volume of stock solution (5 ml)

m = Mass of weighted biodiesel sample (250 mg)

The yield of biodiesel was calculated from the % ME analyzed by GC with the following equation:

$$Yield\ = \frac{(Mass\ of\ biodiesel\ produced/MW\ of\ biodiesel)}{(mass\ of\ oil/\ MW\ of\ oil)\ \times 3} \times (FAME\ content)$$
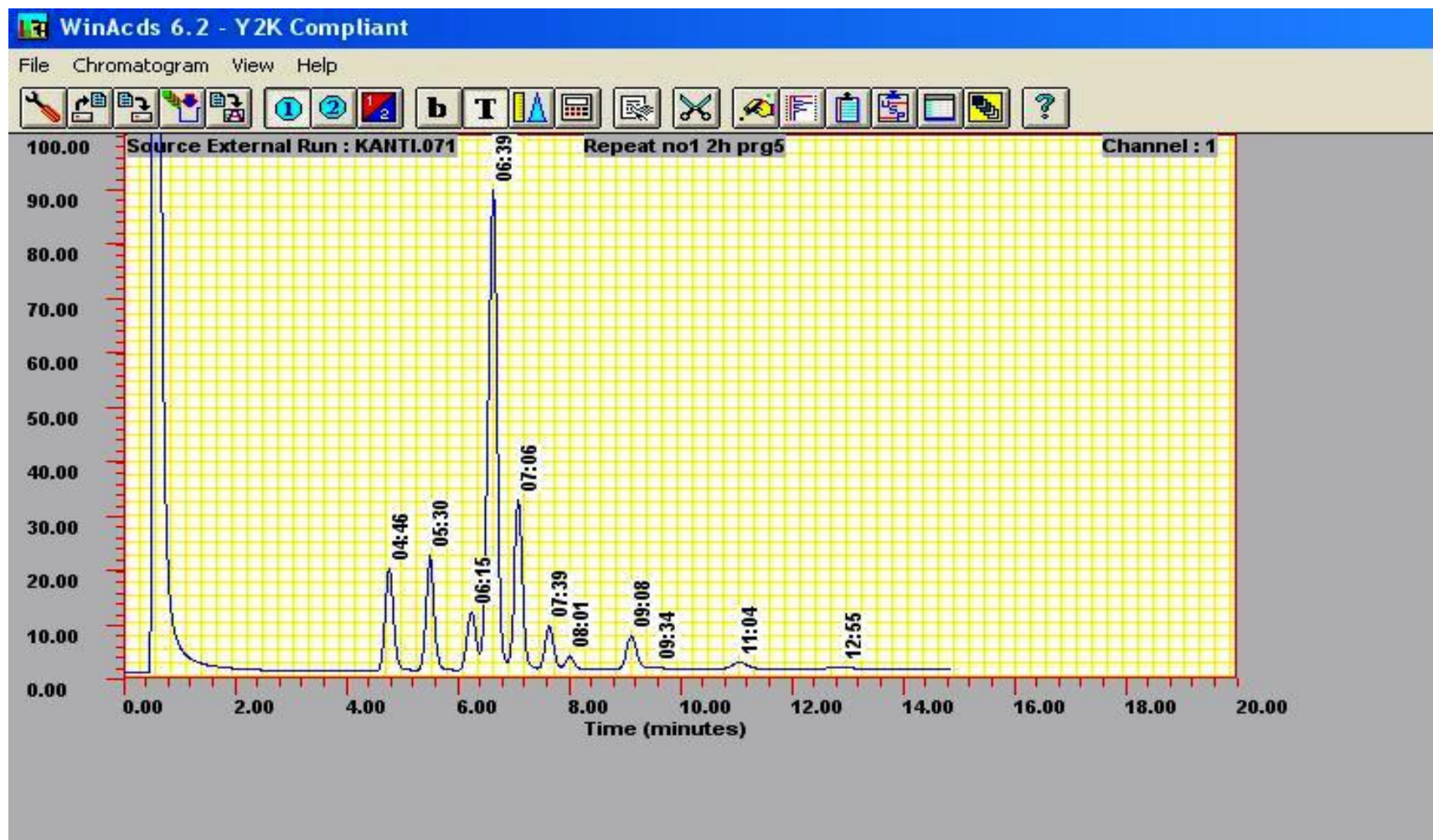
Figure 4.5. Gas chromatogram of Karanja oil methyl esters (KOME)**.**

5.1   Homogeneous transesterification of Soybean oil

Since soybean oil is readily available at any grocery shop, it has been chosen for homogeneous transesterification. In this work, it has been tried to reproduce results of work published by *S.T Keera et al* [18]. Results have been shown in Table 5.1. Reactions were carried out at 60° C with oil to methanol molar ratio 1:6, 1 wt% NaOH and for reaction time of 1 h. Reacting mixture was agitated by magnetic stirrer. Yield obtained in this work are almost same as reported by *S.T Keera et al.* [18]. Authors carried out transesterification of soybean oil and cottonseed oil with methanol using NaOH as catalyst and obtained maximum yield of 90% and 98% respectively. Transesterification of soybean oil was also carried out using KOH as catalyst keeping all reaction conditions same. It is clear from the results that KOH is better than NaOH as an alkaline catalyst for same reaction conditions.

Table 5.1. Homogeneous alkali catalyzed transesterification of Soybean oil

S. N	Reactants (oil to methanol molar ratio)	Catalyst type and amount	Reaction conditions		Yield (%)	Yield(%) reported in Literature	Ref.
			Temperature (^{o}C)	Reaction time (h)			
1	SBO, MeOH (1:6)	NaOH 1wt%	60	1	90.7	90	*S.T. Keera et al.* [18]
2	SBO, MeOH (1:6)	KOH 1 wt%	60	1	93.3		
3	SBO, MeOH (1:6)	KOH 1 wt%	60	1.5	90.5		
4	SBO, MeOH (1:6)	KOH 1.5 wt%	60	1.5	93.7		
5	SBO, MeOH (1:7)	KOH 1 wt%	60	1	94.2		

SBO- Soybean oil   MeOH- Methanol

Then further all reactions were carried out using KOH as homogeneous catalyst. It has been tried to change some reaction conditions like catalyst amount, reaction time and molar ratio; to improve yield of biodiesel. It has been found that increasing reaction time resulted into lower yield when keeping other parameters constant because of reversible reactions [15].

It has been observed that increase in catalyst amount results into higher yield. Maximum yield of 94.2% was obtained when at reaction conditions of 1:7 oil to methanol molar ratio, temperature 60°C, 1 wt% KOH and reaction time of 1 hour.

5.2.   *Heterogeneous transesterification of Karanja oil*

India is a net importer of edible oils hence the emphasis is on non edible oil plants such as Jatropha, Karanja, Neem, Mahua etc. Government of India has found Jatropha and Karanja oil as potential feedstocks for biodiesel production in India to reduce its reliance on foreign countries for petroleum crude oil. Karanja is an oil seed bearing tree which is non edible and underutilized resource [1]. India is a tropical country and offers most suitable climate for the growth of Karanja tree. Karanja oil can be utilized for biodiesel production. Heterogeneous transesterification of Karanja oil has not been studied much. Therefore, Karanja oil has been selected as non edible oil resource for biodiesel synthesis.

5.2.1   *Catalyst characterization*

XRD patterns of pure MgO and K_2CO_3/MgO catalysts were recorded by scanning diffractions of Cu-Kα radiation source and depicted in Figure 5.1. High intensity peaks were obtained at the 2Θ value of 42.9^{o} (200), 62.2^{o} (220) whereas low intensity peaks were obtained at 36.9^{o} (111), 74.7^{o} (311) and 78.6^{o} (222) for pure MgO (JCPDS file no. 74-0430). XRD pattern of MgO indicated its high crystalline and cubic structure. After loading K_2CO_3 on MgO, additional peaks were obtained at the 2θ value of 26.1^{o} (002), 31.7^{o} (130), 32.1^{o} (200) and 34.3^{o} (112) (JCPDS file no. 71-1466) corresponding to K_2CO_3 which also indicates its crystalline and monoclinic structure. Increasing the loading of K_2CO_3 on MgO reduces diffraction intensity of peaks of MgO and increases intensity of peaks corresponding to K_2CO_3. Crystallite size of catalyst was calculated by Scherer's equation. Crystallite size of MgO was found between 22

nm to 35 nm. For K_2CO_3, It was in the range of 55-74 nm. In summary, The XRD patterns of K_2CO_3/MgO catalysts indicated that the catalysts were well crystalline.

FESEM images of MgO and K_2CO_3 loaded on MgO were taken at 10,000 magnification; are shown in Figure 5.2 and 5.3, respectively. Structural morphology of MgO (Figure 5.2) indicates that it has no specific shape. After loading K_2CO_3 on MgO (Figure 5.3), structural morphology of catalyst changes to rod shape.
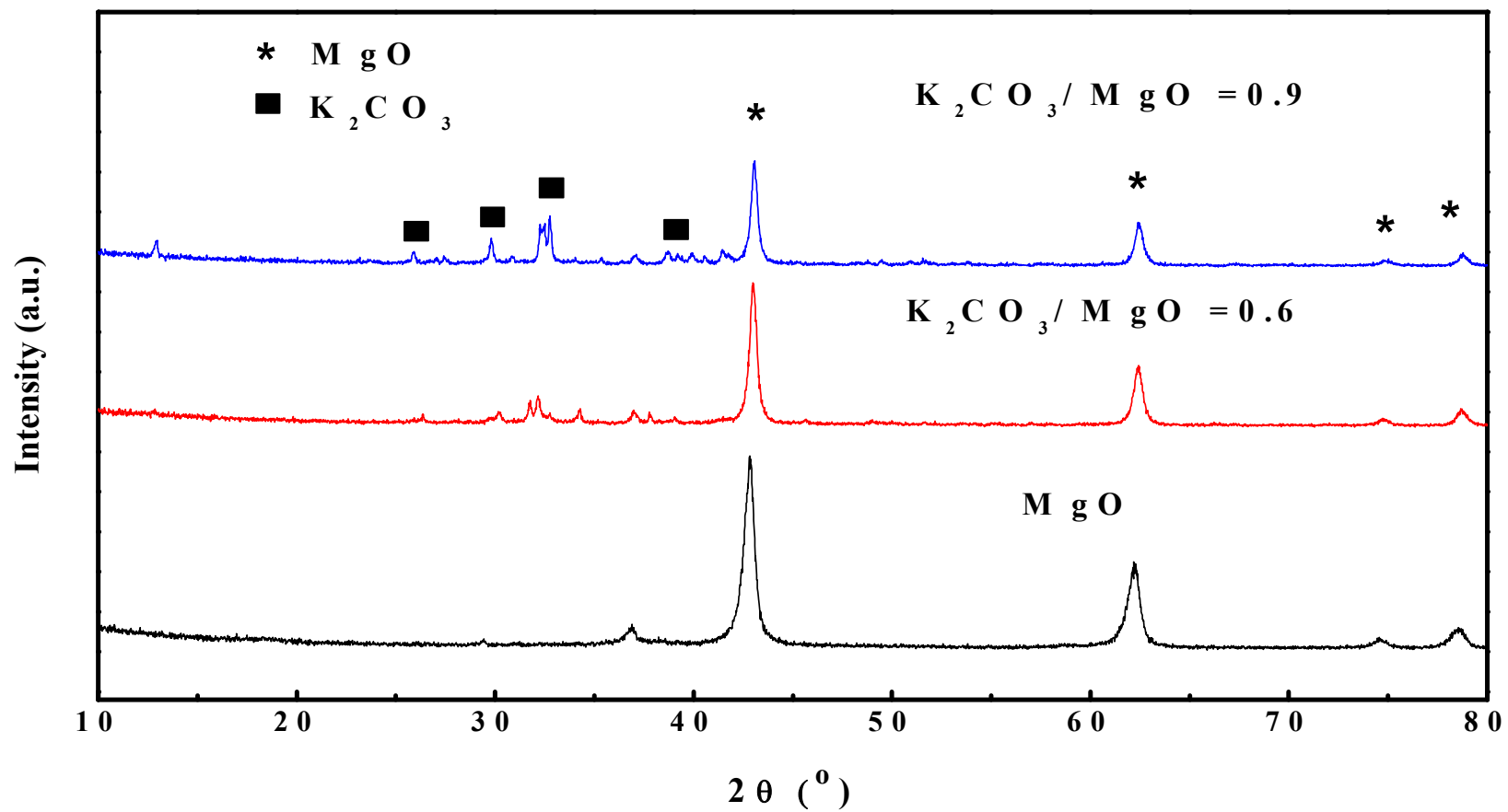
Figure 5.1. XRD patterns of MgO, 0.6 m/m K_2CO_3/MgO and 0.9 m/m K_2CO_3/MgO
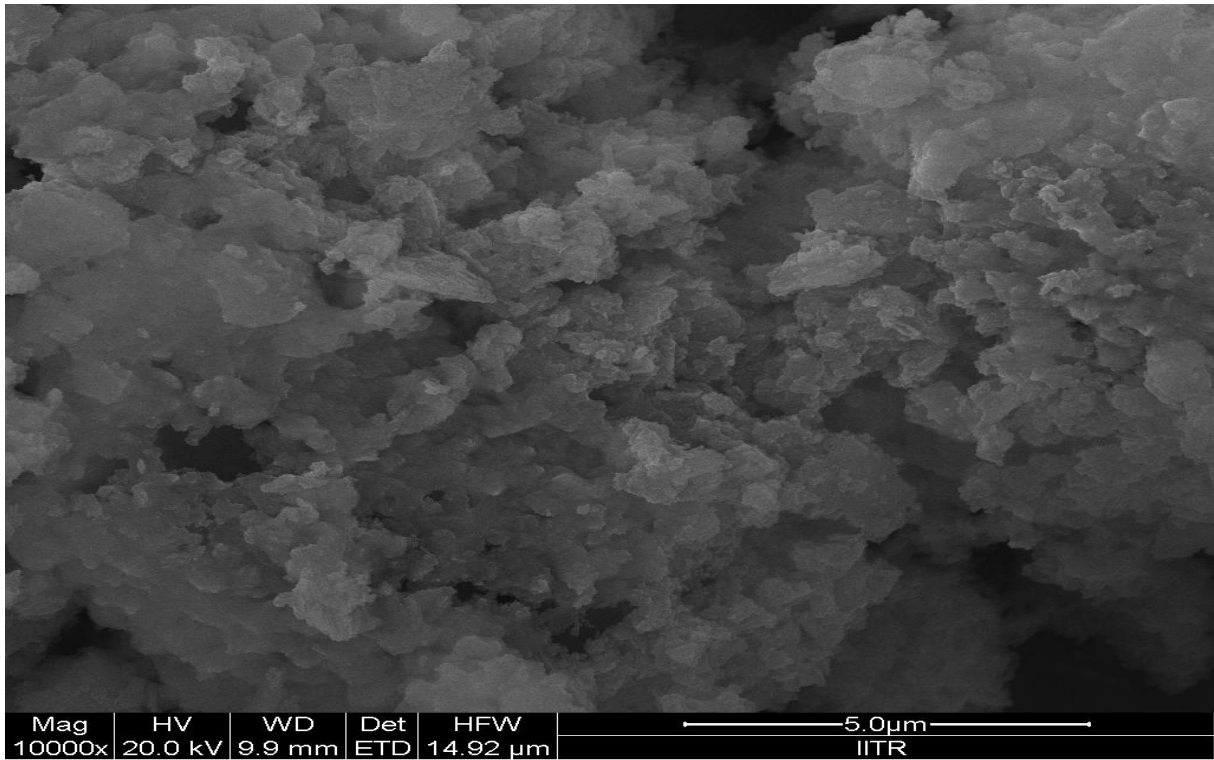
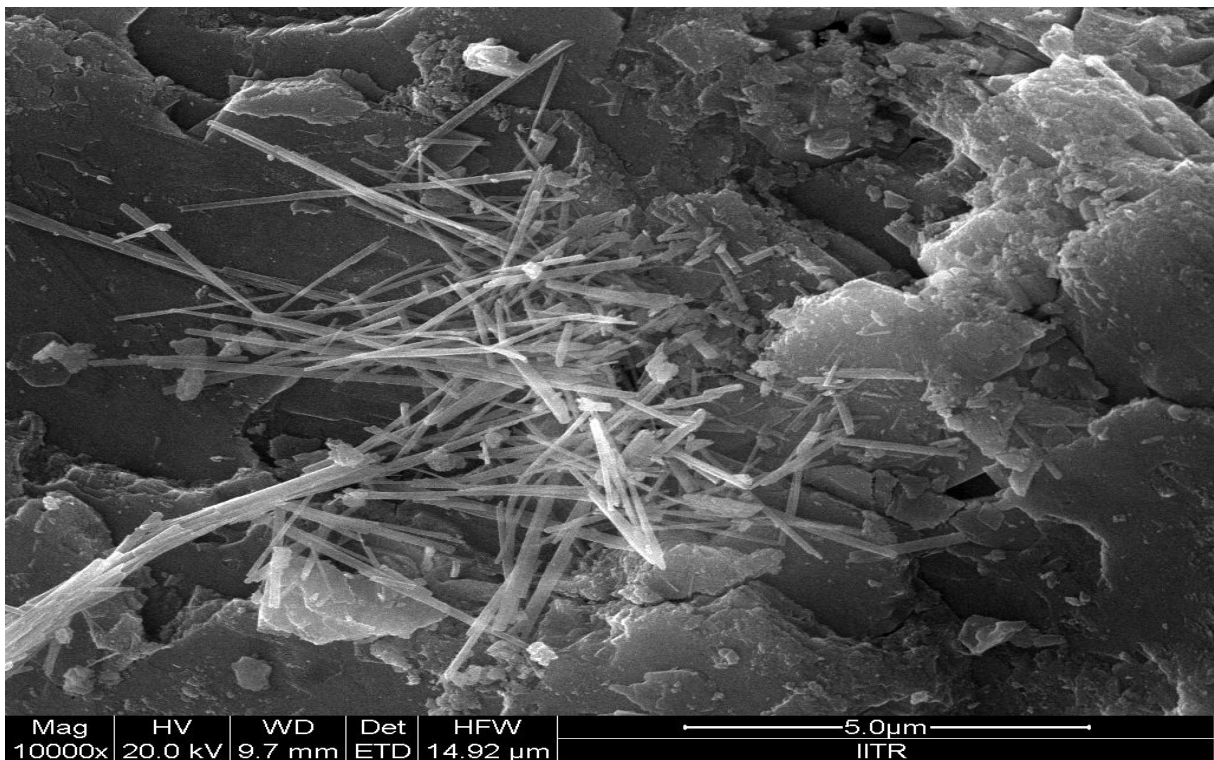**Figure 5.2.** SEM image of pure MgO surface

Figure 5.3. SEM image of K_2CO_3 loaded on MgO

5.2.2. Effect of reaction time

Effect of reaction time on transesterification of Karanja oil with methanol was investigated at 70°C using constant oil to methanol molar ratio (1:9) and 2 wt% catalyst amount for different reaction time. Reaction conditions and results are shown in Table 5.2. Trends of FAME yield with reaction time are shown in Figure 5.4. Reactions were carried out for different reaction time (1 h, 1.5 h, 2 h, 2.5 h, 3 h) keeping all other operating condition same (1:9, 70° C and 2 wt% catalyst). It has been that catalyst was very efficient for transesterification of Karanja oil. It has been found that yield of biodiesel increases from 65.3 to 91.5% with reaction time (1 to 2 h). Increase in reaction time beyond 2 h has negligible effects on the yield.

Table 5.2. Effect of reaction time on heterogeneous transesterification of Karanja oil

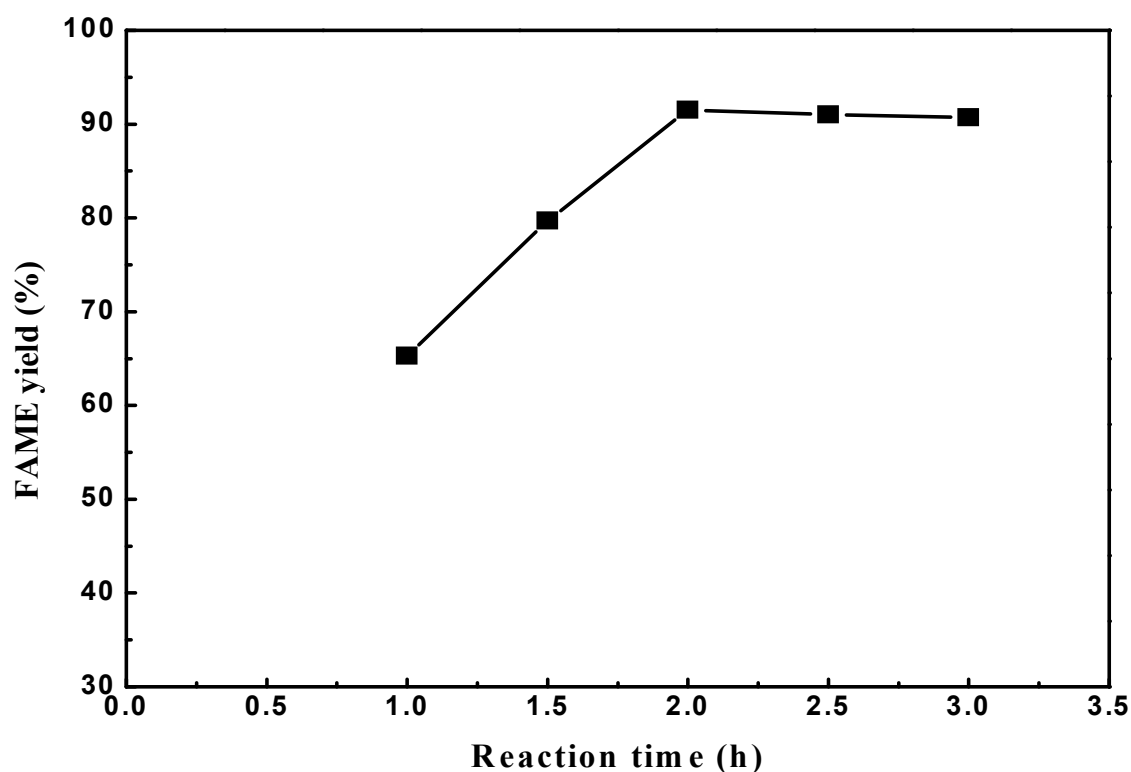| S. N	Reactants	Catalyst	Reaction conditions		Yield (%)
			Temperature (^{o}C)	Reaction time (h)	
1	KO, MeOH (1:9)	2 wt% K_2CO_3/MgO=0.6	70	1.0	65.3
2	KO, MeOH (1:9)	2 wt% K_2CO_3/MgO=0.6	70	1.5	79.7
3	KO, MeOH (1:9)	2 wt% K_2CO_3/MgO=0.6	70	2.0	91.5
4	KO, MeOH (1:9)	2 wt% K_2CO_3/MgO=0.6	70	2.5	91.0
5	KO, MeOH (1:9)	2 wt% K_2CO_3/MgO=0.6	70	3.0	90.7

KO- Karanja oil

MeOH- Methanol

Figure 5.4. Effect of reaction time on biodiesel yield

5.2.3. Effect of reaction temperature

Effect of reaction temperature on transesterification of Karanja oil with methanol was investigated keeping all other conditions constant. Reactions were carried out for reaction time of 2 h keeping constant oil to methanol molar ratio (1:9) and 2 wt% catalyst amount by changing reaction temperature (50, 60, 70, 80, and 90° C). Reaction conditions and results are shown in Table 5.3. When reaction temperature was increased from 50° to 70° C, biodiesel yield increased from 40.5 to 91.3%. Further increase in temperature resulted into lower yield. Trends of FAME yield with reaction temperature are shown in Figure 5.5. It has been found that at temperature of 70°C; catalyst gave maximum yield of 91.3% to methyl esters. To further optimized temperature near 70° C, reactions were also carried out at 65° and 75° C giving yield of 74.6% and 89.9% respectively. It was examined that transesterification of Karanja oil gives maximum yield of 91.3% at 70° C keeping other reaction conditions constant (2%, 1:9, 2 h).

Table 5.3. Effect of temperature on heterogeneous transesterification of Karanja oil

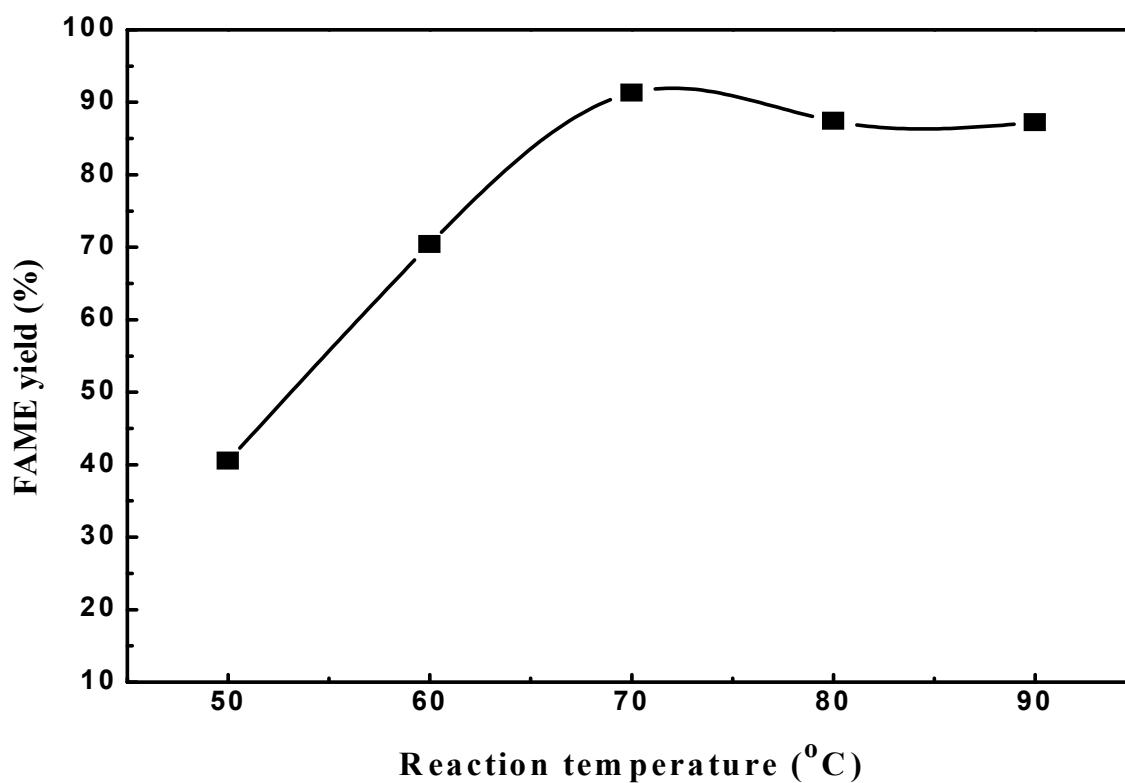| S. N	Reactants	Catalyst	Reaction conditions		Yield (%)
			Reaction time (h)	Temperature (^{o}C)	
1	KO, MeOH (1:9)	2 wt% K_2CO_3/MgO=0.6	2	50	40.5
2	KO, MeOH (1:9)	2 wt% K_2CO_3/MgO=0.6	2	60	70.4
3	KO, MeOH (1:9)	2 wt% K_2CO_3/MgO=0.6	2	70	91.3
4	KO, MeOH (1:9)	2 wt% K_2CO_3/MgO=0.6	2	80	87.4
5	KO, MeOH (1:9)	2 wt% K_2CO_3/MgO=0.6	2	90	87.2

Figure 5.5. Effect of reaction temperature on biodiesel yield

Trends in Figure 5.5 shows that FAME yield first increases and then decreases with increase in temperature. Slow reaction rates were obtained at low temperatures, reaction rate and yield may increase with temperature because of endothermic nature of reaction. Since, boiling point of methanol is 64.5^{o}C, increasing temperature beyond 70°C leads to fast vaporization of methanol and consequently results in lower yields.

5.2.4. *Effect of molar ratio of oil to methanol*

Effect of molar ratio of oil to methanol was investigated. Reactions were carried out with different oil to methanol molar ratio (1:5, 1:7, 1:9, 1:11, 1:13) keeping other process parameters constant as following (reaction temperature 70°C, reaction time 2 h and 2 wt% catalysts). Reaction conditions and results are shown in Table 5.4.

Table 5.4. Effect of molar ratio on heterogeneous transesterification of Karanja oil

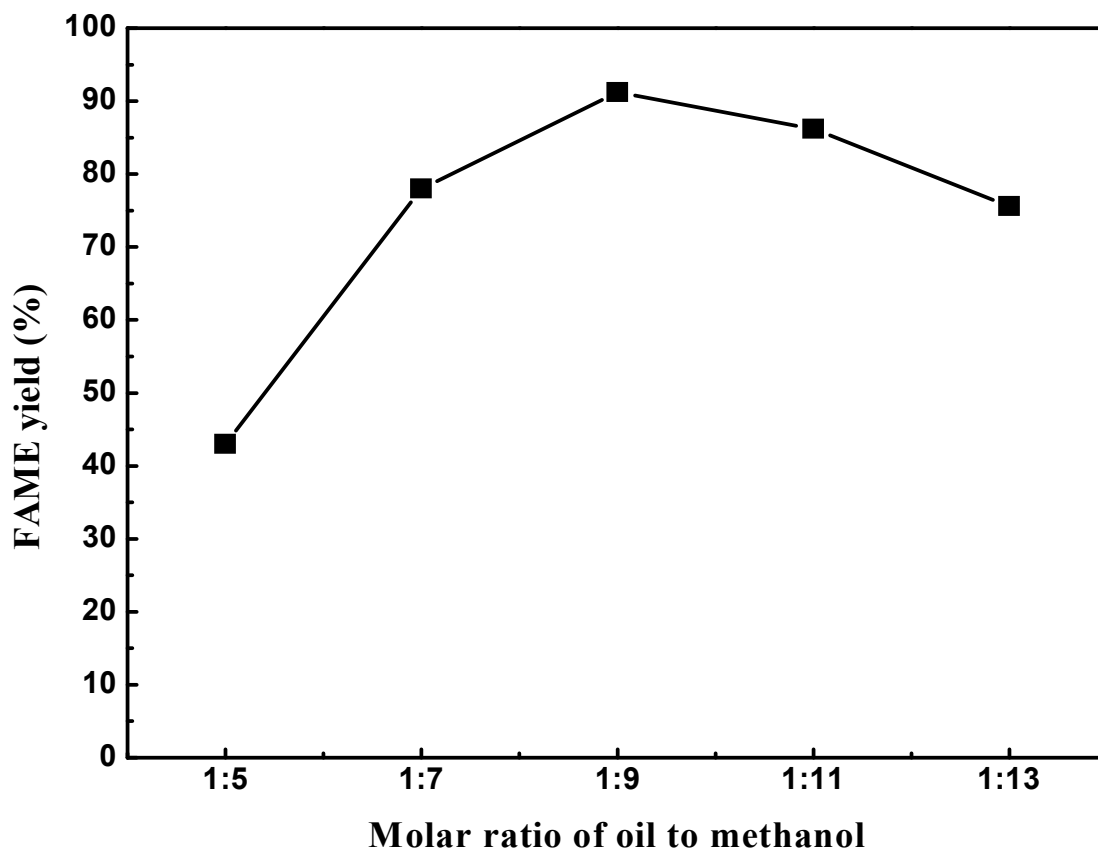| S. N	Reactants	Catalyst	Reaction conditions			Yield %
			Tempe-rature (^{o}C)	Reaction time (h)	Molar ratio	
1	KO, MeOH	2 wt% K_2CO_3/MgO=0.6	70	2	1:5	43
2	KO, MeOH	2 wt% K_2CO_3/MgO=0.6	70	2	1:7	78
3	KO, MeOH	2 wt% K_2CO_3/MgO=0.6	70	2	1:9	91.2
4	KO, MeOH	2 wt% K_2CO_3/MgO=0.6	70	2	1:11	86.2
5	KO, MeOH	2 wt% K_2CO_3/MgO=0.6	70	2	1:13	75.6

Figure 5.6. Effect of molar ratio of oil to methanol on biodiesel yield

Figure 5.6. depicts effect of oil to methanol molar ratio on biodiesel yield. Stoichiometrically, transesterification of Karanja oil requires three moles of methanol for one mole of oil. Because transesterification reaction is reversible, use of excess methanol moves the equilibrium towards product side and consequently results into higher yield of biodiesel. It has been also observed that increasing molar ratio beyond 1:9 leads to lower FAME yield because of diluting effect. It has been found that 1:9 molar ratio of oil to methanol gave maximum yield of 91.2%.

5.2.5. Effect of different supports

Effect of different supports (Al_2O_3 and CaO) on transesterification of Karanja oil with methanol was investigated; keeping all other conditions constant. Reactions were carried out at 70° C for reaction time of 2 h keeping constant oil to methanol molar ratio (1:9) and 2 wt% catalyst amount. Results are shown in Table 5.5 for effect of different supports on biodiesel yield.

Table 5.5. Effect of different supports on biodiesel yield.

S.N	Support	Loading ratio of K_2CO_3 to support (m/m)	Catalyst amount (wt %)	Yield (%)
1	Al_2O_3	0.6	2	72.7
2	CaO	0.6	2	83.2
3	MgO	0.6	2	91.5

It is clear from results that CaO is better than Al_2O_3 because of alkaline nature which leads to higher yield. Furthermore, highest yield of 91.5% obtained using K_2CO_3/MgO.

5.2.6. Fuel properties of biodiesel (Karanja oil methyl esters)

The fuel properties of biodiesel were determined by standard methods and listed in Table 5.6.

Table 5.6. The fuel properties of biodiesel (Karanja oil methyl esters).

Properties	Biodiesel from Karanja oil	Biodiesel standard for B100 ASTM D 6751	Test method
Density (kg/m^3)	873	820-900	ASTM D 4052
Flash point (^{o}C)	160	100-170	ASTM D 93
Cloud point (^{o}C)	10	-3 to 12	ASTM D 97
Pour point (^{o}C)	6	-15 to 16	ASTM D 2500
Kinematic viscosity (mm^2/sec)	8.71	1.9-6.0	ASTM D 445

Pensky Marten flash point tester (closed cup) was used to determined flash point of biodiesel and found within the standards for B100. Redwood viscometer was employed for the determination of kinematic viscosity at 40° C. Biodiesel from Karanja oil cannot be used without blending with petrodiesel because of its high viscosity 8.71 mm^2/sec as compared to maximum allowable 6.0 mm^2/sec for B100 as per ASTM D 6751.

Cloud point and pour point were determined as per ASTM standards and found within range for 100% biodiesel use in CI engines.

In summary, biodiesel prepared in laboratory; had very good fuel properties (flash point, cloud point, pour point and density) except kinematic viscosity. Biodiesel from Karanja oil can be used as alternative, renewable and eco friendly fuel; after blending with petrodiesel in CI engine.

In summary, an environment friendly, inexpensive and highly active K_2CO_3/MgO catalyst for transesterification of Karanja oil (non edible) at moderate reaction conditions is used and gave impressive yield of biodiesel. Effects of different reaction parameters such as reaction time, temperature, molar ratio; have been studied. After 2 h, there is a slight decrease in biodiesel yield. Highest yield obtained at 70° C. Further increasing temperature beyond 70° C causes yield to decrease. When reaction temperature was increased from 50° to 70° C; biodiesel yield increased from 40.5 to 91.3%. Further increasing temperature beyond 70° C causes yield to decrease because of fast vaporization of methanol. Effect of molar ratio oil to methanol has also investigated. Increasing molar ratio from 1:5 to 1:7 increases yield of biodiesel. Reaction conditions have been optimized for transesterification of Karanja oil. A maximum yield of 91.5% has been obtained under optimum reaction conditions temperature at 70^oC, molar ratio of 1:9, for reaction time of 2 h and 2 wt % catalyst amount.

The fuel properties (density, flash point, cloud point, pour point and kinematic viscosity) were determined to check compliance with B100 standards. It was found that because of slightly higher viscosity of Karanja oil methyl esters. It requires blending with petrodiesel to some extent to be used in CI engine.

Future recommendations

1. Reusability of solid catalyst (K_2CO_3/ MgO) need to be investigated.
2. Effect of calcinations temperature for catalyst preparation need to be studied in detail for higher yield of biodiesel.
3. Effect of different loading ratio of K_2CO_3 on MgO can be examined.
4. Kinetic study need to be carried out to get insight into the order of reaction catalyzed by heterogeneous catalysts.

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