

Production of biodiesel from nonedible feedstock (*Pongamia pinnata*) via transesterification

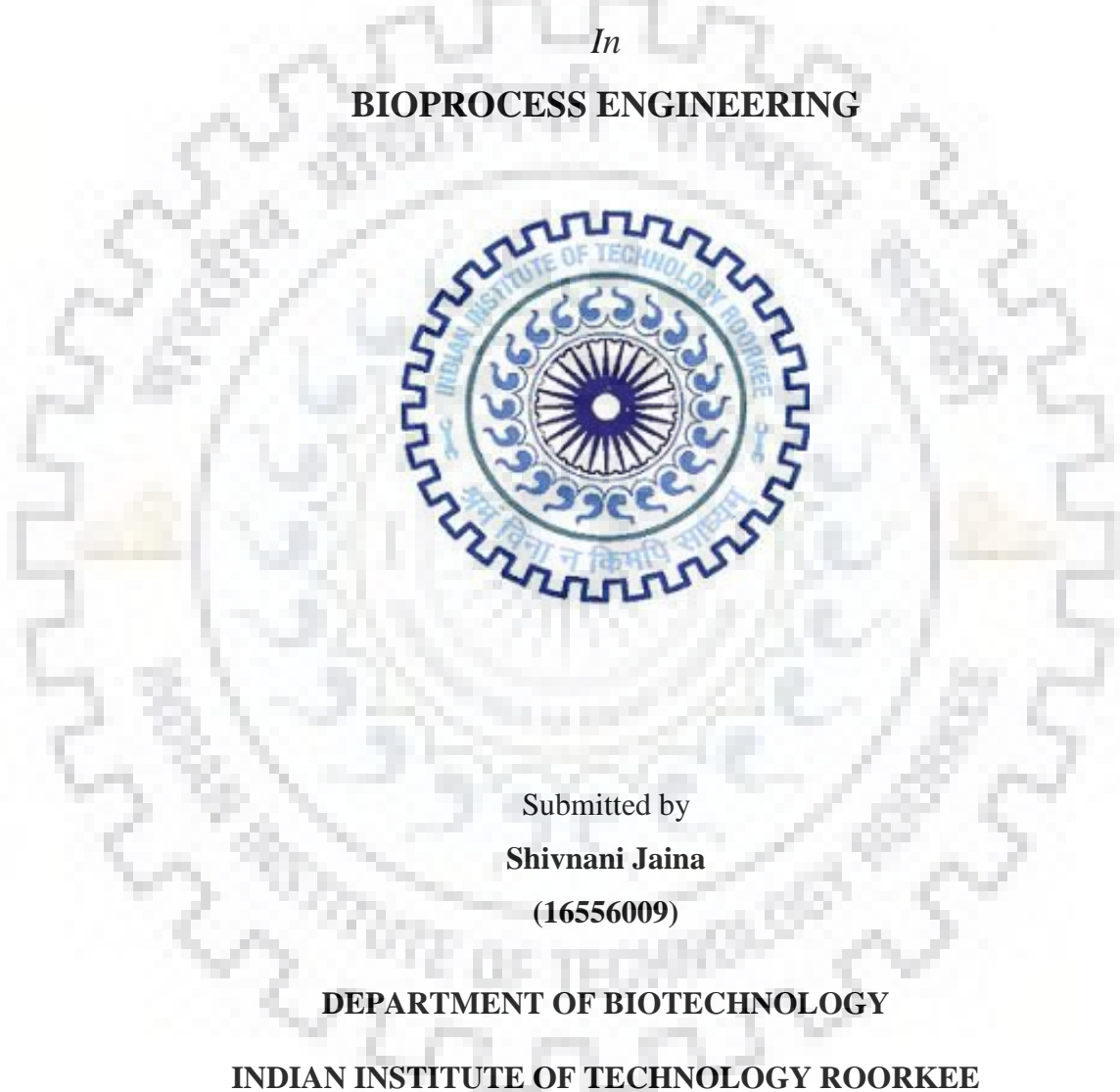
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CANDIDATE DECLARATION

I hereby assure that the work presented in the dissertation entitled “**Production of biodiesel from nonedible feedstock (Pongamia pinnata) via transesterification**” is submitted in partial fulfilment of the course for the award of the degree of Master of Technology in Bioprocess Engineering, to the Department of Biotechnology of Indian Institute of Technology Roorkee, India, is an authentic record of my work carried out by me under the guidance of **Dr. Prakash Biswas**, Associate Professor, Department of Chemical Engineering, and **Dr. Sanjoy Ghosh**, Associate Professor, Department of Biotechnology, Indian Institute of Technology Roorkee, India.

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CERTIFICATE

This is to certify that **Ms. Shivnani Jaina** has completed the dissertation entitled “**Production of biodiesel from nonedible feedstock (Pongamia pinnata) via transesterification**” under our supervision. This is to certify that the above statement made by candidate is correct to the best of my knowledge.

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Abstract

This study focused on the production of biodiesel from the non-edible karanja oil (*Pongamia pinnata*). Two steps esterification process i.e. acid esterification and alkaline esterification was followed due to the high fatty acids (9.5%) content in karanja oil. Acid esterification process reduced the fatty acid percentage to 1.25% and further alkaline transesterification produced methyl esters.

Both homogeneous and heterogeneous catalysts were used for the esterification process. Different heterogeneous catalysts such as K_2CO_3/MgO , K_2CO_3/CaO , Al_2O_3/MgO , and Al_2O_3/CaO were prepared and the reactions conditions i.e. oil to methanol ratio, reaction time, reaction temperature, catalyst weight percentage were optimized for higher fatty acid methyl esters (FAME) content. The maximum FAME content of 97.16% was obtained in presence of K_2CO_3/MgO catalyst (4wt.%) at the oil to methanol mole ration of 1:15.

The physico-chemical properties of the heterogeneous catalysts were characterized by specific surface area (BET) and X-ray diffraction study. Kinetic experiments were conducted to determine the reaction order and activation energy for the formation of biodiesel following Levenspiel method. Kinetic results suggested pseudo-first order reaction. The variation of reaction rate constant with catalyst weight percentage were also determined it showed linear variation up to 8wt.% of the catalyst used for the reaction.

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In the past few decades' petroleum, natural gas and coal have been playing an important role in energy production worldwide (Meher et al., 2006). As a result of which we have seen drastic environmental changes in past couple of years. The amount of greenhouse gasses in the atmosphere has risen to alarming levels (Agarwal et al., 2012). The situation has worsened with the escalating energy consumption worldwide due to rapid population growth and economic development. This has led to many consequences, primarily the cost of crude petroleum oil has increased and secondly these energy producing sources have a detrimental effect on our climatic conditions (Patil PD., and Deng S. 2009). Thus, currently the world is in the need for an alternative energy resource that is renewable, clean, reliable and yet economically feasible solution to the current fossil fuels.

The extensive research in finding renewable fuel has provided us with the solution in form of biodiesel. Some researchers suggest that biodiesel is the fuel of future (Sharma et al., 2008). The prime advantages of biodiesel are (1) It can be manufactured from numerous feed stocks namely edible oil such as canola, soybean and corn (Patil PD. and Deng S., 2009), nonedible oil such as *Madhuca Indica*, *Jatropha Curcas* and *Pongamia pinnata*, animal fat, algal oil, waste cooking oil. (2) It can be manufactured by various methods such as direct use and blending, micro emulsions, transesterification and pyrolysis. (Gupta V and Gupta AK.) (3) It does not emit greenhouse gasses and has relatively less toxic emissions also does not add to existing carbon foot print. (4) It can be manufactured locally and in an environmentally favorable manner. (5) It has low sulphur content, high flash point and also is inherently lubric (Sajja.di B. et al., 2016).

During World War II when petroleum fuels were expensive and low in demand people used vegetable oil to run their engines, which in today's technology would be called biodiesel. Soon after the end of World War II when the petroleum product supplies were restored the concept of biodiesel faded away. Nowadays again as the crude oil prices have reached to heights and these sources are causing environmental pollution we are again searching for alternatives. But today we have improved alternatives, today we can synthesize biodiesel with the help of nonedible oils which in today's scenario a more

preferred option. The production of biodiesel from vegetable oil increases its cost by creating a competition between food and fuel. Thus to avoid rise in food prices nonedible oil sources such as are preferred.

The diverse non edible sources available for biodiesel production are are jatropha seed/kernel, karanja seed/kernel, rubber seed, rice bran, mahua seed, tobacco seed/kernel, Chinese tallow, silk cotton tree, jojoba seed, babassu tree and Euphorbia tirucalli. These non-edible sources are preferred for one primal reason that they avoid food and fuel conflict. Waste cooking oil and animal fats can also be one of the secondary sources after the non-edible oils considered for biodiesel production. With animal fats the advantage is that they are cheap as comparison to the vegetable oils. But these fats contain high unsaturated fatty acid content which is undesirable. The waste cooking oil is preferred less for the mainly two reasons, first is the consistency of the oil, the oil obtained from various sources can be different in fatty acid composition. Secondly the storage and maintenance is a problem. Thus it is observed that non edible oils are a better option in comparison with other sources.

1.1 Factors affecting the choice of feedstock

1.1.1 Oil yield

For a given non-edible feedstock, the quantity of oil extracted is of prime importance. Seeds which produce higher oil content or seeds from which oil is extracted with minimum loses are preferred. The final production cost of the biodiesel is majorly dependent (70-80%) on the initial oil content obtained. Thus we can say that if higher quantity of oil is obtained from the seed, cheaper would the cost be, further if the raw material is cheap the biodiesel produced would cost less.

1.1.2 Oil composition

Biodiesel is produced by transesterification process, which includes incorporation of methyl group to the already existing fatty acids in the oil, due to which the composition of oil has paramount significance. The fatty acids present in the edible and non-edible oils include oleic, linoleic, stearic and palmitic acids. These fatty acids can be present in different forms and composition depending on which the fuel properties of the biodiesel produced are ascertained. Majorly these fatty acids can be present in saturated and unsaturated forms.

The position of double bonds for the same fatty acid might also change the fuel properties of the biodiesel.

Many edible oils have optimum composition of fatty acids to produce biodiesel, but use of such edible oils is still not preferable for majorly two reasons, primarily these oils are not cheap. Secondly these oils contain nutrients which are healthy and essential for human diet. Considering soybean, the oil from soybean contains high protein content (35–40%) (Gui et al., 2008) which are vital for human health. One of the important fatty acid is linoleic acid, which is a polyunsaturated fatty acid and is a member of the essential fatty acid group called omega-6 fatty acids. This particular acid is known to lower the risk of cholesterol and heart disease which makes it imperative for consumption in diet. Considering palm oil, it contains a significant amount saturated fatty acids which are favorable for biodiesel production, but it is also a source polynutrients such as beta-carotene, alpha carotene, Vitamin-E, lycopene, tocotrienols and other carotenoids. These polynutrients should be innate to human diet as these act as antioxidants which makes the immune system of the body stronger, protects from various heart and eye diseases and can prevent various types of cancers.

To avoid the food and fuel conflict, various non-edible oils are considered for biodiesel production. Certain available options are namely jatropha, castor, *P. pinnata*, rubber seed and sea mango. These oils are majorly toxic to human consumption. Like Jatropha contains a toxin called curcin which is present in the seed, fruit and sap. Rubber seeds contain proteins those undergo an enzymatic reaction to produce prussic acid (HCN) which is lethal to consumption. Karanja oil is bitter and non-edible and is used as fish poison. Thus these oils provide a better alternative for biodiesel production than the edible oils.

1.1.3 Cultivation requirements

Another advantage that the nonedible crops offer is the minimum requirement for their growth and maintenance. Jatropha and karanja crops can be grown in a land that is infertile and not suitable for the plantation of edible crops. Also these lands after the plantation of the non-edible crops can improve the nitrogen content of the soil which would

facilitate the growth of other plants. These plants have a healthy life cycle for about 40-50 years, which assures of constant supply of raw material for our biodiesel production.

An additional advantage with *P. pinnata* is that, it is indigenous plant to subtropical environments and can sustain in the areas where the annual rainfall ranges from 500 to 2500mm (Gui et al., 2008). It is also one of the few trees those are nitrogen fixing trees (NFTS) and can produce oil in significant quantity. Since it improves the quality of soil in which it is planted it can be useful to turn highly saline and infertile lands to one that can be used for plantation. *P. pinnata* can also be planted as a decorative plant as has very beautiful flowers. The oil composition from the seed does not vary to much extent so the quality of raw material stays constant which helps in quality of biodiesel yield.

1.2. 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.

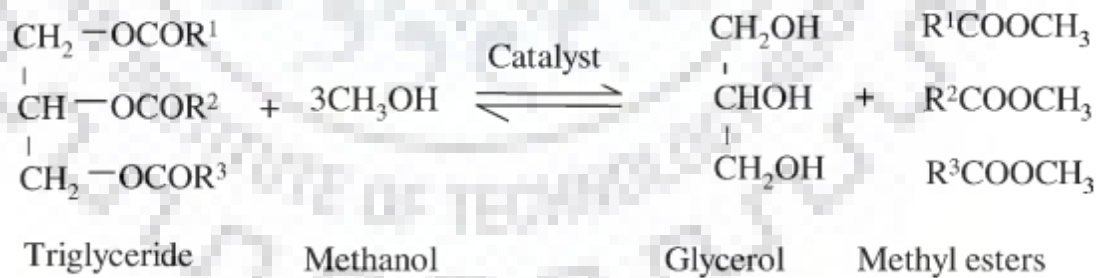
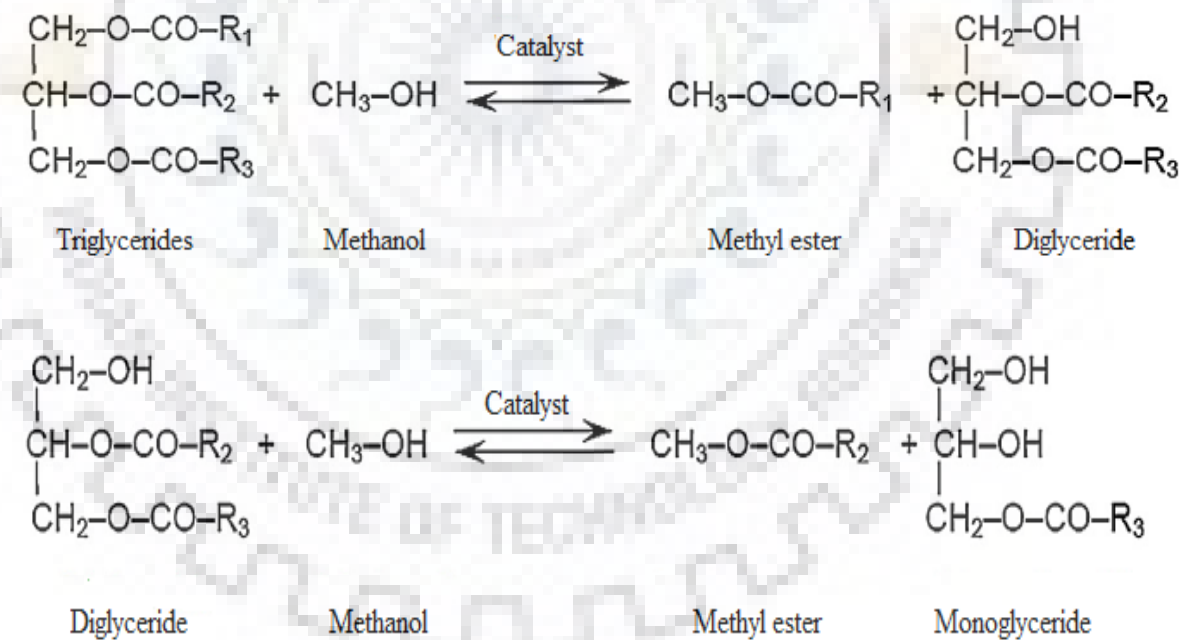


Figure 1.1. Transesterification of triglycerides.

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 most commonly used solvents in the transesterification process. Methanol is the smallest among the alcohols and is selected because of its easy availability and cheaper cost. Also it would fit easy with the huge molecules as compared to 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.



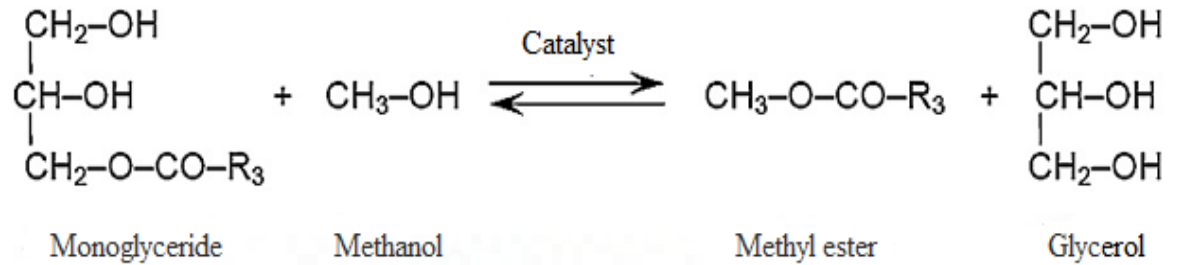


Figure 1.2. Transesterification reaction steps.

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. It is observed that to take the flux of the reaction in the forward direction presence of excess alcohol is necessary, and because methanol is present in excess the forward reaction becomes pseudo first order. It is a common observation that in presence of a alkaline catalyst the reaction becomes faster. (Freedman B, Butterfield RO, et al., 1986).

1.3 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.

1.3.1. 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
- CO₂ neutral (reduction of greenhouse gas emissions)

Table 1.1.

Comparison of the standards for diesel and biodiesel based on ASTM (Patil PD., Deng S, et., 2009)

Property	Diesel	Biodiesel
Standard 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

2.1 Karanja as a potential feedstock

The scientific name of Karanja tree is *Pongamia Pinnata*. This tree grows easily in subtropical environment and takes four to five years to mature. This tree is observed to sustain in all types of environment be it heat, salinity, drought and frost condition. One of important requirements for the growth of this tree is that it requires full overhead light in its early growth days but otherwise it can grow in less amount of sunlight, because of which it is also known as shade tree. Karanja pods are elliptical in shape and contain a single seed. Pods are 2–3 cm wide and 3–6 cm long and are thick walled. Karanja seeds are brown in color and 10–20 mm long in length. Karanja Seed has 27–39% of the oil (Patel and Sankhvara, 2017). This tree is native to Western Ghats, but a lot of trading is also observed in southern states of India such as Tamil nadu, Kerala, Karnataka and Andhra Pradesh

2.1.1 Homogeneous transesterification

Homogeneous catalysts are generally used for transesterification of vegetable oils for biodiesel production. There 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 triglyceride

2.1.2 Acid esterification

The acid value is the amount of the number of acidic functional groups present in the oil sample and is studied in terms of the quantity of potassium hydroxide required to neutralize the sample. The permissible acid value of the oil sample for alkaline transesterification has to be less than 2.0 mg KOH/g. However, other authors advocate it to be less than 4.0 mg KOH/g (Agarwal et al., 2012). The customary catalyst used during acid esterification of oil are sulphuric acid (H_2SO_4), HCl, H_3PO_4 and organic sulfonic acids. Nonetheless, the process has too many numerous shortcomings such as water is produced along with ester from the reaction of FFA with alcohol which restrains the transesterification of triglycerides, it also requires high reaction temperature and time, high oil to alcohol molar ratio, it has slower reaction rate and low catalyst activity. For waste cooking oil the acid employed is sulphuric acid (Talhaand and Sulaiman, 2016). But in this case, the conversion reported is low (82%) and the alcohol required for the reaction is high (200% excess of ethanol). Acid homogeneous transesterification is preferred only for high FFA vegetable oils.

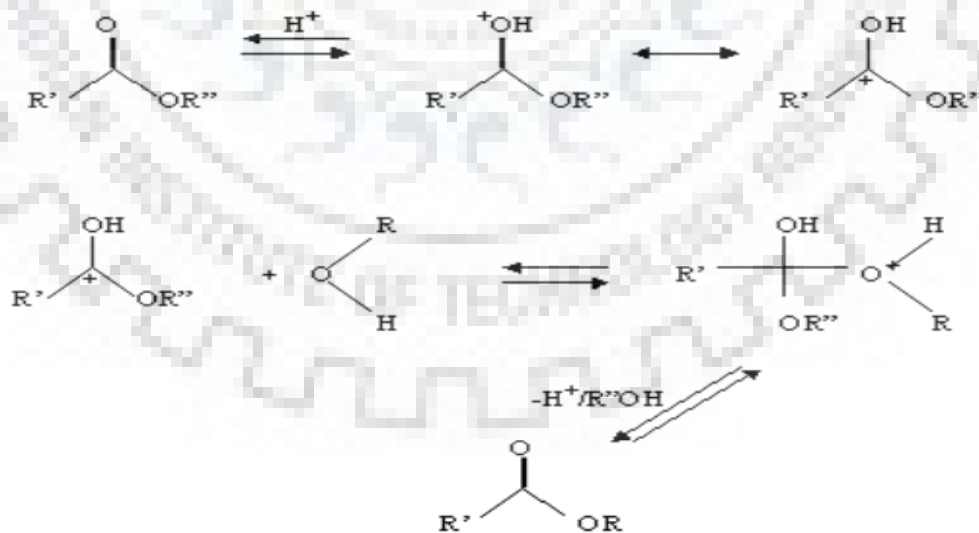


Fig 2.1 Mechanism of acid catalyzed esterification. (Gupta V and Gupta AK., 2004)

2.1.2 Alkaline esterification

Those oil samples whose FFA content is below 2.0%, alkaline transesterification is preferred over the acid catalyzed transesterification as the former is reported to proceed about 4000 (Chuah et al., 2016) times faster than the latter. The most common catalysts that are used during alkaline transesterification at lab level application includes the homogeneous catalysts sodium hydroxide, potassium hydroxide, etc. At industrial level production of biodiesel, the use of homogeneous catalyst such as sodium hydroxide and potassium hydroxide have been successful (Karmee SK. and Chadha A., 2005). This is a 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. The obtained products of transesterification reaction are biodiesel and glycerol, these would be subjected to removal of basic catalysts by washing with hot distilled water

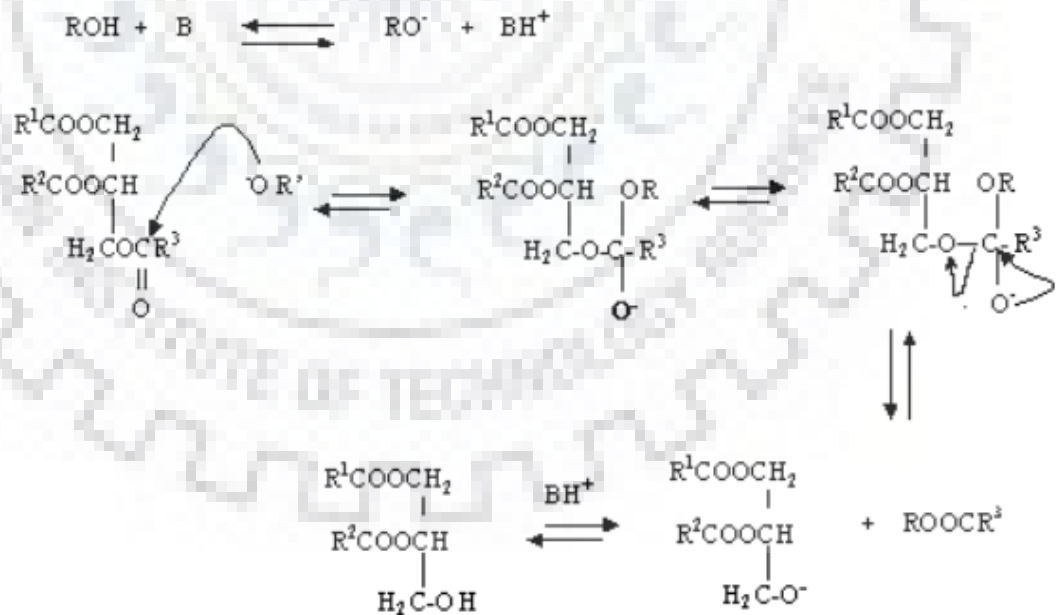


Fig 2.2 Mechanism of base catalyzed esterification. (Gupta V and Gupta AK. 2004)

Freedman B and Mounts T L (1894) 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% CH₃ONa catalyst. Authors also found that acid catalysed transesterification proceeded much slower rate as compared to alkali catalysed reaction.

Georgogianni K G et al., (2008) 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 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., (2006) 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., (2008) studied transesterification of high FFA Karanja oil. Authors carried out esterification of oil using 0.5% H₂SO₄ 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 (2008) achieved optimum yield of 89.5% at 1:8 molar ratio for acid esterification (0.5 % H₂SO₄) and 1:9 molar ratio for alkaline transesterification (0.5% NaOH/KOH) with mechanical stirring. Patil and Deng (2009) 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.

Kinetics of transesterification of soybean oil was investigated by Freedman et al., (1986). 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. As the use of alkaline catalysts gives higher yield and are more efficient than their acid counterparts they are more frequently used. (Gao L, Xu B, et al., 2008). But there are also problems associated with the use of homogeneous catalyst namely difficulty in the removal of the catalysts after the reaction, generation of huge quantity of wastewater and formation of emulsion. In this process, it is essential to utilize feedstock (vegetable oils or animal fats) having low free fatty acids content. With high amounts of free fatty acids the basic catalysts produces soap and water as unwanted by products. This water can hydrolyze the triglycerides to give diglycerides and more free fatty acids (Leung DYC, Wu X, et al., 2010). Homogeneous alkaline catalysts speedup the reaction at moderate temperatures (between 60° and 70° C) (Lopez DE, Goodwin Jr JG, et al., 2005) 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., (2010) 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., (2002) 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 CO₂ 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 (2010) studied the activity of Li ion on CaO. They prepared catalysts by impregnating Li₂CO₃ on CaO having highest surface area of 6.5 m²/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 (2011) 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., (2011) 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., (2011) prepared a new catalyst by impregnation of KOH on Nd₂O₃ and carried out transesterification of soybean oil and reported 92% yield after a reaction time of 1.5h for 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., (2013) investigated activity of modified CaO with bromo-octane and noted nearly 99.5% yield from soybean with oil to alcohol molar ratio of 1:15 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

Different solid catalysts and optimum reaction conditions used for heterogeneously catalyzed transesterification process.

Vegetable oil	Catalyst	Reaction conditions				Biodiesel FAME Yield (%)
		Oil to alcohol ratio	Catalyst amount (wt%)	Temperature (°C)	Reaction time (h)	
Soybean oil	SrO	1:12	3	65	30 min	95
Soybean oil	CaO	1:12	8	65	3	95
Soybean oil	KI/ mesoporous Silica	1:16	5	70	8	95
Soybean oil	Sr(NO ₃) ₂ / ZnO	1:12	5	70	5	94.7
Palm kernel oil	LiNO ₃ / γ - Al ₂ O ₃	1:65	10	60	3	93.4
Palm kernel oil	NaNO ₃ / γ - Al ₂ O ₃	1:65	10	60	3	95.1
Palm kernel oil	KNO ₃ / γ - Al ₂ O ₃	1:65	10	60	3	94.7
Palm kernel oil	Ca(NO ₃) ₂ / γ -Al ₂ O ₃	1:65	10	60	3	94.3
Jatropha curcas oil	CaO/Fe ₃ O ₄	1:15	2	70	80min	95
Jatropha curcas oil	CaMgO and CaZn	1:15	4	65	6	>80
Jatropha oil	Mg-Al hydrotalcite	1:4	1	45	1.5	95.2
Karanja	Li/CaO with Li ion	1:12	5	65	1	99

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

From the literature review it is certain that Karanja oil (*Pongamia pinnata*) has potential for acting as a feedstock for the production of biodiesel. Therefore, following objectives were considered:

- Identification of an appropriate non-edible oil feedstock for biodiesel production.
- To develop a solid base catalyst for heterogeneous transesterification.
- To study the properties of various heterogeneous catalysts via XRD (X-Ray Diffraction) and BET. To optimize the reaction parameters such as oil to methanol mole ratio, reaction temperature, and the reaction time to obtain higher FAME content.
- To optimize the reaction parameters for heterogeneous transesterification such as oil to methanol ratio, reaction temperature, and reaction time.
- To compare the performance of homogeneous and heterogeneous transesterification process.
- To compare between the obtained FAME content by various heterogeneous catalysts.
- To ascertain the fuel properties of the biodiesel obtained.
- To determine the reaction kinetic parameters

4.1 Materials

Karanja oil for experiments was purchased from Arian Enterprise, Shahadara, New Delhi. Potassium hydroxide (>85%), methanol (99.5%) and n-heptane (>99%) were purchased from Merck specialties, India. Methyl heptadecanoate used as internal standard, was obtained from Sigma Aldrich, India.

4.2. Homogeneous transesterification of Karanja oil

4.2.1 Esterification

Experiments were conducted in 100 ml three-necked round-bottomed reaction flask. It was equipped with reflux condenser, magnetic stirrer and thermometer, setup shown in Fig 4.1. Karanja oil contains 6- 20 wt% free fatty acids (Naika *et al.*, 2008). The methyl esters are produced by the reaction between the oil sample and methanol, in the presence of catalyst (KOH). The karanja oil is subjected to a two-step transesterification process. The first step is acid esterification wherein the oil sample was treated with 0.5% sulphuric acid and methanol at 65 °C for 1 h. This pretreatment is carried out to decrease the percentage of free fatty acids in the oil sample

4.2.2 Transesterification- base catalyzed reaction

The transesterification process was studied at catalyst loading (2% KOH wt/wt). Reactions were carried at reaction temperature of 65°C with various oil to methanol molar ratios such as 1:6, 1:8, 1:10, 1:12 and 1:15 for a reaction time of 2.5 hour. Catalyst (KOH) was dissolved into methanol before its addition into reaction flask. 100 ml of the oil along with calculated amount of catalyst and methanol were introduced into the reaction flask (Chitra *et al.*, 2005). After the pre-established temperature was reached, the mixture was rigorously stirred with the help of a magnetic stirrer. After the appropriate time, the mixture was carefully transferred to a separating funnel and allowed to stand there overnight (Meher *et al.*, 2006).



Fig 4.1 Experimental setup for esterification reaction

4.2.3 Purification

After settlement, there were two layers. The upper layer contains biodiesel (methyl esters) with some amount of methanol and traces of the catalyst. The lower layer contains glycerol along with excess methanol and residual catalyst. The bottom layer thrown out. The biodiesel layer was then washed thoroughly by with warm (70°C) distilled water for the purpose of removal of the impurities like methanol, unreacted oil and traces of catalyst.. This purified biodiesel was then analyzed by GC.

4.3. Heterogeneous transesterification of Karanja oil

Due to certain drawbacks of homogenous catalyst the focus has been shifted to heterogeneous catalysts. The advantages of heterogeneous catalysts are namely: these are tolerant to high fatty acid content, also the by products are produced in less quantities as compared to homogeneous catalysts, further these are reusable catalysts. As these are solid basic catalysts they are easily separable and require less purification steps. Thus heterogeneous transesterification is preferred.

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 $80^\circ C$ for 4 hours. After drying; catalyst was calcined at $650^\circ C$ for 3 h in muffle furnace. Loading ratio of K_2CO_3/MgO was taken as 0.6 (wt./wt.) for all the reactions (Liang X, Gao S, et al.,2009).

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- $K\alpha$ radiation source while 2θ kept between 10 and 80° .

BET surface area and pore size distribution of the sample were investigated by using Micrometics Accelerated Surface Area and Porosimetry (ASAP-2020). N_2 adsorption desorption isotherms were recorded at liquid nitrogen temperature ($-196^\circ C$). Prior to the experiment the same were degassed at $150^\circ C$ for 2 h under vacuum. Multipoint Brunauer-Emmet-Teller (BET) method was employed for the determination of surface area by using adsorption isotherm data at relative pressure (P/P_0) range of 0.05-0.3. Whereas the pore size distribution was determined by employing Barret-Joyner-Halenda (BJH) method using the desorption branch of the isotherm.

4.3.3. *Experimental procedures for transesterification*

The transesterification was carried out in 100 ml three-necked round-bottomed reaction flask equipped with reflux condenser, magnetic stirrer and thermometer. 25ml of karanja oil, calculated amount of methanol and catalyst were injected into reaction system. After the pre-established 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 centrifuged 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.



Fig 4.2 Biodiesel (fig left) upper layer biodiesel, lower layer glycerol, (right)After washing upper layer biodiesel and lower layer water.

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. 50 mg of purified biodiesel sample was diluted with 1 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 wax coated BPX70 capillary column for injecting the sample. Nitrogen was used as carrier gas. Oven temperature was increased 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.

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

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:

$$\text{Yield} = \frac{(\text{Mass of biodiesel produced/MW of biodiesel})}{(\text{mass of oil/ MW of oil}) \times 3} \times (\text{FAME content})$$

5.1 Homogeneous transesterification of Karanja Oil

5.1.1 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 (1:6, 1:8, 1:10, 1:12, 1:15) keeping other process parameters constant as following (reaction temperature 65°C, reaction time 2.5 h and 2 wt% catalysts loading). Reaction conditions and results obtained are shown in Table 4.1.

Table 5.1

Effect of molar ratio on homogeneous transesterification of Karanja oil (KO)

Sr. No	Reactants	Catalyst	Reaction conditions			Yield (%)
			Temperature (°C)	Reaction time (h)	Molar ratio	
1	KO, MeOH	2 wt% KOH	65	2.5	1:6	77.4
2	KO, MeOH	2 wt% KOH	65	2.5	1:8	82.5
3	KO, MeOH	2 wt% KOH	65	2.5	1:10	92.2
4	KO, MeOH	2 wt% KOH	65	2.5	1:12	89.7
5	KO, MeOH	2 wt% KOH	65	2.5	1:15	76.3

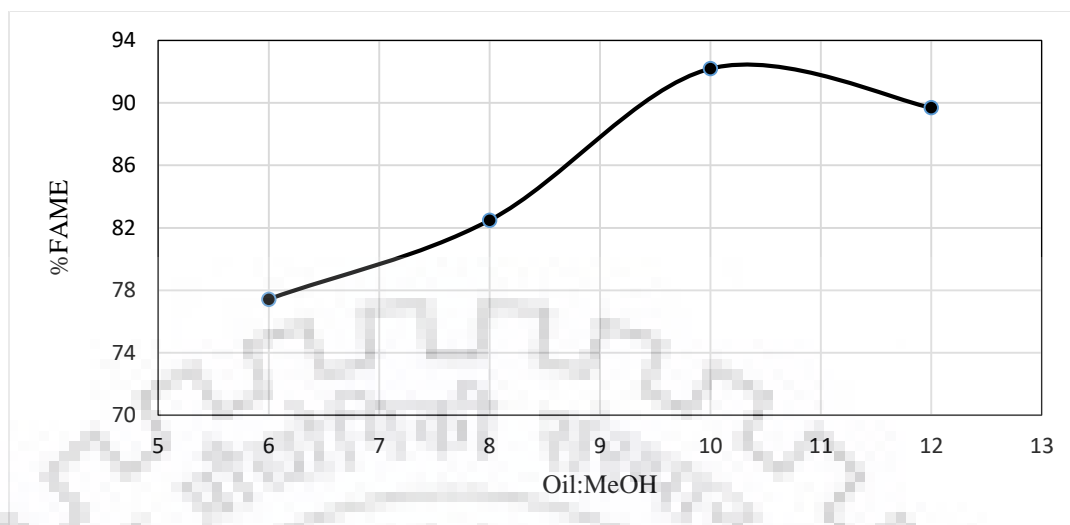


Fig 5.1 Effect of molar ratio of oil to methanol on FAME content

Figure 5.1, depicts the 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. Since transesterification reaction is reversible in nature, use of excess methanol moves the equilibrium towards the product side which results into higher yield of biodiesel. It has been also observed that increasing molar ratio beyond 1:10 leads to lower FAME yield because of diluting effect. It has been found that 1:10 molar ratio of oil to methanol showed the maximum yield of 92.2%.

5.2 Heterogeneous transesterification of Karanja Oil

Heterogeneous transesterification of karanja oil was carried using various solid base catalyst. Previous literature suggested that transesterification reaction requires basic environment. In this study, CaO, MgO were used as support material of the catalyst which is basic in nature. Potassium carbonate (K_2CO_3) and aluminum oxide (Al_2O_3) were used as metal oxides which was deposited on the supports (CaO, MgO). Further, different combination of support and catalyst such as K_2CO_3/CaO , K_2CO_3/MgO , Al_2O_3/CaO and Al_2O_3/MgO were synthesized and the one giving the best FAME percentage was chosen for further experiments. Various reaction parameters have been optimized such as reaction time, reaction temperature, amount of catalyst percentage, oil to methanol molar ratio and the type of catalyst.

5.2.1 Effect of reaction time

The effect of reaction time was studied on the transesterification of Karanja oil with methanol at temperature 68⁰C and at constant oil to methanol mole ratio (1:15). The experimental results are shown in table 5.2 and the change in the FAME yield with respect to change in time is plotted in graph 5.2. The reaction was carried out for 2.5, 3, 3.5, 4, 4.5 h out of which it was observed that the maximum FAME content is obtained when the reaction is carried out for 3.5 hours and the FAME content was 96.23%. The variation of FAME content was observed from 70.15% to 96.23%. After 3.5 hours increasing the reaction time does not increase the FAME yield in significant proportions.

Table 5.2

Effect of reaction time on heterogeneous transesterification of Karanja oil (KO) with catalyst K₂CO₃/MgO

Sl. No	Reactants	Catalyst	Reaction conditions			Yield (%)
			Tempertaure (°C) (±3)	Reaction time (h)	Molar ratio	
1	KO, MeOH	4 wt% K ₂ CO ₃ /MgO =0.6	68	2.5	1:15	70.1489
2	KO, MeOH	4 wt% K ₂ CO ₃ /MgO =0.6	68	3	1:15	89.1488
3	KO, MeOH	4 wt% K ₂ CO ₃ /MgO =0.6	68	3.5	1:15	96.2277
4	KO, MeOH	4 wt% K ₂ CO ₃ /MgO =0.6	68	4	1:15	95.1784
5	KO, MeOH	4 wt% K ₂ CO ₃ /MgO =0.6	68	4.5	1:15	94.0978

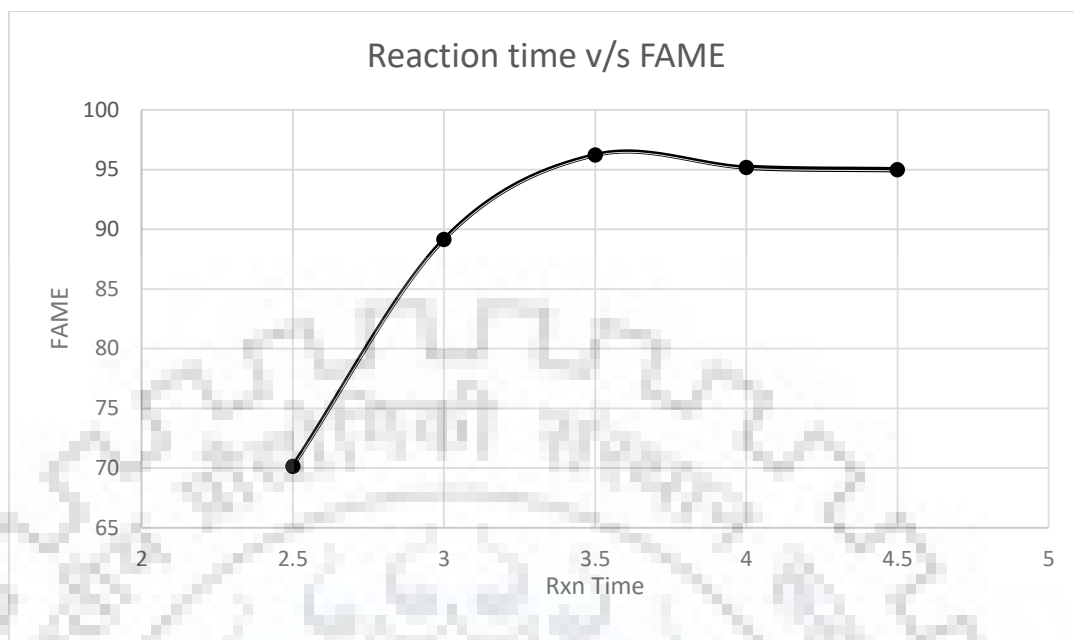


Fig 5.2 Effect of reaction time on FAME content (K_2CO_3/MgO)

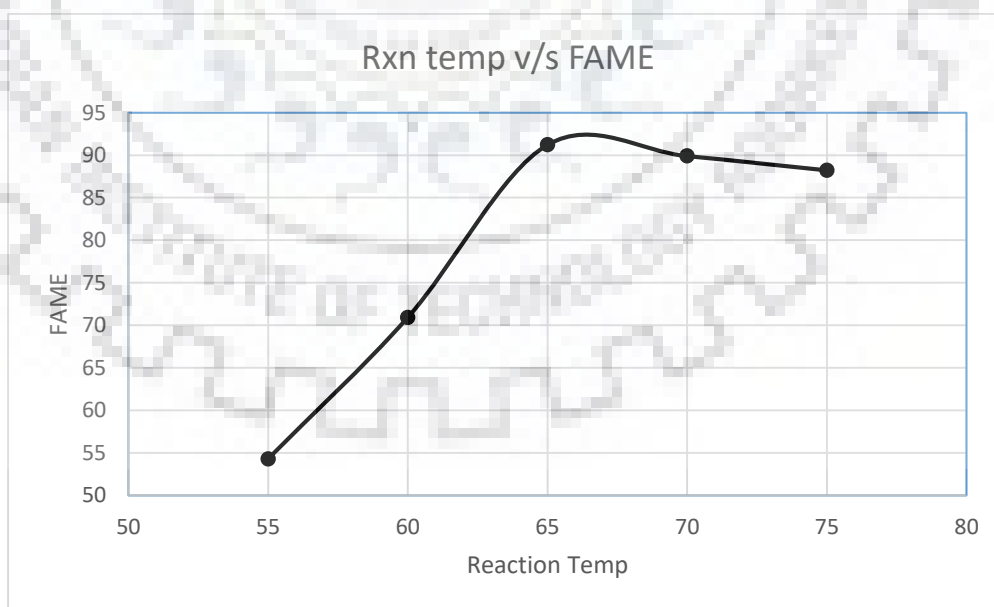
5.2.2 Effect of reaction temperature

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 3.5 h keeping constant oil to methanol molar ratio (1:15) and 4 wt% catalyst amount by changing reaction temperature (55, 60, 65, 70, and 75° C). Reaction conditions and results are shown in Table 5.3. When reaction temperature was increased from 55° to 65° C, biodiesel yield increased from 54.3 to 91.2%. Further when the reaction temperature was increased i.e. from 70 to 75, the FAME content decreased to 89.9% and 88.21%. This decrease was observed because of the fact that methanol has a low boiling of 65⁰C, thus increasing the temperature more than 65, methanol evaporates and is not available for reaction and thus the FAME content decreases.

Table 5.3

Effect of reaction temperature on heterogeneous transesterification of Karanja oil (KO) with catalyst K_2CO_3/MgO

SI .No	Reactants	Catalyst	Reaction conditions			Yield (%)
			Temperature ($^{\circ}C$) (± 3)	Reaction time (h)	Molar ratio	
1	KO, MeOH	4 wt% $K_2CO_3/MgO = 0.6$	55	3.5	1:15	54.28
2	KO, MeOH	4 wt% $K_2CO_3/MgO = 0.6$	60	3.5	1:15	70.95
3	KO, MeOH	4 wt% $K_2CO_3/MgO = 0.6$	65	3.5	1:15	91.20
4	KO, MeOH	4 wt% $K_2CO_3/MgO = 0.6$	70	3.5	1:15	89.88
5	KO, MeOH	4 wt% $K_2CO_3/MgO = 0.6$	75	3.5	1:15	88.21

**Fig 5.3** Effect of reaction temperature on FAME content (K_2CO_3/MgO)

5.2.3 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 (1:10, 1:15, 1:20, 1:25, 1:30) keeping other process parameters constant as following reaction temperature 68°C, reaction time 3.5 h and 4 wt% catalysts loading). Reaction conditions and results obtained are shown in Table 5.4.

Table 5.4

Effect of mole ratio of oil: methanol on heterogeneous transesterification of Karanja oil (KO) with catalyst K₂CO₃/MgO

SI .No	Reactants	Catalyst	Reaction conditions			Yield %
			Temperat ure (°C) (±3)	Reaction time (h)	Molar ratio	
1	KO, MeOH	4 wt% K ₂ CO ₃ /MgO =0.6	68	3.5	1:10	86.76
2	KO, MeOH	4 wt% K ₂ CO ₃ /MgO =0.6	68	3.5	1:15	97.15
3	KO, MeOH	4 wt% K ₂ CO ₃ /MgO =0.6	68	3.5	1:20	96.30
4	KO, MeOH	4 wt% K ₂ CO ₃ /MgO =0.6	68	3.5	1:25	92.75
5	KO, MeOH	4 wt% K ₂ CO ₃ /MgO =0.6	68	3.5	1:30	91.83

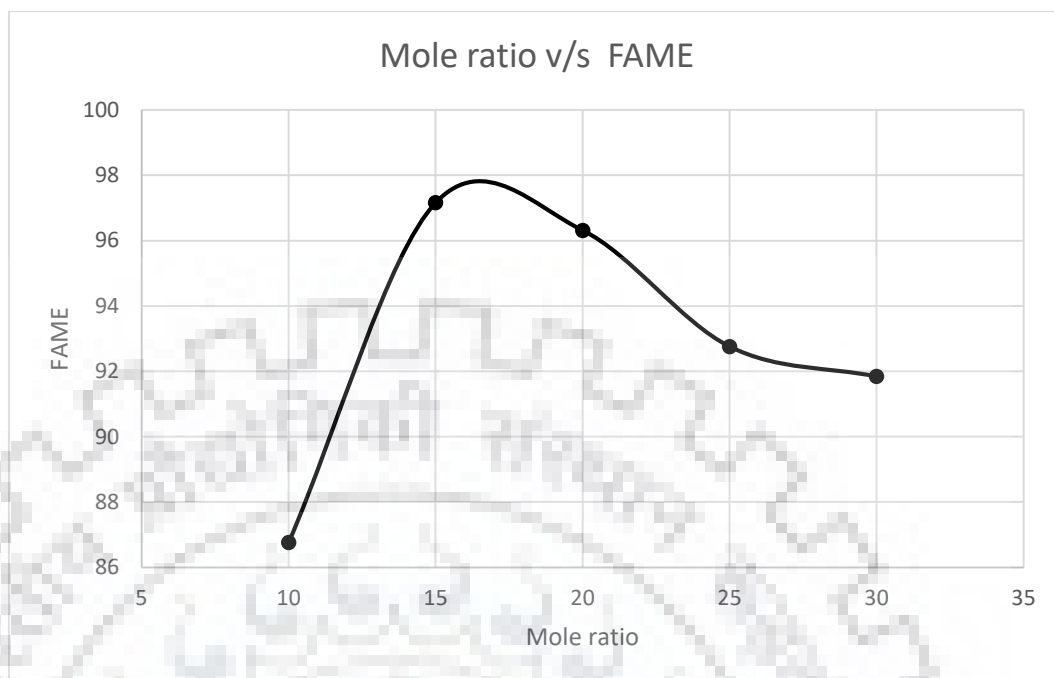


Fig 5.4 Effect of mole ratio on FAME content (K_2CO_3/MgO)

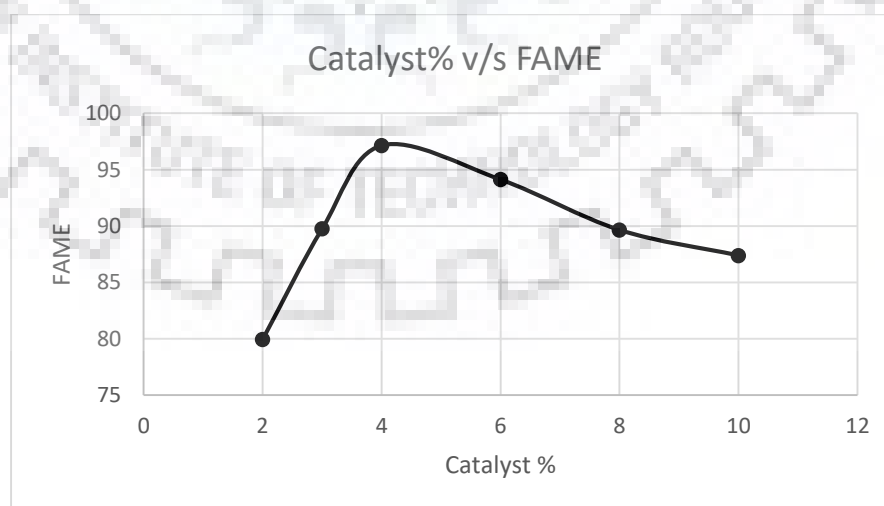
5.2.4 Effect of catalyst weight percentage

Effect of various catalyst weight percentage on FAME yield is shown in Figure 5.5. Various experiments were performed varying the catalyst percentage. The heterogeneous solid catalysts of a definite composition were used in various different weight percentage to study the effect of change on the FAME yield. The weight percent of catalyst was varied from 2 to 10 weight percent and the FAME yield varied from 79.95% to 97.15%. The maximum FAME yield was observed at 4 weight percentage of catalyst and that was 97.15%. Further it was observed that the catalyst weight percentage and the methanol molar ratio should be increased proportionately to increase the FAME yield, increasing only one of the two factors does not impact the FAME yield considerably. This occurs due to the fact that the solid catalyst has to react with methanol to form methoxide which is the actual catalyst that reacts with the fatty acids to form methyl esters. Thus to form methoxide in appropriate amount catalyst weight percentage and methanol ratio should be proportionate. The experimental results are shown in table 5.5 and the trend is plotted in fig 5.5.

Table 5.5

Effect of catalyst weight percentage (K_2CO_3/MgO) on heterogeneous transesterification of Karanja oil (KO)

SI .N o	Reactants	Catalyst	Reaction conditions			Yield %
			Temperatu re ($^{\circ}C$) (± 3)	Reaction time (h)	Molar ratio	
1	KO, MeOH	2 wt% $K_2CO_3/MgO = 0.6$	68	3.5	1:15	79.96
2	KO, MeOH	3 wt% $K_2CO_3/MgO = 0.6$	68	3.5	1:15	89.77
3	KO, MeOH	4 wt% $K_2CO_3/MgO = 0.6$	68	3.5	1:15	97.16
4	KO, MeOH	6 wt% $K_2CO_3/MgO = 0.6$	68	3.5	1:15	94.13
5	KO, MeOH	8 wt% $K_2CO_3/MgO = 0.6$	68	3.5	1:15	89.66
6	KO, MeOH	10 wt% $K_2CO_3/MgO = 0.6$	68	3.5	1:15	87.40

**Fig 5.5** Effect of catalyst(K_2CO_3/MgO) weight percentage on FAME content

5.2.5 Effect of support

Primarily two supports were experimented upon calcium oxide (CaO) and magnesium oxide (MgO). Upon this two supports potassium carbonate and aluminum oxide were doped. Each support was considered with both catalysts and thus there were a total of four catalysts to be worked on. The effect of molar ratio of oil: methanol and catalyst weight percentage was studied on each of the catalyst.

5.2.5.1 Effect of oil: methanol molar ratio for K_2CO_3/CaO

Effect of molar ratio of oil to methanol was investigated. Reactions were carried out with different oil to methanol molar ratio (1:10, 1:15, 1:20, 1:25, 1:30) keeping other process parameters constant as following (reaction temperature 68°C, reaction time 3.5 h and 4 wt% catalysts loading). Reaction conditions and results obtained are shown in Table 5.6.

Table 5.6

Effect of mole ratio of oil: methanol on heterogeneous transesterification of Karanja oil (KO) with catalayst K_2CO_3/CaO .

SI .No	Reactants	Catalyst	Reaction conditions			Yield %
			Temperature (°C) (± 3)	Reaction time (h)	Molar ratio	
1	KO, MeOH	4 wt% $K_2CO_3/CaO = 0.6$	68	3.5	1:10	63.16
2	KO, MeOH	4 wt% $K_2CO_3/CaO = 0.6$	68	3.5	1:15	92.99
3	KO, MeOH	4 wt% $K_2CO_3/CaO = 0.6$	68	3.5	1:20	85.24
4	KO, MeOH	4 wt% $K_2CO_3/CaO = 0.6$	68	3.5	1:25	75.88
5	KO, MeOH	4 wt% $K_2CO_3/CaO = 0.6$	68	3.5	1:30	74.39

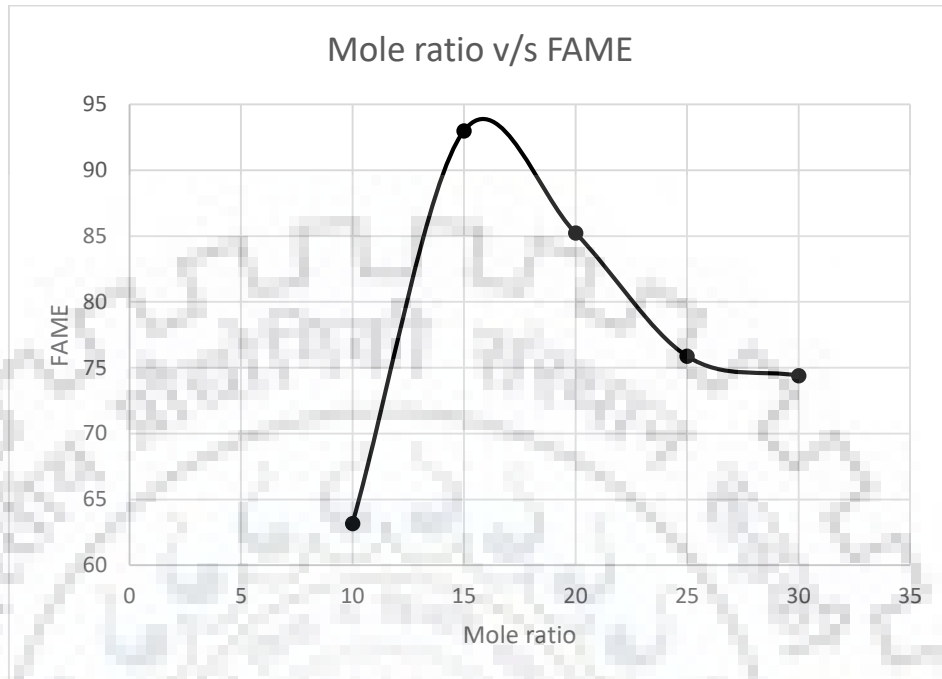


Fig 5.6 Effect of mole ratio on FAME content (K_2CO_3/CaO)

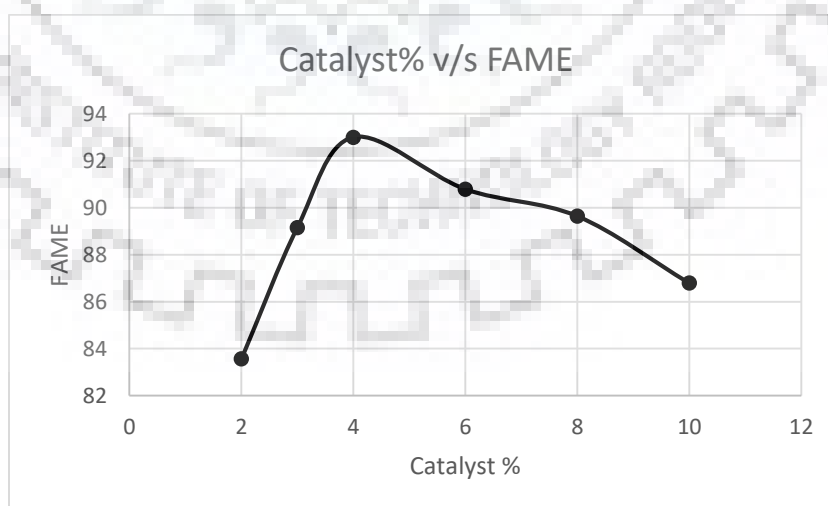
5.2.5.2 Effect of change in catalyst weight percentage for K_2CO_3/CaO

The weight percent of catalyst was varied from 2 to 10 weight percent and the FAME yield varied from 83.56% to 93%. The maximum FAME yield was observed at 4 weight percentage of catalyst and that was 93%. The experimental results are shown in table 5.7 and the trend is plotted in fig 5.7.

Table 5.7

Effect of catalyst weight percentage (K_2CO_3/CaO) on heterogeneous transesterification of Karanja oil (KO)

SI .N o	Reactants	Catalyst	Reaction conditions			Yield %
			Tempertaur e ($^{\circ}C$) (± 3)	Reaction time (h)	Molar ratio	
1	KO, MeOH	2 wt% $K_2CO_3/CaO = 0.6$	68	3.5	1:15	83.56
2	KO, MeOH	3 wt% $K_2CO_3/CaO = 0.6$	68	3.5	1:15	89.15
3	KO, MeOH	4 wt% $K_2CO_3/CaO = 0.6$	68	3.5	1:15	92.99
4	KO, MeOH	6 wt% $K_2CO_3/CaO = 0.6$	68	3.5	1:15	90.78
5	KO, MeOH	8 wt% $K_2CO_3/CaO = 0.6$	68	3.5	1:15	89.63
6	KO, MeOH	10 wt% $K_2CO_3/CaO = 0.6$	68	3.5	1:15	86.79

**Fig 5.7** Effect of catalyst (K_2CO_3/CaO) weight percentage on FAME content

5.2.5.3 Effect of oil: methanol molar ratio for Al_2O_3/CaO

Effect of molar ratio of oil to methanol was investigated. Reactions were carried out with different oil to methanol molar ratio (1:10, 1:15, 1:20, 1:25, 1:30) keeping other process parameters constant as following (reaction temperature 68°C, reaction time 3.5 h and 4 wt% catalysts loading). Reaction conditions and results obtained are shown in Table 5.8. The maximum FAME content obtained was 93%. The experimental results were plotted to study the variation of oil: methanol molar ratio to FAME content and are shown in Fig 5.8.

Table 5.8

Effect of mole ratio of oil: methanol on heterogeneous transesterification of Karanja oil (KO)with catalyst Al_2O_3/CaO .

SI No	Reactants	Catalyst	Reaction conditions			Yield (%)
			Temperature (°C) (±3)	Reaction time (h)	Molar ratio	
1	KO, MeOH	4 wt% $Al_2O_3/CaO.=0.6$	68	3.5	1:10	63.17
2	KO, MeOH	4 wt% $Al_2O_3/CaO.=0.6$	68	3.5	1:15	92.99
3	KO, MeOH	4 wt% $Al_2O_3/CaO.=0.6$	68	3.5	1:20	85.23
4	KO, MeOH	4 wt% $Al_2O_3/CaO.=0.6$	68	3.5	1:25	75.87
5	KO, MeOH	4 wt% $Al_2O_3/CaO.=0.6$	68	3.5	1:30	74.39

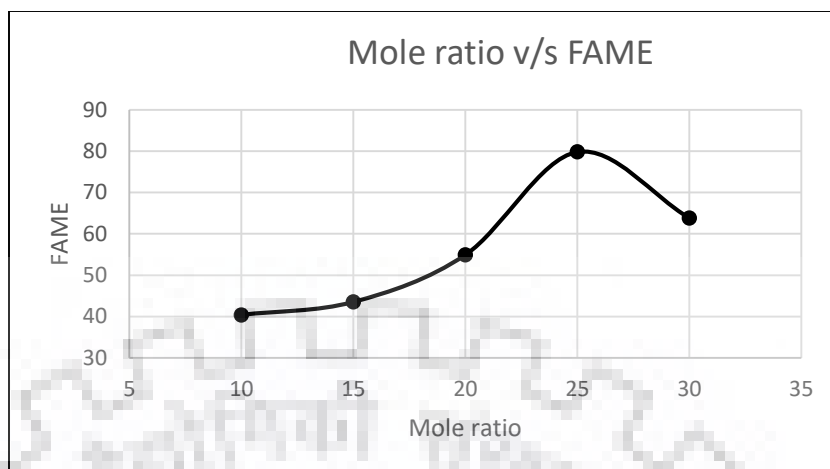


Fig 5.8 Effect of mole ratio on FAME content ($\text{Al}_2\text{O}_3/\text{CaO}$.)

Table 5.9

Effect of catalyst weight percentage ($\text{Al}_2\text{O}_3/\text{CaO}$.) on heterogeneous transesterification of Karanja oil (KO).

S.No	Reactants	Catalyst	Reaction conditions			Yield %
			Temperature ($^{\circ}\text{C}$) (± 3)	Reaction time (h)	Molar ratio	
1	KO, MeOH	2 wt% $\text{Al}_2\text{O}_3/\text{CaO}.$ =0.6	68	3.5	1:15	38.96
3	KO, MeOH	4 wt% $\text{Al}_2\text{O}_3/\text{CaO}.$ =0.6	68	3.5	1:15	43.49
4	KO, MeOH	6 wt% $\text{Al}_2\text{O}_3/\text{CaO}.$ =0.6	68	3.5	1:15	68.57
5	KO, MeOH	8 wt% $\text{Al}_2\text{O}_3/\text{CaO}.$ =0.6	68	3.5	1:15	65.78
6	KO, MeOH	10 wt% $\text{Al}_2\text{O}_3/\text{CaO}.$ =0.6	68	3.5	1:15	52.21

5.2.5.4 Effect of change in catalyst weight percentage for Al_2O_3/CaO

The weight percent of catalyst was varied from 2 to 10 weight percent and the FAME yield varied from 83.56% to 93%. The maximum FAME yield was observed at 4 weight percentage of catalyst and that was 93%. The experimental results are shown in table 5.9 and the trend is plotted in fig 5.9.

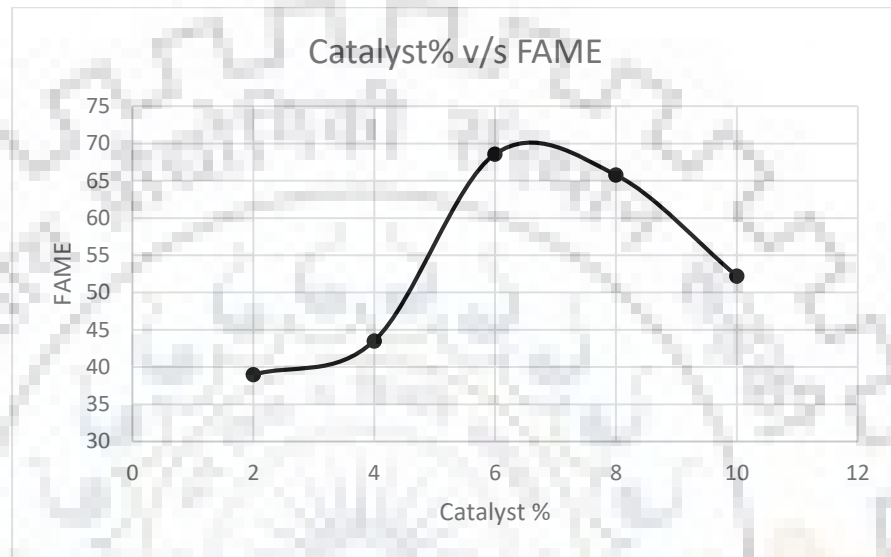


Fig 5.9 Effect of catalyst (Al_2O_3/CaO .) weight percentage on FAME content

5.2.5.5 Effect of change in catalyst weight percentage for Al_2O_3/MgO

The weight percent of catalyst was varied from 2 to 10 weight percent and the FAME yield varied from 83.56% to 93%. The maximum FAME yield was observed at 4 weight percentage of catalyst and that was 93%. The experimental results are shown in table 5.10 and the trend is plotted in fig 5.10.

Table 5.10

Effect of catalyst ($\text{Al}_2\text{O}_3/\text{MgO}$) weight percentage on heterogeneous transesterification of Karanja oil (KO)

SI No	Reactants	Catalyst	Reaction conditions			Yield %
			Temperature ($^{\circ}\text{C}$) (± 3)	Reaction time (h)	Molar ratio	
1	KO, MeOH	2 wt% $\text{Al}_2\text{O}_3/\text{MgO} = 0.6$	68	3.5	1:15	79.9547
2	KO, MeOH	3 wt% $\text{Al}_2\text{O}_3/\text{MgO} = 0.6$	68	3.5	1:15	89.7714
3	KO, MeOH	4 wt% $\text{Al}_2\text{O}_3/\text{MgO} = 0.6$	68	3.5	1:15	97.1575
4	KO, MeOH	6 wt% $\text{Al}_2\text{O}_3/\text{MgO} = 0.6$	68	3.5	1:15	94.1278
5	KO, MeOH	8 wt% $\text{Al}_2\text{O}_3/\text{MgO} = 0.6$	68	3.5	1:15	89.6574
6	KO, MeOH	10 wt% $\text{Al}_2\text{O}_3/\text{MgO} = 0.6$	68	3.5	1:15	87.3971

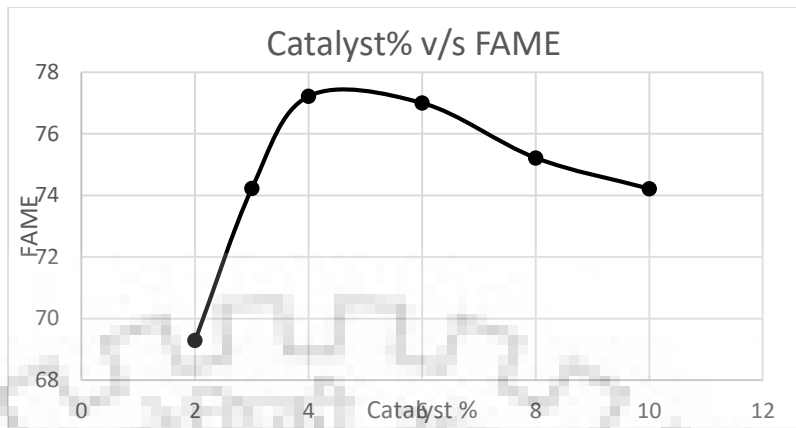


Fig 5.10 Effect of catalyst ($\text{Al}_2\text{O}_3/\text{MgO}$) weight percentage on FAME content

5.2.5.6 Effect of oil: methanol molar ratio for $\text{Al}_2\text{O}_3/\text{MgO}$

Effect of molar ratio of oil to methanol was investigated. Reactions were carried out with different oil to methanol molar ratio (1:10, 1:15, 1:20, 1:25, 1:30) keeping other process parameters constant as following (reaction temperature 68°C , reaction time 3.5 h and 4 wt% catalysts loading.. The experimental results were plotted to study the variation of oil: methanol molar ratio to FAME content and are shown in Fig 5.11.

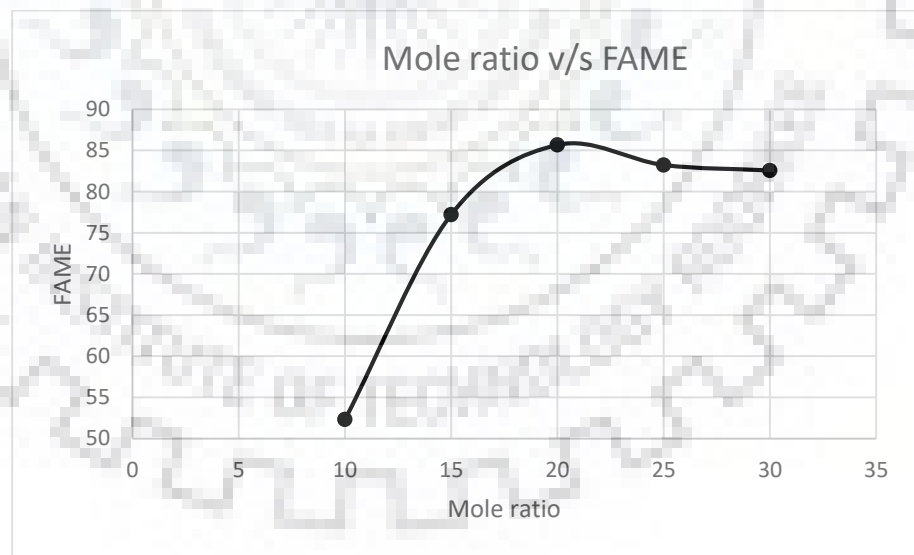


Fig 5.11 Effect of mole ratio on FAME content with catalyst ($\text{Al}_2\text{O}_3/\text{MgO}$)

Table 5.11

Effect of mole ratio of oil: methanol on heterogeneous transesterification of Karanja oil (KO) with catalyst Al₂O₃/MgO

SI No	Reactants	Catalyst	Reaction conditions			Yield (%)
			Temperature (°C) (±3)	Reaction time (h)	Molar ratio	
1	KO, MeOH	4 wt% Al ₂ O ₃ /MgO =0.6	68	3.5	1:10	52.3217
3	KO, MeOH	4 wt% Al ₂ O ₃ /MgO =0.6	68	3.5	1:15	77.2174
4	KO, MeOH	4 wt% Al ₂ O ₃ /MgO =0.6	68	3.5	1:20	85.6589
5	KO, MeOH	4 wt% Al ₂ O ₃ /MgO =0.6	68	3.5	1:25	83.2199
6	KO, MeOH	4 wt% Al ₂ O ₃ /MgO =0.6	68	3.5	1:30	82.5577

5.3 Kinetics of transesterification reaction



The transesterification reaction is a pseudo-first order reaction. It is considered so because one of the two reactants (methanol) is in excess as compared to the other one (oil), thus the rate of reaction depends on the rate of consumption of oil. Thus, we can write it as

$$-\frac{dC_a}{dt} = kC_a$$

C_a : Concentration of reactant A (mol/L)

k : Rate constant (h^{-1})

The negative sign in the equation describes the consumption of the reactant A.

Integrating equation on both sides

$$-\int_{C_{a0}}^{C_a} \frac{dC_a}{C_a} = \int_0^t k dt$$

$$-\ln \frac{C_a}{C_{a0}} = kt$$

The final equation was plotted and the variation of the reaction time with respect to logarithmic ratio of final to initial concentration of the reactant was studied. The slope of curve would give the rate constant value for that particular reaction conditions. The experimental data is tabulated in Table 5.12 and the trend is plotted in Fig 5.12.

Table 5.12

Change in reaction time w.r.t change in logarithmic ratio of final to initial reactant with different oil: methanol molar ratio.

SI .No	Reaction time (h)	ln(Ca/Cao) (1:15)	ln(Ca/Cao) (1:20)	Ca(1:15)	Ca(1:20)	Ca0
1	2.5	0.96	0.82	9.5	11	25
2	3.0	1.27	0.96	7.0	9.5	25
3	3.5	1.71	1.13	4.5	8	25
4	4.0	1.71	1.27	4.5	7	25
5	4.5	1.83	1.27	4	7	25

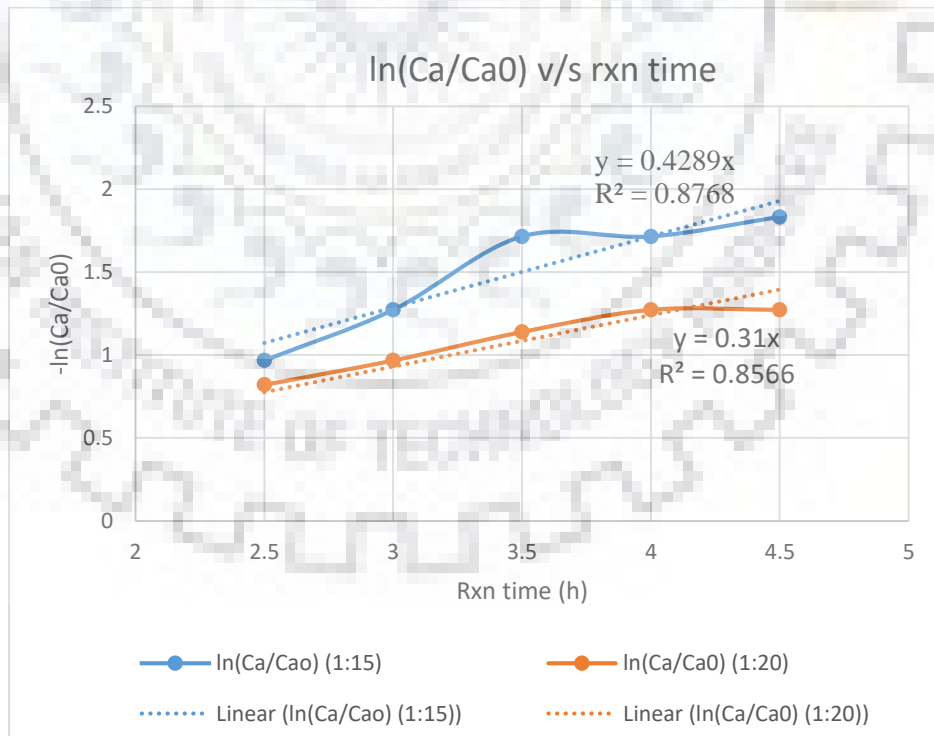


Fig 5.12 Change in reaction time w.r.t change in logarithmic ratio of final to initial reactant

5.3.1 Effect of catalyst weight percentage on rate constant of the reaction

For a particular catalyst amount, experiment for different reaction times were performed. It was seen that by increasing the reaction to the optimum the amount of biodiesel produced increased. All such variations for different catalyst amounts were plotted in Fig 5.13. The slopes of the curve would give the value of rate constant. Further in Fig 5.14 the catalyst weight

Table 5.13

Change in reaction time w.r.t change in logarithmic ratio of final to initial reactant with different catalyst weight percentage

S I . N o	Rx n t i m e	$\ln(\text{Ca}/\text{Cao})$ (2)	$\ln(\text{Ca}/\text{Cao})$ (4)	$\ln(\text{Ca}/\text{Cao})$ (6)	$\ln(\text{Ca}/\text{Cao})$ (8)	$\ln(\text{Ca}/\text{Cao})$ (10)	Ca (2)	Ca (4)	Ca (6)	Ca (8)	Ca (10)	Ca 0
1	2.5	0.51	0.61	0.96	1.51	1.34	15	13.5	9.5	5.5	6.5	25
2	3.0	0.56	0.77	1.20	1.71	1.60	14.25	11.5	7.5	4.5	5	25
3	3.5	0.65	0.91	1.27	1.83	1.77	13	10	7	4	4.25	25
4	4.0	0.73	1.02	1.51	2.30	1.96	12	9	5.5	2.5	3.5	25
5	4.5	0.69	1.02	1.60	2.52	2.12	12.5	9	5	2	3	25

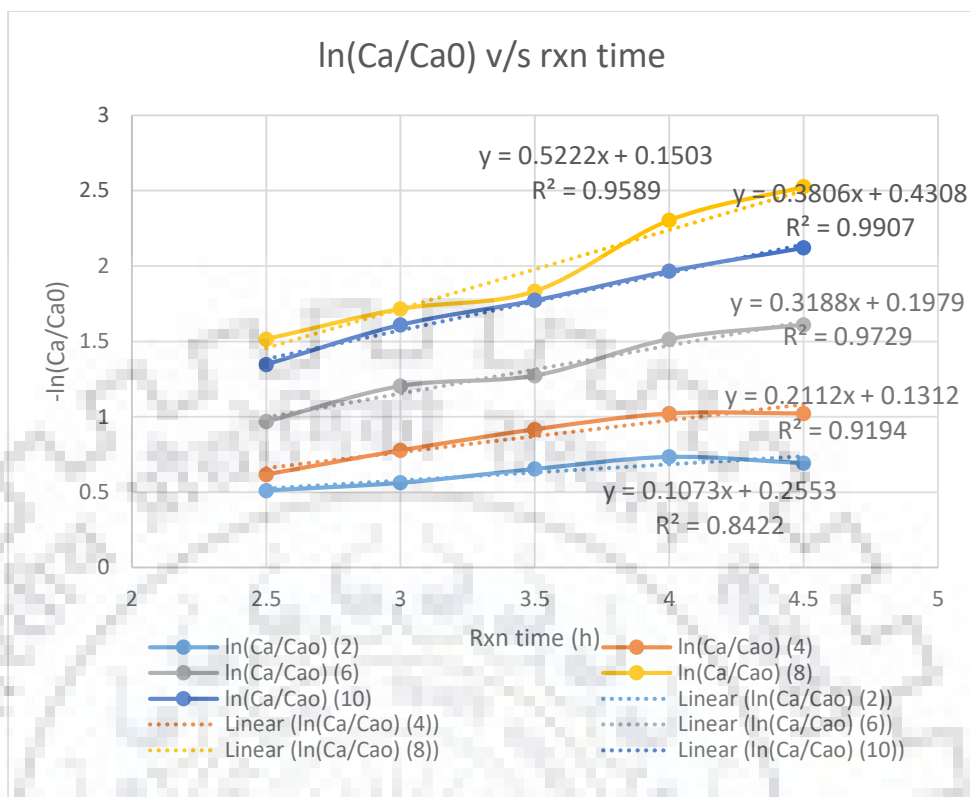


Fig 5.13 Effect of mole ratio on FAME content

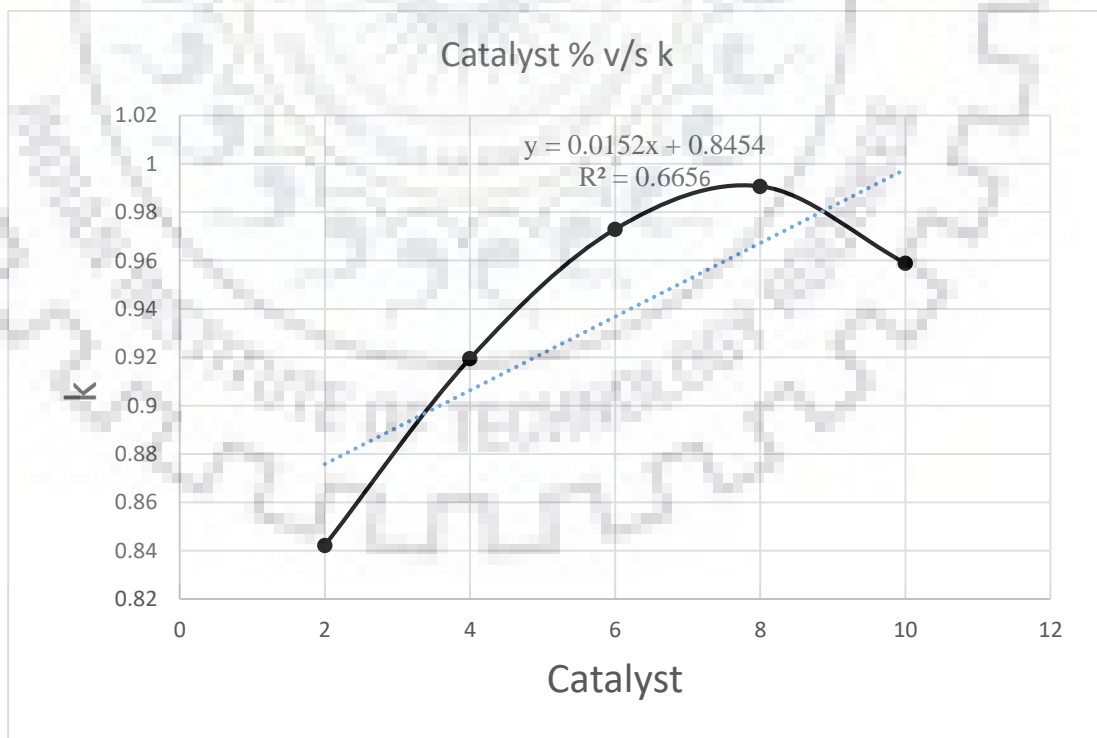


Fig 5.14 Effect of catalyst weight percentage on rate constant

5.4 BET results

The BET analysis thus shows that K_2CO_3/MgO has the highest surface area among all the catalysts i.e $37.88 \text{ m}^2/\text{g}$ and highest pore volume $0.111849 \text{ cm}^3/\text{g}$, these results are in sync with the fact that this same catalyst gives us the highest FAME content. Thus we can say that it is the morphology of the catalyst, the higher surface area and pore volume which are responsible for higher FAME content.

Table 5.14

BET analysis

SI .No	Catalyst	Surface area(m^2/g)	Pore volume (cm^3/g)	Pore size (\AA)
1	K_2CO_3/CaO	0.18	0.00035	76.11
2	K_2CO_3/MgO	37.88	0.12	118.11
3	Al_2O_3/CaO	11.47	0.07	256.06
4	P/TiO_2	7.81	0.03	154.20

It is also seen that the pore size of Al_2O_3/CaO is higher than that of K_2CO_3/MgO , but since the total surface area available in the later is higher the FAME content differs considerably.

5.4 XRD results

XRD patterns of K_2CO_3/CaO , Al_2O_3/CaO , K_2CO_3/MgO , Al_2O_3/MgO catalysts were recorded by scanning diffractions of $Cu-K\alpha$ radiation source and depicted in Figure 5.15 and Figure 5.16.

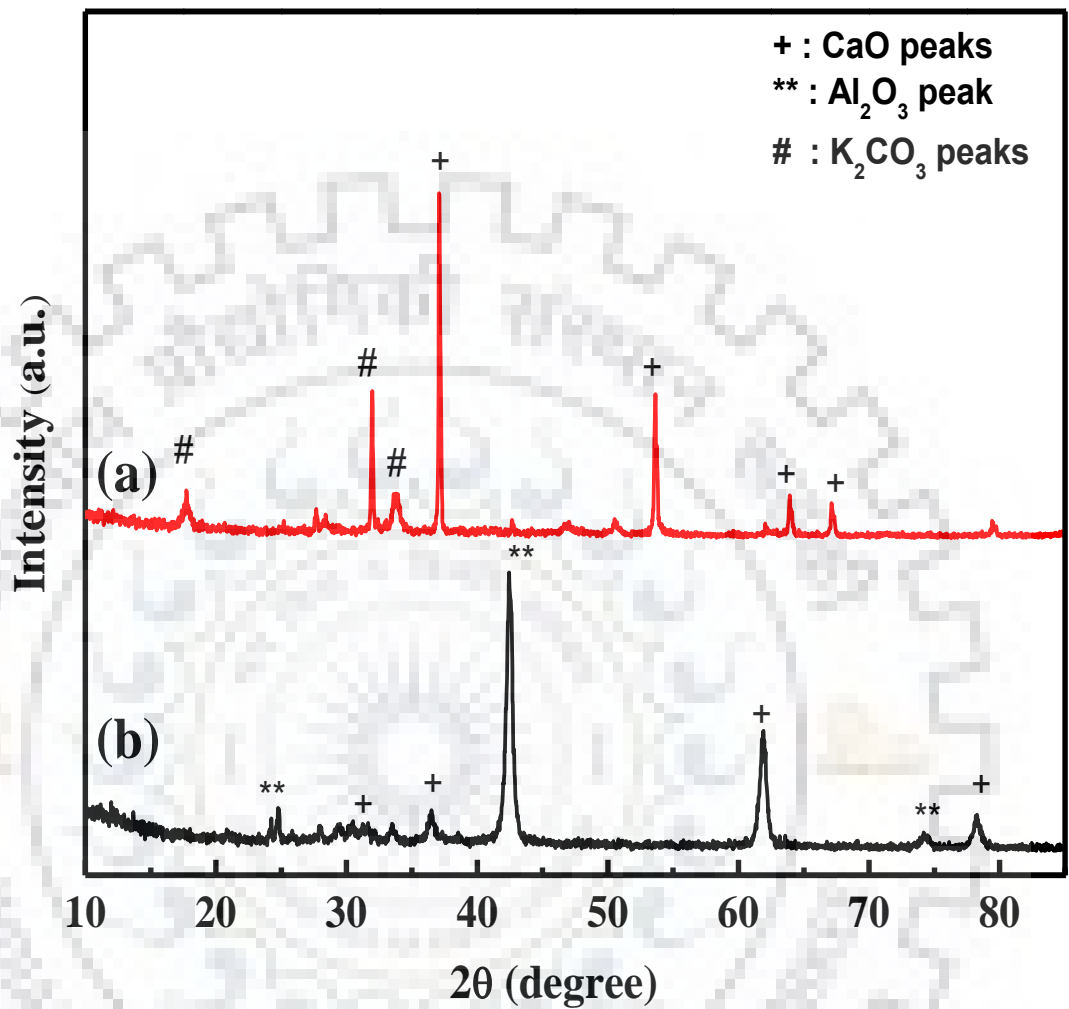


Fig 5.15 XRD patterns of (a) K₂CO₃/CaO (b) Al₂O₃/CaO

- (a) K₂CO₃/CaO: Major peak of K₂CO₃ is obtained 33.21° , minor peaks are obtained at 17.95° and 34° . CaO major peaks are obtained at 37° and 57° , minor peaks are obtained at 64° and 67°
- (b) Al₂O₃/CaO: Major peak of Al₂O₃ is obtained 42.61° , minor peak is obtained at 25.74° . CaO major peak is obtained at 62° , minor peaks are obtained at 32° , 36.5° and 78°

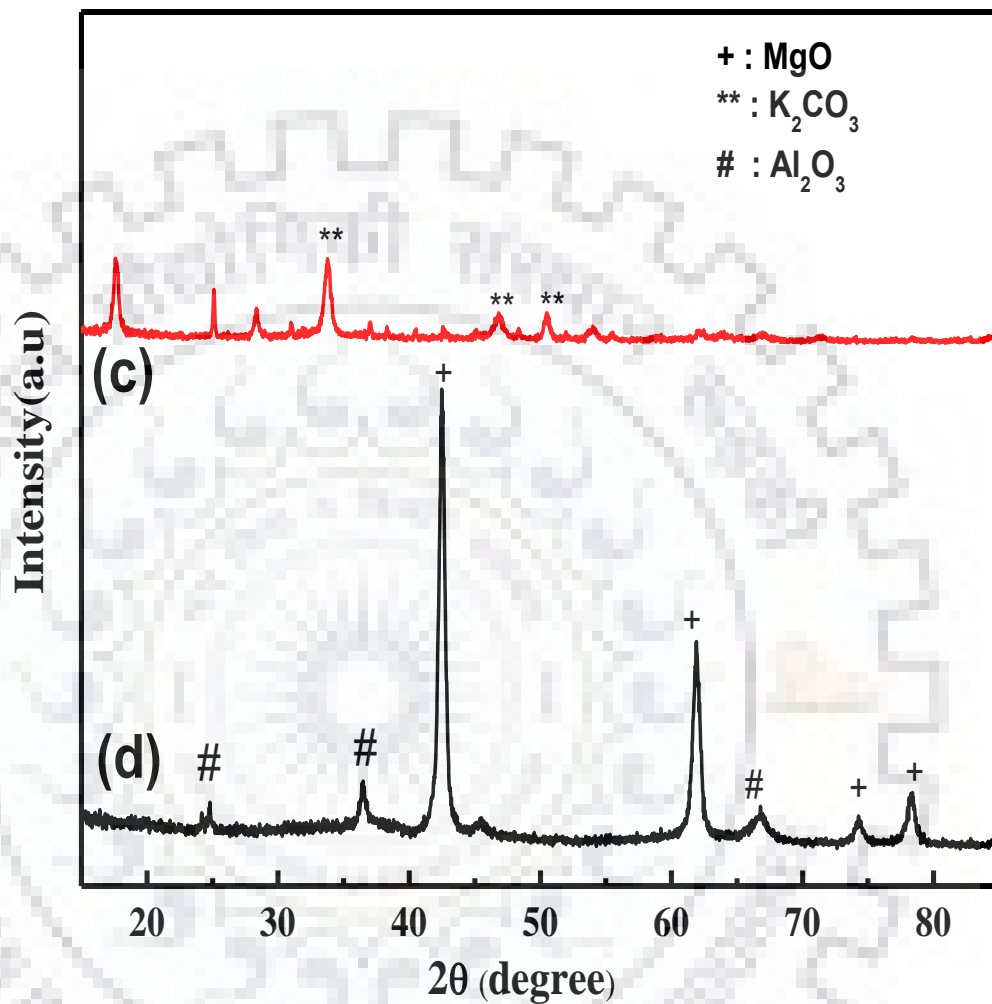


Fig 5.16 XRD patterns of (c) K_2CO_3/MgO (d) Al_2O_3/MgO

- (a) K_2CO_3/MgO :. Minor peaks are obtained at 34° , 47° and 50° . MgO major peaks are obtained at 37° and 57° , minor peaks are obtained at 64° and 67°
- (b) Al_2O_3/MgO : Minor peaks of Al_2O_3 are obtained at 25° , 37° and 66° . MgO major peaks are obtained at 42.4° and 66° , minor peaks are obtained at 74° and 78°

5.5 Fuel properties of biodiesel

Different fuel properties of biodiesel have determined by standard methods available. The resultant data is tabulated in table 5.15. It is observed that all the catalysts have produced biodiesel that has properties under the set limits by the standard methods.

Table 5.15

Fuel properties of biodiesel by various catalysts

SI .N o	Properties	Ho mog eneo us catal yst	Heterogeneous catalyst				Biodies el std (ASTM D 6751)	Test method s
			K/Cao	A/CaO	K/MgO	A/MgO		
1	Density (kg/m ³)	830	875	820	850	844	820-900	ASTM D 4052
2	Flash point (°C)	160	150	149	165	130	100-170	ASTM D 93
3	Cloud point (°C)	8	10	6	7	9.5	-3 to 12	ASTM D 97
4	Pour point (°C)	5	9	8	4	12	-15 to 16	ASTM D 2500

The dissertation work focused on production of biodiesel from non-edible karanja oil. The obtained oil contained high amount free fatty acids. High amount of free fatty acids are a hindrance to production of biodiesel and also increase the production of by products such as soap. Thus, it was necessary to pretreat the oil to produce optimum amount of biodiesel.

Two step esterification process was carried out for the production of biodiesel. Initially the oil was pretreated with 0.5% H_2SO_4 (acid esterification) and further treated with a basic catalyst for production of methyl esters. Majorly two types of alkaline esterification were carried out namely homogeneous and heterogeneous esterification. Homogeneous esterification comprised of basic oxide (KOH). FAME content obtained through this process was 92.2%. Although this process gave high FAME content but has many disadvantages like poor recovery of catalyst, huge effluent generation, higher number of purification steps. Thus heterogeneous catalysts were synthesized.

Different heterogeneous catalysts such as K_2CO_3/MgO , K_2CO_3/CaO , Al_2O_3/MgO , and Al_2O_3/CaO were prepared and the reactions conditions i.e. oil to methanol ratio, reaction time, reaction temperature, catalyst weight percentage were optimized for higher fatty acid methyl esters (FAME) content. The maximum FAME content of 97.16% was obtained in presence of K_2CO_3/MgO catalyst (4wt.%) at the oil to methanol mole ratio of 1:15. The biggest advantage of heterogeneous catalyst was that they could be recycled. These gave a FAME content above 90% for upto 6 cycles. Fig 5.17 shows the catalyst performance of all the heterogeneous catalysts used at oil to methanol mole ratio 1:15, catalyst weight percentage 4% .

The physico-chemical properties of the heterogeneous catalysts were characterized by specific surface area (BET) and X-ray diffraction study. Kinetic experiments were conducted to determine the reaction order and activation energy for the formation of biodiesel following Levenspiel method. Kinetic results suggested pseudo-first order

reaction. The variation of reaction rate constant with catalyst weight percentage were also determined it showed linear variation up to 8wt.% of the catalyst used for the reaction.

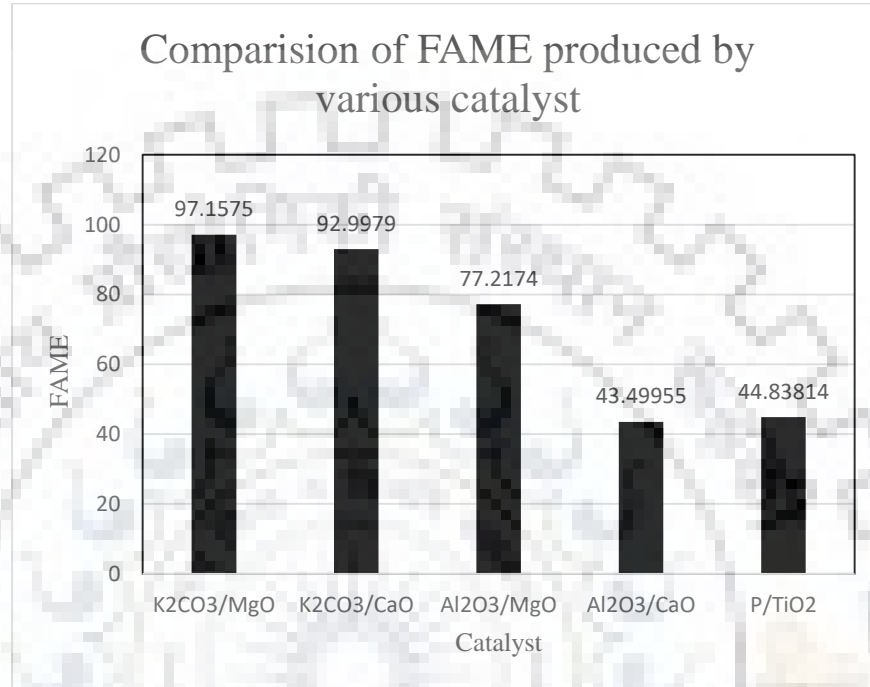


Fig 5.17 FAME yield produced by various catalyst.

Since India is an agrarian country nonedible oil can be considered as a potential feedstock for production of biodiesel. Biodiesel produced by such feedstock is an advantage because it is clean, reliable and renewable source. Also by growing such trees the greenhouse gases in the atmosphere are not added but absorbed as in the case of conventional petroleum products. Thus this ensures us that biodiesel is the fuel of the future.

- Various different types of catalysts such as enzymes or organometallic catalysts can be experimented with, to improve the FAME content of the biodiesel.
- Catalyst characterization can be done extensively, the surface properties of the catalyst can be explored
- Studies on scale up of the reaction can be performed.

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