PRODUCTION OF BIODIESEL BY THE TRANSESTERIFICATION REACTION USING ENVIRONMENTALLY BENIGN CATALYSTS DERIVED FROM LOW COST MATERIALS AND ITS UP-GRADATION IN A PILOT SCALE UNIT

Thesis submitted to the
University of Calicut in partial fulfillment of
the requirements for the degree of

DOCTOR OF PHILOSOPHY IN CHEMISTRY
In the Faculty of Science

By

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CERTIFICATE

This is to certify that the thesis entitled **"Production of Biodiesel by the Transesterification Reaction Using Environmentally Benign Catalysts Derived from Low Cost Materials and its Up-gradation in a Pilot Scale Unit"** bound herewith is a bonafide work done by Mr. Vinu V V under my supervision in the Department of Chemistry, S.N.G.S. College, Pattambi. I also certify that the corrections / suggestions from the adjudicators have been incorporated in the revised thesis.

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Certified that the thesis entitled "**Production of Biodiesel by the Transesterification Reaction Using Environmentally Benign Catalysts Derived from Low Cost Materials and its Up-gradation in a Pilot Scale Unit**", submitted by Mr. Vinu V. V. is an authentic record of research work carried out by him under my supervision at the Research and Post Graduate Department of Chemistry, SNGS College, Pattambi in partial fulfillment of the requirements for the award of degree of Doctor of Philosophy in Chemistry of the University of Calicut, and has not been included in any other thesis submitted previously for the award of any other degree.

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DECLARATION

I hereby declare that the present work entitled "**Production of Biodiesel by the Transesterification Reaction Using Environmentally Benign Catalysts Derived from Low Cost Materials and its Up-gradation in a Pilot Scale Unit**" is an authentic record of the original work done by me under the guidance of Dr. Binitha N. N., Assistant Professor, Research and Post Graduate Department of Chemistry, SNGS College, Pattambi in partial fulfillment of the requirement for the award of degree of Doctor of Philosophy in Chemistry of the University of Calicut, and has not been included in any other thesis submitted previously for the award of any other degree.

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DEDICATED
To
All, who helped to accomplish this venture,

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"Gratitude is the fairest blossom which springs from the soul"

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PREFACE

The non-regenerable fossil fuels are on the verge of their availability. The engine exhaust emission of toxic pollutants by the incomplete combustion of fossil fuels is having serious impact on the environment and living beings. But still, the world employs fossil fuels as the prime energy source and the entire transport system majorly depends on these non renewable resources. Fossil fuels are seen in limited areas in the world. So each country has to seek alternate energy resources to become independent on fuel production. Researchers are working to find out green alternatives that can completely replace the fossil fuels. The best remedy for the pollution causing, depleting and high cost fossil fuels are biofuels that are derived from renewable sources. Among the biofuels, biodiesel got attention as the best suited alternative for petrodiesel. The transport system of the world is mainly concentrated on petrodiesel; biodiesel has the merit of its use as such in the conventional diesel engines without any engine modifications. Biodiesel is a clean, non toxic, biodegradable fuel, which is safe to handle, causing minimum pollutant emission on combustion and is eco-friendly.

Biodiesel is produced from vegetable oils or animal fats by the acid/base catalyzed transesterification reaction with lower alcohols, especially methanol. The feedstock cannot be directly used as a fuel in diesel engines because of the high viscosity of triglycerides. Transesterification of oils/fats converts the feedstock to a fuel, usable in diesel engine with suitable fuel properties. However, the high cost of the feedstock is a major hurdle in biodiesel commercialization, which can be solved by using non edible oils or used cooking oil as the feedstocks. The commercial production of biodiesel is commonly performed by homogeneous base catalyzed transesterification reactions, which are comparably faster than acid catalyzed processes and is also economical. This route has some operational problems such as consumption of the catalyst by soap formation, difficulty in biodiesel separation, requirement of extra neutralization and purification steps as well as emulsion formation on washing, resulting in the loss of biodiesel yield. The best solution for this bottleneck is the use of heterogeneous catalysts for the industrial scale production of biodiesel, which has a lot of promise such as catalyst regeneration, avoiding the washing steps, maximum yield of biodiesel, formation of high purity glycerol by product etc. Thus the use of reusable solid catalysts for biodiesel production makes the entire process greener.

However, the use of solid catalysts in the industrial scale biodiesel production is not yet well established. Relatively high cost and burden in the catalyst preparation limited these catalysts' application in the lab scale biodiesel production. So, there is a need for the easy development of low cost and efficient solid catalysts for the economical eco-friendly industrial scale production of biodiesel from non edible oils. Here, we have developed 4 different sets of solid catalysts from waste materials for the green production of biodiesel. The catalytic activity of these catalysts was investigated by conducting the transesterification reactions with non edible jatropha oil as well as using cooking oil. The feasibility of the developed solid catalysts in the large scale biodiesel production was verified by up-grading the biodiesel production process in a pilot plant with a production capacity of 15 L biodiesel/run. The biodiesel pilot plant was designed and assembled in our laboratory. The vessels and valves of the biodiesel pilot plant are made of polypropylene (cheap material and resistant to a range of chemicals). Use of solid catalysts derived from waste materials and the reusability of most of the prepared catalysts makes the entire process green and cost effective.

This thesis is structured into 7 chapters. Chapter 1 gives an introduction into biodiesel and its production strategies. Chapter 2 explains the materials and methods employed for the catalyst preparation and characterizations and also for the biodiesel production as well as its analysis. Design, assembly and different parts of biodiesel pilot plant are mentioned here. In the chapter 3, preparation of solid catalysts from coconut husk and their applicability in biodiesel production from jatropha as well as using cooking oil is investigated. Chapter 4 describes the development of a heterogeneous catalyst from rice husk ash by sodium incorporation via sol gel method and its feasibility in biodiesel production. Chapter 5 is about the sodium loaded waste borosilicate glass derived sodium silicate catalyst for biodiesel production. In chapter 6, details of the catalyst developed from arecanut husk ash by its chemical reaction with $LiNO_3$ and its use for biodiesel preparation is narrated. Thesis is concluded with chapter 7 that summarizes the present work, which is a promise in biodiesel production in comparison with the present preparation strategies.

CONTENTS

LIST OF PUBLICATIONS AND PATENT FILED

Publication

1. Vinu Vadery, Binitha N. Narayanan, Resmi M. Ramakrishnan, Sudha Kochiyil Cherikkallinmel, Sankaran Sugunan, Divya P. Narayanan, Sreenikesh Sasidharan. Room temperature production of jatropha biodiesel over coconut Husk ash, *Energy*, 2014, *70*, 588-594. DOI: 10.1016/j.energy.2014.04 .045
2. S Padikkaparambil, JP Padi, V Vadery, BN Narayanan. A facile preparation of noble metal free Cu dopped CeO_2 oxidation catalyst suitable for engine exhaust gas treatment, Journal of Environmental Engineering. Accepted.

Patent filed

1. N N Binitha, M R Resmi, V V Vinu, S Sreenikesh, K C Sudha, Preparation of fatty acid alkyl esters (biodiesel) from triglyceride oils using rice husk derived catalysts, Filed an Indian patent, No. 201741025363, July 2017.

Paper communicated/under preparation

1. Vinu Vadery, Sudha Kochiyil Cherikkallinmel, Resmi M Ramakrishnan, Sankaran Sugunan, Binitha N Narayanan, Green route for the production of biodiesel by the transeterification reaction of used cooking oil over catalyst derived from waste borosilicate glass and its pilot scale up-gradation.

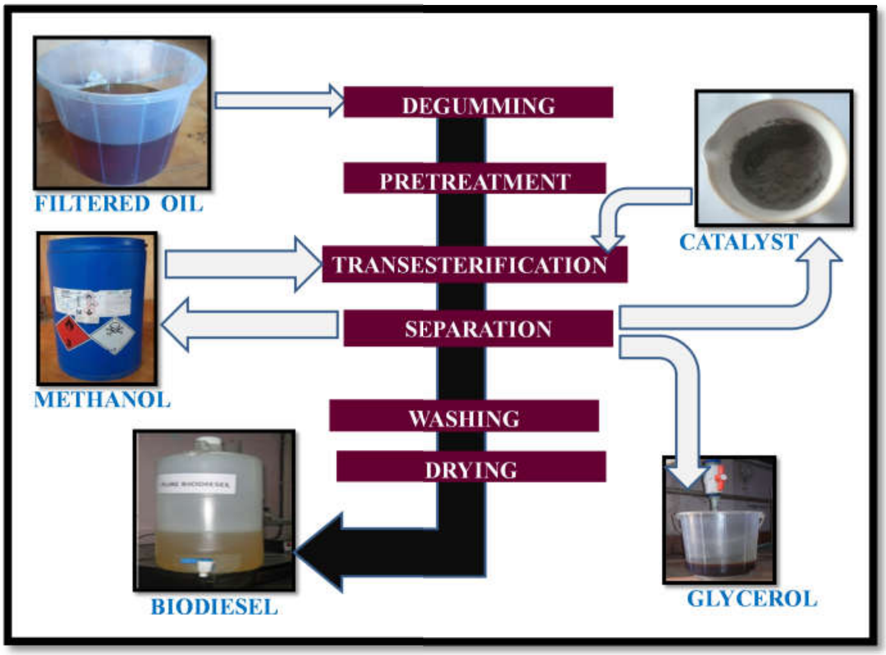
2. Vinu Vadery, Resmi M Ramakrishnan, Sankaran Sugunan, Binitha N Narayanan, Biodiesel production by the transesterification reaction of waste cooking oil over $LiNO_3$ loaded areca nut husk ash catalyst.

LIST OF PAPERS PRESENTED

1. Vinu V. V., Binitha N. N., Engine performance studies and emission analysis of biodiesel prepared from used cooking oil via heterogeneous catalysts, National seminar on Emerging Trends in Nonmaterial's Science and Technology (ENST-2017), Research and Post graduate Department of Chemistry, Sree Neelakanta Government Sanskrit College Pattambi, Palakkad, 19-20 December 2017.
2. Vinu V. V., Binitha N. N., Eco-friendly scalable catalyst for Biodiesel Production: Evaluation in Diesel Engine, HORIZON' 15, A national level students symposium on innovative catalysis, Department of Chemistry, NIT Tiruchirappalli, 11-12 September 2015.
3. Vinu V. V., Binitha N. N., Doping of lanthanum over K/Al_2O_3 catalysts for the transesterification of jatropha oil , National ,Seminar on Advanced Trends in Chemistry, St. Aloysius College, Elthuruth, Thrissur, November 30th and December 1st, 2012.

CHAPTER 1

BIODIESEL AND BIODIESEL PRODUCTION STRATEGIES



1.1 Introduction

Energy resources are one of the main driving forces in the growth of every country [1]. The world's energy requirement is satisfied mainly by the fossil fuels, especially the petroleum fuels [2]. The global population has been increasing by a rate of 1.1% per year, which has now reached to 7.6 billion and is growing continuously [3]. As a result, the energy consumption is also increasing with a rate of 2.5% per annum [3]. The finite reserves of petroleum based fuels are mainly concentrated in certain regions of the world. Since, these resources are finite, it is necessary to look towards alternative fuels [4]. The increased use of the fossil fuels creates its deficiency and its prolonged use causes serious environmental issues. Based on the current consumption of fossil fuels, it is expected that it will end up within the upcoming 30-60 years [5]. The combustion of fossil fuels emits hazardous gases like CO_2, nitrogen oxides (NO_x), hydrocarbons (HC), SO_2 etc [7]. Increase in the atmospheric CO_2 level creates global warming, which cause the melting of ice bergs, rising of the sea level etc. Nowadays, in effect, climate changes occur much faster in an unpredictable way [8]. Thus, both the energy crisis and environmental impacts demand the search for alternate energy resources. Production of energy from renewable sources is the only alternate solution for the crisis created by the depletion of fossil fuels and environmental degradation. Renewable energy resources are clean and eco-friendly; they have least contribution to green house gas and other pollutant's emission. Solar, geothermal, wind, hydroelectric, biomass, ocean and hydrogen are the most important renewable energy resources [9]. With proper development in the technology, those reserves can satisfy the global energy demands in future [10]. The transport sector accounts for ~25% of the world's energy demand and it consumes ~62% of all the petroleum fuels produced [11]. The promising alternative fuels for transportation in future are liquid biofuel, hydrogen fuel, biogas, methane etc. Biofuels from biomass get more attention because of its natural availability and easy production [12, 13]. Among the various biofuels present, biodiesel is the most promising alternative fuel for petrodiesel, since it can be a direct substitute for petrodiesel in conventional diesel engines [14]. Present energy usage profile is narrated in figure 1.1 [15]

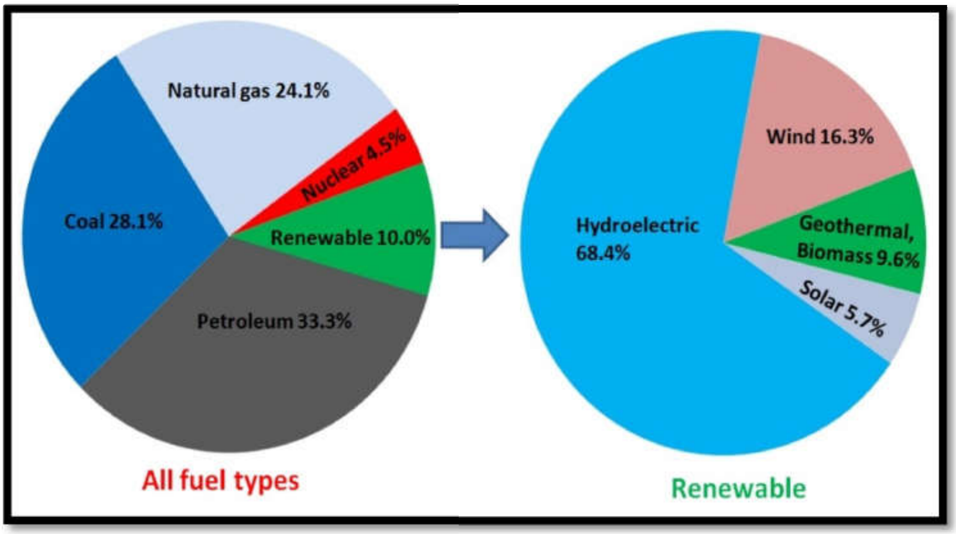


Fig 1.1 Global energy consumption in fraction, 2016

1.2 Biodiesel as an alternative fuel

Biodiesel is a liquid biofuel made from vegetable oils by chemical transformation called transesterification reaction [16]. Chemically, biodiesel is the monoalkyl esters of long chain fatty acids derived from triglyceride molecules (oil/fat) by the transesterification reaction with lower alcohols. Lower alcohols like methanol or ethanol are the commonly used ones and the produced biodiesel is known as fatty acid methyl ester, if methanol is used. Biodiesel can be used as such in conventional diesel engines without any modifications [17-19]. The fuel properties of biodiesel are comparable with the petrodiesel fuel and it performs in the diesel engine as same as or much better than the petrodiesel fuel. Biodiesel is a green fuel, which has renewable origin, non-toxic and biodegradable nature and it is safe and easy to handle when compared to petrodiesel fuel. It is an eco-friendly fuel; it's reduced emission on combustion in comparison with diesel fuel reducing its hazardous impact on the environment. Biodiesel enhances fuel lubricity and improves the anti-wear properties while blending with petrodiesel. It is an oxygenated fuel and additionally, the growth of oil crop balances the total CO_2 emission to the atmosphere [20-23]. Fuel grade biodiesel or its blends with petrodiesel can be used in vehicles. Fuel grade biodiesel is the selection criteria for biodiesel to be used in a diesel engine. It is based on both physical and chemical properties of biodiesel fuel [24-26]. The relevant biodiesel fuel properties and its requirements are described in the following sections.

1.3 Fuel properties of biodiesel

For the long term use of biodiesel in diesel engine without any technical problems, the physical and chemical characteristics of the biodiesel fuel must satisfy the quality requirements. The fuel properties and hence the quality of biodiesel are affected by the fatty acid composition of the parent vegetable oil or animal fat, the entire biodiesel production process, handling, storage etc. Some of the major fuel parameters needed for the efficient performance of fuel in diesel engine are mentioned here. Changes in these properties strongly affect the performance and the emission characteristics of the fuel [26-30].

1.3.1 FAME content

The most important parameter ascribing the use of biodiesel as a fuel is its monoalkyl ester content. Commonly, fatty acid methyl ester (FAME) is the monoalkyl ester while using methanol as the transesterifying alcohol. According to European standard fuel specification, EN 14214, the biodiesel should contain a minimum of 96.5% ester content in it for assigning it as a standard fuel [31, 32].

1.3.2 Free glycerol and total glycerol

Glycerol is an undesirable by-product in the biodiesel production and is thus separated from the biodiesel sample; but it has some value added uses on purification. There will be a chance for the presence of trace amount of glycerol in the separated biodiesel and is referred as free glycerol. The unconverted triglycerides and partially reacted di- and monoglycerides are collectively called as bound glycerol in the biodiesel sample. Total glycerol corresponds to both the free and bound glycerin in the biodiesel fuel [33-35].

Presence of free and bound glycerol in biodiesel cause negative effects while performing in the diesel engine. High levels of free glycerine can cause injector deposits as well as clogged fuelling systems, and can result in the accumulation of free glycerine at the bottom of storage and fuelling systems.

1.3.3 Acid value

Acid value is a measure of the amount of free fatty acids (FFA) present in the biodiesel sample. Presence of FFA in the sample causes degradation and thermal instability of biodiesel. FFA undergoes oxidation and break down into aldehydes, ketones, epoxides and alcohols. FFA corrodes the engine parts [36- 38].

1.3.4 Water content

Water is accumulated in the biodiesel during its production process and washings, especially in the homogeneous catalyzed route [39]. Presence of water adversely affects the biodiesel quality such as it enhances the growth of microorganisms. In addition, the esters get rancid and its chemical structure will also be affected. Hydrolysis of the ester with water increases the FFA content leading to corrosion of the storage tank, emulsification and sediment formation; and additionally makes the biodiesel susceptible to hydrolytic oxidation [40]. These things negatively affect the engine performance.

1.3.5 Iodine value

Iodine value of the biodiesel sample indicates the amount of unsaturation present in the molecule. Presence of double bonds makes the biodiesel sample highly susceptible to oxidation and it negatively affects the stability of biodiesel by polymerization and gum formation. It is clear that, higher the iodine value of the sample lower will be its oxidation stability [41-43].

1.3.6 Viscosity

High viscosity is the major reason for avoiding the use of oils as fuel in the diesel engines. Branched structure of oil is changed into linear chain in biodiesel and thus biodiesel has lower viscosity than the parent oil. The viscosity varies with fatty acid chain length and unsaturations. The high viscosity of fuels leads to operational problems in engines and decrease the combustion efficiency due to poor atomization in the injector. The viscosity of biodiesel fuel is generally higher than petrodiesel fuel as a result of its comparatively high molecular mass [44-46].

1.3.7 Density

Density is an important fuel property. Normally the biodiesel fuel has higher density than the diesel fuel. Density of biodiesel varies with its chemical composition. Fuel density affects the injection system [47]. Higher the density, a mass injection creates poor atomization in the fuel-air mixture. It causes incomplete combustion and thus causes more pollutant emission [48, 49].

1.3.8 Flash point and fire point

Flash point and fire point of biodiesel are the properties independent with the engine performance, but connected with the safety requirements in storage and transport. As compared to diesel fuels, biodiesel has higher flash point and fire point, making it non hazardous to transport. Lower flash and fire points of biodiesel are an indication of dissolved methanol in the biodiesel and it should be removed to increase the flash point/fire point [50-53].

1.3.9 Cetane number

The cetane number (CN) indicates how efficiently a fuel undergoes combustion inside the compression ignition engine. This property is related with the time delay between the starting of the fuel injection and its combustion. CN of biodiesel depends on its fatty acid profile; the value varies from 45 to 67. Biodiesel from saturated fats has higher cetane index and they performed well in the engine. Compared to diesel, biodiesel has higher cetane number and thus higher combustion efficiency in the engine [54, 55].

1.3.10 Calorific value

The heat content of the fuel, referred as calorific value is a measure of energy released as a result of combustion of a fuel [56]. A fuel with higher calorific value is mostly preferred since it improves the efficiency of the engine by high power generation [57]. Compared to diesel fuel, usually, biodiesel has lower calorific value [58].

1.3.11 Cold-flow properties

The cold flow properties of a fuel are the indication of its efficiency at low temperatures. Cloud point, pour point and cold filter plugging point are the cold-flow properties of biodiesel. Cloud point is the temperature at which small crystals of wax are observed upon cooling of biodiesel. It is connected with the filter plugging point, where the fuel begins to clog filters hence causing hindrance to the engine performance. Pour point is the lowest temperature at which the fuel flow is possible. All these properties highly influence the engine performance of vehicles at cold weather [59, 60].

1.3.12 Oxidation stability

Biodiesel having vegetable origin is highly susceptible for oxidation [61]. Oxidation stability is one of the important factors concerning the storage stability of biodiesel [62]. Presence of water/moisture, FFA, traces of metals, unsaturation in the fatty acid chain etc are the internal factors affecting the oxidation stability of biodiesel. Also air, light and heat cause a detrimental effect on biodiesel storage resulting in its oxidation [63]. Increased viscosity is one of the adverse effects as a result of the presence of oxidation products in biodiesel, which affects the engine performance [64].

Oxidation stability of biodiesel fuel can be determined by the copper strip corrosion method [65].

1.4 Standard fuel specifications for biodiesel

For the commercial use of biodiesel as a fuel in diesel engines, it must satisfy some quality requirements. So as to yield better fuel performance and reduced emissions, standard specifications for biodiesel were established and are also being developed in each country so that the engine manufacturers and biodiesel producers use similar standards for fuel quality assessment [66]. The most accepted standard fuel specifications for biodiesel are the European standard, EN 14214 and the USA standard, (American Society for Testing and Materials) ASTM D 6751 [67, 68]. The physical and chemical properties of biodiesel may vary with its origin. The biodiesel fuel must satisfy the criteria assigned by the standard specifications for its effective performance. Some of the relevant physical and chemical properties of biodiesel fuel are already mentioned in the section 1.3, which directly influence the performance of biodiesel in the engines. There are specific ranges of values for each of the fuel properties. The slight differences in the standard values for different regions are due to the climate-related requirements for biodiesel in different countries [69]. All modern diesel engines are compatible for the use of biodiesel as long as the fuel meets the standard specifications. The standard values as specified by EN 14214 and ASTM D 6751 for the fuel parameters of biodiesel are provided in Table 1.1 and 1.2 [70, 71].

Table 1.1 European standard fuel specifications for biodiesel (EN 14214)

Fuel property	Test method	Limits	Units
Ester content	EN 14103	96.5 min	% (m/m)
Density; 15 °C	EN ISO 3675, 12185	860-900	Kg/m^3
Viscosity, 40 °C	EN ISO 3104, ISO 3105	3.5-5.0	mm^2/s
Flash point	EN ISO 2719, 3679	101 min	°C
Sulfur content	EN ISO 20846, 20884	10.0 max	mg/kg
Carbon residue (10% dist. res.)	EN ISO 10370	0.30 max	% (m/m)
Cetane number	EN ISO 5165	51 min	-
Sulfated ash	ISO 3987	0.02 max	% (m/m)
Water content	EN ISO 12937	500 max	mg/kg
Total contamination	EN 12662	24 max	mg/kg
Copper strip corrosion (3h, 50 °C)	EN ISO 2160	1	-
Oxidative stability, 110 °C	EN 14112, 15751	6.0 min	h
Acid value	EN 14104	0.50 max	mg KOH/g
Iodine value	EN 14111	120 max	mg I/100g
Linolenic acid content	EN 14103	12 max	%(m/m)
Methanol content	EN 14110	0.20 max	% (m/m)
Monoglyceride content	EN 14105	0.80 max	% (m/m)
Diglyceride content	EN 14105	0.20 max	% (m/m)
Triglyceride content	EN 14105	0.20 max	%(m/m)
Free glycerine	EN 14105, 14106	0.02 max	%(m/m)
Total glycerine	EN 14105	0.25max	%(m/m)
Alkali metals (Na + K)	EN 14108, 14109, 14538	5.0 max	mg/kg
Earth alkali metals (Ca + Mg)	prEN 14538	5.0 max	mg/kg
Phosphorus content	EN 14107	4.0 max	mg/kg

Table 1.2 American standard fuel specifications for biodiesel (ASTM D 6751)

Fuel property	Test method	Limits	Units
Flash point (closed cup)	D 93	93 min	°C
Methanol content	EN 14110	0.2 max	% volume
Water and sediment	D 2709	0.050 max	% volume
Kinematic viscosity, 40 °C	D 445	1.9-6.0	mm^2/s
Sulfated ash	D 874	0.020 max	% mass
Sulfur	D5453	0.05 or 0.0015 max	% mass
Copper strip corrosion	D 130	No. 3 max	-
Cetane number	D 613	47 min	-
Cloud point	D 2500	Report	°C
Carbon residue	D 4530	0.050 max	% mass
Acid number	D 664	0.50 max	mg KOH/g
Free glycerin	D 6584	0.020	% mass
Total glycerin	D 6584	0.240	% mass
Phosphorus content	D 4951	0.001 max	% mass
Distillation temperature	D 1160	360 max	°C
Sodium and potassium, combined	EN 14538	5 max	ppm (µg/g)
Calcium and magnesium, combined	EN 14538	5 max	ppm (µg/g)
Oxidation stability	EN 15751	3 min	hours
Cold soak filterability	D7501	360 max	sec

In India, Bureau of Indian Standards (BIS) established IS 15607 standards for biodiesel fuel [72]. This standard is developed from European EN 14214 and American ASTM D 6751 standard fuel specifications for biodiesel fuel. Fuel quality parameters according to the Indian standards are provided in the table 1.3 [73].

Table 1.3 Indian standard fuel specifications for biodiesel (IS 15607)

Fuel property	Test method	Limits	Units
Ester content	EN 14103	96.5 min	% (m/m)
Density; 15 °C	ISO 3675/P 32	860-900	Kg/m^3
Viscosity, 40 °C	ISO 3104/P 25	2.5-6.0	mm^2/s
Flash point (closed cup)	P 21	120 min	°C
Sulfur content	D 5443/P 83	50.0 max	mg/kg
Carbon residue (10% dist. res.)	D 4530	0.05 max	% (m/m)
Cetane number	ISO 5156/P 9	51 min	-
Sulfated ash	ISO 6245/P 4	0.02 max	% (m/m)
Water content	D 2709 / P 40	500 max	mg/kg
Total contamination	EN 12662	24 max	mg/kg
Copper strip corrosion (3h, 50 °C)	ISO 2160/P 15	1	-
Oxidative stability, 110 °C	EN 14112	6.0 min	h
Acid value	P 1	0.50 max	mg KOH / g
Iodine value	EN 14104	To report	mg I/100g
Methanol content	EN 14110	0.20 max	% (m/m)
Free glycerine	D 6584	0.02 max	%(m/m)
Total glycerine	D 6584	0.25max	%(m/m)
Alkali metals (Na + K)	EN 14108	To report	mg/kg
Earth alkali metals (Ca + Mg)	-	To report	mg/kg
Phosphorus content	D 4951	10.0 max	mg/kg

1.5 Biodiesel feedstocks

The most common feedstocks for biodiesel production are triglycerides. Generally vegetable oils, animal fats, algal oils and used cooking oils are employed [74, 75]. Vegetable oils have higher viscosity in the range of 35-50 mm^2s^{-1}, so it cannot be directly used as fuel in the diesel engine [76]. Reduction of viscosity is the effective way for using these renewable materials in diesel engine. Several ways are available for reducing the viscosity of the oil/fat such as blending of oil with petrodiesel, pyrolysis, micro emulsification and transesterification [77]. Among these, transesterification is the cost effective, efficient and widely used method, which produces fatty acid monoalkyl esters called biodiesel. Biodiesel has viscosity in the range of petrodiesel and comparable fuel properties of diesel [78].

Vegetable oils are of two types, edible oils (coconut oil, sunflower oil, palm oil, soybean oil, peanut oil, sesame oil, mustard oil, rice bran oil etc) and non edible oils (jatropha oil, karanja oil, pongamia oil, castor oil, rubber seed oil etc), which are good sources of biodiesel [79-81]. Biodiesel production from edible oils is not much recommended because of their high cost and resulting competition with food uses. So non edible oils are the suitable option, but the cultivation of these crops requires land use that will also cause competition with the land for food production [80]. Thus, the use of non-edible crops, such as *jatropha curcas*, which can grow even in barren lands, is highly recommended since the extensive use of these crops can significantly reduce the cost of biodiesel production. Recently, many researchers investigated the utilization of used cooking oil (UCO) for biodiesel production, which can also effectively make the biodiesel production economical [81]. Moreover, the use of UCO as a feedstock for biodiesel production provides an alternative way of its disposal. The marketing feasibility of the use of biodiesel depends on the cost of the feedstock. The cheapest feedstocks are waste restaurant oils and rendered animal fats [82].

1.5.1 *Jatropha curcas* oil (JCO)

Jatropha curcas is a flowering plant belonging to the family *Euphorbiaceae* and grows in tropical and subtropical countries. Jatropha is native to Mexico, Central America, Africa, India, Brazil, Argentina and Paraguay [83]. In India, it has variety of names and in Kerala it is often called kattavanakku [84]. It is a semi-evergreen shrub or small tree, grows up to a height of 6 m or above. The name "jatropha" is a resultant of its medicinal value i.e. from two latin words jatros (doctor) and trophe (food). It is non edible because it contains phorbol esters, which are toxic [85].

Jatropha plant get attention among various oil crops since it can grow even in barren lands with ecological advantages at the worst climate conditions [86]. Without sacrificing the fertile land, jatropha plants can survive and thus is a promise for reclaiming of barren lands. Jatropha growth is not demanding any care in the cultivation and additionally it makes the land fertile. Jatropha plant and its parts have some medicinal applications [86]. Depending on the variety, the oil content in the jatropha seed will vary from 30-50%. Linoleic and oleic fatty acid are the major constituents in jatropha oil [87]. The FFA content in jatropha oil is found to be varied in a range of 2.5 to 65% [88]. The presence of toxic components in jatropha oil makes it non edible but it has the properties required for its use as a fuel in common diesel engines. Table 1.4 contains the fatty acid profile of the jatropha oil [89, 90]. Figure 1.2 shows the plant, seed and oil of *jatropha curcas*.

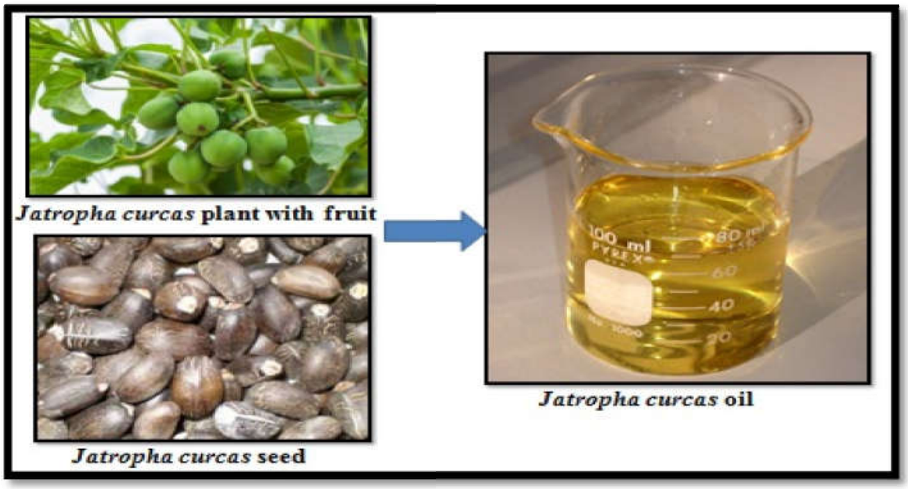


Fig 1.2 *Jatropha curcas* plant, seeds and oil

Table 1.4 Fatty acid profile of *jatropha curcas* oil

Fatty Acid (no. of carbon: double bond)	Percentage (%)
Oleic (18:1)	44.7
Linoleic (18:2)	32.8
Palmitic (16:0)	14.2
Stearic (18:0)	7.0
Palmitoleic (16:1)	0.7
Linolenic (18:3)	0.2
Arachidic (20:0)	0.2
Margaric (17:0)	0.1
Myristic (14:0)	0.1
Saturated	21.6
Monounsaturated	45.4
Polyunsaturated	33

1.5.2 Used cooking oil (UCO)

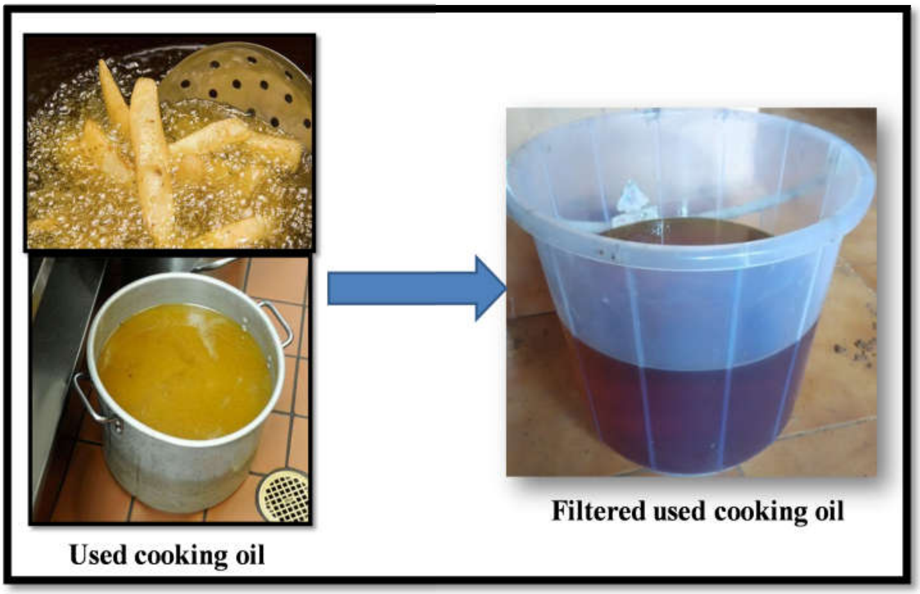
With the growth of human population and changes in the food habits, the amount of UCO generated increases. Repeated use of cooking oil for frying purposes etc. cause serious health hazards. Studies revealed that the polyunsaturated fatty acid containing oils such as soya, canola, sunflower, and corn oil degrade easily to toxic compounds when heated [91]. Prolonged consumption of burnt oils led to atherosclerosis, inflammatory joint disease, and development of birth defects [92]. Thus it should be disposed after one or two repeated uses. Management of such oils and fats poses significant challenges because of their disposal problems and possible contamination of the water and land resources. Thus the alternative use of UCO in biodiesel production is of great attention. But, high FFA content (varies from 3.5 to 70%) is a problem faced in the base catalyzed biodiesel production using UCO [93]. The fatty acid profile of the palm oil and coconut oil, two common cooking oils in our state, are provided in the table 1.5 and 1.6 respectively [94, 95].

Table 1.5 Fatty acid profile of palm oil

Fatty Acid (no. of carbon: double bond)	Percentage (%)
Oleic (18:1)	39.2
Linoleic (18:2)	10.1
Palmitic (16:0)	44.0
Stearic (18:0)	4.5
Linolenic (18:3)	0.4
Myristic (14:0)	1.1
Lauric 12:0	0.2
Saturated	21.6
Monounsaturated	45.4
Polyunsaturated	33

Table 1.6 fatty acid profile of coconut oil

Fatty Acid (no. of carbon: double bond)	Percentage (%)
Caprylic (8:0)	7.0
Decanoic (10:0)	5.4
Lauric 12:0	48.9
Myristic (14:0)	20.2
Palmitic (16:0)	8.4
Oleic (18:1)	6.2
Linoleic (18:2)	1.4
Saturated	91
Monounsaturated	6
Polyunsaturated	2



Used cooking oil

Filtered used cooking oil

Fig 1.3 Crude and filtered used cooking oil

1.6 Different stages in biodiesel production

Biodiesel production from triglyceride oils proceeds through different steps which is depicted in the figure 1.4. The key step is the transesterification reaction of refined triglycerides with lower alcohols in the presence of a suitable catalyst [96, 97]. Before that the raw material oil requires some pretreatments. In the case of virgin oils, if they do not contain FFA, direct transesterification reaction can be done. But in most of the cases, feedstocks require pretreatment procedures [98, 99]. The impurities such as gums, FFAs and moisture present in the oil adversely affect biodiesel production process by reducing the product yield. So, they should be removed from the feedstock before subjecting to the transesterification reaction [100, 101]. Degumming, acid pretreatment and drying are the procedures adopted for the removal of gum, FFA and moisture respectively.

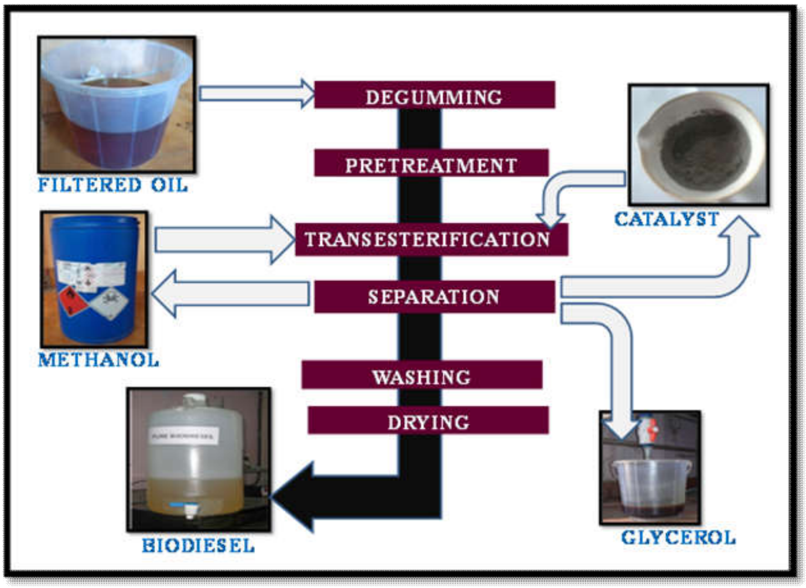


Fig 1.4 Different stages in biodiesel production

1.6.1 Degumming of oil

Before degumming, the feedstock is subjected to filtration for the removal of insoluble impurities present in the feedstock. Gums are soluble impurities present in the crude vegetable oils other than residual metals like Ca, Mg, etc. Gums are inherently present in the feedstocks by biological means. Gums in vegetable oils refer to a variety of compounds including hydratable and non-hydratable phosphatides, lecithin, and other impurities which are responsible for metal contamination. Gums present in the oil have severe affects in transesterification, in addition to its hindrance to the activity of catalyst and thus reducing the biodiesel yield, it also creates difficulties in diesel engine performance. Degumming of filtered oil was performed by thermal treatment with water with the assistance of degumming agents [102-105].

1.6.2 Pretreatment of oil

Another important step is the acid pretreatment of the degummed oil. It is done for the removal of FFA present in the feedstock oil. Almost all the non edible and waste cooking oils are the prime hosts for FFAs. The pretreatment of oil is carried out to reduce the FFA to < 1% before the base catalyzed biodiesel production. Esterification is the common pretreatment procedure. Acid catalysts are most effective in the esterification of the FFAs to the corresponding esters within a short duration of time. So biodiesel production from feedstocks having high FFA content is achieved by two steps; acid pre-esterification followed by base catalyzed transesterification reactions. Acid pretreatment is generally conducted with high FFA bearing feedstocks and lower alcohols (methanol) using concentrated acids as catalysts (HCl or H_2SO_4). Acid esterification provides an extra benefit as it retains the FFA as its ester, thereby eliminating the problems such as soap formation, emulsification, decrease in biodiesel yield etc [106-109].

1.6.3 Transesterification reaction

Transesterification is the key chemical reaction employed in biodiesel production. Among the various processes available for converting vegetable oils/fats as fuel in diesel engines, transesterification is the universally accepted and widely used method. As we know, the main components of oil/fat are triglycerides with different fatty acid chains attached to glycerol. The nature and properties of the oil/fat is the characteristic of the fatty acid chain present in it. Transesterification converts these fatty acid triglycerides to the corresponding monoalkyl esters using a lower alcohol with the aid of a catalyst [110-112]. Figure 1.5 shows the scheme of transesterification.

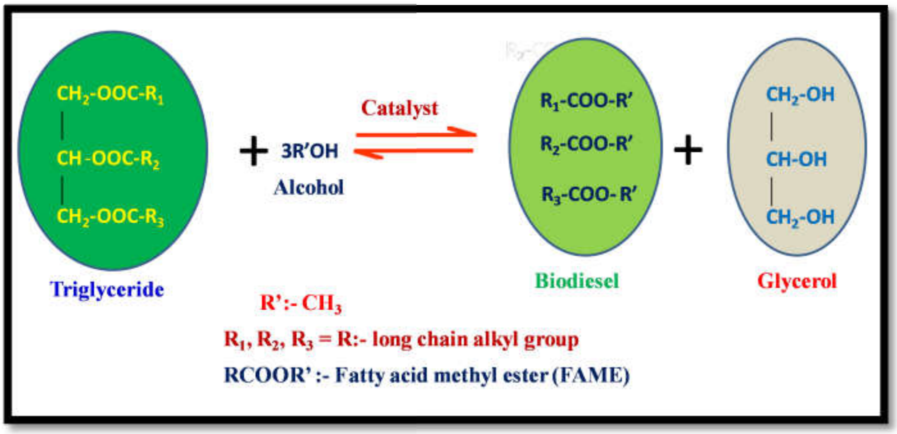


Fig 1.5 Scheme for transesterification reaction

Transesterification is not a single step reaction; it proceeds through different consecutive and reversible steps [113, 114]. Initially, the triglyceride (TG) is converted into diglycerides (DG) then to monoglycerides (MG) and finally to glycerol. In each step, one molecule of FAME is produced. The different steps are depicted in the figure 1.6. Efficiency of the transesterification reaction and thereby the biodiesel quality depends on many factors. The remaining stages in biodiesel production are its separation from glycerol and catalyst as well as biodiesel purification.

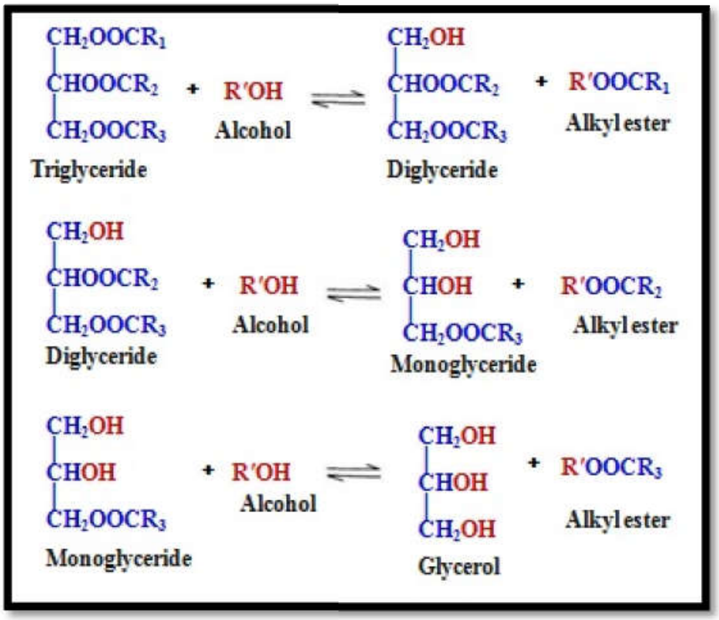


Fig 1.6 Different steps in transesterification reaction

1.7 Factors affecting the transesterification

Transesterification is a reversible process, which reduces the viscosity of the triglyceride oil by converting it into monoalkyl esters

[115, 116]. The transesterification reaction is strongly influenced by several factors including the molar ratio of alcohol/oil, nature and amount of the catalyst, presence of water/moisture, free fatty acid in the oil samples, reaction temperature, reaction time and agitation speed.

1.7.1 Alcohol/oil molar ratio

In a typical transesterification reaction, one molecule of oil is reacted with 3 molecules of alcohols to produce 3 molecules of biodiesel and one glycerol molecule. In most of the cases methanol/oil molar ratio greater than 3 is required to get maximum conversion to FAME. Here, excess alcohol can act as a solvent that can ensure proper contact between the reagent molecules and catalysts by providing effective mixing. This can result in maximum conversion of biodiesel within a short period of time. There is an optimum amount of alcohol required in the transesterification reaction that also depends on the feedstock and the catalyst. Further increase in the amount of alcohol will not lead to increase in the biodiesel yield. Excess methanol stops the reversible reaction but adds the recovery cost of excess methanol which is a negative impact. Similarly, the chain length of the alcohol used is also important. Lower alcohols, especially methanol are commonly used, which is highly reactive in the transesterification reaction. The reactivity of alcohols in transesterification will be reduced on increase in the chain length. Formation of soap, emulsion and difficulties in biodiesel-glycerol separation are the problems associated with the alcohols having higher alkyl chains [117-119].

1.7.2 Nature of the catalyst and its concentration

Transesterification is highly influenced by the catalyst; there is no reaction under normal temperature and pressure conditions without the use of a catalyst. The nature of the catalysts also influences the biodiesel yield. Details of transesterification catalysts in biodiesel production are given in the section 1.8. The concentration of catalyst is another factor; insufficient amount of catalyst will result in incomplete conversion. So there is a minimum amount of catalyst required in all the transesterification reactions and excess quantity may negatively affect the reaction by catalyst leaching or soap formation [120-123].

1.7.3 Reaction temperature

Temperature promotes the reaction by increasing the rate of the forward reaction, thereby reducing the reaction time. Especially, the reflux temperature of the alcohol is found to be the best reaction temperature in most of the cases [124]. At higher temperatures the viscosity of the oil got reduced which leads to the effective mixing and contact between the reactant molecules and catalyst, yielding maximum product. Elevated temperature is not favored for the transesterification due to the possible cause of saponification of oil instead of biodiesel production [125].

1.7.4 Reaction time

Initially, the transesterification reaction will be very slow till the effective mixing of the components (oil, alcohol and catalyst) and after that the rate will get increased with increase in time. Time needed for the completion of reaction depends on other reaction parameters such as temperature, catalyst and the amount of alcohol too. Reaction conducted for a longer time may cause a negative effect by decreasing the product yield since transesterification is a reversible process. Soap formation from the product ester is also possible with increased reaction time [126-128].

1.7.5 Water content

Water content in the feedstock oil as well as in the reaction medium adversely affects the transesterification reaction. Presence of more than 0.5 wt% of water in the feedstock has a negative effect on biodiesel production. Moisture present in the oil causes hydrolysis and increases the free fatty acid content in the feedstock. In the base catalyzed biodiesel preparation, water content leads to the formation of soap and hence reduces the biodiesel yield. For better results, the reaction must be water free [129-132].

1.7.6 Free fatty acid (FFA) content

FFA content is a critical factor in the biodiesel production. For a base catalyzed transesterification, the FFA content in the feedstock must be less than 1%. Otherwise, it will cause some hurdles in the production process i.e., it react with the catalyst and soap is formed. In addition, consumption of catalyst leads to the reduction in biodiesel yield. Soap formation causes difficulties in biodiesel layer separation and results in emulsion formation during the washing of the biodiesel product. For a feedstock with high FFA content, pretreatment is essential [133-135].

1.7.7 Agitation speed

Effective mixing of the reactants and catalysts ensures the proper contact, thereby increasing the reaction rate. So agitation speed has a role in the transesterification. Oil is viscous in nature and is immiscible with alcohol so the best way for the proper contact of these molecules under normal conditions is continuous agitation [136-138].

1.8 Catalysts in biodiesel production

Catalyst plays an important role in the production of biodiesel via the transesterification of triglyceride molecules [139]. Without catalyst there is no active reaction under normal conditions. The catalyst selection for the biodiesel production mainly depends on the feedstock and its FFA content. Biodiesel catalysis is a relevant area of research and varieties of catalysts are developed for the transesterification process [140, 141]. Generally, biodiesel is produced over homogeneous and heterogeneous catalysts. Different types of catalysts in biodiesel production are depicted in figure 1.7.

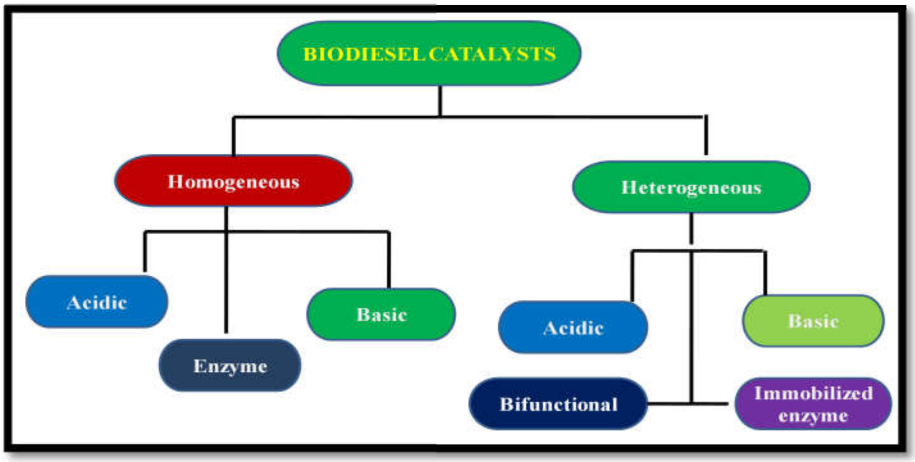


Fig 1.7 Catalysts in biodiesel production

In homogeneous catalysis, concentrated acids (HCl, H_2SO_4, HNO_3 etc), bases (KOH, NaOH, NaOMe etc) and enzymes (eg; lipase from various sources) are the most commonly used catalytic systems in biodiesel production [142, 143]. In this case, both the reactants and the catalysts are in same phase, which enhances the catalytic activity in the reaction yielding high oil conversion. In an economical point of view, homogeneous base catalyzed biodiesel production is favored and commonly employed since it gives maximum conversion within short duration of reaction. But it has some operational problems i.e., catalysts are used up, causes difficulties in final separation and purification of biodiesel, corrosion of the production vessels, requirement of extra neutralization and washing steps etc that increases the total cost of production. Use of heterogeneous catalysts overcomes the problems associated with the production of biodiesel via homogeneous catalysis. It is a greener and cost effective method [144-146].

The heterogeneous catalysts are always non-corrosive and environmentally benign. Much easier product and catalyst separation as well as formation of high purity glycerol by product are the main attractions of heterogeneous catalyzed biodiesel production [147]. In heterogeneous catalysis, solid materials or active materials supported on solids are used. Here the reactants and catalysts are in different phase and the reaction initiates via adsorption. We can easily recover the catalyst after the reaction by simple filtration/centrifugation. Regeneration and reusability for several times are the highlights of heterogeneous catalysis. Less or no washing of produced biodiesel is required, which make the process economically and ecologically benign. A variety of solid acids and solid bases as well as few bifunctional solid and supported enzyme catalysts are used as heterogeneous catalysts for biodiesel production [148]. For the industrial scale production of biodiesel, heterogeneous catalysis is mostly preferred considering the problems associated with homogeneous catalyzed route [149, 150]. However, the uses of solid catalysts in commercial production plants are limited. Non availability, high cost and catalyst preparation difficulties restricted the heterogeneous catalysts to the laboratory scale production of biodiesel [151]. Researchers are still seeking and developing the new and sustainable solid catalysts for the commercial production of biodiesel [152]. Some of the solid catalysts mainly based on acid, alkali, bifunctional and supported enzyme catalysts are shown in the table 1.7, which are used for the laboratory preparation of biodiesel from different oil sources.

Table 1.7 Heterogeneous catalysts used in transesterification

Sl. No:	Catalyst (Catalyst weight wt%)	Feedstock oil (Oil: methanol molar ratio)	Reaction temperature (°C), Reaction time (min)	FAME conversion (%)	Reference
1	CaO (5)	Used cooking oil (1:6)	65, 180	92.00	153
2	Li/CaO (5)	Karanja oil (1:6)	65, 60	99.00	154
3	Li/CaO (5)	Jatropha oil (1:6)	65, 120	99.00	154

4	CaO/NiO (5)	Jatropha oil (1:15)	65, 300	86.30	155
5	CaO/Nd_2O_3 (5)	Jatropha oil (1:15)	65, 360	82.20	156
6	CaO/La_2O_3 (4)	Jatropha oil (1:24)	65, 360	86.50	156
7	Na/SiO_2 (3)	Jatropha oil (1:9)	15	>98	157
8	Li/CaO (5)	Pongammia oil (1:12)	65, 60-120	>99.00	158
9	$CaO\text{-}La_2O_3$ (3)	Jatropha oil (1:25)	160, 180	98.76	159
10	Ca/Al_2O_3 (1)	Soybean oil (1:32)	120, 360	94.70	160
11	Na/Al_2O_3 (1)	Soybean oil (1:32)	120, 360	97.10	160
12	K/Al_2O_3 (1)	Soybean oil (1:32)	120, 360	98.90	160
13	CaO/Al_2O_3 (5.97)	Palm oil (1:14)	64.29, 300	98.64	161
14	$CaO/KI/\gamma\text{-}Al_2O_3$ (6)	Palm oil (1:42)	65, 300	95.00	162
15	CaO/Fe_3O_4 (2)	Jatropha oil (1:15)	70, 80	95.00	163
16	CaO/mesoporous silica (5)	Soybean oil (1:16)	60, 8	95.20	164
17	MgO (3)	Canola oil (3:20)	190, 120	82.80	165
18	Template MgO (3)	Canola oil (3:20)	190, 120	98.20	165
19	SrO (5)	Olive oil (1:6)	65, 15	82.00	166
20	SrO (5)	Used cooking oil (1:6)	65, 180	86.00	153
21	K_3PO_4 (5)	Used cooking oil (1:6)	65, 180	78.00	153
22	$CaZn(OH)_4$ (3)	Sunflower (1:20)	78, 180	95.00	167
23	Na_2ZrO_3 (3)	Soybean oil (1:3)	65, 180	98.30	168

24	$Sr_3Al_2O_6$ (1.3)	Soybean oil (1:25)	60, 61	95.70	169
25	Ce-Hydrotalcite (5)	Soybean oil (1:9)	67, 240	90.00	170
26	MgAlFe hydrotalcite (3)	Soybean oil (1:21)	65, 240	81.00	171
27	propyl-SO_3H-SBA-15 (6)	Palm oil (1:20)	140, 120	72.00	172
28	arene-SO_3H-SBA-15 (6)	Palm oil (1:20)	140, 120	78.00	172
29	Nb-MCM 41 (7.5)	Sunflower oil (1:12)	200, 240	95.00	173
30	$Fe(HSO4)_3$ (1)	Used cooking oil (1:15)	205, 240	94.50	174
31	KNO_3/CaO (1)	Rapeseed oil (1:6)	65, 180	98.00	175
32	MgO/ZnO (3)	Jatrophaoil (1:25)	120, 180	83.00	176
33	Magnetic $CaFe_2O_4$/ $CaFe_2O_5$ (4)	Jatropha oil (1:15)	100, 30	>80	177
34	Lipozyme TL IM (15)	Castor oil (1:3)	45, 24 h	67.58	178
35	KF/CaO (4)	Chinese tallow seed oil (1:12)	65, 150	96.80	179
36	Mo-Mn/gamma-Al_2O_3-MgO (5)	Used cooking oil (1:27)	100, 240	91.40	180
37	KNO_3/CaO (1)	Rapeseed oil (1:6)	65, 180	98.00	175
38	$Zn/Ca/Al_2O_3$ (6)	Palm oil (1:24)	65, 180	97.64	181
39	KNO_3/ Al_2O_3 (6)	Jatropha oil (1:12)	70, 360	84.00	182
40	Fe_2O_3-MnO-SO_4^{2-}/ZrO_2 (3)	Used cooking oil (1:20)	180, 240	>95	183
41	Li/MgO (9)	Soybean oil (1:12)	60, 120	93.90	184

42	KOH/MgO (4)	Mutton fat (1:22)	65, 20	>98	185
43	La/Mn oxide (3)	soybean oil (1:12)	180, 60	>99	186
44	SO_3H-MCM-41 (14.5)	Para rubber seed oil (1:16)	129.6, 48	>80	187
45	KI/Mg-Al mixed-metal oxides (5)	Soybean oil (1:20)	70, 480	>90	188
46	CaMgO and CaZnO (4)	Jatropha oil (1:15)	65, 360	>80	189
47	Cu/ZnO (12)	Used cooking oil (1:8)	55°C, 50	97.71	190
48	CaO–MoO_3–SBA-15 (6)	Soybean oil (1:50)	65, 50	83.20	191
49	KF/Ca-Al hydrotalcite (5)	Palm oil (1:12)	65, 300	97.98	192
50	$Ca_{3.5x}Zr_{0.5y}Al_xO_3$ mixed oxide (2.5)	Palm oil (1:12)	150, 300	87.00	193
51	CaFeAl/LDO (6)	Soybean oil (1:12)	60, 60	90.00	194
52	KOH/ZrO_2 (6)	Silybum marianum oil (1:6)	60, 2	90.80	195
53	Na/Zr-SBA-15 (12)	Canola oil (1:6)	70, 6	99.00	196
54	Bi_2O_3–La_2O_3 (2)	Jatropha oil (1:15)	150, 4	93.00	197
55	sulfonated pyrolyzed rice husk (5)	Used cooking oil (1:20)	110, 15	87.57	198
56	KBr /CaO (3)	Used cooking oil (1:12)	65, 1.8	83.60	199
57	K_2O/CaO-ZnO (6)	Soybean Oil (1:15)	60, 4	81.08	200
58	Fe^{3+}/Mn/Molybdenum Oxide /ZrO_2 (4)	Used cooking oil (1:25)	200, 5	95.60	201

59	CaO–La_2O_3 mixed (3) metal oxide (3)	Jatropha oil (1:25)	160, 180	98.76	202
60	Fe^{3+}–Mn doped Tungstated ZrO_2 (4)	Used cooking oil (1:25)	200, 240	96.00	203
61	Na/NaOH/ γAl_2O_3 (1g)	soybean oil (1:9)	60, 120	94.00	204
62	Li_2CO_3 (12)	soybean oil (1:32)	65, 120	97.20	205
63	Li/ZrO_2 (3)	soybean oil (1:13)	65, 180	98.20	206
64	Sulfonated C. pentandra stalks (1.5)	C. pentandra seed oil (1:18)	220, 150	99.00	207
65	K_2CO_3/Al-Ca hydrotalcite (2)	Soybean oil (1:13)	65, 120	95.10	208
66	Phosphazenium hydroxide/SiO_2 (3.8)	Soybean oil (1:60)	75, 12	90.00	209
67	1,3-dicyclohexyl-2-octylguanidine/ SBA-15 (8)	Soybean oil (1:15)	65, 15	92.60	210
68	K-doped hydroxyapatite catalysts (8)	Palm oil (1:9)	65, 1.5	96.40	211
69	Amberlyst-36 (6)	Palm oil (1:20)	140, 120	32.00	172
70	SiO_2-Tosicacid (6)	Palm oil (1:20)	140, 120	65.00	172
71	Nb-MCM 41 (7.5)	Sunflower oil (1:12)	200, 240	95.00	212
72	15%WO_3/Zr-MCM41 (1.50 g)	Sunflower oil (1:12)	200, 150	82.00	213
73	30%WO_3/$AlPO_4$ (5)	Soybean oil (1:30)	180, 300	72.50	214
74	30%Tungstosicicacid/ zeolite Hβ (200 mg)	Soybean oil (1:4)	65, 480	95.00	215

75	Sulfonated carbon (7.50)	Polanga oil (1:30)	180, 300	99.00	216
76	20%K/TiHT (6)	Canola oil (1:36)	65, 120	100	217
77	$NaAlO_2$ (1.5)	Soybean oil (1:12)	65, 60	93.90	218
78	KF/ZnO (3)	Soybean (1:10)	65, 540	87.00	219
79	TiSBA-15-Me-$PrSO_3H$ (2)	Palmitic acid (1:3)	65, 120	94.00	220
80	Na_3PO_4 (3)	Rapeseed oil (1:9)	70, 20	100	221

1.9 Mechanism of transesterification reaction

Mechanism of the acid catalyzed transesterification reaction is depicted in the figure 1.8. In the first step, protonation of the carbonyl group of the triglyceride ester results in the formation of a carbocation followed by nucleophilic attack of the alcohol moiety with the formation of an intermediate. This intermediate eliminates the glycerol part to form a monoalkyl ester and diglyceride with the regeneration of the catalyst [222- 224]. This process repeats twice more to form the free glycerol and finally results in the formation of 3 molecules of monoalkyl ester.

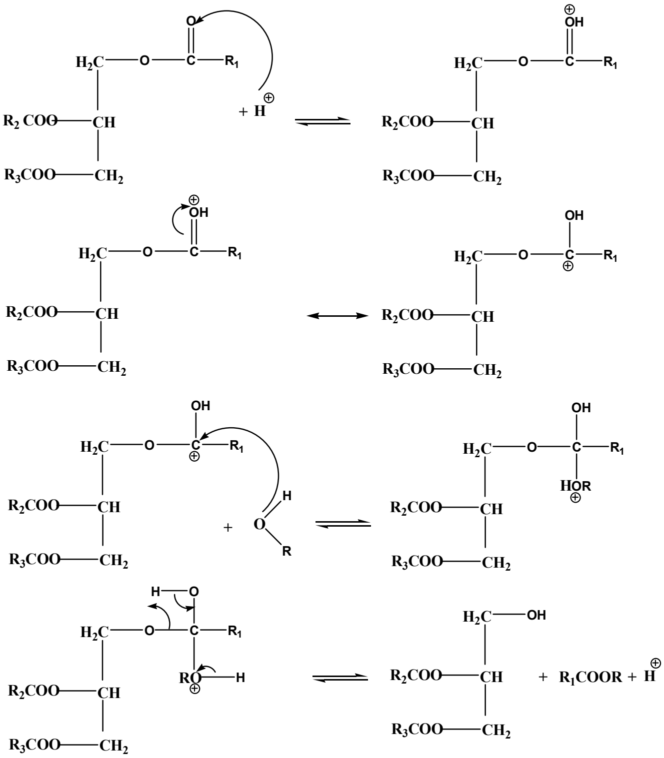


Fig 1.8 Mechanism of the acid catalyzed transesterification reaction

Base catalyzed transesterification reaction proceeds through three steps which are shown in the figure 1.9. In the reaction, a base (B) abstracts a proton from the alcohol moiety (ROH) to produce an alkoxide ion (RO^-). This alkoxide ion (nucleophile) attacks on the carbonyl carbon atom of the triglycerides molecule to form a tetrahedral intermediate which undergo rearrangement to form monoalkyl ester and diglyceride anion. Then, the diglyceride ion reacts with the protonated base, (BH^+) forming diglyceride with the regeneration of the base. This base will further abstract a proton from the alcohol and this process will continue until the complete formation of monoalkyl esters from triglyceride molecules [225-228].

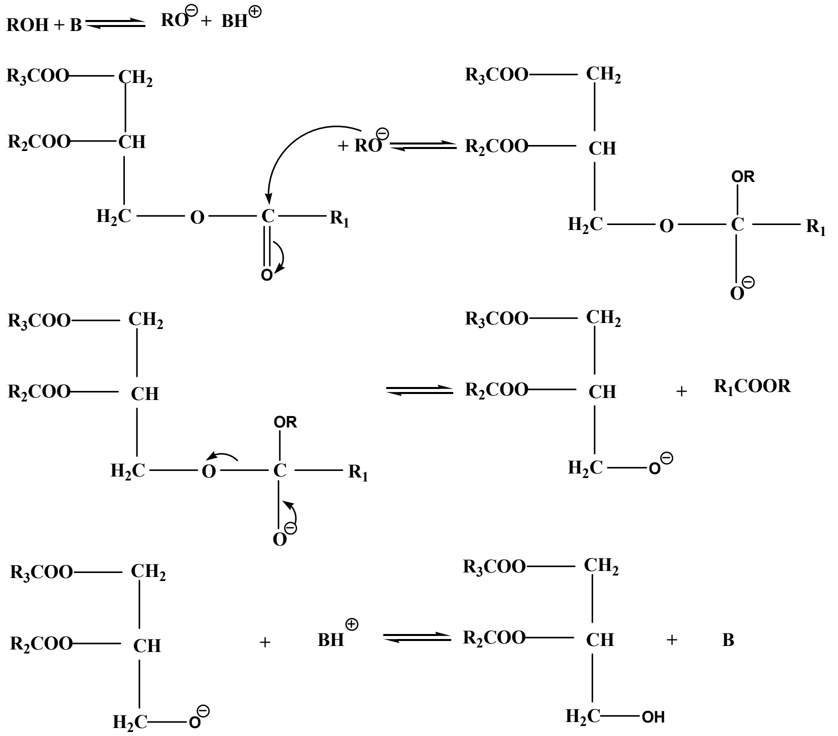


Fig 1.9 Mechanism of the base catalyzed transesterification reaction

1.10 Catalysts from waste materials

Recently, various heterogeneous catalysts derived from natural resources have been reported for the transesterification of triglycerides [229, 230]. A lot of works are there based on CaO catalysts derived from various waste egg shells, waste shells of creatures and animal bones for the laboratory scale preparation of biodiesel. Some of them are chicken egg shell [231], oyster egg shell [232], turtle shell [233], mollusks [234], cockle [235], snail shell [236], waste fish scales [237], waste chicken bone [238], waste mud crab shell [239], waste animal bone [240] etc. These materials are good source of CaO and have high commercial value as a catalyst. Easy availability, biocompatibility and environmental acceptability can make the possibility of these materials as catalysts for the large scale biodiesel production. However, catalyst leaching is the major defect of CaO based catalysts in the biodiesel production [241-243]. Utilization of various waste materials as solid catalysts or catalyst supports in biodiesel production opens a route to the value addition of recycling of waste [151, 229, 230 and 244]. The catalysts derived from renewable biomass are considered as green catalysts and the production of biodiesel over these catalysts is highly promising. Searching and developing economically viable, eco-friendly, and renewable heterogeneous catalysts from waste materials for biodiesel production is therefore very attractive. Plant derived waste materials, especially ashes from several plant materials are also getting much attention since they are good source for basic metal oxides (K_2O, Na_2O etc) or silica [245-247]. Palm empty fruit bunch [248], wood ash [249], coco pod husk ash [250], banana plant waste [251], bamboo powder [252], rice husk ash [253-255] etc were successfully utilized for catalysts development in biodiesel production by chemical modifications. Some of the solid catalysts derived from waste materials are described in table 1.8. Large scale production of biodiesel over solid catalysts derived from such waste materials are not yet reported. The loss of operational feasibility or hurdle in up-gradation in large scale process may be the bottleneck for the industrialization [256, 257]. There should be a thorough investigation required through pilot scale studies, to make the use of these materials as catalyst in industrial biodiesel production.

Table 1.8 Heterogeneous catalyst derived from waste materials for biodiesel production

Sl. No:	Catalyst (Catalyst weight wt%)	Feedstock oil (Oil: methanol molar ratio)	Reaction temperature (°C), Reaction time (min)	FAME conversion (%)	Reference
1	Calcined scallop shell (5)	Used cooking oil (1:6)	65, 120	86.00	258
2	CaO/Fly ash (6)	Palm oil (1:12)	60, 120	>90	259
3	Chicken bones (5g)	Used cooking oil (1:15)	65, 240	89.33	260
4	Li/waste eggshell (5)	Nahor oil (1:10)	65, 240	94	261
5	Mussel shell derived CaO (12)	Soybean oil (1:24)	60, 480	94.10	262
6	Egg shell CaO (3)	Sunflower oil (1:9)	60,240	94.73	263
7	Crab shell derived CaO (3)	Sunflower oil (1:6)	60, 240	83.10	263
8	Ostrich eggshell derived CaO (1.5)	Used cooking oil (1:12)	65, 120	96.00	264
9	Zeolite ZSM-5 from rice husk (0.5)	Vegetable oil (1:3)	60, 300	92.75	265

10	Dolomite (6)	Palm kernel oil (1:30)	60, 180	98.00	266
11	animal bones (20)	Rapeseed oil (1:18)	65, 240	96.78	219
12	Snail shells (2)	UCO (1:6.03)	60, 420	99.58	267
13	Oyster shells (25)	Soybean (1:6)	65, 300	96.50	268
14	CaO from natural calcites (1.5)	Palm olein oil (1:15)	60, 45	95.70	269
15	LiCO3/ peanut husk (5)	Soybean (1:12)	65, 240	98.40	270
16	Clam shell (3)	Used cooking oil (1:6.03)	60, 180	>89	271
17	Biont shells (3)	Rapeseed oil (1:9).	180	97.50	272
18	Palm empty fruit bunch (20)	Jatropha oil (1:15)	65, 90	98.54	248
19	KOH/ Palm empty fruit bunch (15)	Jatropha oil (1:15)	65, 45	99.45	248
20	Calcined wood ash (3)	Jatropha oil (1:12)	65, 180	97.70	249
21	Chemically activated wood ash (3)	Jatropha oil (1:12)	65, 210	98.50	249
22	Coco pod husk ash (1)	Soybean oil (1:6)	65, 60	98.70	250
23	Coco pod husk ash/MgO (1)	Soybean oil (1:6)	65, 120	91.40	250
24	Banana plant waste (20)	n-Butyl cinnamate (1:100)	29, 360	80.00	251

25	Na_2SiO_3@Ni / bamboo powder char (7)	Soybean oil (1:9)	65, 100	98.10	252
26	(Li/Na/K)/ Rice Husk silica (3)	Used cooking oil (1:9)	65, 60	96.5-98.2	273
27	NaOH/Rice husk ash (2.5)	Palm oil (1:12)	65, 30	97.00	274
28	NaOH/Rice husk ash (2.5)	Palm oil (1:12)	RT, 150	94.00	274
29	$LiCO_3$/ Rice husk ash (4)	Soybean oil (1:24)	65, 180	99.50	275
30	Calcined egg shell/ Rice husk ash (7)	Palm oil (1:9)	65, 240	91.50	276

1.11 Pilot plant

A pilot plant is a pre-commercial production system which is crafted to make a realistic investigation about a process or problems faced during the venture on a manageable scale within a reasonable time frame [277]. The importance of pilot scale study is that, we can identify and solve the operational problems to be faced in the large scale industrial plants before its construction [278]. Pilot plants are typically smaller than the large scale industrial plants and are intended for learning or evaluation purpose. It also offers training for persons before large scale operation [279]. Pilot plants are less expensive to build and it has operational flexibility which reduces the risks associated with the trials in large scale plants. Depending upon the purpose, pilot plants having variety of sizes are being constructed. Pilot plant provides the valuable data for the complete design of a large scale plant. The merit of pilot scale study is that, we can change the design more easily and cheaply at the pilot scale level before the construction of big plants. Pilot scale study is also informative about the processes, corrosiveness of the vessels/parts, and the technical difficulties in the operation. Redesign of the production process can also be possible in the pilot scale level [280].

Major steps behind the construction of a custom pilot plant are

1. Designing: - Designing is the master step in the construction of a custom pilot plant. It requires a meticulous knowledge about the process and keen engineering skill for designing the plant so as to meet all the theoretical and technical aspects of the process. It includes drawings of the entire process systems with vessels, equipment's layouts positions, connections, pipings, electric connections and whatever required for achieving the project goal.
2. Fabrication and assembling: - A genuine selection of the material by understanding the chemistry of the process is required for the fabrication. Fabrication of the entire components required for the process operation and its assembling will be achieved in a cost effective way within a short duration of time in the pilot scale processes.

3. Testing: - Working of the individual components will be tested to ensure its operational feasibility. Leak checking, flows, pressure controls, temperature, stirring speeds etc are properly checked and verified here.

4. Installation and start: - Once the plant is fabricated and tested, the next is its operation to ensure the plant's feasibility in the process. Redesign and alteration of the process can be done at this stage.

After the successful design, installation and working of the pilot plant, it can also be used to demonstrate the feasibility of the process in the industrial scale production [281. 282].

1.12 Pilot plants in biodiesel production

Chaturvedi and coworkers designed and developed a batch biodiesel pilot plant for rural applications [283]. It is a cost effective working plant having the production capacity of 100 liters of biodiesel from edible/non edible oils and UCO via base catalyzed route. A methanol recovery unit in the plant made the entire process economical [283]. Ramesh and coworkers constructed a cost effective pilot plant having a biodiesel production capacity of 250 litres/day via homogeneous base catalyzed route at Tamilnadu Agricultural University [284]. The biodiesel pilot plant was made of stainless steel vessels consisting of reaction vessels with heater, stirrer, chemical mixing tank, three glycerol settling tanks and a washing tank [284]. Bouaid et al prepared 100 L biodiesel per run in the pilot plant from *brassica carinata* oil using methanol with KOH as the catalyst [285]. The transesterification reaction was carried out at fixed pressure and temperature conditions in a completely stirred tank reactor made of glass having a production capacity of 200 L, which is equipped with a turbine agitator, temperature, pressure and stirring speed controllers [285]. Alptekin et al. compared the fuel properties of the corn oil and animal fat derived biodiesel produced in the pilot scale biodiesel production unit assembled at the Alternative Fuels Research and Development Center in Kocaeli University [286]. Biodiesel was produced via a two step production process (pre esterification and transesterification) in the pilot plant with the capacity of about 100 kg per day [286]. They found that the biodiesel produced in pilot scale unit have no significant differences in the fuel properties of methyl esters produced in the laboratory scale experiments [286]. Liu et al constructed a pilot plant with a production capacity of 30 metric tonnes of crude biodiesel per day from waste oil using polyferric sulphate catalysts in a stirred tank. The reactions were carried out at temperature of 100-110 °C, at a catalyst dosage of 1.5-2.0 wt% for 2 h reaction. For most of the batches, conversion of waste oil to fatty acid methyl esters was found to be above 98% at a lower methanol molar ratio of 1.5 [287]. Tint and Mya produced biodiesel from unrefined jatropha oil with methanol and ethanol using KOH in a pilot plant made of stainless steel having a production capacity of 30 gal/day. They achieved 92% (methyl ester) and 90% (ethyl ester) conversion at optimized reaction conditions of 1 wt% catalyst, at a methanol to oil reaction molar ratio of 6:1 at 65 °C for 1 h reaction [288]. Sahu and coworkers produced biodiesel from jatropha and karanja oil using methanol (6:1) and KOH (1 wt%) for a 3 h reaction at 65 °C in the pilot plant (designed and developed Centre for Rural Development & Technology, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110016, India) of production capacity 30-50 L/run [289]. Kavita et al designed and fabricated a modular and mobile bio-diesel stainless steel reactor plant for the production of 45 liters of biodiesel a day (from a total of 3 batches). Biodiesel conversion of 99-100% was achieved from waste vegetable oil under the optimized reaction conditions of catalyst NaOH 0.75 wt%, methanol to oil molar ratio of 5:1 at a temperature of 60 °C for 1 h reaction [290]. Kumar et al constructed a pilot plant using polypropylene (PP) vessels for the production of biodiesel, especially methyl esters from different non edible oil feedstocks under mild reaction conditions. The biodiesel pilot plant contains reaction vessel, catalyst tank, settling and washing chamber, evaporation chamber, and methanol recovery system. They strongly recommend the use of PP for the construction of reaction vessels for the economic production of biodiesel [291]. Still there the methanol recovery unit was made of stainless steel.

1.13 Commercial production of biodiesel over solid catalysts

Commercial biodiesel production is more affordable than ever before and the leading countries in biodiesel production and consumption are Argentina, Australia, Brazil, Belgium, Canada, China, European Union, France, Germany, India, Indonesia, Israel, Italy, Spain, Singapore, Malaysia, Taiwan, Thailand, United Kingdom, United States etc[292]. The commercial biodiesel production is mainly achieved via homogeneous catalyzed route (KOH or NaOH or NaOMe) [293]. This route has the advantage of a lower reaction time and low cost for the catalysts [294]. However, it causes operational difficulties, since the homogeneous base catalysts are highly sensitive towards moisture and free fatty acid content in the feedstock [295]. So, development of new and effective solid catalysts is necessary for the green production of biodiesel. Some of the major heterogeneous catalysts successfully employed in the commercial production of biodiesel are described below.

Bournay et al used zinc aluminate as the heterogeneous catalyst for the commercial production of biodiesel [296]. They had employed a reaction temperature of 200 °C and a pressure of 62 bar. Institut Français du Pétrole (IFP) developed this patented technology and is being commercialized by Axen in the trade name of Esterfip-H^{TM} and they have an annual production of 160,000 tonne biodiesel in the unit at Séte France [297]. Benefuel Inc., USA, in their ENSEL Process employed two catalysts; one is a double-metal cyanide (DMC) and the other one a metal oxide catalyst developed by NCL, Pune [298]. The process showed high tolerance against higher FFA level and water content [299]. A nontoxic heterogeneous catalyst named T300 developed by the researchers at Iowa State University and DOE's Ames National Laboratory was commercialized for biodiesel production by Catilin, USA and the catalyst works well as at standard pressure and temperature conditions [300]. Dossin et al developed a heterogeneous MgO catalyst for the industrial scale production of biodiesel and they achieved a production of 1,00,000 tonnes of biodiesel per year in a continuous stirred reactor of 25 m^3 containing 5700 kg of MgO catalyst [301].

1.14 Significance of the present work

Biodiesel is the most suited alternative for the conventional petrodiesel fuel. It is meant to be used in standard diesel engines without or less engine modifications making it a direct replacement for petrodiesel. The renewable origin and reduced engine exhaust emissions projected it as a green fuel. Most heavy vehicle transportation is mainly focused on diesel engines. So, in this era of depleting fossil fuel reserves, use of biodiesel has high relevance. The industrial scale biodiesel production is mainly achieved via homogeneous catalyzed transesterification reaction, which has some disadvantages. In an eco-friendly point of view, heterogeneous catalyzed biodiesel production is most preferred for the large scale biodiesel production. Unfortunately there are limited uses of solid catalysts for the commercial production of biodiesel even though many heterogeneous catalysts are reported so far for the laboratory scale transesterification reaction. It is mainly due to the non availability of efficient and low cost solid catalysts. Here, we developed solid catalysts using waste materials (coconut husk, rice husk, areca nut husk and waste borosil glass) which are mostly discarded in landfills. The present catalysts are prepared by cost effective methods and the entire process is eco-friendly. All the prepared catalysts are highly efficient in the transesterification of jatropha oil as well as used cooking oil and produces fuel grade biodiesel meeting the European as well as American international standard specifications for the biodiesel fuel.

We have designed and assembled a pilot plant consisting of vessels and valves made of PP for biodiesel production, aiming the industrial scale up straight forward. The reactions in the pilot plant are carried out at normal pressure and temperature conditions compared to most of the industrial scale production units that are operating under high pressure and temperature conditions. Another highlight of the present design is methanol recovery unit, which reduces the total production cost. The pilot plant is suitable to operate via heterogeneous catalyzed route; there is provision for the separation of catalyst enabling its reuse. The feasibility of the pilot plant in the biodiesel production is investigated by upgrading one of the best suited conditions of transesterification reaction obtained from laboratory scale experiments over one among each set of the catalysts. The custom pilot plant is a skid mount unit which can be easily transported to other places. The details of the pilot plant are discussed in the chapter 2 in the sections 2.8 and 2.9.

1.15 Objectives of the present work

The major objective of the present work is to provide a route for the effective industrial scale up for the solid catalyzed biodiesel production process. We have designed and assembled a biodiesel pilot plant in our laboratory for providing an easy industrial scale up of the process used in our studies. Some of the specific objectives in this regards are;

1. Preparation of solid catalysts using waste materials (coconut husk, rice husk, areca nut husk and waste borosil glass) and alkali metal precursors
2. Characterization of the prepared catalysts to determine the active phase responsible for its catalytic activity
3. Investigation of the effect of reaction parameters on the catalytic transesterification reaction
4. Design and assembling of pilot plant for biodiesel production
5. Up-gradation of one of the best suited reaction condition in the pilot plant
6. Analysis of the fuel properties of the biodiesel produced in the pilot plant.

References

1. http://www.bibalex.org/search4dev/files/348889/181672.pdf.
2. IEA's World Energy Outlook. Oil Gas Eur. Mag. 4, 170 (2011).
3. https://en.wikipedia.org/wiki/Population_growth#cite_note-2.
4. C. Junjie and X. Deguang, *Journal of Advancement in Engineering and Technology*, 2014, **2**, 1-7.
5. A. Demirbas, *Energy Edu. Sci. Technol. C*, 2016, **8**, 17-48.
6. A. K. Agarwal, *Prog. Energy Combust. Sci.*, 2007, **33**, 233-271.
7. R. N. Colvile, E. J. Hutchinson, J. S. Mindell and R. F. Warren, *Atmos. Envir.*, 2001, **35**, 1537-1565.
8. A. M. Ramakrishnan, *J. Pet. Environ. Biotechnol.*, 2015, 7, 1-6.
9. http://www.ed.gov.nl.ca/edu/k12/curriculum/documents/science/highschool/ES3205_student_text_chapter_18.pdf.
10. K. Sharma, *Electrical India*, 2002, **42**, 20-21.
11. A. O. Phebe and A. Samuel, *Cogent Engineering*, 2016, **3**, 1-14.
12. https://www.bp.com/content/dam/bp/pdf/energy-economics/statistical-review-2016/bp-statistical-review-of-world-energy-2016-full-report.pdf.
13. S. Yaman, *Energy Convers. Manage.*, 2004, **45**, 651-671.
14. Demirbas, *Energy Convers. Manage.*, 2002, **43**, 2349-2356.
15. http://www.columbia.edu/~mhs119/EnergyConsump/WorldPrimaryEnergy2016_pies.pdf.
16. A. Demirbas, *Energy Convers. Manage.*, 2003, **44**, 2093-2109.

17. B. K. Bala, *Energy Educ. Sci. Technol.*, 2005, **15**, 1-43.

18. M. Balat, *Energy Educ. Sci. Technol.*, 2005, **16**, 45-52.

19. https://umexpert.um.edu.my/file/publication/00003184_93153.pdf.

20. V. Kumar and P. Kant, Res. J. Chem. Sci., 2013, **3**, 64-68.

21. W. M. J. Achten, L. Verchot, Y. J. Franken, E. Mathijs, V. P. Singh, R. Aerts and B. Muys, *Biomass Bioenergy*, 2008, **32**, 1063-1084.

22. L. Bournay, D. Casanave, B. Delfort, G. Hillion and J. A. Chodorge. *Catal. Today*, 2005, **106**, 190-192.

23. HannuJl, https://www.dieselnet.com/tech/fuel_biodiesel_std.php.

24. K.Y. Ashok, E. K. Mohd, M. D. Alok and P. Amit, *Case Studies in Thermal Engineering*, 2016, **8**, 236-244.

25. M. H. Jayed, H. H. Masjuki, M. A. Kalam, T. M. I. Mahlia, M. Husnawan and A. M. Liaquat, *Renewable Sustainable Energy Rev.*, 2011, **15**, 220-235.

26. W. Yuan, A. C. Hansen and Q. Zhang, *Trans ASAE*, 2003, **46**, 1487-1493.

27. Y.C Su, Y.A. Liu. *Ind. Eng. Chem. Res.*, 2011, **50**, 6809-6836.

28. E Akbar, N. N. Binitha, Z Yaakob, S. K. Kamarudin, J. Salimon. *Green Chem.*, 2009, **11**, 1862-1866.

29. C. A. P. Singh and A. K. Sarma, *Renewable Sustainable Energy Rev.*, 2011, **15**, 4378-4399.

30. B. Sangita, K. V. A. Pradeep. *J. Sci. Ind. Res.*, 2010, **69**, 575-579.

31. EN 14103: Fat and oil derivatives – Fatty Acid Methyl Esters (FAME) -Determination of ester and linolenic acid methyl esters content.

32. Thermo Scientific Application Note #AN10212: Determination of Total FAME and Linolenic Acid Methyl Ester in Pure Biodiesel (B100) by GC in Compliance with EN 14103. www.thermo.com.

33. EN 14105: Fat and oil derivatives – Fatty Acid Methyl Esters (FAME) - Determination of free and total glycerol and mono-, di-, tri-glyceride content.

34. ASTM D6584: Standard Test Method for Determination of Free and Total Glycerin in B-100 Biodiesel Methyl Esters By Gas Chromatography.

35. Thermo Scientific Application Note #AN10192: Determination of Free and Total Glycerin in B-100 Biodiesel via Method ASTM D6584. www.thermo.com.

36. https://www.intechopen.com/books/biofuel-s-engineering-process-technology/biodiesel-production-and-quality.

37. X. Zeng, M. K. Danquah, X. D. Chen and Y. Lu, *Renewable Sustainable Energy Rev.*, 2011, **15**, 3252-3260.

38. http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.463.383&rep=rep1&type=pdf.

39. R. A. Korus, T. L. Mousetis, *J. Am. Oil Chem. Soc.*, 1984, **61**, 537-540.

40. G. Knothe, *J. Am. Oil Chem. Soc.*, 2002, **79**, 847-854.

41. M. Shahabuddin, M. A. Kalam, H. H. Masjuki, M. M. K. Bhuiya and M. Mofijur. *Energy*, 2012, **44**, 616-622.

42. R. E. Tate, K. C. Watts, C. A. W. Allen and K. I. Wilkie, *Fuel*, 2006, **85**, 1010-1015.

43. R. Kwangdinata, I. Raya and M. Zakir, *Sci. World*, 2014, **2014**, 1-5.

44. E. Alptekin and M. Canakci, *Renewable Energy*, 2008, **33**, 2623-2630.

45. S. Lee, D. Tanaka, J. Kusaka and Y. Daisho, *JSAE Rev.*, 2002, **23**, 407-414.

46. C.Y. Choi and R. D. Reitz, *J. Eng. Gas Turbines Power*, 1999, **121**, 31-37.

47. Y. Ali, M. Hanna and S. Cuppett, *J. Am. Oil Chem. Soc.*, 1995, **72**, 1557-1564.

48. J. H. F. Boog, E. L. C. Silveria, L. B. de Caland and M. Tubina, *Fuel*, 2011, **90**, 905-907.

49. N. D. D. Carareto, C. Y. C. S. Kimura, E. C. Oliveira, M. C. Costa and A. J. A. Meirelles, *Fuel*, 2012, **96**, 319-326.

50. M. O. Bagby, B. Freedman and A.W. Schwab, ASAE Paper No. 87-1583, presented at the International Winter Meeting of the ASAE, Chicago (1987).

51. W. E. Klopfenstein, *J. Am. Oil Chem. Soc.*, 1985, **62**, 1029-1031.

52. G. Knothe, A. C. Matheaus and I. T.W. Ryan, Fuel, 2003, **82**, 971-975.

53. G. I. Martins, D. Secco and H. A. Rosa, *Renewable Sustainable Energy Rev.*, 2015, **42**, 154-157.

54. K. J. Harrington, *Biomass*, 1986, **9**, 1-17.

55. M. Canakci and H. Sanli, *J. Ind. Microbiol. Biotechnol.*, 2008, **35**, 431-441.

56. Y. Ali, M. Hanna and S. Cuppett, *J. Am. Oil Chem. Soc.*, 1995, **72**, 1557-1564.

57. I. Lee, L. Johnson and E. Hammond, *J. Am. Oil Chem. Soc.*, 1995, **72**, 1155-1160.

58. A. Demirbas, *Energy Convers. Manage.*, 2009, **50**, 14-34.

59. C. D. Bannister, C. J. Chuck, M. Bounds, J. G. Hawley, *Proc IMechE Part D: J Automobile Engineering*, 2011, **225**, 99-114.

60. R. L. McCormick, S. R. Westbrook, *Energy Fuels*, 2010, **24**, 690-698.

61. E. Choe, D. B. Min, *Compr. Rev. Food Sci. Food Saf.*, 2006, **5**, 169-186.

62. H. Masjuki, M. Hassan and A. Kalam, *Procedia Eng.*, 2013, **56**, 39-53.

63. Y. Zahira, N. N. Binitha, P. Silija, U. K. Surya, P. M Akbar, *Renewable Sustainable Energy Rev.*, 2014, **35**, 136-153.

64. P. V. Rao, *World Academy of Science, Engineering and Technology* 2011, **75**, 855-868.

65. M. H. Jayed, H. H. Masjuki, M. A. Kalam, T. M. I. Mahlia, M. Husnawan and A. M. Liaquat, *Renewable Sustainable Energy Rev.*, 2011, **15**, 220-235.

66. A. Demirbas, *Biodiesel: a realistic fuel alternative for diesel engines*, Springer, London, 2008.

67. EN 14214: Automotive fuels – Fatty Acid Methyl Esters (FAME) for dieselengines- requirements and test methods.

68. ASTM D 6751: Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels.

69. https://www.worldenergy.org/wp-content/uploads/2012/10/PUB_Biofuels_Policies_Standards_and_Technologies_2010_WEC.pdf.

70. A. E. Atabani, A. S. Silitonga, H. C. Ong, T. M. I. Mahlia, H. H. Masjuki, A. B. IrfanFayaz, *Renewable Sustainable Energy Rev.*, 2013, **18**, 211-245.

71. A. Murugesan, C. Umarani, T. R. Chinnusamy, M. Krishnan, R. Subramanian and N. Neduzchezhain, *Renewable Sustainable Energy Rev.*, 2009, **13**, 825-834.

72. http://www.tistr.or.th/APEC_website/Document/2nd%20APEC%20biodiesel/2nd%20APEC%2016Jul%2008/7.%20Biodiesel%20Situation%20in%20India.pdf.

73. https://cdn.intechopen.com/pdfs-wm/23666.pdf.

74. M. M. Gui, K. T. Lee and S. Bhatia, *Energy*, 2008, **33**, 1646-1653.

75. S. P. Singh and D. Singh, *Renewable Sustainable Energy Rev.*, 2010, **14**, 200-216.

76. J. C. Juan, D. A. Kartika, T. Y. Wu and T. Y. Hin, *Bioresour. Technol.*, 2011, **102**, 452-460.

77. A. W. Schwab, M. O. Bagby and B. Freedman, *Fuel*, 1987, **66**, 1372-1378.

78. B. K. Barnwal and M. P. Sharma, *Renewable Sustainable Energy Rev.*, 2005, **9**, 363-378.

79. M. Mofijur, H. H. Masjuki, M. A. Kalam, M. A. Hazrat, A. M. Liaquat and M. Shahabuddin, *Renewable Sustainable Energy Rev.*, 2012, **16**, 5007-5020.

80. V. B. Borugadda and V. V. Goud, *Renewable Sustainable Energy Rev.*, 2012, **16**, 4763-4784.

81. M. M. Gui, K. T. Lee and S. Bhatia, Energy, 2008, **33**, 1646-1653.

82. M. G. Kulkarni and K. D. Ajay, *Ind. Eng. Chem. Res.*, 2006, **45**, 2901-2913.

83. https://www.cabi.org/isc/datasheet/28393.

84. R. V. Nair, *Controversial Drug Plants*, Universities press (India), Hyderabad, 2004.

85. T. B. Gudeta, *Journal of Biology, Agriculture and Healthcare*, 2016, **6**, 45-59.

86. R. Brittaine, N. Lutaladio, Jatropha: A Smallholder Bioenergy Crop: The Potential for Pro-Poor Development, Food and Agriculture Organization of the United Nations (FAO), Rome, Italy, 2010.

87. R. M. Jingura, R. Matengaifa, D. Musademba and K. Musiyiwa, *Biomass Bioenergy*, 2011, **35**, 2080-2086.

88. A. M. Faiz, R. Yunus, T. I. M. Ghazi and T.C.S Yaw, *Int. J. Eng. Technol.*, 2008, **5**, 92-98.

89. G. M. Gubitz, M. Mittelbach and M. Trabi, *Bioresour. Technol.*, 1999, **67**, 73-82.

90. E. Akbar, Z. Yaakob, S. K. Kamarudin, M. Ismail and J. Salimon, *Eur. J. Sci. Res.*, 2009, **29**, 396-403.

91. S. G. Stevenson, M. Vaisey-Genser, N. A. M. Eskin, *J. Am. Oil Chem. Soc.*, 1984, **61**, 1102-1108.

92. F. Soriguer, G. Rojo-Martinez, M. C. Dobarganes, J. M Garcia-Almeida, I. Esteva, M. Beltran, M. S. Ruiz De Adana, F. Tinahones, J. M. Gomez-Zumaquero, E. Garcia-Fuentes and S. Gonzalez-Romero. *Am. J. Clin. Nutr.*, 2003, **78**, 1092-1097.

93. A. B. M. S. Hossain and A. N. Boyce, *Bulgarian Journal of Agricultural Science*, 2009, **15,** 312-317.

94. D. O. Edem, *Plant. Foods Hum. Nutr.*, 2002, **57**, 319-341.

95. J. A. Banzon and A. P. Resurreccion, *Phillip. J. Coco. Studies*, 1979, **4**, 1-8.

96. K. P. Saroj and R. K. Singh, *J. Chem. Pharm. Res*, 2011, **3**, 39-49.

97. S. Y. No, *Renewable Sustainable Energy Rev.*, 2011, **15**, 131-149.

98. A. Kumar and S. Sharma, *Renewable Sustainable Energy Rev.*, 2011, **15**, 1791-800.

99. M. Chai, Q. Tu, M. Lu and Y. J. Yang, *Fuel Process. Technol.*, 2014, **125,** 106-113.

100. Z. Oybek, S. Stefan and S. Stanislav, *Acta Chim. Slovaca,* 2008, **1**, 321-328.

101. B. Cleenewerck and A. J. Dijkstra, *Fat Sci. Technol.*, 1992, **94,** 317-322.

102. N. G. Shemelis and M. M. Jorge, *AIMS Energy*, 2017, **5**, 425-457.

103. T. Verleyen, U. Sosinska, S. Ioannidou, R. Verhe, K. Dewettinck, A. Huyghebaert and W. Greyt, *J. Am. Oil Chem. Soc.*, 2002, **79,** 947-953.

104. N. Ochoa, C. Pagliero, J. Marchese and M. Mattea, *Sep. Purif. Technol.*, 2001, **22,** 417-422.

105. Y. Bo, W. Y. Hua and J.J. Guo, *J. Am. Oil Chem. Soc.*, 2006, **83,** 653-658.

106. A. Ahmad, G. Barat, R. O. Mohammad and N. Gholamhassan, *Energy Convers. Manage.*, 2012, **63**, 138-148.

107. M. Canakci and J. V. Gerpen, *Am. Soc. Agric. Eng.*, 1999, **42**, 1203-1210.

108. W. Yong, O. Shiyi, L. Pengzhan and Z. Zhisen, *Energy Convers. Manage.*, 2007, **48,** 184-188.

109. M. P. Dorado, E. Ballesteros, J. A. de Almeida, C. Schellert, H. P. Lohrelein and R. Krause, *Trans ASAE*, 2002, **45,** 525-529.

110. G. Knothe, R. O. Dunn and M. O. Bagby, Biodiesel: the use of vegetable oils and their derivatives as alternative diesel fuels. In: Fuels and Chemicals from Biomass, 1st edn. American Chemical Society, New York, 1997.

111. J. V. Gerpen, B. Shanks, R. Pruszko, D. Clements and G. Knothe, (2004) Biodiesel production technology. National Renewable Energy Laboratory, NRRL/SR-510-36244.

112. H. Fukuda, A. Kondo and H. Noda, *J. Biosci. Bioeng.*, 2001, **92,** 405-416.

113. F. Ma and M. A. Hanna, *Bioresour. Technol.*, 1999, **70**, 1-15.

114. Y. Chisti, *Biotechnol. Adv.*, 2007, **25,** 294-306.

115. H. D. Hanh, N. T. Dong, K. Okitsu, R. Nishimura and M. Yasuaki, *J. Jpn. Pet. Inst.*, 2007, **50**, 195- 199.

116. M. P Dorado, E. Ballesteros, M. Mittelbach and F. J. Lopez, *Energy Fuels*, 2004, **18**, 1457-1462.

117. I. A. Musa, *Egypt. J. Pet.*, 2016, **25**, 21-31.

118. D. Wen, H. Jiang and K. Zhang, *Prog. Nat. Sci.*, 2009, **19**, 273-284.

119. N.N.A.N. Yusuf, S.K. Kamarudin and Z. Yaakub, *Energy Convers. Manage.*, 2011, **52,** 2741-2751.

120. I.M. Atadashi, M.K. Aroua, A.R.A. Aziz and N.M.N. Sulaiman, *J. Ind. Eng. Chem.*, 2013, **19**, 14-26.

121. A. Banerjee and R. Chakraborty, *Resour. Conserv. Recycl.*, 2009, **53**, 490-497.

122. S. Gryglewicz, *Bioresour. Technol.*, 1999, **70**, 249-259.

123. Z. Helwani, M. R. Othman, N. Aziz, W. J. N. Fernando, and J. Kim, *Fuel Process. Technol.*, 2009, **90**, 1502-1514.

124. L.C. Meher, D. V. Sagar and S. N. Naik, *Renewable Sustainable Energy Rev.*, 2006, **10**, 248-268.

125. M. Mathiyazhagan and A. Ganapathi, *Research in Plant Biology*, 2011, **1,** 1-5.

126. B. Freedman, R. O. Butterfield and E. H. Pryde, oil. *J. Am. Oil Chem. Soc.*, 1986, **63,** 1375-1380.

127. D. Y. C. Leung and Y. Guo, *Fuel Process. Technol.*, 2006, **87,** 883-890.

128. T. Eevera, K. Rajendran and S. Saradha, *Renewable Energy*, 2009, **34**, 762-765.

129. J. M. Encinar, J. F. Gonzalez and A. R. Reinares, *Ind. Eng. Chem. Res.*, 2005, **44**, 5491-5499.

130. B. Freedman, E. Pyrde and T. Mounts, *J. Am. Oil Chem. Soc.*, 1984, **61**, 1638-1643.

131. F. Ma, L. D. Clements and M. A. Hanna, *Trans ASAE*, 1998, **41**, 1261-1264.

132. D. Kusdiana and S. Saka, *Bioresour. Technol.*, 2004, **91**, 289-295.

133. R. Banani1, S. Youssef, M. Bezzarga and M. Abderrabba, *J. Mater. Environ. Sci.*, 2015, **6**, 1178-1185.

134. A. Demirbas, *Prog. Energy Combust. Sci.*, 2005, **31,** 466-487.

135. S. V. Ghadge and H. Raheman, *Biomass Bioenergy*, 2005, **28,** 601-605.

136. A. Srivastava and R. Prasad, *Renewable Sustainable Energy Rev.*, 2000, **4**, 111-133

137. U. Rashid and F. Anwar, *Fuel*, 2008, **87**, 265-273.

138. B. K. Barnwal and M. P. Sharma, *Renewable Sustainable Energy Rev.*, 2005, **9**, 363-378.

139. G. Vicente, M. Marchtinez, J. Aracil and A. Esteban, *Ind. Eng. Chem. Res.*, 2005, **44**, 5447-5454.

140. M. R. Avhad and J.M. Marchetti, *Renewable Sustainable Energy Rev.*, 2015, **50**, 696-718.

141. H. H. Mardhiah, H. C. Onga, H. H. Masjuki, S. Lim and H. V. Lee, *Renewable Sustainable Energy Rev.*, 2017, **67**, 1225-1236.

142. A. V. Marjanovic, O. S. Stamenkovic, Z. B. Todorovic, M. L. Lazic and V. B. Veljkovic, *Fuel*, 2010, **89**, 665-671.

143. D. Y. C. Leung, X. Wu and M. K. H. Leung, *Appl. Energy*, 2009, **87**, 1083-1095.

144. A.P. S. Chouhan and A.K. Sarma, *Renewable Sustainable Energy Rev.*, 2011, **15**, 4378– 4399.

145. M. D. Serio, R. Tesser, L. Pengmei and E. Santacesaria, *Energy Fuels*, 2008, **22**, 207-217.

146. Y. C. Sharma, B. Singh and J. Korstad, *Biofuels*, *Bioprod. Bioref.*, 2011, **5,** 69-92 (2011).

147. A. F. Lee, J. A. Bennett, J. C. Manayil and K. Wilson, *Chem. Soc. Rev.*, 2014, **43**, 7887-7916.

148. M.E. Borges and L. Diaz, *Renewable Sustainable Energy Rev.*, 2012, **16**, 2839– 2849.

149. H. Fukuda, A. Kondo and H. Noda, *J. Biosci. Bioeng.*, 2001, **92**, 405-416.

150. J. A. Melero, J. Iglesias and G. Morales, *Green Chem.*, 2009, **11**, 1285-1308 .

151. N. S. Talha and S. Sulaiman, *ARPN J. Eng. Appl. Sci.*, 2016, **11**, 439-448.

152. A. H. West, D. Posarac and N. Ellis, *Bioresour. Technol.*, 2008, **99**, 6587-6601.

153. E. Viola, A. Blasi, V. Valerio, I. Guidi, F. Zimbardi, G. Braccio and G. Giordano, *Catal. Today*, 2012, **179**, 185-190.

154. M. Kaur and A. Ali, *Renewable Energy*, 2011, **36**, 2866-2871.

155. S. H. Teo, U. Rashid and Y. H. Taufiq-Yap, *Fuel*, 2014, **136**, 244252.

156. Y. H. Taufiq-Yap, S. H. Teo, U. Rashid, A. Islam, M. Z. Hussien and K. T. Lee, *Energy Convers. Manage.*, 2014, **88**, 1290-1296.

157. D. Kumar, G. Kumar, Poonam and C. P. Singh, *Ultrason. Sonochem.*, 2010, **17**, 839-844.

158. M. Kaur and A. Ali, *Renewable Energy*, 2011, **36**, 2866-2871.

159. H. V. Lee, J. C. Juan and Y. Y. H. Taufiq, *Renewable Energy*, 2015, **74**, 124-132.

160. G. M. Tonetto and J. M. Marchetti, *Top. Catal.*, 2010, **53**, 755-762.

161. M. Zabeti, W. M. A. W. Daud and M. K. Aroua, *Fuel Process. Technol.*, 2010, **91**, 243-248.

162. P. A. Nyoman, P. Bambang, A. P. Diah, S. Suprapto and R. Achmad, *Energy Syst. Manage.*, 2015, **1**, 159-169.

163. C. Liu, P. Lv, Z. Yuan, F. Yan and W. Luo, *Renewable Energy*, 2010, **35**, 1531-1536.

164. C. Samart, C. Chaiya and P. Reubroycharoen, *Energy Convers. Manage.*, 2010, **51**, 1428-1431.

165. H. Jeon, D. J. Kim, S. J. Kim and J. H. Kim, *Fuel Process. Technol.*, 2013, **116**, 325-331.

166. C. L. Chen, C. C. Huang, D. T. Tran and J. S. Chang, *Bioresour. Technol.*, 2012, **113**, 8-13.

167. J. M. R. Caballero, J. S. Gonzalez, J. M. Robles, R. M. Tost, M. L. A. Castillo and E. V. Alonso, *Fuel*, 2013, **105**, 518-522.

168. N. S. Torres, I. C. R. Ibarra and H. Pfeiffer, *Fuel Process. Technol.*, 2014, **120**, 34-39.

169. E. Rashtizadeh, F. Farzaneh and Z. Talebpour, *Bioresour. Technol.*, 2014, **154**, 32-37.

170. A. P. S. Dias, J. Bernardo, P. Felizardo, M. J. N. Correia, *Energy*, 2012, **41**, 344-353.

171. S. H. Wang, Y. B. Wang, Y. M. Dai and J. M. Jehng, *Appl. Catal. A: Gen.*, 2012, **439-440**, 135-41.

172. J. A. Melero, L. F. Bautista, G. Morales, J. Iglesias and R. S. Vazquez, *Chem. Eng. J.*, 2010, **161**, 323-331.

173. C. G. Sancho, R. T. Moreno, J. M. M. Robles, J. S. Gonzalez, A. J. Lopez and P. M. Torres, *Appl. Catal. B: Environ.*, 2011, **108– 109**, 161-167.

174. F. H. Alhassan, R. Yunus, U. Rashid, K. Sirat, A. Islam and H. V. Lee, *Appl. Catal. A: Gen.*, 2013, **456**, 182-187.

175. J. M. Encinar, J. F. Gonzalez, A. Pardal and G. Martinez, *Fuel Process. Technol.*, 2010, **91**, 1530-1536.

176. H. V. Lee, Y. H. Taufiq-Yap, M. Z. Hussein and R. Yunus, *Energy*, 2013, **49**, 12-18.

177. X. Bao-jin, L. Jia, Z. Fan and F. Zhen, *Energy*, 2014, **68**, 584-591.

178. E. Maleki, M. K. Aroua and N. M. N. Sulaiman, *Fuel Process. Technol.*, 2013, **112**, 129-132.

179. W. Libai, W. Yun, L. Donglian, H. Shengyang and H. Heyou, *Fuel*, 2010, **89**, 2267-2271.

180. F. Muhammad, R. Anita, N. Abdul, S. Muhammad, *RSC Adv.*, 2016, **6**, 872-881.

181. M. K. Norhasyimah, W. A. W. A. Bakar and R. Ali, *Energy Convers. Manage.*, 2017, **137**, 113-120.

182. A. P. Vyas, N. Subrahmanyam, P. A. Patel, *Fuel*, 2009, **88**, 625-628.

183. H. A. Fatah, R. Umer and Y. H. Taufiq-Yap, *Fuel*, 2015, **142**, 38-45.

184. W. Zhenzhong, Y. Xinhai, T. T. Shan, Y Jinyue and D. Erik, *Appl. Energy*, 2010, **87**, 743-748.

185. M. Vishal, S. Satnam and A. Amjad, *Renewable Energy*, 2011, **36**, 2253-2258.

186. N. Sadia, H. Liu, S. Dejan, W. Amir and W. Liang, *Fuel Process. Technol.*, 2015, **131**, 290-296.

187. S. Chanatip, K. Surachai, C. Chaiyan, R. Prasert, S. Ruengwit and C. Metta, *Arabian J. Chem.*, 2015, DOI:10.1016/j.arabjc.2014.12.034.

188. J. Tantirungrotechai, P. Chotmongkoolsap and M. Pohmakotr, *Microporous Mesoporous Mater.*, 2010, **128**, 41-47.

189. Y. H. Y. Taufiq, H. V. Lee, M. Z. Hussein and R. Yunus, *Biomass Bioenergy*, 2011, **35,** 827-834.

190. B. Gurunathan and A. Ravi, *Bioresour. Technol.*, 2015, **188**, 124-127.

191. X. Wenlei and Z. Liangliang, *Energy Convers. Manage.*, 2014, **79**, 34-42.

192. G. Lijing, T. Guangyuan, X. Guomin and W. Ruiping, *Biomass Bioenergy*, 2010, **34**, 1283-1288.

193. H. Amani, Z. Ahmad and B. H. Hameed, *Renewable Energy*, 2014, **66**, 680-685.

194. Y. Lu, Z. Zhang Y. Xu, Q. Liu and G. Qian, *Bioresour. Technol.*, 2015, **190**, 438-441.

195. T. Mohammed, Z. Min, F. Weiwei, C. Yao, Z. Ting, J. C. Samuel, Y. Liuqing, W. Xiangyang, *Energy Convers. Manage.*, 2014, **80**, 117-125.

196. K. C. Wen, H. T. Hui, C. W. Ming, C. S. En and I. C. Ching, *Int. J. Hydrogen Energy*, 2014, **39**, 19555-19562.

197. N. M. F. Rabiah, Y. Y. H. Taufiq, R. Umer, H. T. Siow, N. Z. A. Shajaratun and A. Islam, *Energy Convers. Manage.*, 2014, **88**, 1257-1262.

198. L. Ming, Z. Yan, C. Yixin and Z. Xifeng, *Bioresour. Technol.*, 2014, **154**, 345-348.

199. S. E. Mahesh, R. Anand, K. M. M. S. Begum and N. Anantharaman, *Energy Convers. Manage.*, 2015, **91**, 442-450.

200. I. Istadi, S. I. Prasetyo and T. S. Nugroho, *Procedia Environ. Sci.*, 2015, **23**, 394-399.

201. F. H. Alhassan, U. Rashid and Y. Y. H. Taufiq, *J. Oleo Sci.*, 2015, **64**, 505-514.

202. H. V. Lee, J. C. Juan and Y. Y. H. Taufiq, *Renewable Energy*, 2015, **74,** 124-132.

203. F. H. Alhassan, R. Umer , Y. Robiah, S. Kamaliah, M. I. Lokman and Y. Y. H. Taufiq, Int. J. *Green Energy*, 2015, **12**, 987-994.

204. H. J. Kim, B. S. Kang, M. J. Kim, Y. M. Park, D. K. Kim, J. S. Lee and K. Y. Lee, *Catal. Today*, 2004, **93-95**, 315-320.

205. J. X. Wang, K. T. Chen, S. T. Huang, K. T. Chen and C. C. Chen, *J. Am. Oil Chem. Soc.*, 2012, 89, 1619-1625.

206. D. Yuqi, S. Hui, D. Jinzhao, C. Ping, L. Hui and Z. Xiaoming, *Catal. Commun.*, 2011, **12**, 606-610.

207. S. P. Karuppiah and P. Muthiah, *RSC Adv.*, 2015, **5**, 11180-11187.

208. S. Chuanjia, F. Qiu, D. Yang and B. Ye, *Fuel Process. Technol.*, 2014, **126**, 383-391.

209. M. J. Kim, M. Y. Kim, O. Z. Kwon and G. Seo, *Fuel Process. Technol.*, 2011, **92**, 126-131.

210. X. Wenlei, Y. Xinli and F. Mingliang, *Renewable Energy*, 2015, **80**, 230-237.

211. C. Guanyi, S. Rui, S. Jiafu, L. Changye and Y. Beibei, *Energy Convers. Manage.*, 2015, **98**, 463-469.

212. C. G. Sancho, R. M. Tost, J. M. M. Robles, J. S. Gonzalez, A. J. Lopez and P. M. Torres, *Appl. Catal. B: Environ.*, 2011, **108–109,** 161-167.

213. A. J. Lopez, I. J. Morales, J. S. Gonzales and P. M. Torres, J. Mol. *Catal. A: Chem.*, 2011, **335,** 205-209.

214. W. Xie and D. Yang, *Bioresour. Technol.*, 2012, **119**, 60-65.

215. N. Narkhede and A. Patel, *Ind. Eng. Chem. Res.*, 2013, **52**, 13637-13644.

216. F. A. Dawodu, O. Ayodele, J. Xin, S. Zhang and D. Yan, *Appl. Energy*, 2014, **114**, 819-826.

217. D. Salinas, S. Guerrero, A. Cross , P. Araya and E. E. Wolf , *Fuel*, 2016, **166**, 237-244.

218. T. Wan, P. Yu, S. Wang and Y. B. Luo, *Energy Fuels*, 2009, **23**, 1089-1092.

219. W. Xie and X. Huang, *Catal. Lett.*, 2006, **107**, 53-59.

220. C. I. S. Leon, D. Song, F. Su, S. An, H. Liu, J. Gao, Y. Guo and J. Leng, *Microporous Mesoporous Mater.*, 2015, **204,** 218-225.

221. S. T. Jiang, F. J. Zhang and L. J. Pan, *Braz. J. Chem. Eng.*, 2010, **27**, 137-144.

222. R. Sridharan and I. M. Mathai, *J. Scient. Ind. Res.*, 1974, **33**, 178-187.

223. E. W. Eckey, JAOCS, 1956, **33**, 575-579.

224. P. M. Ejikeme, I. D. Anyaogu, C. L. Ejikeme, N. P. Nwafor, C. A. C. Egbuonu, K. Ukogu and J. A. Ibemesi, *E-J. Chem.*, 2010, **7**, 1120-1132.

225. W. Stoffel, F. Chu and E. H. Ahrens, *Anal. Chem.*, 1959, **31**, 307-308.

226. K. Narasaka, M. Yamaguchi and T. Mukaiyama, *Chem. Lett.*, 1977, **6**, 959-962.

227. J. P. Guthrie, *J. Am. Chem. Soc.*, 1991, 113, 3941-3949.

228. M. W. Formo, *J. Am. Oil Chem. Soc.*, 1954, **31**, 548-559.

229. B. Sanjay, *Res. J. Chem. Sci.*, 2013, **3**, 95-101.

230. R. Chakraborty, S. Chatterjee, P. Mukhopadhyay and S. Barman, *Procedia Environ. Sci.*, 2016, **35**, 546-554.

231. Z. Wei, C. Xu, and B. Li, *Bioresour. Technol.*, 2009, **100**, 2883-2885.

232. N. Nakatani, H. Takamori, K. Takeda, and H. Sakugawa, *Bioresour. Technol.*, 2009, **100**, 1510–1513.

233. J. Xie, X. Zheng, A. Dong, Z. Xiao and J. Zhang, *Green Chem.*, 2008, **11**, 355-364.

234. N. Viriya-empikul, P. Krasae, B. Puttasawat, B. Yoosuk, N. Chollacoop and K. Faungnawakij, *Bioresour. Technol.*, 2010**,** **101**, 3765-3767.

235. P. L. Boey, G. P. Maniam, S. A. Hamid and D. M. H. Ali, *Fuel*, 2011, **90**, 2353-2358.

236. A. Birla, B. Singh, S. N. Upadhyay and Y. C. Sharma, *Bioresour. Technol.*, 2012**, 106**, 95-100.

237. R. Chakraborty, S. Bepari and A. Banerjee, *Bioresour. Technol.*, 2011, **102**, 3610-3618.

238. M. Farooq, A. Ramli and A. Naeem, *Renewable Energy*, 2015, **76**, 362-368.

239. P. L. Boey, G. P. Maniam and S. A. Hamid, *Bioresour. Technol.*, 2009, **100**, 6362-6368.

240. A. Obadiah, G. A. Swaroopa, S. V. Kumar, K. R. Jeganathan and A. Ramasubbu, *Bioresour. Technol.*, 2012, **116**, 512-516.

241. K. Urasaki, S. Takagi, T. Mukoyama, J. Christopher, K. Urasaki, S. Kato, A. Yamasaki, T. Kojima and S. Satokawa, *Appl. Catal. A: Gen.*, 2012, **411-412**, 44-50.

242. M. Kouzu and J. Hidaka, *Fuel*, 2012, **93**, 1-12.

243. M. L. Granados, D. M. Alonso, I. Sadaba, R. Mariscal and P. Ocon, *Appl. Catal. B: Environ.*, 2009, **89**, 265-272.

244. P. Kumar, A. K. Sarma, M. K. Jha, A. Bansal and B. Srivasatava, Bull. *Chem. React. Eng. Catal.*, 2015, **10**, 221-229.

245. M. K. Misra, K. W. Ragland and A. J. Baker, *Biomass Bioenergy*, 1993, **4**, 103-116.

246. O. Babajide, L. Petrik, N. Musyoka, B. Amigun and F. Ameer, *Pet. Coal*, 2010, **52**, 261-272.

247. F. Ezebor, M. Khairuddean, A. Z. Abdullah and P. L. Boey, *Energy*, 2014, **70**, 493-503.

248. Y. Zahira, S. B. S. Irwan, N. N. Binitha, R. S. A. Siti and I. Manal, *Bioresour. Technol.*, 2012, **104**, 695-700.

249. M. Sharma, A. A. Khan, S. Puri and D. Tuli, *Biomass Bioenergy*, 2012, **41**, 94-106.

250. C. O. Boateng and K. T. Lee, *Chem. Eng. J.*, 2013, **220**, 395-401.

251. S. Pathak and D. C. Deka, *J. Chem. Pharm. Res.*, 2016, **8**, 486-491.

252. F. Zhang, X. H. Wu, M. Yao, Z. Fang and Y. T. Wang, *Green Chem.*, 2016, **18**, 3302-3314.

253. W. Roschat, T. Siritanon, B. Yoosuk and V. Promarak, *Energy Convers. Manage.*, 2016, **119**, 453-462.

254. G. Y. Chen, R. Shan, J. F. Shi and B. B. Yan, *Fuel Process. Technol.*, 2015, **133,** 8-13.

255. K. T. Chen, J. X. Wang, Y. M. Dai, P. H. Wang, C. Y. Liou, C. W. Nien , J. S. Wu and C. C. Chen, *J. Taiwan Inst. Chem. Eng.*, 2013, **44,** 622-629.

256. C. Lingfeng, X. Guomin, X. Bo and T. Guangyuan, *Energy Fuels*, 2007, **21**, 3740-3743.

257. G. Teng, L. Gao, G. Xiao and H. Liu, *Energy Fuels*, 2009, **23**, 4630-4634.

258. S. Suchada, A. Maidinamu, G. Guoqing, S. Chanatip, A. Shawket, H. Xiaogang, K. Katsuki and A. Abuliti, *Energy Convers. Manage.*, 2015, **95**, 242-257.

259. H. Hadiyanto, P. L. Sri, A. Abdullah, W. Widayat and S. Heri, *Int. J. Energy Environ. Eng.*, DOI 10.1007/s40095-016-0212-6.

260. M. Farooq, A. Ramli and A. Naeem, *Renewable Energy*, 2015, **76**, 362-368.

261. B. Jutika, L. J. Konwar and D. Deka, *Fuel Process. Technol.*, 2014, **122**, 72-78.

262. R. Rezaei, M. Mohadesi and G. R. Moradi, *Fuel*, 2013, **109**, 534-541.

263. L. M. Correia, R. M. Saboya, N. S. Campelo, J. A. Cecilia, E. R. Castellon, J. C. L. Cavalcante and R. S. Vieira, *Bioresour. Technol.*, 2014, **151**, 207-213.

264. Y. H. Tan, M. O. Abdullah, C. N. Hipolito and Y. H. Taufiq-Yap, *Appl. Energy*, 2015, **160**, 58–70.

265. U. Septiani, R. A. Putri and N. Jamarun, *Der. Pharmacia. Lettre.*, 2016, **8**, 86-91.

266. C. Ngamcharussrivichai, P. Nunthasanti, S. Tanachai and K. Bunyakiat, *Fuel Process. Technol.*, 2010, **91,** 1409-1415.

267. A. Birla, B. Singh, S. N. Upadhyay and Y. C. Sharma, *Bioresour. Technol.*, 2012, **106**, 95-100.

268. N. Nakatani, H. Takamori, K. Takeda and H. Sakugawa, *Bioresour. Technol.*, 2009, **100**, 1510-1513.

269. B. Yoosuk, P. Udomsap, B. Puttasawat and P. Krasae, *Chem. Eng. J.*, 2010**, 162,** 135-141.

270. Y. M. Dai, K. T. Chen, Y. J. Wang and C. C. Chen, *Int. J. Chem. Eng. Appl.*, 2014, **5**, 276-280.

271. P. Nair, B. Singh, S. N. Upadhyay and Y. C. Sharma, *J. Cleaner Prod.*, 2012, **29-30**, 82-90.

272. J. Xie, X. Zheng, A. Dong, Z. Xiao and J. Zhang, *Green Chem.*, 2008, **11**, 355-364.

273. N. Hindryawati, G. P. Maniam, M. R. Karim and K. F. Chong, *Engineering Science and Technology, an International Journal*, 2014, **17,** 95-103.

274. W. Roschat, T. Siritanon, B. Yoosuk and V. Promarak, *Energy Convers. Manage.*, 2016, **119,** 453-462.

275. K. T. Chen, J. X. Wang, Y. M. Dai, P. H. Wang, C. Y. Liou, C. W. Nien, J. S. Wu and C. C. Chen, *J.Taiwan Inst. Chem. Eng.*, 2013, **44**, 622-629.

276. G. Y. Chen, R. Shan, J. F. Shi and B. B. Yan, *Fuel Process. Technol.*, 2015, **133**, 8-13.

277. B. H. Junker, *Pilot Plants: Design and Operation. Encyclopedia of Industrial Biotechnology*, John Wiley & Sons, 2009.

278. J. G. Lowenstein, Chem. Eng., 1985, **92,** 62-76.

279. P. Richard, *Pilot Plants: Design, Construction and Operation*, McGraw-Hill, New York, 1992.

280. D. Anderson and D. Masterson, International Palm Oil Conference, 2003, 6-9.

281. J. Frishammar, P. Soderholm, K. Backstrom, H. Hellsmark and H. Ylinenpaa, *Technol. Anal. Strateg. Manage.* 2014, **27**, 1-18.

282. H. Hellsmark, J. Frishammar, P. Soderholm and H. Ylinenpaa, *Research Policy*, 2016, **45**, 1743-1761.

283. O. P. Chaturvedi, S. Mande, P. Rajan, and K. Kundu, *ZENITH International Journal of Multidisciplinary Research*, 2013, **3**, 46-52.

284. D. Ramesh, A. Samapathrajan and P. Venkatachalam, *The Jatropha Journal*, 2006, **18**, 1-6.

285. A. Bouaid, Y. Diaz, M. Martinez and J. Aracil, *Catal. Today*, 2005, **106**, 193-196.

286. E. Alptekina, M. Canakci and H. Sanli, *Waste Manage.*, 2014, **34**, 2146-2154.

287. R. Liu, C. Li, H. Zhang, Z. Xiao, A. Zhang and J. Chen, *Energy Sources, Part A*, 2017, **39**, 29-35.

288. T. T. Kywe and M. M. Oo, *World Academy of Science, Engineering and Technology*, 2009, **50**, 477-483.

289. G. Sahu, L. M. Das, B. K. Sharma and S. N. Naik, *Asia-Pac. J. Chem. Eng.*, 2011, **6,** 38-43.

290. S. H. Kavita, V. Krishnamurthy, M. N. C. Prabha and R. Makam, *Kathmandu University Journal of Science, Engineering and Technology*, 2015, **11**, 61-68.

291. R. K. Kumar, Channarayappa, K. T. Prasanna and B. Gowda, *Biomass Convers. Bioref.*, 2013, **3**, 79-86.

292. https://en.wikipedia.org/wiki/Biodiesel_by_region.

293. W. Zhou and D. B. G. Boocock, *J. Am. Oil Chem. Soc.*, 2006, **83**, 1041-1045.

294. A. V. Tomasevic and S. S. S. Marinkovic, *Fuel Process. Technol.*, 2003, **81**, 1-6.

295. Z. Helwani, M. R. Othman, N. Aziz, W. J. N. Fernando and J. Kim, *Fuel Process. Technol.*, 2009, **90**, 1502-514.

296. L. Bournay, D. Casanave, B. Delfort, G. Hillion and J. A. Chodorge, *Catal. Today.*, 2005, **106**, 190-192.

297. R. Stern, G. Hillion and J. J. Rouxel, Process for the production of esters from vegetable oils or animal oils alcohols. (1999) US Patent 5: 908–946.

298. Benefuel - www.benefuel.net.

299. Phil Thane, "Breaking Away from Potassium Hydroxide" Biofuels International, Nov. (2008) 53.

300. http://biodieselmagazine.com/articles/3536

301. T. F. Dossin, M. F. Reyniers, R. J. Berger and G. B. Marin, *Appl. Catal. B*, 2006, **67**, 136-148.

CHAPTER 2

MATERIALS AND METHODS

Designed, Assembled and Installed a Biodiesel Pilot Plant made of Polypropylene Vessels for the Pilot Scale Production of Biodiesel

2.1 Introduction

The conventional homogeneous catalyzed industrial biodiesel production process is associated with operational problems and challenges [1]. For industrial purposes, heterogeneous catalysis is more suitable and it overcomes the problems associated with the homogeneous catalyzed biodiesel production [2]. Only limited successful reports are available for the large scale production of biodiesel via heterogeneous catalyzed route because of the high cost and non-availability of the catalyst as well as the tedious steps required in the catalyst development. Additionally, the catalyst production requires extra care in controlling pH, stirring rate, temperature etc [3]. Solid catalysts derived from natural resources or biomaterials as well as waste materials can effectively replace the conventional homogeneous catalysts thereby solving most of the hurdles in the biodiesel production processes [4]. Development of solid catalysts from renewable sources or from waste materials makes the process eco-friendly and economically viable [5]. Here we could develop 4 different sets of solid catalysts from waste materials; and among them, three sets are prepared by their reaction with alkali metal precursors. The catalyzed production of biodiesel from used cooking oil (UCO) and jatropha oil (JCO) is also effectively scaled up in the pilot plant designed and assembled in our laboratory. Simple methods and mild conditions are employed for the preparation of all the catalysts that makes the process greener, aiming the industrial scale-up straightforward and cost-effective. This chapter mentions the materials employed in the preparation of biodiesel and catalysts, characterization and analytical techniques used to explore the nature and the active phases of the catalysts prepared, procedures of the laboratory scale experiments done for the investigation of the effect of reaction parameters and catalyst reusability in the biodiesel preparation, design and assembling of the parts of biodiesel pilot plant, detailed description of the scale up of the reaction under the selected conditions in the pilot plant, methanol recovery and purification of the biodiesel etc and also the fuel property analysis of the produced biodiesel samples.

2.2 Materials Used

All the materials used in the preparation of biodiesel in the laboratory scale and in the pilot plant including catalyst precursors are tabulated in the table 2.1. All the chemicals used were of analytical grade and only deionised water was used in the experiments.

Table 2.1 Materials used

Sl. No	Material	Manufacturer/Supplier
1	Waste Cooking oil	Catering centers at Pattambi
2	*Jatropha curcas* oil	Extracted from *jatropha curcas* seeds using oil expeller (Rajkumar Agro Engineers Pvt Ltd, Nagpur, India)
3	Methanol	Merck Specialities Pvt. Ltd.
4	Isopropyl alcohol	NICE Chemicals Pvt. Ltd.
5	Phosphoric acid	NICE Chemicals Pvt. Ltd.
6	Con. HCl (35%)	NICE Chemicals Pvt. Ltd.
7	Anhydrous sodium sulphate	NICE Chemicals Pvt. Ltd.
8	Coconut husk	Local coconut farm

9	Areca nut husk	Local areca nut farm
10	Sodium hydroxide	NICE Chemicals Pvt. Ltd.
11	Rice husk	RARS pattambi
12	Anhydrous Lithium nitrate	NICE Chemicals Pvt. Ltd.
13	Broken borosil® glass beakers	From our laboratory
14	Citric acid mono hydrate	NICE Chemicals Pvt. Ltd.
15	Iodine monochloride	NICE Chemicals Pvt. Ltd.
16	Potassium iodide	NICE Chemicals Pvt. Ltd.
17	Sodium thiosulfate	NICE Chemicals Pvt. Ltd.
18	Starch	NICE Chemicals Pvt. Ltd.
19	*N*-Methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA)	Sigma Aldrich Pvt. Ltd India
20	Heptane	Merck Chemicals Pvt. Ltd
21	Biodiesel standards	Sigma Aldrich Pvt. Ltd India

2.3 Analytical techniques

The catalysts prepared by the reaction between waste materials and alkali metal precursors as well as by the combustion of coconut husks are analyzed using different techniques to find out their composition, structure and morphology in order to determine the active sites that are responsible for catalysis. Fourier Transform Infrared (FTIR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron Microscopy (TEM), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), temperature programmed desorption (TPD) of CO_2 etc are the various techniques used for the characterization of the prepared catalysts. Gas chromatography (GC) is used to evaluate the fatty acid methyl ester

(FAME) content in the biodiesel samples. FAME content in the biodiesel is compared with the quantity mentioned in the fuel specification of the biodiesel according to European (EN 14214) as well as American standards (ASTM D 6751). The percentage chemical composition of the biodiesel fuel was analyzed with gas chromatography-mass spectroscopy (GCMS). The fuel properties of biodiesel produced in the pilot plant, such as FAME content, acid value, iodine number, viscosity, water content, density etc are determined and compared with the standard fuel specifications.

2.3.1 Fourier transform infrared (FTIR) spectroscopy

Infra red spectroscopy is a spectroscopic technique used to identify the chemical compounds and to investigate and elucidate the composition of unknown samples by recording the absorption spectra of the substances in the near, mid and far infrared regions. This technique deals with the interaction of a molecule with radiation in the IR region of the electromagnetic spectrum. Molecular vibrations of the atoms in the compounds are responsible for the FTIR spectrum which is recorded with the intensity of infrared radiation as a function of frequency or wavelength. The spectrum is obtained by passing infrared radiation through the sample and analyzing the radiation absorbed/transmitted, which corresponds to the energy (frequency) of vibration of a part of the sample molecule and recorded as a peak. The light transmitted through the sample contains information about the material to be studied and this technique is irrespective of the phase of the material (solid, liquid or gas). The most useful IR region for sample analysis lies between 4000 cm^{-1} to 400 cm^{-1} where we can study the fundamental vibrations and associated rotational vibrations of the molecules. The region 4000 cm^{-1}-1450 cm^{-1} is known as the functional group region, where the most useful information obtained from an IR spectrum is about the functional groups present within the molecule. IR region below 1450 cm^{-1} contains complicated series of absorption peaks mainly due to all manners of bending vibrations within the molecule, known as the fingerprint region; here the spectra tend to be more complex and much harder to assign. In the case of metal oxide related species, even stretching bands occurs below 1450 cm^{-1} and provides useful information about the structure of the materials [6-10].

In the present study, the catalysts prepared by the treatment of alkali metal precursors with different waste materials as well as catalysts derived from coconut husks were analyzed using FTIR spectral techniques. The FTIR spectra gave an idea about the chemical bonding, composition and material formation in the catalyst systems. The FTIR spectral analysis of the catalyst derived from coconut husk were done using NICOLET6700 FTIR Thermo scientific in the region of 400-4000 cm^{-1} by means of KBr pellet method. For the analysis of the catalysts derived from rice husk, areca nut husk and waste borosil® glass, the FTIR spectra were recorded using THERMO NICOLET AVATAR 370 in the region of 400-4000 cm^{-1}.

2.3.2 X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) is a non destructive analytical technique employed for the qualitative and quantitative analysis of the crystal structure and chemical composition of the materials and thin films. X-ray diffraction technique investigates the crystal structure and atomic spacing of the materials by quantifying the scattered intensity of the X-ray beam hit on the sample as a function of incident and scattered angle. It is based on constructive interference of monochromatic X-rays and a crystalline sample. X-rays are electromagnetic radiation with wavelengths between about 0.02 Å and 100 Å and they are of higher energy that can penetrate to the matter more easily. Their ability to penetrate to the matter depends on the density of the matter. When X-ray radiation passes through the matter, it interacts with the electrons in the atoms, resulting in its scattering. If the atoms are organized in planes (i.e., the matter is crystalline) and the distances between the atoms are of the same magnitude as the wavelength of the X-rays, constructive and destructive interference will occur. The interaction of X-rays with crystalline substances produces diffraction pattern when constructive interference takes place and is called X-ray diffraction and the condition can be expressed by Bragg's law, $n\lambda = 2d \sin\theta$, where, 'λ' is the wavelength of X-rays, 'd' is the inter-planar distance and 'θ' is the angle of diffraction. X-ray diffraction is of two types, powder and single crystal diffraction. Here we are using the powder diffraction technique to analyze the catalysts. The powder sample is assumed to be consisted of a number of crystallites which are oriented in a random manner. When monochromatic X-rays are allowed to fall on the powder sample, diffraction takes place from the planes which are properly oriented at the correct angle to satisfy the Bragg's law. The observed diffraction pattern is recorded by a diffractometer. The diffraction pattern thus formed is unique for each material. If the sample consists of different phases, then each phase produces its own diffraction patterns. Lattice spacing for different planes and percentage of amorphous and crystalline phases of samples can be obtained from XRD analysis [11-15].

In the present study, the crystal structure, crystalline phase and chemical composition of the prepared solid catalysts is determined using XRD analysis. The active phase responsible for the catalytic activity of the catalysts in the transesterification reaction is also verified from by the XRD measurements and is compared with the standard JCPDS database. The powder diffraction patterns of the catalysts derived from coconut husk ash and rice husk ash were recorded on a Bruker AXS D8 Advance diffractometer using Cu Kα radiation as X-ray source (Kα =1.542 Å). In XRD analysis, all the samples were scanned in the 2θ range of 3°-80°. Rigaku Mini flex 600 diffractometer is used for the XRD analysis of the catalysts from arecanut husk and waste glass.

2.3.3 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is an advanced non destructive technique used to analyze the surface structure of solid samples by magnifying the image of the samples to a resolution range of few nanometers using high energy electron beams. In the SEM analysis, the electron beam is produced with the help of an electron gun and is swept in a raster over the surface of the specimen. The interaction of electron beam with surface atoms of the sample will produce signals corresponding to secondary electrons, back scattered electrons, characteristic X-rays, cathodoluminescence, auger electrons, specimen current, transmitted electrons etc, depending on the nature of the sample and it provides informations about the surface morphology, composition and electrical conducting properties of the samples. The signals developed by the instrument is recorded on a screen as a three dimensional image containing the morphology of the sample. Generally, SEM analysis is conducted under vacuum and the samples are prepared by coating on a carbon tape (conducting) and in the case of non conducting samples, sputter coating with gold is used [16-20]. On combination with EDS, we can find out the percentage composition of the elements in the samples.

Surface morphology of the catalytic systems prepared in the present work were analyzed by the Jeol JSM - 6390LV scanning electron microscope. From the SEM analysis, macroporous structures of the solid catalysts are revealed which is beneficial for the activity of catalysts in the transesterification reaction. The elemental analysis and hence the percentage composition of the catalytic systems prepared from coconut husk was performed with the SEM-EDS combination using OXFORD XMX N energy dispersive spectrometer.

2.3.4 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is a high magnification and ultra resolution microscopic technique used to analyze the morphology and topography of the samples. It gives a clear picture about the microstructure of the specimens including crystalline structure and composition. In the operation, TEM resembles the working of an optical microscope, where the electron beams are used instead of light rays and the electromagnetic condenser lenses replaces the normal optical lenses. Compared to the optical microscope, TEM gives high magnification of about one million times and ultra resolution even in less than 1 nanometer range.

In TEM, high energy electron beam produced by the electron gun is focused on the sample through the condenser lens and the electrons transmitted after the interaction with the sample are magnified and focused to the imaging device to get a two dimensional black and white image of the sample. Depending upon the structure and nature of the materials, the interaction of electron with the sample may cause diffraction, transmission and scattering which produces scattered electrons i.e., elastic and inelastic scattered electrons, transmitted electrons, X-rays, Auger electrons, etc. For a sample to show a good TEM image, it must be transparent to the electron (thin or porous materials) and must be able to withstand vacuum.

Using TEM, we can identify the particle size, grain and crystallite size, particle size distribution as well as lattice fringes and hence the structure of the material can be illustrated [21-25]. The TEM analysis of the catalysts was done using Jeol JEM - 2100 transmission electron microscope. The macroporous nature of the catalysts beneficial for the activity in the transesterification is also confirmed from the TEM analysis.

2.3.5 Inductively coupled plasma-atomic emission spectroscopy (ICP-AES)

By the inductively coupled plasma-atomic emission spectroscopic (ICP-AES) technique, the metal composition in the sample can be analyzed. ICP-AES is an emission spectroscopic technique usually used to detect the metals present even at minor or trace quantity in the sample. Around 60 elements can be analyzed at a time using a single source. In this technique, inductively coupled plasma is used to excite the atoms or ions in the sample to higher energy levels and returned to the ground state by emitting the radiation characteristic to the elements. Normally, samples for analysis are prepared by making a solution with concentrated acids and the diluted sample solution is aspirated to the instrument. Atomization or ionization of the elements will be achieved and they reach the plasma with the help of argon gas at an elevated temperature of about 7000 °C; here the excitation of the outer shell electrons takes place. These excited electrons emit radiation having a wavelength characteristic to the element with intensity corresponding to the concentration of the element [26-30]. In the present study, we use SPECTRO ACROS simultaneous ICP spectrometer in the spectral range 130 nm to 770 nm to a approximate resolution of 0.009 nm and Thermo Electron IRIS

INTREPID II XSP DUO in the spectral range 165 to >1000 nm of resolution 0.005 nm at 200 nm for the elemental analysis of catalyst derived from coconut husk and waste borosilicate glass respectively. ICP-AES analysis gave the percentage composition of the elements present in the catalyst and thus confirmed its nature.

2.3.6 Temperature-programmed desorption (TPD) of CO_2

The basicity or acidity of the catalysts can be analyzed using temperature programmed desorption (TPD) technique. This method of analysis was introduced by Amenomiya and vetanovic in 1963. In this method, desorption of adsorbed gases on the samples occurs by means of programmed heating and eluted gas is analyzed. In a typical TPD experiment, a definite amount of the catalyst is kept in a reactor and heated to a programmed temperature with the aid of a furnace. At first an inert carrier gas, usually argon, nitrogen or helium flows over the catalyst and a suitable adsorbate is then injected to the carrier column where it gets adsorbed on the surface of the catalyst. After a sufficient time of exposure, the gas that is not adsorbed is flushed out of the system. Then the catalyst is heated where the temperature rises linearly with time. A suitable gas chromatographic detector is used to analyze the changes in the carrier gas stream. As the catalyst is heated, the adsorbate is desorbed into the carrier gas stream and is detected by the detector. The spectrum thus obtained depends on the nature of the catalyst, heating rate and surface coverage. In TPD, the strength of basic or acidic sites in the sample can be calculated from the amount of desorbed gas. The information obtained from the desorption studies includes the surface concentration and the nature of the active sites. Higher the desorption temperature of CO_2, stronger will be the basic sites because strongly bound molecules have high binding energies which increases the desorption temperatures. The catalysts usually shows weak, medium and strong basic sites corresponding to desorption peaks obtained at a temperature range of room temperature to 200 °C, 200 °C-400 °C and above 400 °C respectively [31-34].

The basicity of the catalysts prepared from waste borosilicate glass and arecanut husk were investigated using the instruments BELCAT II Version 0.4.5.16 and Micromeritics Chemisorb 2750 respectively via temperature programmed desorption (TPD) of CO_2 by using Helium as the carrier gas. The amount of CO_2 desorbed is taken as a measure of the basicity and the desorption temperature indicated the strength of basic sites [35].

2.3.7 Gas chromatography

Chromatographic methods are used to separate mixtures of compounds based on their physical properties. The important chromatographic methods are gas chromatography (GC) and liquid chromatography (LC, often termed as high-performance liquid chromatography (HPLC)). In GC, the mixture is separated mainly based on the difference in the polarity, boiling point and the structure of the individual compounds. To carry out a GC analysis, the sample is usually dissolved in low concentrations in an organic solvent and then injected into the gas chromatograph. In some cases, the sample needs to be derivatized with a specific reagent in order to obtain a useful gas chromatogram. Derivatization with MSTFA is required for biodiesel analysis. The main intention of the derivatization is to make the sample volatile. After injection of the volatile sample into the gas chromatograph, it is carried through the column by a carrier gas and the components are separated. A column is a long, thin path (usually capillary tube) that contains a material with which the sample components interact more or less strongly depending on their structure (may be polarity). The separated components reach the detector while heating; one of the common detectors, i.e. flame ionization detector, is used in the present study. When the detector detects a material eluted from the column at a certain retention time, this will be shown by a peak in the chromatogram. Generally, the integrated value of the peak amplitude over time is proportional to the amount of material. This constitutes the usefulness of GC in quantifying the amounts of components in a mixture. Glycerol and mono- and diacylglycerols containing free hydroxyl groups, is not performing well in the GC. Derivatization improves their performance considerably. Derivatization can provide better resolution between compounds with similar properties. Often standards are used in GC, which are known compounds that will indicate the presence of those compounds in the mixture based on their retention time in the column. Standards are therefore very useful in establishing the presence of specific compounds in a mixture [36-40].

Here biodiesel is analyzed using Thermo Fisher Trace GC 700 Gas Chromatograph equipped with MXT® biodiesel TG column and flame ionization detector as per the standard procedure. The condition for GC analysis of biodiesel sample of the present study as per ASTM D 6584 specification is given below.

Injector

Cool on column injection: Programme, oven track Sample size: 1μL

Mode: Splitless Column Flow: 30 mL/min , Injection Volume: 1 μL

Injector Temperature Programme

Temp1: 55 °C Time1: 1 min Rate1: 15°/min Temp2: 180 °C
Time2: 0 min Rate2: 7°/min Temp3: 230 °C Time3: 0 min
Rate3: 30°/min Temp4: 360 °C Time4: 10 min Rate4: 0°/min

Detector

Type: Flame Ionization Temperature : 350 °C Carrier Gas : Nitrogen

Oven

Column: MXT® biodiesel TG column

Oven Temperature Programme

Temp1: 55 °C Time 1: 1 min Rate 1: 15°/min Temp 2: 180 °C

Time 2: 0 min Rate2: 7°/min Temp 3: 230 °C Time 3: 0 min

Rate 3: 30°/min Temp 4: 360 °C Time 4: 10 min Rate4: 0°/min

2.3.8 Gas chromatography-mass spectrometry

The percentage composition of each of the methyl esters present in the biodiesel were evaluated by gas chromatography–mass spectrometry (GC-MS). It is an analytical method that combines the features of gas chromatography and mass spectrometry to identify different substances within a test sample. The GC-MS instrument separates chemical mixtures in the GC component and identifies the components at the molecular level in the MS component. It is one of the most accurate tools for analyzing organic samples. In the GC, mixture will separate into individual substances when heated. As the separated substances emerge from the column opening, they flow into the MS. MS identifies the compounds by determining the mass of the analyte molecule and then by comparing it with the standard mass spectral library of known mass spectra of known compounds, covering several thousand compounds. MS is considered as the only definitive analytical detector in GC [41-45]. Here the UCO biodiesel was analyzed using PerkinElmer Autosystem XL GC TurboMass Gold Mass Spectrometer with TurboMass 6.1.0.1963 software and JCO biodiesel using Agilent 6890 GCMS with MSD chemstations software for investigating the fatty acid profile in the samples.

2.4 Purification of oil feedstock

UCO was collected from a local catering center. It was filtered using a fine cotton cloth to remove all the insoluble impurities. JCO was expelled from *jatropha curcas* seeds and filtered by means of an oil expeller and filtration unit (Rajkumar Agro Engineers Pvt Ltd, Nagpur, India). Both the oils are then subjected to degumming to remove the soluble gums inherently present in the oil feedstocks.

2.5 Initial studies on the influence of reaction variables on the transesterification reaction of oil feedstocks

A series of transesterification reactions were performed in the laboratory scale by varying the reaction parameters such as reactants' molar ratio, catalyst/oil weight percentage, the temperature at which the reaction was conducted, and the duration of the reaction. In a typical run, 5 g of oil (UCO/JCO) (usually with FFA < 1% attained via pretreatment) was mixed with the desired amount of catalyst and methanol in a 50 mL RB flask fitted with a water condenser. The reaction was carried out at a specified temperature with constant stirring at 450 rpm. After each run, the reaction mixture was centrifuged for 15 minutes and the top methyl ester phase was separated from the dense glycerol phase after removing the settled catalyst. 3 mL of deionized water was added to the methyl ester part for washing in order to remove any impurities if present. The washing process was repeated 3 times and the obtained biodiesel was dried over anhydrous sodium sulphate. The reactions were also repeated with oils having varying amount of FFA and water content in order to study the effect of these parameters on the catalytic activity.

2.6 Reusability of the catalyst

One of the highlights of the solid heterogeneous catalyst is its reusability. Solid catalyst can be recovered by means of simple filtration and can be reused directly or by activating at its calcination temperature [46-50]. In the present study, reusability of the most active catalysts in each series is investigated under one of the best suited reaction conditions. After the reaction, the contents were centrifuged and filtered. The catalyst residue was washed with methanol to remove the contaminated impurities and after that, the catalyst was dried and activated at its calcination temperature for 1 h. Then, the second cycle of the transesterification process was conducted using the regenerated catalyst and the procedure was repeated after each reaction till the catalyst losses its activity.

2.7 Biodiesel analysis

For the use of biodiesel as an alternate fuel for petrodiesel, the FAME content in the biodiesel should be greater than 96.5% as per the European specification of standard biodiesel fuel. In the present study, the FAME content and hence the fuel quality of the biodiesel is determined mainly by the GC analysis. Thermo Fischer Trace GC 700 gas chromatograph equipped with MXT biodiesel column and flame ionization detector is used to determine the FAME content in the biodiesel by a test method of ASTM D 6584 [51-53]. Sample preparation for GC measurements is the important step in biodiesel analysis. The glycerol, mono-, di- and triglycerides must be derivatized to reduce their polarity and improve the thermal stability of the molecule. The derivatization technique used is silylation. The derivatization reagent used is MSTFA. The reaction involves the replacement of the active hydrogen of the hydroxyl group by a trimethylsilyl group. The derivatization procedure for both standards and samples is identical. 100 mg of biodiesel samples were weighed into a clean dry 10 mL septa vial followed by internal standards and it was derivatized exactly with 100 μL of MSTFA. The mixture was shaken well and allowed to stand at room temperature for 15-20 min. Approximately 8 mL of n-heptane was added to the vial and mixed well. One microlitre of the reaction mixture was then injected into the cool-on column port and the analysis was started. Injector program was oven track, (details are mentioned in section 2.3.7). Mono-, di-, and triglycerides were determined by a comparison with mono-olein, diolein, and triolein standards. Chromatogram and peak integration reports were collected and the FAME content was determined [54-56].

2.8 Biodiesel pilot plant: design and assembling

With a thorough knowledge and experience in the laboratory scale biodiesel preparation, we can scale up the entire biodiesel production process to pilot scale. Here we have designed a pilot scale set up having a production capacity of 15 L biodiesel per run. Figure 2.1 shows the schematic of the designed pilot plant (SNGS model1).

In the pilot plant, we ensured the presence of different components/operational facilities required in the laboratory scale biodiesel preparation. The biodiesel pilot plant consists of the following parts/vessels; provision for feedstock pretreatment (**j**), transesterification reactor (**c**), catalyst filtration port (**f**), glycerol settling vessel (**g**), methanol recovery unit (**k**) and provision for the purification of biodiesel (**o**, **m** & **p**). The entire vessels and valves are made of polypropylene (PP), which are resistant to biodiesel and a range of chemicals. The connections are done using tygoethane tubing, which is also resistant to a range of chemicals and biodiesel. The top of all the main vessels (pretreatment tank, reaction vessel and methanol distillation tank) are equipped with a condensers made of PVC pipe and copper coil. Cold water (from chiller (**s**)), is circulated through the condensers using a tulu pump for the condensation of methanol in the pretreatment vessel, reaction vessel and methanol recovery tank.

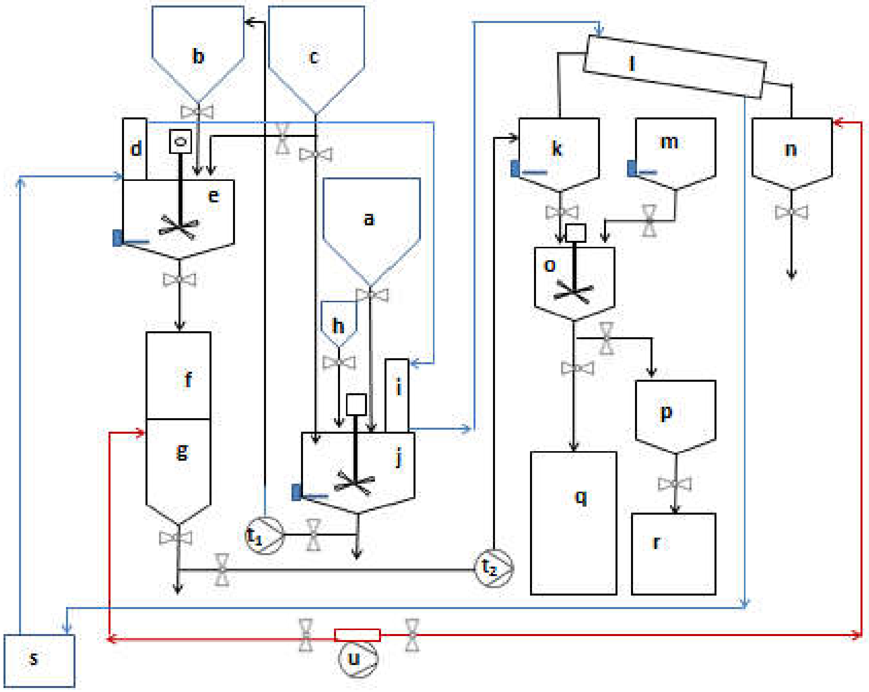
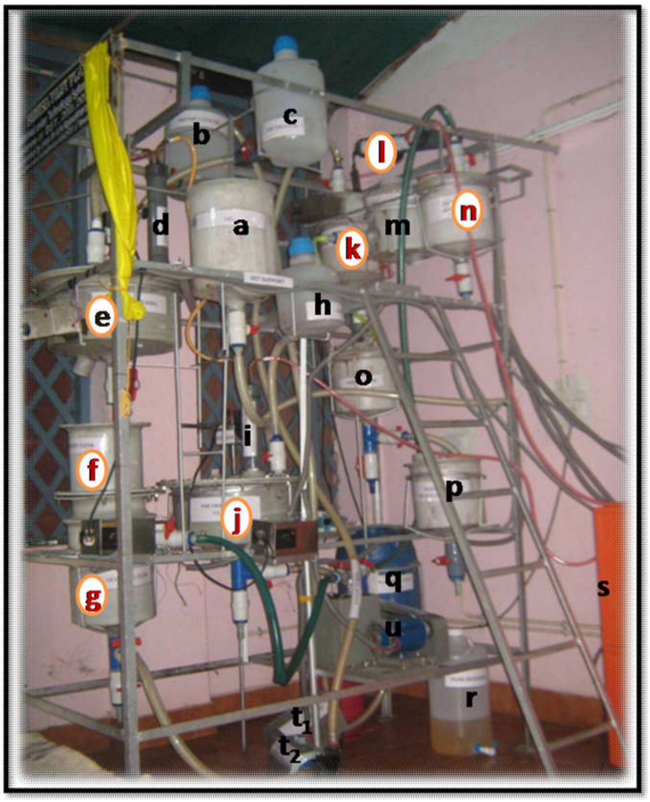


Fig 2.1 Schematic representation of Biodiesel pilot plant SNGS model1

⋈ -Valve, **a**- Oil tank, **b**- Pretreated oil tank, **c**- Methanol tank, **d**- Condenser, **e**- Reaction vessel, **f**- Catalyst separation port, **g**-Glycerol settling tank, **h**- Acid tank, **i**- Condenser, **j**- Pretreatment vessel, **k**- Methanol distillation tank, **l**- condenser for methanol from distillation tank, **m**- Hot water tank, **n**- Recovered methanol tank, **o**- Water washing tank, **p**- Drying tank, **q**- Waste water tank, **r**- Pure biodiesel tank, **s**- Chiller, $\mathbf{t_1}$ & $\mathbf{t_2}$- pump, **u**- vacuum pump

There is a provision for the removal of solid catalyst from the reaction mixture after the reaction, a filtration port (**f**), where the catalyst is separated by filtration under suction. The liquid mixture of biodiesel, methanol and glycerol is allowed to separate to two layers in the separation/settling tank (**g**). Two motor pumps ($\mathbf{t_1}$ & $\mathbf{t_2}$) are engaged; one for the supply of pretreated oil to the reaction vessel via tank (**b**) and the second for the pumping of glycerol separated biodiesel to the methanol distillation tank (**k**). The top of the methanol distillation tank is equipped with a condenser (**l**) and it is connected to the methanol collection tank (**n**). The vacuum pump (**u**) employed for providing suction during filtration of the catalyst is also used for giving vacuum for the distillation of methanol. Washing tank (**o**), hot water tank (**m**) and drying tank (**p**) are meant for the purification of the crude biodiesel.

All the components of the pilot plant engaged in the production of biodiesel are properly mounted on a stand according to the design. The connections of the vessels through valves are done using tygoethane tubing. Electric connections are assembled in a control panel which controls and monitors the temperature as well as regulates the speed of mechanical stirrers inside the tanks. The photograph of the pilot plant assembled with all the vessels and accessories are shown in the figure 2.2.



e:- Reaction Vessel, f & g:- Filtration and Settling Unit,
j:- Pretreatment Vessel , k, l & n:- Methanol Recovery Unit

Fig 2.2 Photograph of Biodiesel pilot plant SNGS Model1 (important components markings are highlighted)

2.9 Different components of biodiesel pilot plant

2.9.1 Pretreatment and Reaction vessels

The transesterification reaction vessel and esterification pretreatment vessel are exactly same with only changes in the number of openings and valves in the top portion. Both are conical bottom cylindrical 50 L polypropylene vessels equipped with a mechanical stirrer (1100 W motor). The stainless steel (SS) stirring rad in the reaction vessel composed of two stainless steel crosses in the end at a distance of 7 cm in between. The bottom cross is projected to the valve tubing to avoid settling of the solid catalyst in the valve tubings. Teflon stirring rad of the same type is used in the pretreatment vessel. The speed of the stirrer is variable and has a maximum stirring speed of 700 rpm. In the pretreatment vessel, the required temperature is achieved by using a 2 kW dry coil heater kept inside a medium thick glass tube (since SS corrods in concentrated acids) and in the reaction vessel, 2 kW SS immercible coil heater is used. The top of both the vessels are equipped with water condensers made of copper coil covered with a PVC jacket. Chilled water is circulated through the copper coils to ensure the condensation of methanol vapors inside the PVC tube during the reaction. This provision avoids the risk in operating the vessels since there is no high pressure generation, where the excessive formation of methanol vapors are avoided by its continuous condensation. The PVC condensers are sealed to prevent the accumulation of atmospheric moisture on the copper coils. The oil and the methanol for the biodiesel production are transferred from the corresponding storage vessels to the pretreatment/reaction vessels via tygoethane tubing (tygothane polyurethane 1” ID x 1 3/8” OD). The images of both the pretreatment and reaction vessels and their accessories are shown in the figure 2.3 and figure 2.4 respectively. Drawing of the vessel is also shown in figure 2.3.

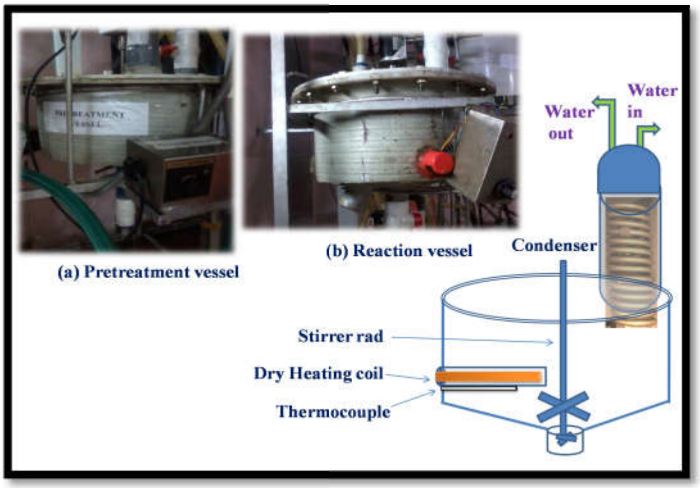


Fig 2.3. Images and sketch of pretreatment and reaction vessels

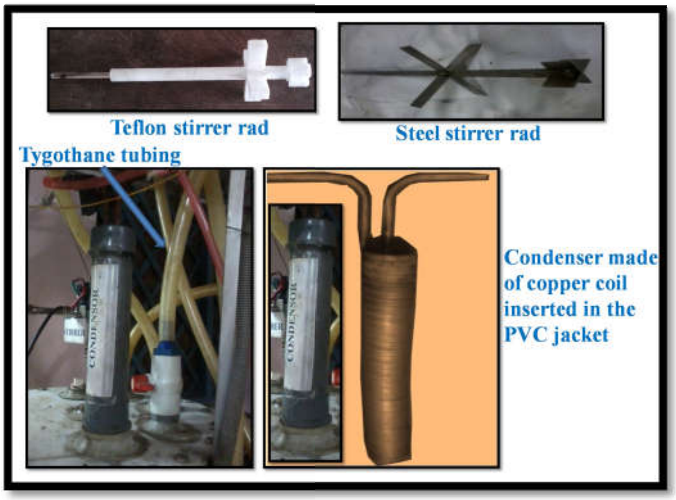


Fig 2.4. Accessories of pretreatment and reaction vessels

2.9.2 Filtration and Settling unit

There is a provision for the removal of solid catalyst from the reaction mixture after the reaction, a filtration port (**f**) made of PP, where the catalyst was separated by filtration using whatman no.1 filter paper under suction. A vacuum pump (**u**) is connected to the settling tank for providing suction in the catalyst separation stage. This will also helps for the easy layer separation of the glycerol-biodiesel mixture. The filtration port is a flat bottom cylindrical vessel having sieve like provision. Filter paper was properly placed at the bottom of the vessel. The liquid mixture of biodiesel, methanol, and glycerol after filtration can be allowed to settle in the separation tank (**g**). After the settling, the glycerol separated biodiesel layer can be pumped to the methanol distillation tank (**k**) via pump **t$_2$**. The image of filtration and settling units are provided in the figure 2.5.

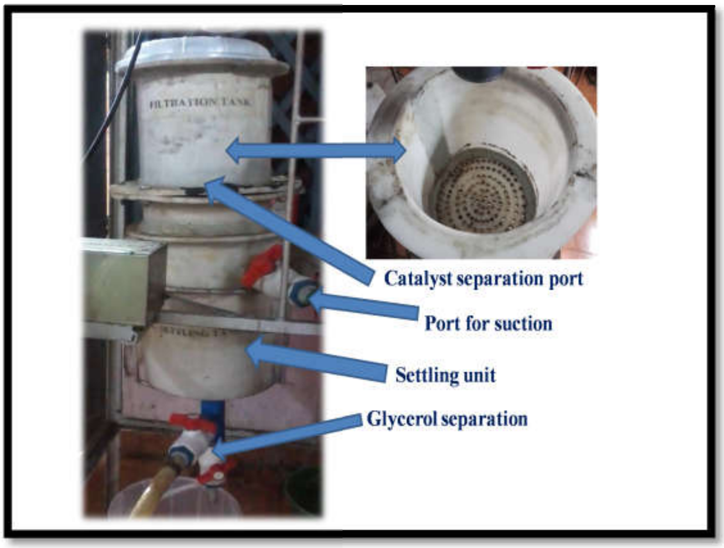


Fig 2.5 Filtration and settling unit

2.9.3 Methanol recovery unit

In the present pilot plant, there is also a provision for the recovery of excess methanol used for the reaction, which makes the entire process cost effective. The methanol distillation tank (**k**) contains a 2 kW SS coil heater. The top of the methanol distillation tank is equipped with a condenser (**l**) made of PVC and copper coil, and it was connected to the methanol collection tank (**n**). The copper coil was connected to the distillation tank via a 4 cm diameter SS 316 tube. The entire system was sealed to achieve the required vacuum. The excess methanol can be collected (in tank **n**) here under vacuum at a temperature of 50 °C. The same vacuum pump (**u**) is meant for the filtration of the catalyst. Figure 2.6 shows the image and schematic of the methanol recovery unit and the condensation port respectively.

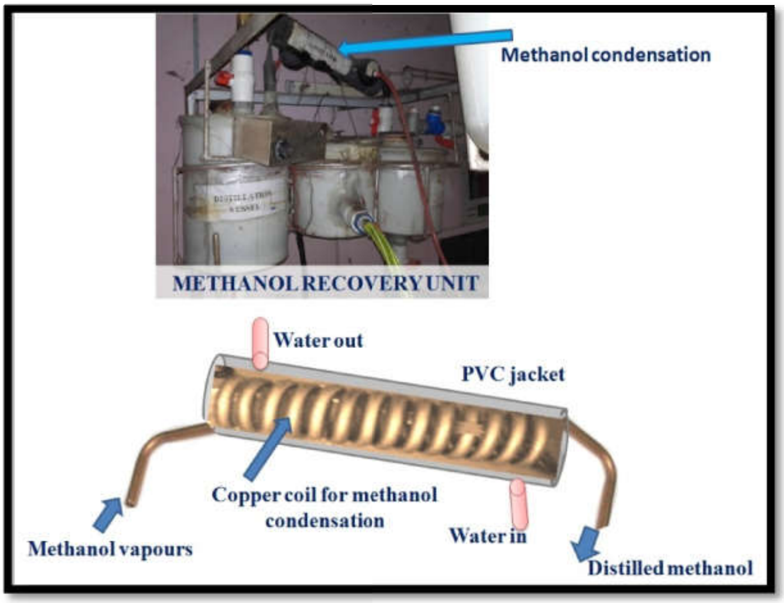


Fig 2.6 Methanol recovery unit and schematic of condensation port

2.9.4 Biodiesel purification

Beside the major components, there is a provision for the purification of the biodiesel produced in the pilot plant. Washing tank (**o**) equipped with stirrer, hot water tank (**m**) equipped with heating coils and drying tank (**p**) are meant for the purification of the crude biodiesel.

In summary, we have skillfully designed and expertly assembled the components of the pilot plant for the pilot scale economic production of biodiesel which has the promise of easy industrial scale up. Thus constructed biodiesel pilot plant is designated as SNGS Model 1. Since the components are made of PP vessels, it makes the entire unit become cost effective, light weight and offers a lot of promise for an easy and economical industrial scale up. The pilot plant is a skid mount unit, which is movable and can be easily transported from one place to other. The temperature inside the vessels is controlled digitally and the maximum temperature engaged in the biodiesel production is 65 °C. Continuous condensation of methanol inside the reaction vessels avoids the high pressure generation inside the vessels and hence the entire process is safe. The filtration port ensures the separation of solid catalyst and the catalyst may be recycled and reused, which makes the process further green and economical. Methanol recovery unit in the biodiesel pilot plant is another peculiarity and thus the recovered excess methanol can be reused. The production capacity of the biodiesel pilot plant is 15 L biodiesel/run. The entire set up was cost effective, eco-friendly and highly feasible for the industrial scale up.

2.10 Catalyst preparation unit

A cylindrical PP vessel equipped with heating coils and mechanical stirrer is used for the bulk scale preparation of the catalyst. The capacity of the PP vessel is 120 L. The stirring speed of the mechanical stirrer is varied by a controller and the required temperature inside the vessel is controlled and maintained using digital temperature controller. The catalyst preparation vessel set up is also employed for the degumming of the oil feedstock. The photograph of the set up is shown in the figure 2.7.

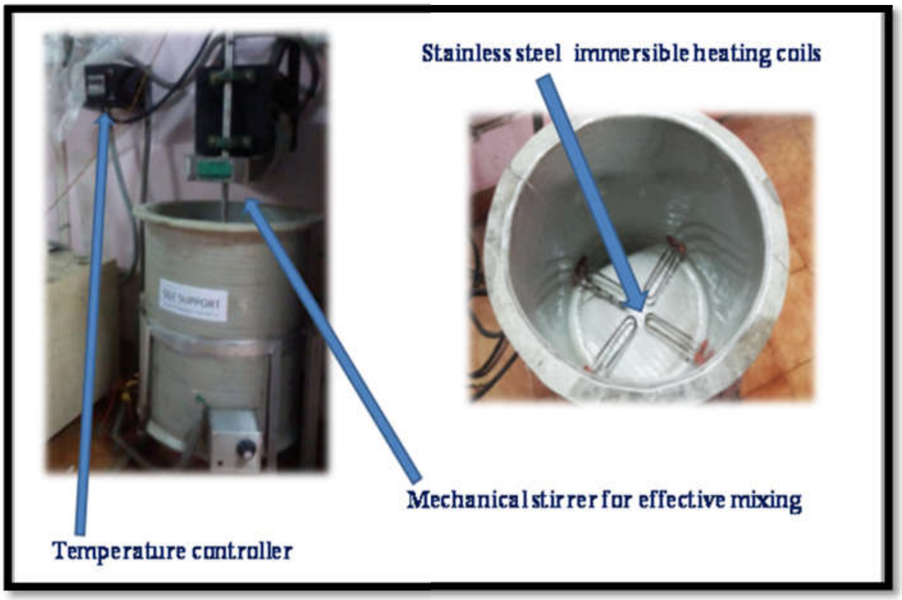


Fig 2.7 Degumming and catalyst preparation unit

2.11 Degumming of oil feedstocks

Degumming of filtered oil (JCO/UCO) was done to eliminate phospholipids and was performed by thermal treatment with water with the assistance of a degumming agent, phosphoric acid [57, 58]. Figure 2.8 shows the settled gum from the oil

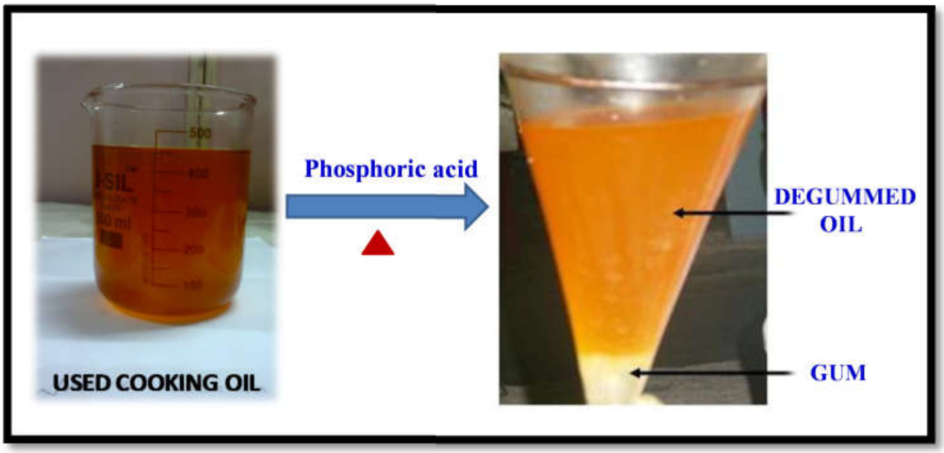


Fig 2.8 Degumming of used cooking oil in the laboratory scale

In bulk, degumming was done in the catalyst preparation unit, which is a cylindrical PP vessel equipped with heating coils and mechanical stirrer (section 2.11, figure 2.7). In this process, the filtered oil was first heated to a temperature of 60 °C. As the temperature was achieved, 0.01% phosphoric acid by weight of oil was added to the oil and the mixture was then stirred for 30 minutes with heating. 2 wt% of water was added to the above mixture followed by increasing the temperature and maintained at 70 °C-80 °C for 15 minutes [59, 60]. Gums present in the oil settled at the bottom were drained off. The oil was dried using anhydrous Na_2SO_4.

2.12 Biodiesel production in the pilot plant

The detailed procedure for the biodiesel production in the pilot plant is provided below. JCO and UCO were used as the feedstocks for the biodiesel production over different catalysts. The different stages in the biodiesel production are discussed in the following sections.

2.12.1 Pretreatment of Degummed Oil

There is no change in the experimental procedure between laboratory scale and pilot scale pre esterification reactions, the only difference is in the equipments where the reaction was carried out. In the laboratory scale, experiments were conducted in round bottom flasks made up of Borosil glass that was fitted with Liebig condenser. Temperature was maintained in the oil bath where the reactions were performed. The figure 2.9 shows the pretreatment process in the laboratory scale set up.

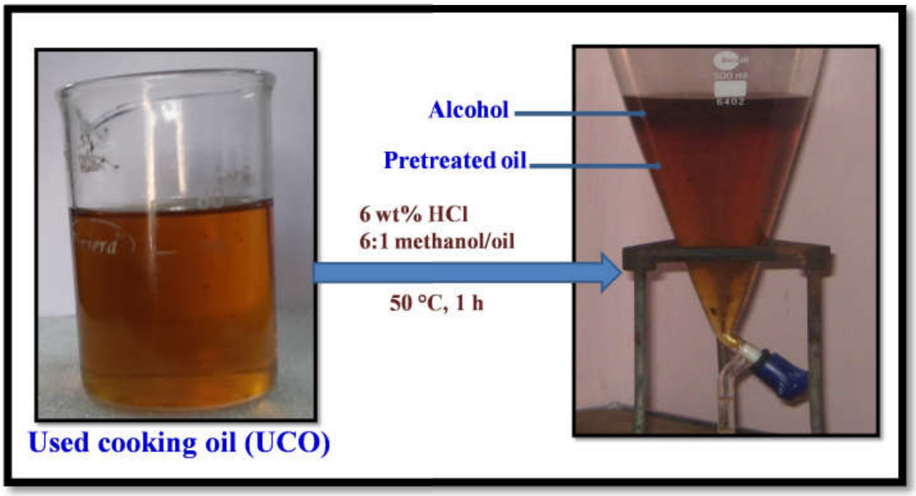


Fig 2.9 set up of pretreatment of used cooking oil in laboratory scale

In the pilot plant, experiments were performed on PP vessels. Separate provisions were available for each step of the biodiesel production process. At first, degummed oil (from tank **a**) was added to the pretreatment vessel (**j**). Adequate amount of methanol (6:1 w.r.t oil) (from methanol storage tank **b**) and acid (HCl, 6 wt%) (from acid storage tank **h**) were added to the oil in the pretreatment vessel and then mixed thoroughly with stirring. Pretreatment was done at a temperature of 50 °C for 1 h [61, 62]. Water was poured to the vessel following the pretreatment and after layer separation, bottom layer was discarded and washing was repeated thrice to remove remaining acid from the oil. The washed pretreated oil was then transferred to the storage tank via pump (**t_1**). The pretreated oil was made water free using anhydrous Na_2SO_4.

2.12.2 Transesterification reaction in the pilot plant; catalyst and glycerol separation

The pretreated oil (~15 kg) was passed to the reaction vessel (**e**) and was mixed with specified amount of methanol (from tank **c**) with stirring. Required amount of catalyst was added through the opening on the top of the reaction vessel while stirring and the reaction mixture was heated to the desired reaction temperature for specified reaction time. Then the reaction mixture was transferred into the filtration port (**f**) and the catalyst was separated by filtration under suction. The liquid mixture of biodiesel, methanol, and glycerol were collected in the separation tank (**g**) and allowed to settle the glycerol with layer separation. The lower glycerin layer was drawn off from the bottom of the separation tank.

2.12.3 Methanol recovery

The crude biodiesel was then passed into the methanol distillation vessel (tank **k**) via pump (**t_2**). The unreacted methanol was recovered under vacuum at a temperature of 50 °C and was collected (tank **n**).

2.12.4 Purification of biodiesel

The methanol separated biodiesel was passed to the washing tank (tank **o**) to purify with warm deionized water from the hot water tank (**m**). As in the case of a homogeneous catalyzed process, there is no step required to neutralize the biodiesel since the catalyst was already separated. Washing with water was performed with gentle agitation so as to ensure complete removal of any traces of methanol, glycerol or any other impurities present in the biodiesel. The washed biodiesel was then passed to the moisture remover tank (**p**), where the remaining water was separated using anhydrous sodium sulfate. Pure biodiesel was then collected and stored.

2.13 Determination of fuel properties of biodiesel

Two major fuel specifications establishing the quality requirements for mono alkyl ester based biodiesel as fuels are the ASTM D 6751 in USA and the EN 14214 in Europe [63-67]. Fuel properties of the biodiesel made in the pilot plant were determined using standard test procedures. The fuel properties like ester content, free and total glycerol, mono, di and triglycerides etc were analyzed by GC analysis (method ASTM D 6584) and some of the other parameters such as acid value, iodine number, water content, density, viscosity etc, were determined using standard analytical test methods described in the following sections and thus obtained biodiesel properties can be compared with standard fuel specifications to assess its quality [63-68].

2.13.1 FAME content

FAME content is meant to be a guide to the purity of biodiesel by way of measuring the conversion of triglycerides to methyl esters. In order to commercialize biodiesel as pure biofuel or blending stock for diesel fuels, it must meet the standard specifications for biodiesel fuel (FAME content of 96.5% by EN 14214). Ester content was usually analyzed using GC [63-68]. Mono-, di-, and tri- glycerides are also determined by the GC analysis.

2.13.2 Total and free glycerol

The most important criterion for a good-quality biodiesel is the completion of the transesterification reaction. The incomplete reaction will cause the presence of bound glycerol in the form of un-reacted triglycerides and intermediate mono- and di- glycerides. Another contaminant found in biodiesel is the free glycerol, which was not removed during the water washing of biodiesel.

The combination of the bound and free glycerol is referred to as total glycerol. These datas are calculated directly from the gas chromatogram on the basis of the ASTM D 6584, which is the prescribed standard method for measuring free and total glycerol. The total glycerol in a biodiesel sample is calculated using the formula [63-68].

$$\text{Total glyceride} = G+(0.25*MG)+(0.15*DG)+(0.10*TG)$$

G- Free glycerol, MG-Monoglyceride, DG- Diglyceride, TG-Triglyceride

Besides the acylglycerols, residual alcohol (methanol) can contaminate the final biodiesel product. Amount of methanol can also be analyzed via GC.

2.13.3 Acid value

Acid value of the oil/fat/biodiesel sample indicates quantitatively the presence of free fatty acid in it. It is generally estimated by neutralizing the FFA in the sample with KOH solution of known concentration. Titration method is employed here to determine the FFA content in the sample. In a typical procedure, 1 g of biodiesel sample was accurately weighed in an Erlenmeyer flask and was dissolved in 10 mL isopropyl alcohol. Then, to the mixture, two drops of phenolphthalein was added and thoroughly shaken. It was then titrated with standardized KOH solution until a permanent pink color appears. The acid value was calculated from the titer value using the following formula [63-68].

$$\text{Acid Value} = (A \times N \times 56.1) / W$$

Where, ‘A’ represents Volume of KOH solution, ‘N’ represents the normality of the KOH solution and ‘W’ represents the weight of the biodiesel sample. According to the standard fuel specifications, the acid value should be less than 0.50 mg KOH/g (ASTM D 6751).

2.13.4 Water content

Water content is a detrimental factor affecting the quality of biodiesel by causing its auto oxidation, hence increasing the FFA concentration [63-68]. Water content in the biodiesel sample was analyzed by drying the sample using calcium chloride [69]. 10 mL of biodiesel sample is added to the previously weighed dry beaker and the mass of the sample is accurately weighed on a four digit electronic balance. Next, 1g of calcium chloride was separately weighed and added to the beaker containing the biodiesel sample. Then the beaker was kept inside a hot air oven at a temperature of 100 °C for 1 h. After that, the sample was cooled and accurately weighed and mass of the dried biodiesel sample alone was calculated [69].

$$\text{Water Content} = (d / t) \times 100$$

Where: d, represents the difference in oil weights in g.

t, represents the mass of the oil before heating in g.

2.13.5 Iodine number

Iodine value (IV) or iodine number of oil is the measure of total unsaturation in the fatty acid chain and it is one of the quality determining factors for the use of biodiesel in diesel engines. IV is determined by calculating the number of moles of iodine added directly to the double bonds present in the fatty acid chain [63-67]. In a typical procedure for IV determination, 1 g of biodiesel sample was accurately weighed in an Erlenmeyer flask and about 25 mL of Wij's solution was added to this sample. The solution was thoroughly mixed and kept at room temperature for 30 minutes. After that, 10 mL of 15% KI solution was added and again shaken for 2 minutes. The solution was then titrated with 0.1 N sodium thiosulfate. When the color of the solution becomes pale yellow, 1 mL of starch solution was added as the indicator. Then titration was continued until the blue color of the solution was disappeared and then the volume of the thiosulfate solution used up was noted. Similarly, a blank titration was also conducted without using biodiesel sample. From the titre values, the iodine number was calculated using the following formula [63-68].

$$\text{Iodine value} = \frac{\text{Eq. wt of iodine} \times \text{vol. of } Na_2S_2O_3 \times \text{Normality of } Na_2S_2O_3 \times 100 \times 10^{-3}}{\text{Weight of biodiesel sample}}$$

2.13.6 Viscosity

Viscosity of the biodiesel sample was determined using Ostwald's viscometer apparatus. Ostwald viscometer is a commonly used viscometer, which consists of a U-shaped glass tube held vertically. For more accurate measurements, it is held in a controlled temperature bath. The liquid biodiesel sample was allowed to flow through its capillary tube between two etched marks (A and B) and the time of flow of the liquid was measured using a stopwatch.

Similarly the time of flow for reference sample, usually water was also calculated. The viscosity is calculated from the relation,

$$\eta/\eta^* = dt/d^*t^*$$

Where: η^* is viscosity coefficient of the reference sample (water), d^* is the density of the reference sample, and t^* is the time of flow of the reference sample. The other variables are viscosity coefficient (η), density (d), and time of flow (t) of the biodiesel sample [63-68].

2.13.7 Density

Density is mass of the substances occupying unit volume. It is an important fuel property, which is directly related to the engine performance and emission characteristics. The density was determined by measuring the volume of biodiesel accurately and its weighing was performed in a four digital electronic balance. 10 mL of biodiesel sample was accurately measured and transferred to a pre-weighed dried beaker and weighed the total mass. From the difference between weight of sample and beaker, the weight of the sample alone can be found out [63-68]. Then, the density of biodiesel sample is calculated using the formula,

$$\text{Density} = w/v$$

Where, ‘w’ represents the weight and ‘v’ represents the volume of the biodiesel sample.

References

1. M. S. Azhari, Y. Robiah, I. M. G. Tinia and C. S. Y. Thomas, *Pertanika J. Sci. Technol.*, 2012, **20**, 165- 173.
2. A.S. Yusuff, O.D. Adeniyi, M.A. Olutoye and U.G. Akpan, *J.Appl. Sci. Process Eng.*, 2017, **4**, 142-157.
3. G. Teng, L. Gao, G. Xiao and H. Liu, Energy *Fuels*, 2009, **23,** 4630-4634.
4. B. Sanjay, *Res. J. Chem. Sci.*, 2013, **3**, 95-101.
5. P. Kumar, A. K. Sarma, M. K. Jha, A. Bansal and B. Srivasatava, Bull. Chem. React. Eng. Catal., 2015, **10**, 221-229.
6. S. P. Davis, M. C. Abrams and J. W. Brault, *Fourier Transform Spectrometry*, Academic Press, San Diego, 2001.
7. R. P. Wodehouse, *Pollen grains*, McGraw-Hill Book Company, New York, 1935.
8. B. H. Stuart, *Infrared Spectroscopy: Fundamentals and Applications*, Wiley, 2004.
9. R. M. Silverstein, G. C. Bassler and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, Wiley, New York, 1981.
10. R. J. Bell, *Introductory Fourier Transform Spectroscopy*, Academic press Inc. New York and London, 1972.
11. H. Lipson, and H. Steeple, *Interpretation of X-ray powder diffraction patterns*, Macmillan, London, 1970.
12. C. Whiston, *X-ray Methods-Analytical Chemistry*, John Wiley, New York , 1987.
13. https://engineering.jhu.edu/labs/wp-content/uploads/sites/76/2016/04/Phillips-Basic-XRD-Theory.pdf.
14. M. Birkholz, *Thin Film Analysis by X-Ray Scattering*, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2006.

15. N. Kasai, M. Kakudo, *X-ray diffraction by macromolecules*, Springer, Tokyo: Kodansha ; Berlin ; New York, 2005.

16. http://chanl.unc.edu/assets/pdf_files/operations/microscopy/S4700.pdf.

17. J. Goldstein, D. Newbury, D. Joy, C. Lyman, P. Echlin, E. Lifshin, L. Sawyer and J. Michael, *Scanning Electron Microscopy and X-ray Microanalysis*, Springer, New York, 2003.

18. http://fy.chalmers.se/~f10mh/Halvarsson/EM_intro_course_files/SEM_intro.pdf.

19. W. Zhou, R. Apkarian, Z. L. Wang, D. Joy, *Scanning Microscopy for Nanotechnology*, Springer-Verlag, New York, 2007.

20. P. Echlin, *Handbook of Sample Preparation for Scanning Electron Microscopy and X-Ray Microanalysis*, Springer US, 2009.

21. A. Muller and J. Grazul, J. Electron Microsc., 2001, **50**, 219-226.

22. P. R. Buseck, J. M. Cowley and L. Eyring, *High-Resolution Transmission Electron Microscopy and Associated Techniques*, Oxford University Press, Oxford, 1988.

23. Spence JCH, *High-Resolution Electron Microscopy*, Oxford University Press, Oxford, 1988.

24. S. J. Pennycook and P. D. Nellist, *Scanning Transmission Electron Microscopy*, Springer, New York, 2011.

25. G. Thomas and M. J. Goringe, *Transmission Electron Microscopy of Materials*, Wiley-Interscience, New York, 1979.

26. https://en.wikipedia.org/wiki/Inductively_coupled_plasma_atomic_emission_spectroscopy.

27. http://www.ncm.unn.ru/files/2015/11/applecture212.pdf.

28. M Thompson and J. N. Walsh, *Analysis of metals by ICP-AES. In: Handbook of Inductively Coupled Plasma Spectroscopy*, Springer, Boston, 1989.

29. A. Varma, *CRC Handbook of Inductively Coupled Plasma Atomic Emission Spectroscopy*, CRC Press, Boca Raton, Florida, U.S.A., 1991.

30. A. A. Warra and W. L. O. Jimoh, *Int. J. Chem. Res.*, 2011, **3**, 41-48.

31. P. A. Redhead, *Vacuum*, 1962, **12**, 203-211.

32. N.J. Clark, *M.Sc. Thesis*, Texas State University, USA, 2009.

33. R. J. Cvetanovic and Y. Amenomiya, *Catal. Rev.: Sci. Eng.*, 1972, **6,** 21-48.

34. H. Tsuji, F. Yagi, H. Hattori and H. Kita, *Stud. Surf. Sci. Catal.*, 1992, **75,** 1171-1183.

35. P.T. Dawson and P.C. Walker, *Experimental Methods in Catalytic research*, Academic press, New York, 1976.

36. F. A. Settle, *Handbook of Instrumental Techniques for Analytical Chemistry*, Prentice Hall PTR, Upper Saddle River, New Jersey, 1997.

37. C. M. Marvin, *GC/MS A practical user's guide*, John Wiley & Sons, Inc, USA, 2008.

38. B. Jonathan and M. M. James, *Analytical chemistry in a GMP environment*, John Wiley & Sons, Inc., USA, 2000.

39. R.L. Grob, *Modern Practice of Gas Chromatography*, Wiley, New York, 1995.

40. W. Harris and H. Habgood, *Programmed Temperature Gas Chromatography*, J. Wiley & Sons, New York, 1966.

41. H. J. Hubschmann, *Handbook of GC-MS: Fundamentals and Applications*, Wiley-VCH, Weinheim, 2009.

42. S. Ahuja and N. D. Jespersen, *Modern Instrumental Analysis*, Elsevier, Amsterdam, 2006.

43. O. D. Sparkman, Z. Penton and F. G. Kitson, *Gas Chromatography and Mass Spectrometry*: A Practical Guide, Academic Press, Oxford, 2011.

44. https://www.restek.com/pdfs/PCAN2559-UNV.pdf.

45. S Sharmila and L. J. Rebecca, *J. Chem. Pharm. Res*., 2012, **4**, 4883-4887.

46. N. Oueda, Y. L. B. Coulibaly, I. W. K. Ouedraogo, Mater. Sci. Appl., 2017, **8**, 94-122.

47. N. Hindryawati, G. P. Maniam, M. R. Karim and K. F. Chong, *Eng. Sci. Technol*., 2014, **17,** 95-103.

48. A.P.S. Dias, J. Bernardo, P. Felizardo and M. J. N. Correia, *Fuel Process. Technol*., 2012, **102**, 146-155.

49. A. Piker, B. Tabah and N. A. G. Perkas, *Fuel*, 2016, **182**, 34-41.

50. S. Yan, C. DiMaggio, S. Mohan, M. Kim, S. O. Salley and K. Y. S. Ng, *Top. Catal.*, 2010, **53**, 721-736.

51. D 6585 Test Method for Determination of Free and Total Glycerine in B-100 Biodiesel Methyl Esters by Gas Chromatography, ASTM International, 100 Bar Harbor Drive, West Conshohocken, PA, USA, 2003.

52. American Society for Testing and Materials (ASTM), D6751 Standard Specification for biodiesel fuel blend stock (B100) for middle distillate fuels. ASTM, West Conshohocken, PA, 2008.

53. Y. Zahira, S. B. S. Irwan, N. Binitha, R. S. A. Siti and I. Manal, *Bioresour. Technol.*, 2012, **104**, 695-700.

54. British-Adopted European Standard, Fat and Oil Derivatives e Fatty Acid Methyl esters (FAME) e Determination of Free and Total Glycerol and Mono-, Di-, Triglyceride Contents (Reference Method), BS EN 14105:2003, 2003.

55. E. D. Dodds, M. R. McCoy, L. D. Rea and J. M. Kennish, *Lipids*, 2005, **40**, 419-428.

56. R.E. Paul, *J. Chromatogr. Sci.*, 2011, **49**, 384-396.

57. M. Chai, Q. Tu, M. Lu and Y. J. Yang, *Fuel Process. Technol.*, 2014, 125, 106-113.

58. N. G. Shemelis and M. M. Jorge, *AIMS Energy*, 2017, **5**, 425-457.

59. A. Choukri, M. A. Kinany, V. Gibon, A. Tirtiaux and S. Jamil, *J. Am.* Oil *Chem. Soc.*, *2001*, **78**, 1157-1160.

60. V. Vadery , B. N. Narayanan , R. M. Ramakrishnan , S. K. Cherikallinmel, S. Sugunan, D. P. Narayanan and S. Sasidharan, *Energy*, 2014, **70,** 588-594.

61. M. P. Dorado, E. Ballesteros, J. A. de Almeida, C. Schellert, H. P. Lohrelein and R. Krause, *Trans ASAE*, 2002, **45**, 525-529.

62. K.C. Sudha, G. Anila, Y. Zahira, M.R. Resmi, S. Sugunan and N. N. Binitha, *RSC Adv.*, 2015, **5**, 46290-46294.

63. S. P. Singh and D. Singh, *Renewable Sustain Energy Rev.*, 2010, **14**, 200-216.

64. G. Knothe, *Fuel Process. Technol.*, 2005, **86,** 1059-1070.

65. European Committee for Standardization (CEN), Standard EN 14214, Automotive fuels - fatty acid methyl esters (FAME) for diesel engines - Requirements and test methods, CEN, Brussels, 2003.

66. EN 14214: Automotive fuels – Fatty Acid Methyl Esters (FAME) for diesel engines - requirements and test methods.

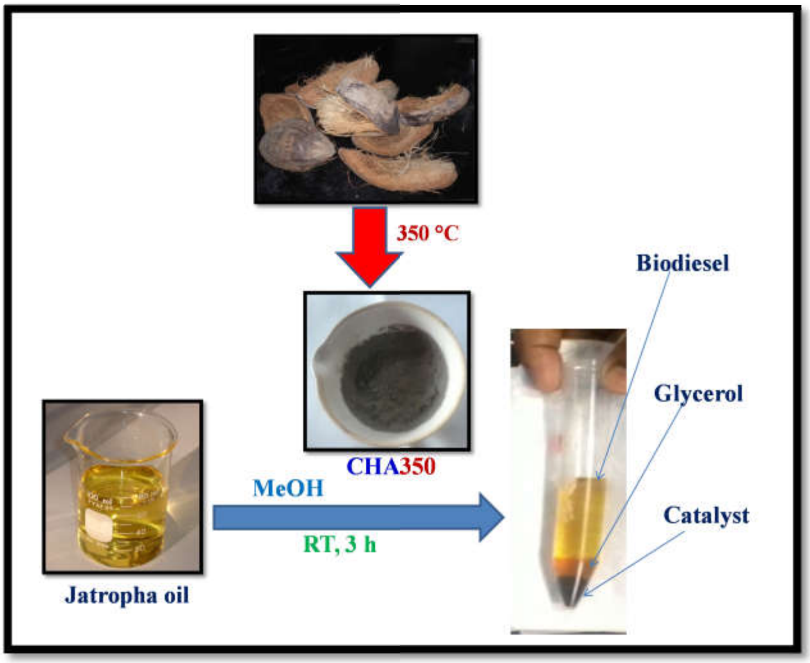
67. ASTM D 6751: Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels.

68. A. Okullo, A. K. Temu, P. Ogwok and J. W. Ntalikwa, *Int. j.Renewable Energy Res.*, 2012, **2**, 47-52.

69. http://www.odec.ca/projects/2009/guru9s2/Procedure.htm.

CHAPTER 3

PRODUCTION OF BIODIESEL USING COCONUT HUSK ASH CATALYST



Coconut husk ash is effectively used in the production of fuel grade biodiesel even by room temperature transesterification reaction of non-edible/used triglyceride oils

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3.1 Introduction

As an important source of oil and income, coconut tree is an inevitable part of Kerala life [1]. The name Kerala has the meaning “the land of coconut” (kera in malayalam), which is called so due to the abundance of coconut tree [2]. Among the wide variety of useful components from the coconut tree, coconut husk has been considered as an agricultural waste material. Coconut oil and coconut water processing firms generate a lot of coconut husk and in most of the cases it is usually discarded or burned [3]. The improper treatments of these materials will result in land and air pollution. The coconut husk has been used as a biomass fuel since it contains a high amount of lignin and cellulose, and hence possesses high calorific value [4]. The coconut husk can be used as a value-added clean combustion fuel, which can replace wood and other traditional fuel sources. The combustion of coconut husk produces a lot of ash as waste. Coconut is a permanent crop and there is no scarcity of the husks. Both in terms of its availability and cost, coconut husk has good potential for use in power plants. The coconut husk bears 40% of coconut fruit and it contains 30% fiber with a chemical composition of cellulose, lignin, tar, tannin, potassium etc [5]. At present, coconut husks are used as a fuel for coconut processing, as a domestic fuel and as a source of fiber for making rope and mats. The charcoal made from coconut husk by direct combustion method has a number of applications [6]. The activated carbon derived from coconut husk is highly efficient for wastewater treatment processes [7]. Manju et al have used copper impregnated coconut husk carbon as an adsorbent for the removal of arsenic from contaminated water [8]. Chromium (VI) is removed from aqueous solutions using activated carbon produced from coconut husk fiber [9]. Phenol, acid red 27 dye, and Cu^{2+} ions are also removed by employing activated carbon from coconut fiber using CO_2 and phosphoric acid as the activators [10]. Cationic dyes like methylene blue has been removed by adsorption on coir pith carbon [7]. Coconut husk carbon is used as an additive in the preparation of activated carbon from digested sewage sludge using $ZnCl_2$ as an activating agent [11]. There are some other reports related to the use of coconut husk ash as a stabilizing agent for improving the quality of infertile lateritic soil, as an enhancement of concrete for improving the toughness torsion and the tensile stress of concrete whereas the coconut fibers also ensures long-term durability of the concrete [12]. Furthermore, fermentable sugar extracted from relatively abundant lignocellulosic material obtained by suitable pretreatment of coconut husk makes it a cheap and potential substrate for the bioethanol production through enzymatic hydrolysis [13].

In the present work, coconut husk is utilized for the preparation of a base catalyst in the production of biodiesel. Since it is inexpensive and locally available in plenty, it is a suitable raw material for the bulk production of catalyst. The use of ash based materials for biodiesel production offers the best route for waste management and its natural availability, environmental friendliness, renewable nature and low cost stimulate its importance in making a solid catalyst for biodiesel production [14]. The use of palm empty fruit bunch ash [15], rice husk ash [16], cocoa pod husk ash [17], wood ash [18] etc as precursors of the catalyst or as catalyst supports for biodiesel production is already established and is already mentioned in chapter 1, in section 1.12. However, in all those cases higher amount of catalyst of around 20 wt% of the oil is required for the production of biodiesel or high calcination temperature is required for the catalyst development [15, 18]. The catalytic performance was further improved by chemical treatment with K or Ca containing compounds [15-18]. Here, the catalyst preparation from coconut husk has been done by a simple procedure, by means of controlled heat treatment (combustion) alone without any chemical processing. The ash obtained is used as such as catalyst for the preparation of biodiesel. The advantage of coconut husk derived catalyst is the presence of high potassium content, which is sufficient for giving excellent catalytic activity for the production of biodiesel that meets international standards even by room temperature reaction. A simple method of heat treatment employed for the bulk scale preparation of ash from coconut husk makes the pilot scale production of biodiesel easy and economically viable.

3.2 Experimental

3.2.1 Preparation of coconut husk ash

Coconut husks were washed with deionized water and dried under sunlight. Then the catalysts were prepared by the combustion of coconut husk at different temperatures starting from 300 °C to 500 °C with an interval of 50 °C. The calcination (combustion of coconut husk) was performed by placing the dried coconut husk as such into a cleaned muffle furnace under the selected temperature for 1 h. The different catalytic systems thus prepared were designated as **CHAT**, where **CHA** is the short form of coconut husk ash and **T** indicates the catalyst treatment temperature in °C. For example, the catalyst treated at 350 °C is designated as CHA350. The ash content of coconut husk is found to be ~5%. The preparation of catalyst from coconut husk is depicted in figure 3.1.

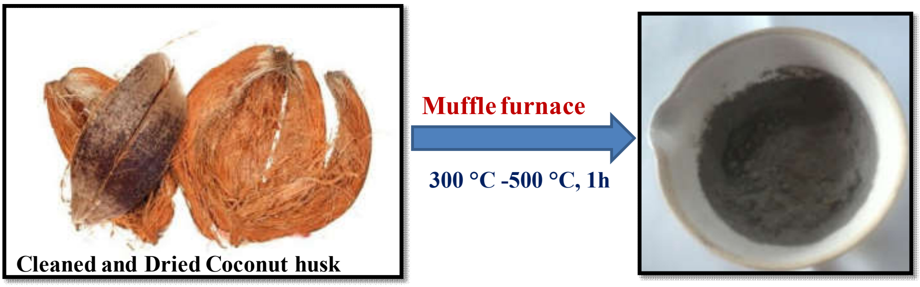


Fig 3.1 Preparation of coconut husk ash catalyst

The ashes prepared by the controlled combustion of coconut husk at different temperatures were analyzed thoroughly using FTIR spectroscopy, XRD and SEM-EDS characterization techniques. The catalytic activity of the coconut husk ash derived catalysts in the biodiesel production was investigated in the transesterification of *jatropha carcus* oil. The activity of CHA350 in UCO transesterification is also analyzed. The detailed procedures for the investigation of reaction parameters in the transesterification reaction, pilot scale production of biodiesel from *jatropha carcus* oil as well as used cooking oil, biodiesel analysis, and the determination of fuel properties are explained in chapter 2 in the sections 2.5, 2.12.2, 2.7 and 2.13 respectively.

3.3 Results and discussion

The coconut husks treated at different calcination temperatures were characterized using various techniques in order to find out the active components and surface morphology of the systems. Initially, the catalytic activity of the coconut husk derived ash based catalysts was investigated in the laboratory scale by the transesterification of jatropha oil with methanol at different reaction conditions. The influence of calcination temperature on the activity was monitored first. Effect of the reaction parameters such as methanol to oil molar ratio, dosage of catalyst, duration of the reaction and reaction temperature of the catalytic reaction was investigated. The biodiesel production was upgraded in the pilot plant at the best suited reaction condition to ensure its applicability in the large scale production process.

3.3.1 Catalyst characterization

3.3.1.1 SEM-EDS analysis

The mass percentage of the components of coconut husk and the heat treated varieties as obtained from EDS analyses are given in Table 4.1. It is seen that carbon and oxygen content of the coconut husk decreased upon combustion. It can be concluded from the nature of the components that K is the main active ingredient responsible for the high activity of these catalysts in biodiesel production. From the elemental analysis data, it is observed that majority of potassium exists as its chloride.

The SEM images of the coconut husk and its thermally treated systems are provided in the figure 3.2. Images of the heat treated samples reveal the presence of mineral aggregates of complex morphology with macropores. It is evident from the SEM images that, CH has no porous structure and it displayed a flake like structure. Temperature treatment caused the elimination of organic matter and created pores in the remaining ash. There are many reports on macroporous heterogeneous catalysts active for biodiesel production [19-21].

Table 4.1. SEM-EDS analysis data of coconut husk/coconut husk treated at various temperatures

Catalyst	Element (mass %)							
	C	O	Na	Mg	Si	Cl	K	Others
CH	61.77	16.43	-	-	-	8.06	10.91	2.82
CHA300	8.47	6.35	1.95	2.05	1.68	33.54	41.73	4.23
CHA350	1.29	4.44	2.92	1.21	3.25	43.57	42.90	0.43
CHA400	2.22	6.63	3.63	1.36	4.25	34.34	46.71	0.87
CHA450	1.72	6.34	0.98	0.69	4.92	29.54	55.81	-
CHA500	-	5.71	0.92	-	3.20	35.7	54.47	-

Elemental analysis via CHNS is also performed. The result indicated the presence of S (0.23%) in CHA350 in addition to C (4.29%), H (0.99%) and N (0.03%).

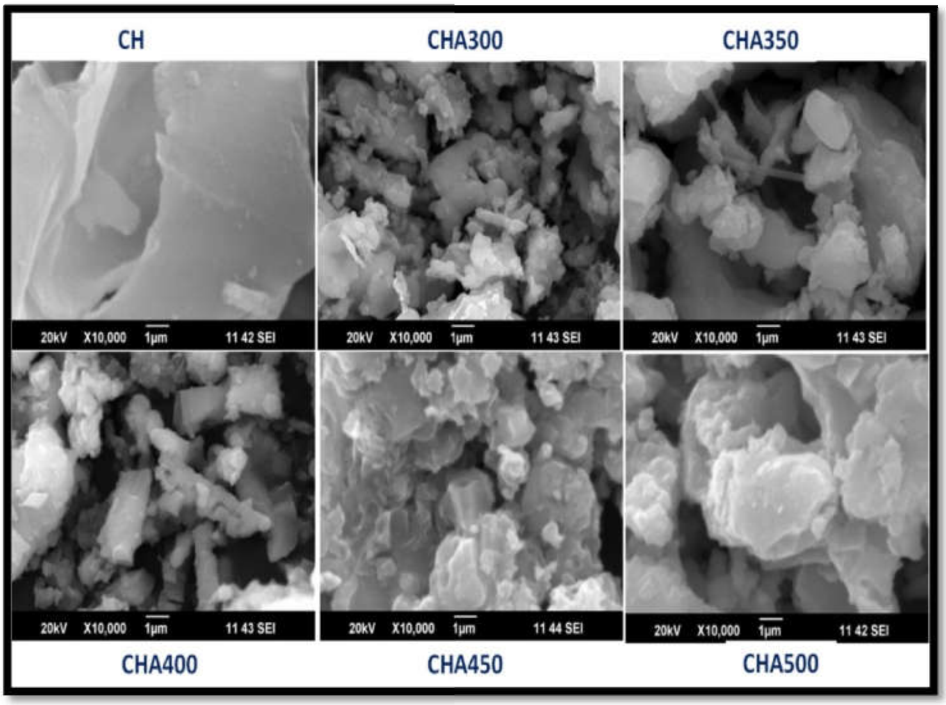


Fig 3.2 SEM image for CH and heat treated varieties

3.3.1.2 FTIR spectral analysis

The FTIR spectra of different ash samples derived from coconut husk are shown in figure 3.3. All the systems showed similar spectral patterns with little variation in the spectral band intensities. The peaks observed around 3400 cm^{-1} and 1640 cm^{-1} correspond to stretching and bending vibrations of adsorbed water or surface hydroxyl groups [22]. The absorption of atmospheric CO_2 on the basic sites may be the reason for the presence of band for basic carbonates in the range of 1300-1500 cm^{-1} [23]. Peak around 1000 cm^{-1} may be due to the silica component; i.e., stretching of Si-O-Si bond [24].

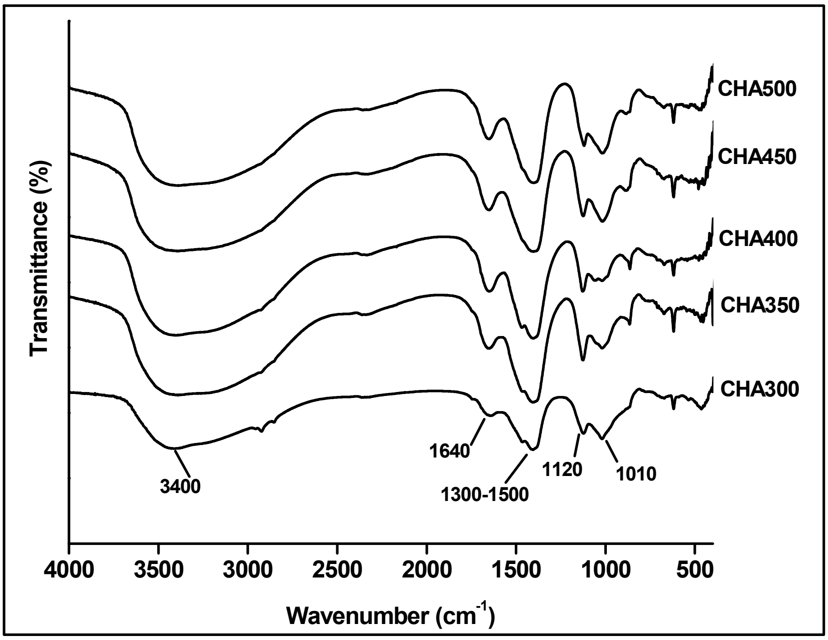


Fig 3.3 FTIR spectra of coconut husk treated at various temperatures

3.3.1.3 XRD analysis

The components responsible for the activity of the coconut husk ash in biodiesel production are revealed from the X-ray diffraction analysis. Figure 3.4 shows the XRD patterns of the catalysts prepared at different calcination temperatures. The 2θ values corresponding to the diffraction from various components of ash such as KCl, $K_2Si_2O_5$, K_2SO_4, K_2S_3, $KAlO_2$, $K_4CaSi_3O_9$, $Ca_2FeAl_2BSi_4O_{15}(OH)$ etc., as matched with the JCPDS (73-0380, 04-

010-3964, 005-0613, 31-1095, 00-053-0809, 00-039-1427 and 070-1856) data [15, 18]. The diffraction bands at 2θ values of 28.3°, 40.5°, 50.2°, 66.4° and 73.7° corresponds to the (002), (022), (222), (024) and (224) respective planes of KCl in the cubic lattice. The diffraction bands at 2θ values 32.7°, 34.3° and 38.6° from the (221), (202) and (222) planes of K_2S_3 in the crystal lattice is also visible.

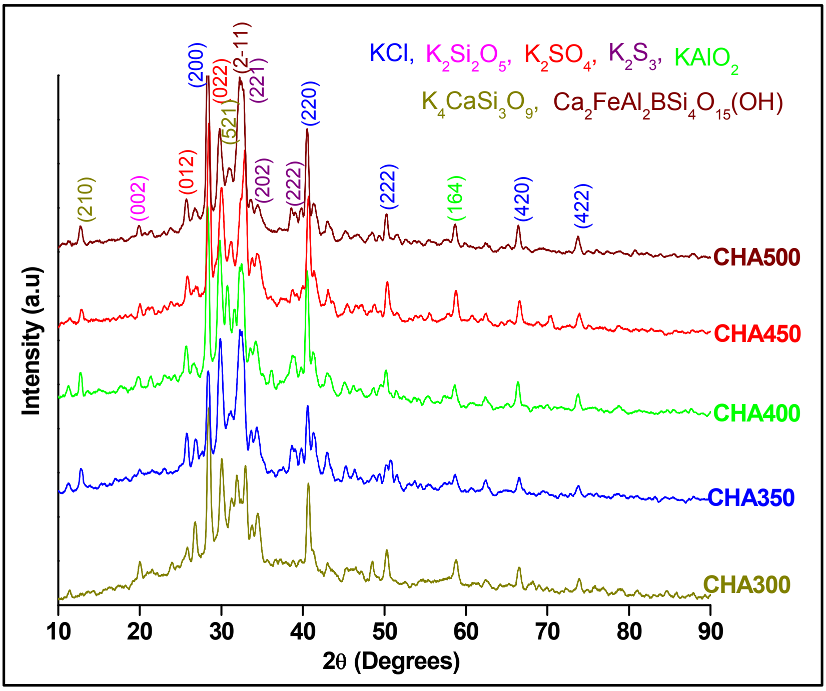


Fig 3.4 XRD of coconut husk treated at various temperatures

3.3.2 Catalytic activity studies

The catalytic activity of the prepared systems is initially analyzed in the transesterification of JCO with methanol. At first, the suitable calcination temperature for the preparation of coconut husk ash catalyst was determined.

3.3.2.1 Effect of calcination temperature

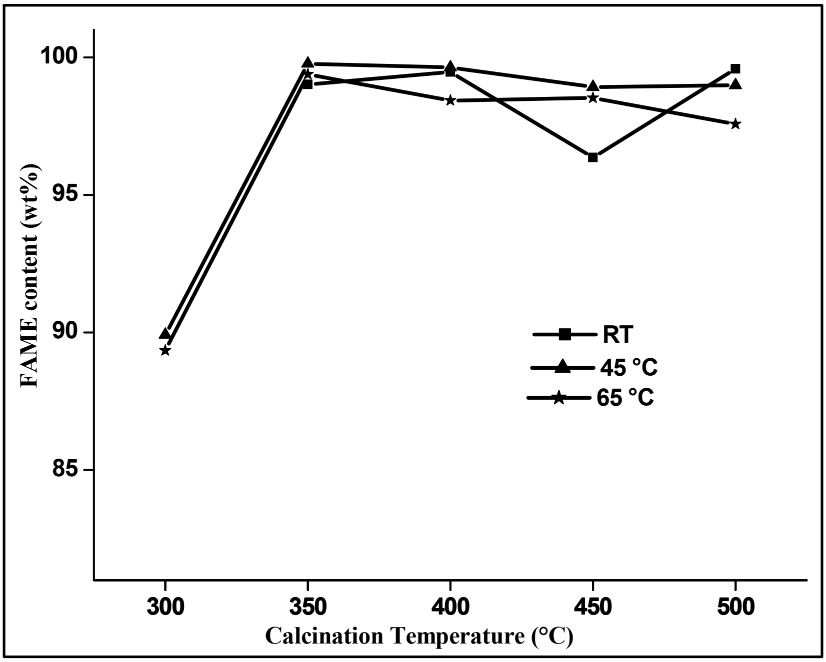


Fig 3.5 Effect of calcination temperature on FAME content under the reaction conditions of catalyst weight 5 wt%, methanol to oil molar ratio 15:1 and at 45 °C and 65 °C for 1h

Among the different catalysts prepared from the coconut husk, CHA350, the coconut husk treated at 350 °C was found to show the highest activity at different reaction temperatures and is evident from the results shown in figure 3.5. Room temperature reaction was conducted for 3 h. The catalyst is superior to other basic ash based catalysts used for biodiesel production [15-18]. So this particular catalyst production process and hence the biodiesel preparation is much more energy efficient compared to the other ash based catalysts. The effects of other reaction parameters, methanol/oil molar ratio, catalyst weight, reaction time and reaction temperature are analysed over CHA350 catalyst.

3.3.2.2 Effect of methanol/oil molar ratio

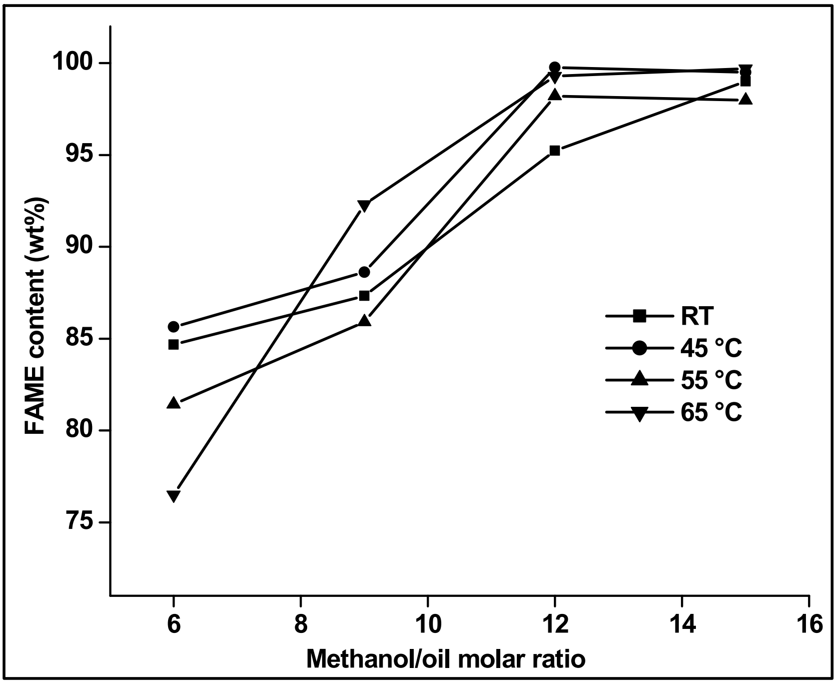


Fig 3.6 Effect of methanol/oil molar ratio on FAME content under the reaction conditions of catalyst weight 5 wt%, at reaction temperatures of RT, 45 °C, 55 °C and 65 °C over CHA350

Figure 3.6 shows the effect of methanol/oil molar ratio on the transesterification of jatropha oil over CHA350 catalyst at various reaction temperatures. All the reactions are carried out for 1 h, except for room temperature reaction, which was conducted for 3 h. A FAME content of about 80% is achieved even at a lower methanol/oil ratio of 6:1 at high temperatures. Further increase in the amount of methanol consequently raised the FAME content and acquired a fuel grade value of above 96.5% from a methanol/oil molar ratio of 12:1 onwards. Within 1 h of reaction, excellent results were obtained for a methanol/ oil molar ratio of 12:1 at reaction temperatures of 45 °C and 65 °C. It can be concluded from the plots shown in figure 4.5 that 45 °C is the best-suited lowest reaction temperature for the transesterification of jatropha oil over coconut husk ash catalyst at 12:1 methanol/oil molar ratio and the best suited methanol/oil ratio for room temperature reaction was 15:1 when 5 wt% of the catalyst is used for 3 h reaction.

3.3.2.3 Influence of catalyst dosage

From the figure 3.7, it is observed that increase in the catalyst weight will result in high conversion at all the selected temperatures. For a dosage of 5 wt% of the CHA350 catalyst, a FAME content of 99.77% is achieved and a further increase in catalyst weight resulted in more or less similar FAME content and thus we selected a catalyst weight percentage of 5 wt% for further studies.

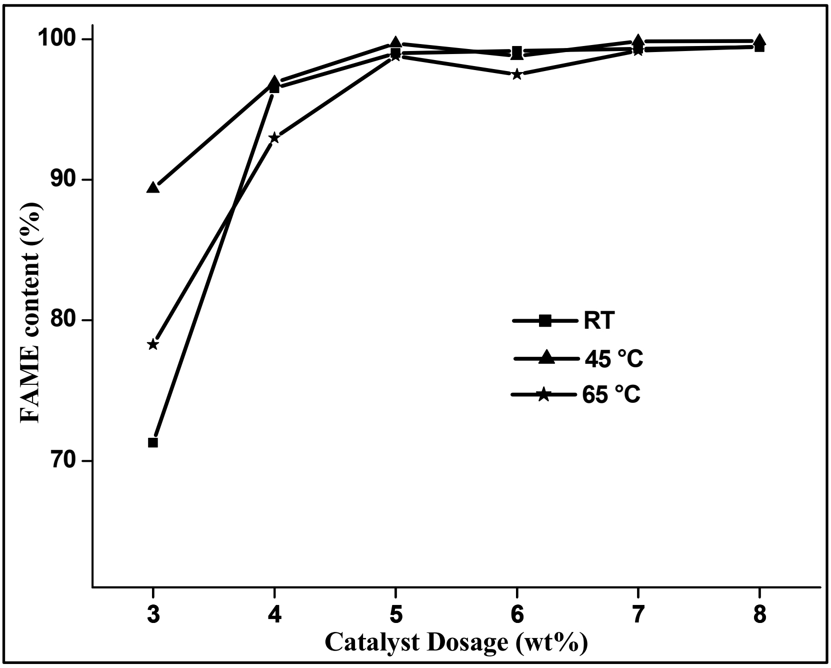


Fig 3.7 Effect of catalyst weight on FAME content under the reaction conditions of 12:1 methanol/oil for reaction temperatures of 45 °C and 65 °C and 15:1 for RT over CHA350

3.3.2.4 Effect of time

Production of biodiesel at a faster rate is economically viable and preferred in industrial scale applications. Here the duration for transesterification reaction is varied at room temperature, 45 °C and 65 °C (figure 3.8 and figure 3.9).

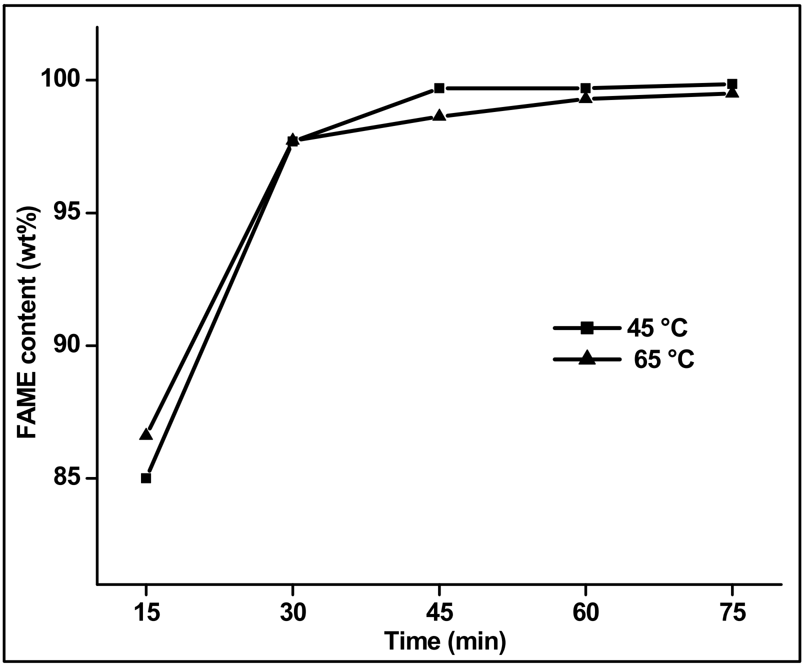


Fig 3.8 Effect of reaction time on FAME content under the reaction conditions of 12:1 methanol/oil for reaction temperatures of 45 °C and 65 °C over CHA350

It is seen that fuel grade biodiesel with FAME content of more than 96.5% is obtained within 30 minutes of the reaction from 45 °C onwards. At room temperature, it requires 3 h to obtain fuel grade biodiesel at a methanol/oil molar ratio of 15:1. Further raise in the reaction time maintained the FAME content above 99% at 15:1 and 12:1 methanol/oil molar ratios.

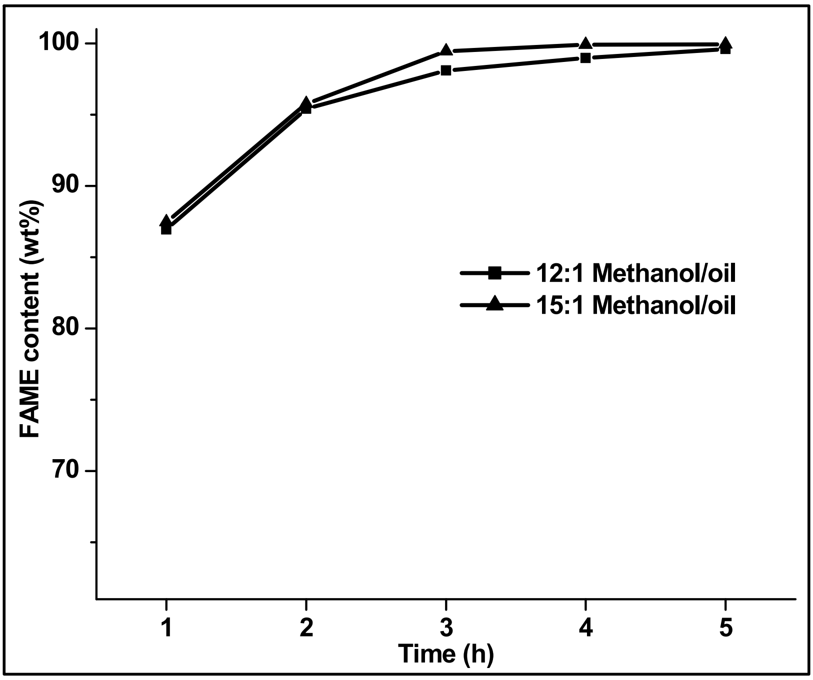


Fig 3.9 Effect of reaction time on FAME content under the reaction conditions of 15:1 and 12:1 methanol/oil at room temperature over CHA350

3.3.3 Reusability of CHA350

Reusability of the CHA350 catalyst was investigated at the reaction conditions of 5 wt% of catalyst at a methanol/oil molar ratio of 12:1 at reaction temperature of 65 °C for 1 h. Catalyst recovered from the reaction medium was washed with methanol to remove the traces of biodiesel and was dried. The catalyst was then activated at 350 °C for 1 h and repeated the reaction. It found that the catalyst lost its activity. It may be caused by leaching of the active components responsible for the reaction.

3.3.4 Leaching studies of CHA350

Leaching study of CHA350 is performed to investigate the nature of the catalytic process, since the catalyst was found to be inactive in the second cycle itself. The catalyst corresponding to 5 wt% of oil was first stirred with methanol for 1 h at 65 °C. It was then filtered and the filtrate was used for the transesterification reaction with oil in such a way that the methanol to oil molar ratio was 12:1. The FAME content obtained with the leached out homogenous catalyst was 96.1%. The result is compared with the reaction done at 65 °C for 1 h over 5 wt% of the solid catalyst; more efficient performance (above 99% FAME) is obtained by the use of the solid catalyst as such under the selected reaction conditions and the total time required for the entire reaction was also found to be less. The activity of the residue after the reaction is checked and it is found that the solid residue is not active in the reaction. It is possible that the active component in the catalyst is leached to methanol and removed during the filtration process losing the activity of the solid material.

So as to get an idea about the components of the catalyst that are reached out to the reaction mixture, elemental analysis of the fresh CHA350 and used up catalyst was investigator via ICP-AES analysis. The amount of metal components (in mg/g catalyst) are Al: 1. 3342 (1.2764), Ca: 21.5366 (19.8516), Fe: 2.2352 (2.2857), K: 336.49 (92.4741), Mg: 17.349 (17.5163) and Na: 41.98 (23.0274). Data in the parenthesis stands for the used catalyst. The results reveal the leaching of Potassium and Sodium species to the reaction mixture, while retaining other components. This further confirms the role of potassium in the reaction.

3.3.5 Pilot scale production of biodiesel

The feasibility for the scale-up of the low cost solid CHA350 catalyst in biodiesel production is analyzed by performing the reaction in the pilot scale setup. At the reaction condition of 12:1 methanol/oil ratio at a temperature of 45 °C, the transesterification of JCO as well as UCO is upgraded in the pilot plant over 5 wt% of CHA350 catalyst for 1 h reaction. The biodiesel produced from JCO and UCO contains the FAME contents of 99.77% and 99.97% respectively indicating the high efficacy of the process.

3.3.6 Fuel properties of biodiesel

The fuel properties of the JCO and UCO biodiesel produced in the pilot plant are analyzed using various test methods [25, 26]. From the data shown in table 3.3, it is evident that the prepared biodiesel samples meet the international standard specifications.

Table 3.3 Fuel properties of biodiesel produced from JCO and UCO over CHA350 catalyst

Parameters	Unit	Limits	Standards	JCO	UCO
Ester content	% m/m	96.5 min	EN 14214	99.77	99.97
Monoglyceride	% m/m	1.00max	D 6751	0.00	0.00
Triglyceride	% m/m	0.25max	D 6751	0.04	0.02
Free glycerol	% m/m	0.02 max	D 6751	0.00	0.00
Total glycerol	% m/m	0.38 max	D 6751	0.03	0.01
Acid value	mg KOH/g	0.80 max	D 6751	0.00	0.24
Water content	Vol.%	0.50 max	D 6751	0.00	0.00
Iodine value	mg I/100 g	120 max	EN 14214	109	92
Viscosity	mm2/s	1.96-6.0	D 6751	4.07	3.78
Density	kg/ m3	860-890	D 6751	873	868

3.3.7 Composition of biodiesel

The percentage composition of the fatty acid methyl esters present in the biodiesel sample obtained from jatropha oil are given in Table 3.4; and it matches the reported data of fatty acid profile of jatropha oil [27].

Table 3.4 Percentage composition of fatty acid methyl ester found in the biodiesel produced from JCO over CHA350 catalyst

Faty acid	No. of carbon in the fatty acid chain: Double bond	Weight (%)
Myristic	14:0	<0.01
Palmitic	16:0	15.48
Stearic	18:0	6.61
Arachidic	20:0	<0.01
Behenic	22:0	<0.01
Palmitoleic	16:1	0.86
Oleic	18:1	37.05
Linoleic	18:2	37.42
Linolenic	18:3	<0.01
Others		2.55

3.4 Conclusions

A highly efficient ash based catalyst has been developed from coconut husk for the large-scale production of fuel grade biodiesel in a cost-effective way that made the entire process economically viable. The catalyst activity is excellent in the transesterification reaction even at room temperature. At a reaction temperature of 45 °C, with the catalyst CHA350, prepared from coconut husk at a low calcination temperature of 350 °C, the FAME content of biodiesel was found to be more than 97% within 30 minutes of reaction time. The biodiesel produced from JCO and UCO at the selected reaction conditions in the pilot plant over CHA350 met the international standard specifications for the biodiesel fuel. The most attractive factor of the present cost-effective, solid catalyst developed from waste material for biodiesel production is its low temperature activity.

References

1. H.P. Singh, V. T. Markose and R. Gopalakrishnan, *30 Years of Coconut Industry in India*. Coconut Development Board, Kochi, 1999.

2. Mukharjee, Pippa, *Nature Guides - Common Trees of India, World Wild Fund for Nature - India*, Oxford University Press, Bombay,1983.

3. J. A. Banzon and J. Velasco, *Coconut: Production and Utilisation. Philippine Coconut Research and Development Foundation*, Pasig, Metro Manila, Philippines, 1982.

4. T. Y. Ding, S. L. Hii and L. G. A. Ong, *BioResources*, 2012, **7**, 1540-1547.

5. J. R. Oluremi, S. I. Adedokun and O. M. Osuolale*, IJERT*, 2012, **1**, 1-9.

6. K.S. Low and C. K. Lee, *Pertanika*, 1990, **13**, 221-228.

7. D. Kavitha and C. Namasivayam, *Bioresour. Technol*., 2007, **98**, 14-21.

8. G. N. Manju, C. Raji and T. S. Anirudhan, *Wat. Res*., 1998, **32**, 3062-3070.

9. W. T. Tan, S. T. Ooi and C. K. Lee, *Environ. Technol*., 1993, **14**, 277-282.

10. I. A.W. Tan, A. L. Ahmad and B. H. Hameed, *J. Hazard. Mater*., 2008, **153,** 709-717.

11. J. H. Tay, X. G. Chen, S. Jeyaseelan and N. Graham, *Chemosphere*, 2001, **44**, 45-51.

12. J. R. Oluremi, S. I. Adedokun and O. M. Osuolale, *The Pacific Journal of Science and Technology*, 2012, **13**, 499-507.

13. Muhaimin, S. Sudiono, *AIP Conference Proceedings* 1823, 020092 (2017); doi: 10.1063/1.4978165.

14. P. Kumar, A. K. Sarma, M. K. Jha, A. Bansal and B. Srivasatava, Bull. Chem. React. Eng. Catal., 2015, **10**, 221-229.

15. Z. Yaakob, I. S. B. Sukarman, B. Narayanan, S. R. S. Abdullah and M. Ismail, *Bioresour. Technol.*, 2012, **104**, 695-700.

16. G. Y. Chen, R. Shana, J. F. Shi and B. B. Yan, *Fuel Process. Technol.*, 2015, **133**, 8–13.

17. C. O. Boateng and Lee KT, *Chem. Eng. J.*, 2013, **220**, 395-401.

18. M. Sharma, A. A. Khan, S. K. Puri, D. K. Tuli, *Biomass Bioenergy*, 2012, **41,** 9 4-1 0 6.

19. W. Guang, Y. Zifeng, S. Marianne, Z. Peng and W. Ben, *Fuel*, 2010, **89,** 2163-2165.

20. Y. Liu, T. Liu, X. Wang, L. Xu and Y. Yan, Energy Fuels 2011, **25,** 1206-1212.

21. W. Boyang, L. Shufen, T. Songjian, F. Rihua and M. Yonglu, *Fuel*, 2013, **104,** 698-703.

22. K. Nakamoto, *Infrared spectra of inorganic and coordination compounds*, John Wiley, New York, 1970.

23. S. M. Park, J. W. Park, H. P. Hab, H. S. Han and S. Gon, *J. Mol. Catal. A: Ch. E.m*, 2007, **273,** 64-71.

24. NN Binitha and S. Sugunan, *Micropor Mesopor Mater.*, 2006, **93,** 82-89.

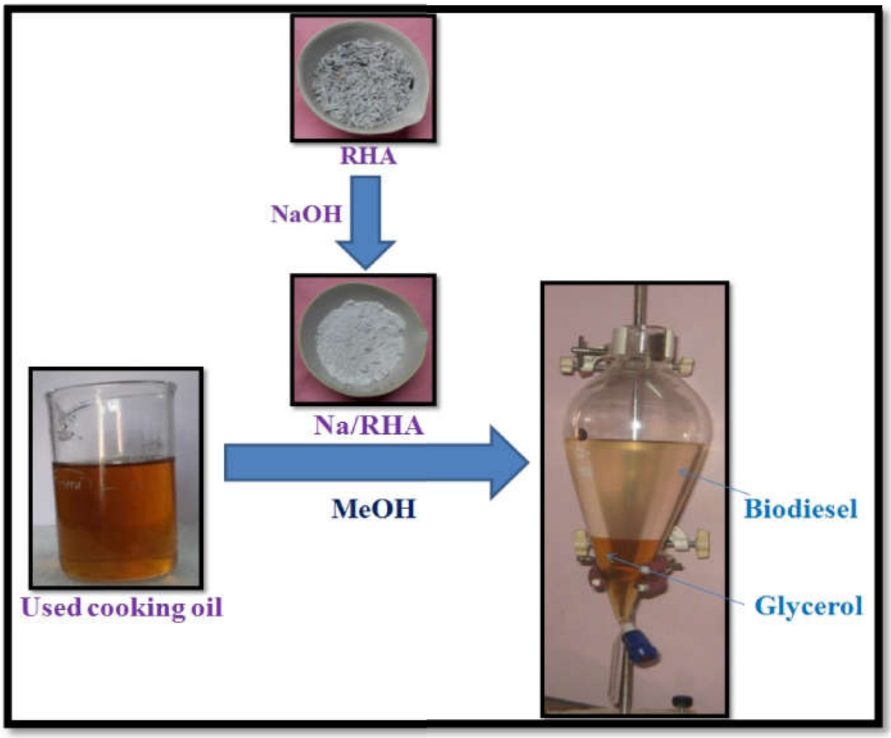
25. S. P. Singh and D. Singh, *Renewable Sustainable Energy Rev.*, 2010, **14,** 200-216.

26. G. Knothe, *Fuel Process. Technol.*, 2005, **86,** 1059-1070.

27. G. M. Gubitz, M. Mittelbach and M. Trabi, *Bioresour. Technol.*, 1999, **67,** 73-82.

CHAPTER 4

SINGLE STEP BIODIESEL PRODUCTION OVER Na LOADED RICE HUSK ASH CATALYST



Sodium modified rice husk ash catalyst was effectively used in the single step production of biodiesel from triglyceride oils

4.1 Introduction

Rice husk (RH) is an agricultural waste generated in the production of rice [1]. The rice milling industries discarded plenty of rice husks and the utilization of this waste material for value-added purposes could solve its disposal problem and thus can reduces the cost of waste management [2]. Due to the presence of high organic content (cellulose and lignin) and hence the high calorific value (13-16 MJ/kg), RH has been used as fuel in rice processing and also in power plants [3]. In Kerala, charcoal (umikkari) from rice husk has been used as a traditional ayurvedic tooth cleanser [4]. The combustion of RH produces rice husk ash (RHA, ~ 18%), which is largely disposed of in landfills. The major constituent of RHA is silica (content varies from 83-98%) with minor amounts of metallic elements [5]. The incinerating methods and conditions under which the RHA is produced, can affect the silica content and properties of the ash [6]. Controlled burning of RH under specific conditions produces active RHA, which contains high purity amorphous silica that has variety of applications in electronics, ceramic, and polymer material industries [7]. Ultrafine size and high surface area of silica obtained from RH could offer many applications, such as thixotropic agents, as thermal insulators, as composite fillers, as adsorbents and as catalyst precursors/supports for organic synthesis etc [8]. The high silicon content in the RHA makes it a major source for the preparation of elementary silicon and silicon-based compounds [9]. RH derived silica is more attracted in catalysis, for the production of materials like zeolites and mesoporous silicates [10]. Effective tuning of the properties of silica derived from RHA by chemical treatment can enhance its catalytic activity and thus has been employed as a heterogeneous catalyst in a variety of organic transformations [11].

As a catalyst support or precursor for biodiesel production, silica from RHA is also used. Wang et al prepared a heterogeneous lithium silicate catalyst from RHA for the transesterification of soybean oil [12]. Hindryawati and coworkers utilized RH silica for the impregnation of alkali metals (Li, Na, and K) for its effective use in the transesterification of used cooking oil [13]. Roschat et al prepared RH derived sodium silicate and employed as a solid catalyst for the conversion of triglycerides to biodiesel [14].

In the present work, a green heterogeneous catalyst was developed from RHA by treating it with NaOH for the production of biodiesel by a one-step, facile transesterification of used cooking oil (UCO) as well as jatropha oil (JCO). The characterization of the catalyst using various techniques revealed that the active phase of the catalyst is sodium silicate, which is distributed over cristobalite silica. Reports are there on the use of sodium silicate (which is prepared by different methods) as a solid catalyst for the production of biodiesel from rapeseed oil [15], soybean oil [16], cottonseed oil [17], jatropha oil [18] and palm oil [19]. All these works have at least one of the following demerits such as limited reusability of the catalyst, catalyst leaching, high cost of the catalyst, requirement of high methanol/oil molar ratio in the reaction, high reaction temperature, low FFA tolerance, long duration for the reaction and/or the need of high pressure conditions. The present catalyst is highly efficient and operated under mild reaction conditions even at lower methanol/oil molar ratios. The major highlight of the sodium loaded rice husk ash derived catalyst is its reusability for 8 repeated cycles of operation. The catalyst is found to be resistant to high FFA content (up to 20%) in the oil, thereby eliminating the requirement of pre-esterification step. It also tolerates moisture content even up to 4 weight percent of the oil. Pilot scale production of fuel grade biodiesel over the catalyst under mild reaction conditions revealed the feasibility of the process for industrial scale operations.

4.2 Experimental

4.2.1 Preparation of Rice husk ash (RHA)

RH was cleaned first to remove the dust and other impurities. Then it was thoroughly washed with deionized water and dried at 90 °C in a hot air oven. The dried RH was calcined in a muffle furnace at 650 °C for 3 h and powdered to get RHA.

4.2.2 Preparation of Na/RHA catalyst

The solid catalyst from RHA was developed by Na incorporation via sol-gel method. In a typical procedure, RHA was added to NaOH solution (0.25 N) so as to attain a Na:Si molar ratio of 1:1 (50/50). The suspension was stirred by heating at 80 °C to dissolve the silica present in the rice husk ash. The insoluble part is filtered out from the obtained sol. The stirring and heating of the sol were continued till the transparent sol got gelated and was then dried. The gel was transferred to a china dish and dried in an oven at 90 °C. Calcination was performed at different temperatures from 450 °C to 750 °C at an interval of 50 °C. After calcination, the samples were powdered and refluxed with methanol for 1 h for removing the methanol soluble fraction and further activated at the calcination temperature for one more hour. The procedure is depicted in the figure 4.1. The catalyst calcined at a temperature of 650 °C was found to be more suitable for the reaction and thus it was selected for further catalytic activity studies. A series of catalysts calcined at 650 °C was also prepared by varying the molar ratio of Na/Si to 30:70, 40:60 and 60:40. The catalyst prepared at a Na/Si molar ratio of 50:50 and calcined at 650 °C, designated as Na/RHA was analyzed through FTIR spectroscopy, XRD, TEM and SEM analyses.

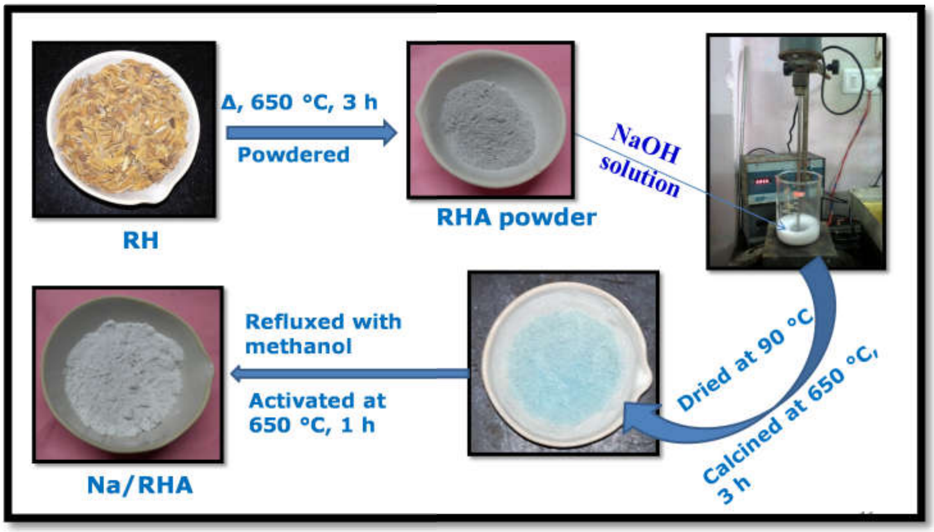


Fig 4.1 Preparation of Na loaded RHA catalyst

The activity of all the catalytic systems prepared was analyzed by investigating its performance in the transesterification of used cooking oil (UCO). The detailed procedures for the investigation of the effect of reaction parameters in the transesterification reaction, pilot scale production of biodiesel from used cooking oil as well as *jatropha carcus* oil (JCO) under the selected reaction conditions, biodiesel analysis and determination of fuel properties are explained in chapter 2, sections 2.5, 2.12.2, 2.7 and 2.13 respectively.

4.3 Results and Discussion

The catalysts were prepared by sol-gel method using RHA and NaOH at different Na/Si molar ratios. The system prepared at a Na/Si molar ratio of 50:50 treated at 650 °C was designated as Na/RHA and was selected for the detailed catalytic activity studies. The active components and the surface morphology of the Na/RHA catalyst was analyzed through various characterization techniques. Laboratory scale experiments were conducted in order to study the effect of catalyst calcination temperature, methanol to oil molar ratio, dosage of the catalyst, duration of the reaction and the reaction temperature in the transesterification reaction of used cooking oil with methanol over the Na/RHA catalyst. At one of the selected reaction conditions, biodiesel production is upgraded in the pilot plant which ensured the feasibility of the process in the large scale production.

4.3.1 Catalyst characterizations

4.3.1.1 FTIR Spectral analysis

In the FTIR spectrum (Figure 4.2), the band around 1450 cm^{-1} can be attributed to the vibration characteristic of the presence of carbonate aroused by atmospheric CO_2 adsorption [20]. The Si-O-M or Si-O-Na vibration is observed around 990 cm^{-1} [21, 22]. Additionally, the O-H stretch of surface-bound water is seen as broadband around 3400 cm^{-1} [23]. Si-O-Si symmetric stretching vibration is observed around 742 cm^{-1}. The bands around 594 cm^{-1} and 496 cm^{-1} are attributed to the O-Si-O as well as Si-O-Si bending vibrations [24].

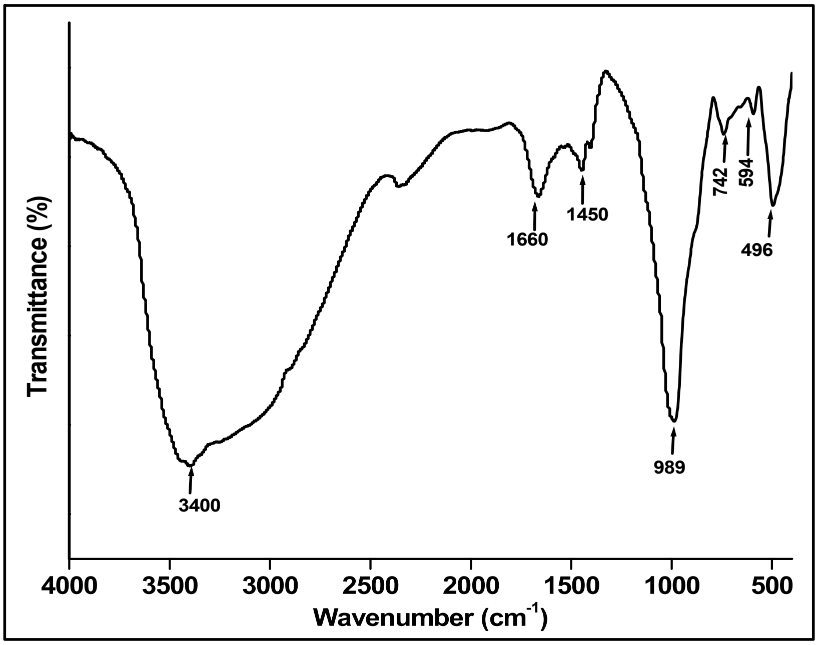


Fig.4.2 FTIR spectra of Na/RHA catalyst

4.3.1.2 XRD Analysis

The XRD pattern (Figure 4.3) revealed that Na_2SiO_3 (JCPDS card nos. 00-016-0818) and cristobalite SiO_2 (JCPDS card no. 01-082-1235) are the major crystalline phases of the material [25, 26]. Cristobalite SiO_2 may interact with Na_2SiO_3, thus increasing the heterogeneity of the highly active Na/RHA catalyst in the transesterification reactions. The diffraction bands at 2θ values 16.7°, 24.7°, 29.1°, 34.6°, 36.9°, 45.4°, 47.9°, 49.3°, 51.8°, 60.1°, 64.0° and 65.5° corresponds to the respective planes; (100), (101), (110), (220), (002), (210), (112), (211), (300), (103), (221) and (302) of Na_2SiO_3 in the hexagonal crystal structure. The diffraction bands at 2θ values 22.2°, 42.9°, 53.8° and 58.0° are characteristic for the cristobalite SiO_2.

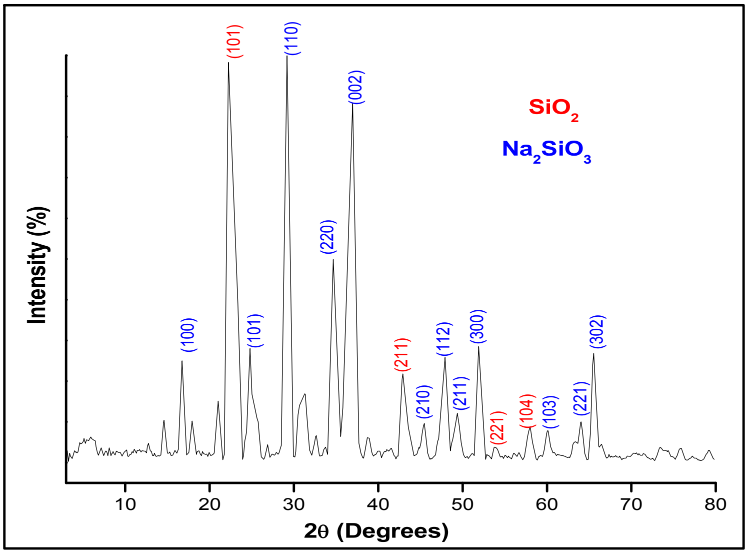


Fig.4.3 XRD image of Na/RHA catalyst

4.3.1.3 SEM Analysis

In the SEM image (figure 4.4), homogeneous interconnected sheet like structure with macroporous rough morphology is observed, which is favorable for biodiesel production [14, 27].

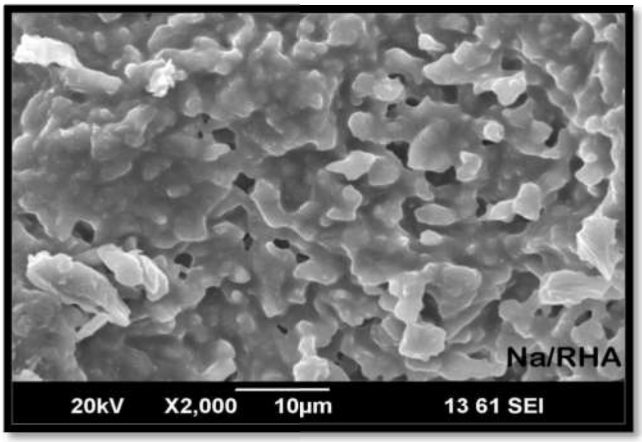


Fig.4.4 SEM image of Na/RHA catalyst

4.3.1.4 TEM Analysis

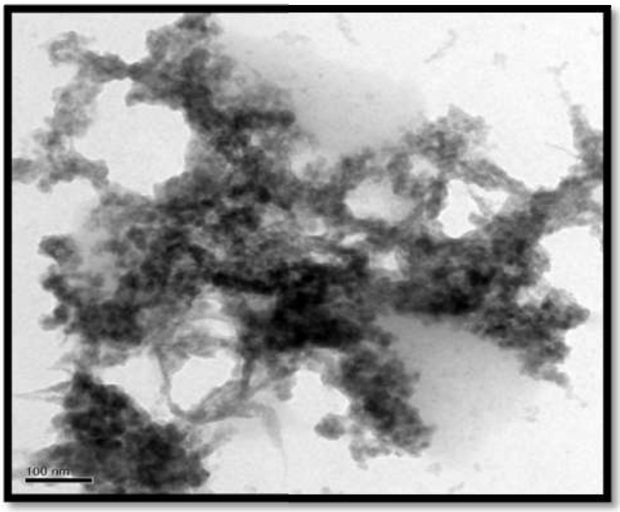


Fig.4.5 TEM image of Na/RHA catalyst

In the TEM, interparticle agglomeration and macropores are observed.

4.3.2 Activity studies of RHA derived catalysts

The catalytic efficiency of RHA derived catalysts at varying conditions was investigated using UCO.

4.3.2.1 Effect of catalyst calcination temperature

The calcination temperature of 1:1 Na/Si catalyst is varied from 450 °C to 750 °C, whereas at 650 °C maximum conversion of biodiesel is obtained and is thus selected as the suited calcination temperature of the catalyst. The results are shown in the figure 4.6.

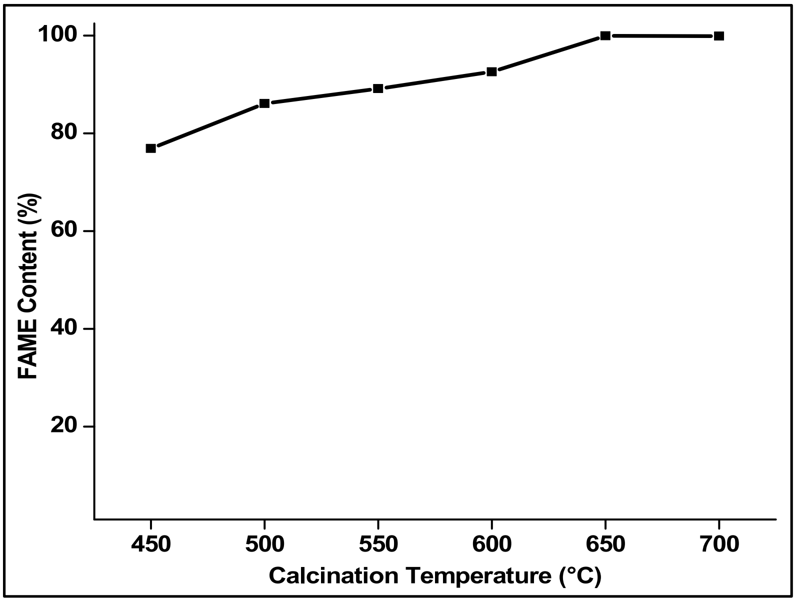


Fig 4.6 Effect of calcinations temperature on FAME content under the reaction conditions of catalyst weight 6 wt%, 15:1 methanol/oil molar ratio, at a reaction temperature of 65 °C over Na/RHA catalyst for 75 minutes

4.3.2.2 Effect of Na/Si molar ratio

The molar ratio of Na:Si is varied to choose the best composition of the catalyst. Activity increased linearly with Na loading up to 50:50 which further decreased at a 60:40 molar ratio of Na:Si in the transesterification reaction of UCO. Then the catalyst with 1:1 Na/Si molar ratio was selected as the best catalytic system for further investigations. The results are plotted in the figure 4.7. The effect of reaction parameters influencing the catalytic activity of Na/RHA catalyst in the biodiesel production from UCO was then investigated. At one of the best reaction conditions, transesterification of JCO was also conducted.

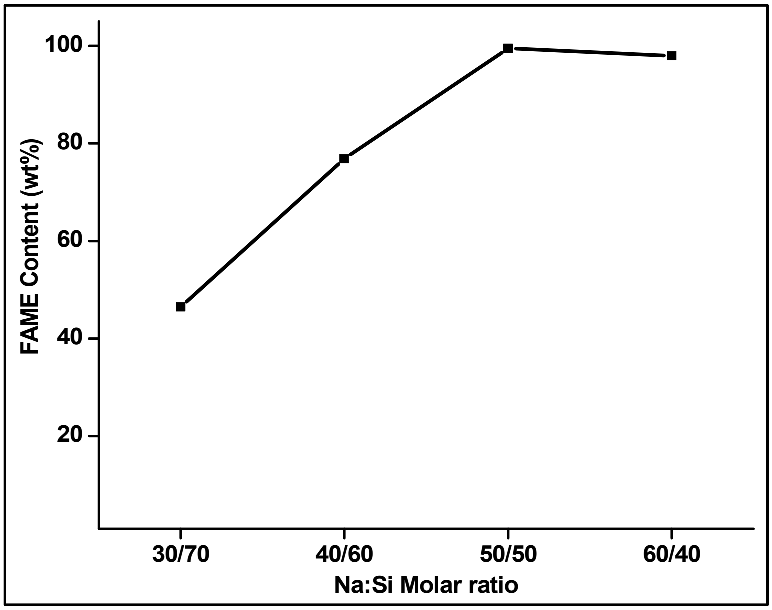


Fig 4.7 Effect of Na/Si molar ratio on FAME content under the reaction conditions of catalyst weight 6 wt%, 15:1 methanol/oil molar ratio, at reaction temperature of 65 °C over Na/RHA catalyst for 75 minutes reaction

4.3.2.3 Effect of methanol/oil molar ratio

The high molar ratio of methanol to oil is highly beneficial in the transesterification reactions since methanol has the additional role as a solvent and also in promoting the forward reaction [28, 29]. Activity increased linearly with methanol/oil ratio. It is found that 12:1 is the most suited methanol/oil ratio in the transesterification reaction using Na/RHA catalyst, whereas the biodiesel content in the samples produced from UCO matches the international standard specifications at a ratio of 12:1. The observations are shown in the figure 4.8.

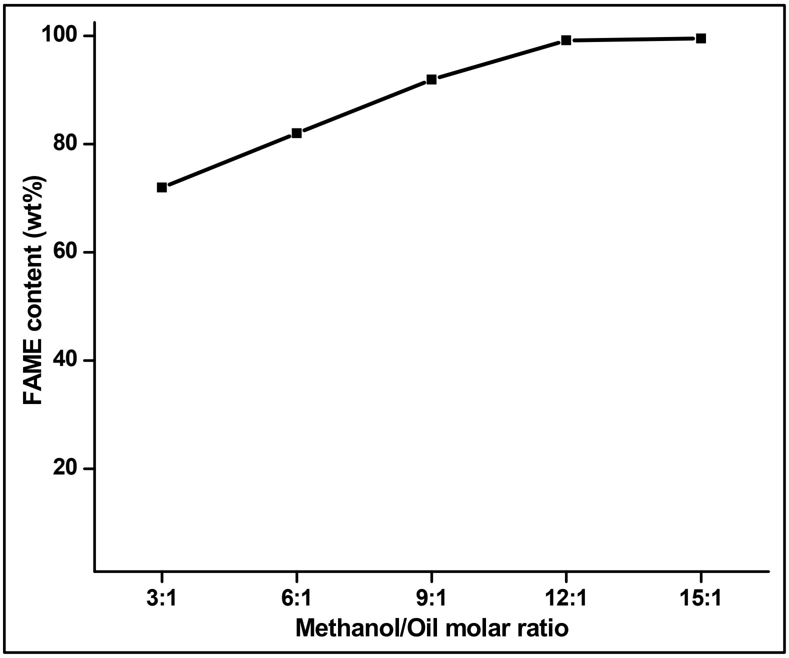


Fig 4.8 Effect of methanol/oil molar ratio on FAME content under the conditions of catalyst weight/oil 6 wt%, at a reaction temperature of 65 °C over Na/RHA catalyst for 60 minutes reaction

4.3.2.4 Effect of catalyst weight

The catalyst weight is varied and it is found that the FAME content matches the EN14214 specification (above 96.5%) for the reactions conducted over a dosage of 4 wt% of catalyst/oil onwards. The results are shown in the figure 4.9. 100% FAME content is achieved at a catalyst weight of 6 wt% onwards and thus it is selected for further experiments.

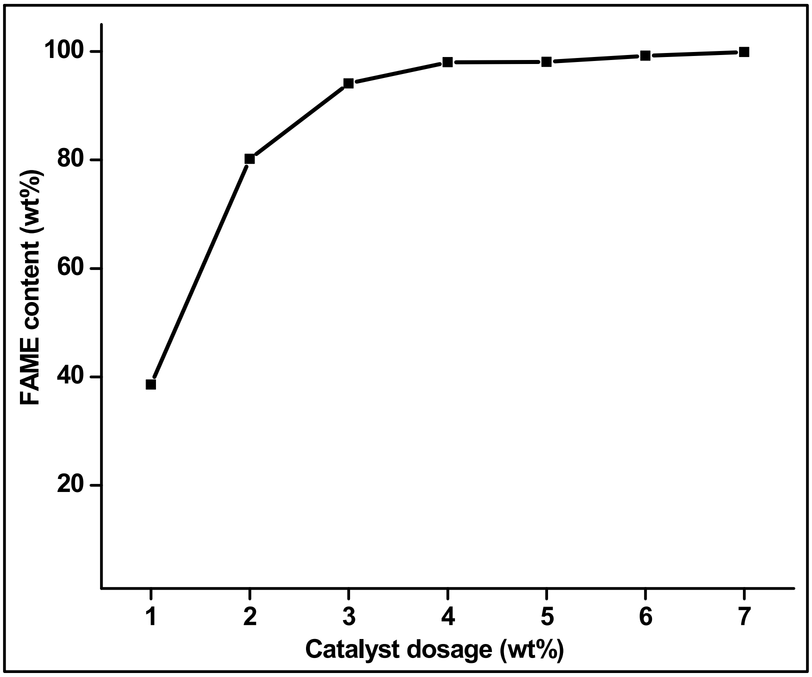


Fig 4.9 Effect of catalyst weight on FAME content under the reaction conditions of 12:1 methanol/oil molar ratio at a temperature of 65 °C over Na/RHA catalyst for 60 minutes reaction

4.3.2.5 Effect of reaction time

The reaction time is increased and it can be seen from the data in figure 4.10 that the FAME content is more than 96.5% from 45 min onwards. The maximum conversion of the triglycerides to the corresponding mono alkyl esters is achieved within 60 minutes.

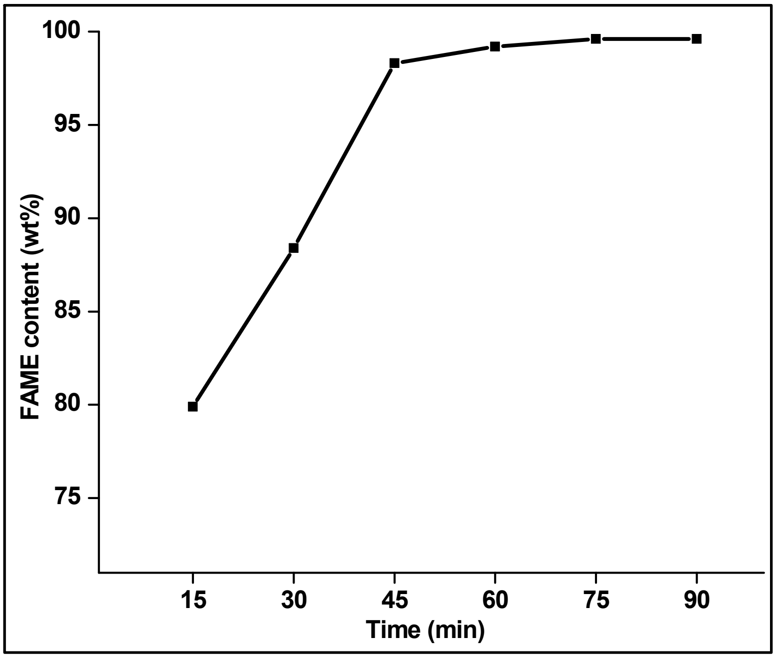


Fig 4.10 Effect of reaction time on FAME content under the conditions of catalyst weight 6 wt%, at a temperature of 65 °C over Na/RHA catalyst at a methanol/oil molar ratio of 12:1

4.3.2.6 Effect of reaction temperature

The reaction temperature is varied, and from 55 °C onwards, the FAME content meets the standard fuel specifications of biodiesel. It is found that the reflux temperature of the alcohol (methanol), i.e. 65 °C, is the most suited temperature to obtain maximum conversion within a short duration of the transesterification reaction. Results are shown in the figure 4.11.

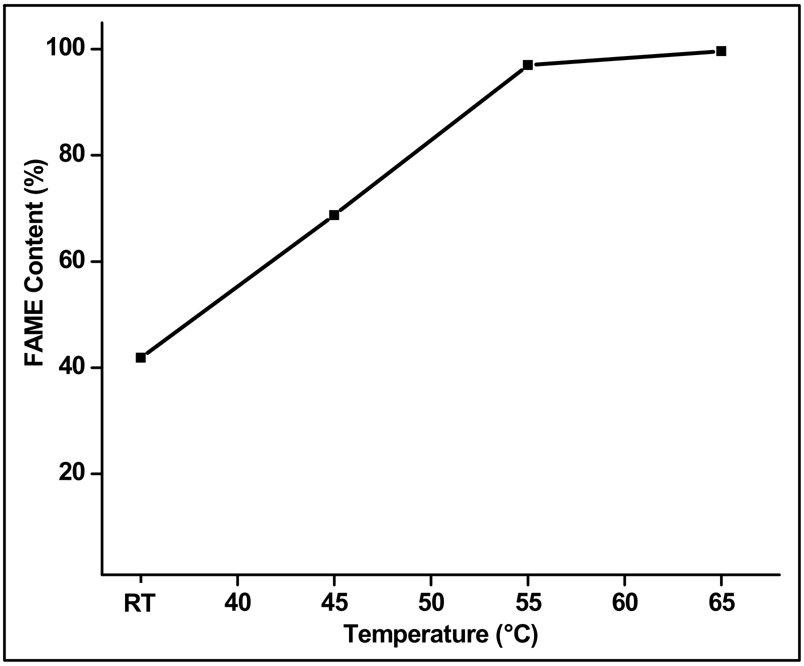


Fig 4.11 Effect of reaction temperature on the FAME content under the conditions of catalyst weight/oil 6 wt%, 12:1 methanol/oil molar ratio over Na/RHA catalyst for 75 minutes reaction

4.3.2.7 Effect of water content

Presence of moisture is a detrimental factor to biodiesel production. Usually, a moisture/water content of more than 0.5% diminishes the catalytic activity and reduces the biodiesel yield [30]. But in the case of low cost feedstocks such as UCO, the presence of trace amount of water is unavoidable [31]. We conducted a series of experiments by varying the water content in the oil and it found that for 75 minutes reaction, the catalyst was tolerant up to 2 wt% of water in the feedstock. When the reaction time was increased to 3 h, it is tolerant up to 4 wt% of water and the FAME content was sufficiently high (99.40%) when compared to that required as per the EN 14214 international standard specification of biodiesel. The results are shown in figure 4.12.

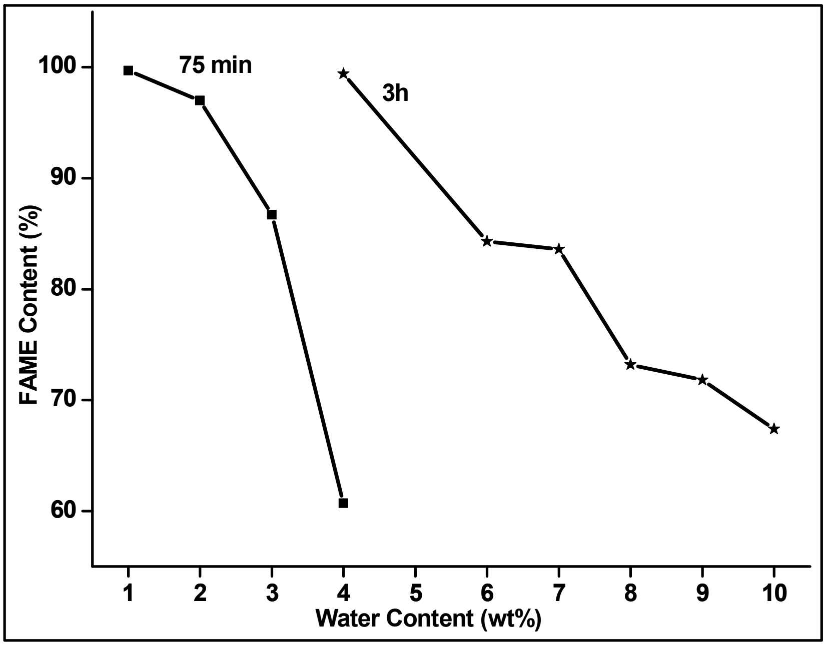


Fig 4.12 Effect of water content on the FAME content under the selected conditions of catalyst weight 6 wt%, 12:1 methanol/oil at 65 °C over Na/RHA catalyst for 75 minutes and 3 h reactions

4.3.2.8 Effect of free fatty acid

Effect of FFA content in the feedstock on the activity of Na/RHA is investigated since the amount of FFA usually negatively affects the biodiesel preparation using base catalysts [32]. Pre-esterification with acid catalyst is necessary for the high FFA containing feedstocks like UCO and JCO before the transesterification reaction [33]. The present Na/RHA catalyst was tolerant up to 6 wt% FFA content in the UCO for the reactions conducted for 75 minutes. By increasing the duration of reaction to 3 h, the catalyst showed a FFA tolerance up to 20 wt% of the oil. Results are in the table 4.1. Thereafter soap formation was also the resultant of the reaction.

Table 4.1 Effect of FFA on FAME content over Na/RHA catalyst

Amount of FFA added (wt% of oil)	FAME Content (wt%)
1	99.9
2	100.0
3	99.0
4	99.8
5	99.4
6	99.2
7	96.4
8	96.4
9	96.4
10	94.5
11	85.0
9*	100
12*	99.8
15*	98.8
20*	97.0

Reaction conditions: Catalyst dosage/oil 6 wt%, 12:1 methanol/ oil molar ratio at 65 °C over Na/RHA catalyst for 75 minutes and *3 h reaction

4.3.3 Catalyst reusability

The reusability of the present catalyst in the transesterification of UCO is investigated and it is found that the catalyst is effectively reusable in 8 repeated cycles without any loss in its catalytic activity.

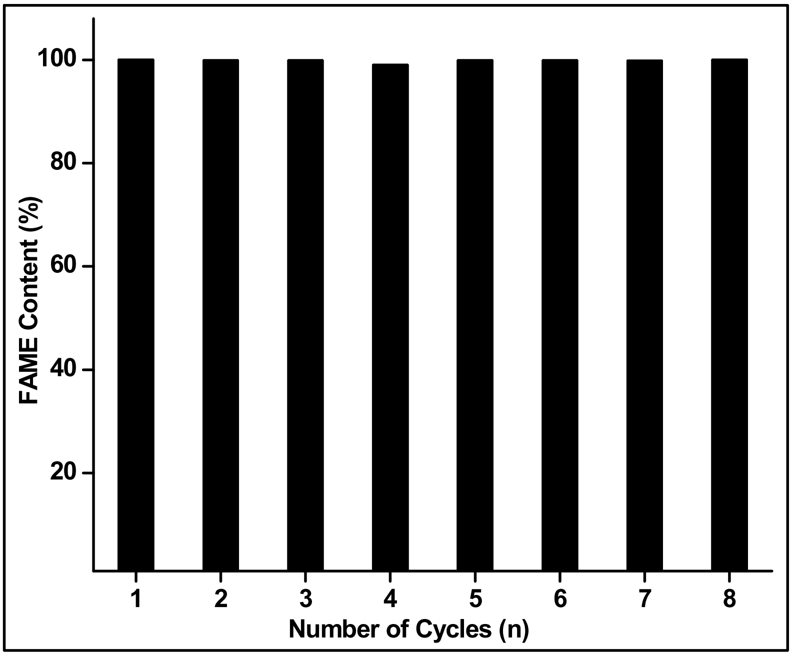


Fig 4.13 Reusability of the Na/RHA catalyst under the reaction conditions of a catalyst weight 6 wt%, 12:1 methanol/oil molar ratio at 65 °C for 75 minutes reaction

4.3.4 Pilot scale production of biodiesel over Na/RHA catalyst

15 L of fuel grade biodiesel is also produced over Na/RHA catalyst by performing the reaction in the pilot plant at the selected reaction conditions of catalyst weight 6 wt%, 12:1 methanol/oil molar ratio at a temperature of 65 °C for 75 minutes reaction and thus the catalyst is shown to be effective for the large scale economic

production of biodiesel. Here the transesterification reaction could be performed even without any acid pre-treatment process.

4.3.5 Fuel properties of the biodiesel produced in the pilot plant over Na/RHA catalyst

Table 5.2 shows the fuel properties of the biodiesel produced in the pilot plant from UCO over Na/RHA catalyst. Standard test methods are used to determine the fuel properties of the produced biodiesel [34, 35]. It evidently meets the international standard specifications for biodiesel fuel. Fuel properties of JCO biodiesel are also provided.

Table 4.2 Fuel properties of the UCO and JCO biodiesel produced over Na/RHA catalyst

Parameters	Unit	Limits	Standards	UCO	JCO
Ester content	% m/m	96.5 min	EN 14214	99.60	99.20
Monoglyceride	% m/m	1.00max	D 6751	0.00	0.08
Triglyceride	% m/m	0.25max	D 6751	0.08	0.20
Free glycerol	% m/m	0.02 max	D 6751	0.00	0.00
Total glycerol	% m/m	0.38 max	D 6751	0.05	0.10
Acid value	mg KOH/g	0.80 max	D 6751	0.40	0.58
Water content	Vol.%	0.50 max	D 6751	0.00	0.00
Iodine value	mg I/100 g	120 max	EN 14214	42	110
Viscosity	mm^2/s	1.96-6.0	D 6751	3.78	4.07
Density	kg/m^3	860-890	D 6751	866	875

4.4 Conclusion

Green and highly efficient low cost heterogeneous catalysts were developed from rice husk ash by sodium loading and it was successfully used for the biodiesel production from UCO and JCO feedstocks. The best catalyst, with 1:1 Na/Si molar ratio, treated at 650 °C retained 100% of its initial activity till 8 repeated cycles. The catalyst was found to be tolerant to high free fatty acid and moisture content in the UCO feedstock. The reaction was performed under mild conditions and the entire process is greener compared to the existing methods and also the biodiesel produced in the pilot plant met the international standard specifications for biodiesel fuel.

References

1. J. Alvarez, G. Lopez, M. Amutio, J. Bilbao and M. Olazar, F*uel*, 2014, **128**, 162-169.

2. M. Balakrishnan, V. S. Batra, S. J. Hargreaves and I. D. Pulford, *Green Chem*., 2011, **13**, 16-24.

3. D. An, Y. Guo, Y. Zhu and Z. Wang, *Chem. Eng. J.*, 2010, **162**, 509-514.

4. D. Prasetyoko, Z. Ramli, S. Endud, H. Hamdan and B. Sulikowski, *Waste Manage*., 2006, **26**, 1173-1179.

5. http://cgpl.iisc.ernet.in/site/Portals/0/Technologies/Precipitated Silica.pdf.

6. L. Armesto, A. Bahillo, K. Veijonen and J. Otero, *Biomass Bioenergy*, 2002, **23**, 171-179.

7. U. Kalapathy and A. Proctor, *Bioresour. Technol*., 2000, **73,** 257-262.

8. B. R. Abu, R. Yahya and S. N. Gan, *Procedia Chem*., 2016, **19**, 189-195.

9. V. P. Della, I. Kuhn and D. Hotza, *Mater. Lett*., 2002, **57**, 818-821.

10. A. Farook, N. A. Jimmy and A. Iqbal, *Catal. Today*, 2012, **190,** 2-14.

11. A. B. James, W. Karen and F. L. Adam, *J. Mater. Chem. A*, 2016, **4**, 3617-3637.

12. K. T. Chen, J. X. Wang, Y. M. Dai, P. H. Wanga, C. Y. Liou, C. W. Nien, J. S. Wua and C. C. Chen, *J. Taiwan Inst. Chem. Eng*., 2013, **44**, 622-629.

13. N. Hindryawati, G. P. Maniam, M. R. Karim and K. F. Chong, *Eng. Sci. Technol*., 2014, **17,** 95-103.

14. W. Roschat, T. Siritanon, B. Yoosuk and V. Promarak, *Energy Convers. Manage.*, 2016, **119**, 453-462.

15. Y. D. Long, F. Guo, Z. Fang, X. F. Tian, L. Q. Jiang and F. Zhang, *Bioresour. Technol.*, 2011, **102**, 6884-6886.

16. F. Guo, Z. G. Peng, J. Y. Dai and Z. L. Xiu, *Fuel Process. Technol.*, 2010, **91**, 322-328.

17. X. Gui, S. Chen and Z. Yun, *Chin. J. Chem. Eng.*, 2016, **24**, 499-505.

18. Y. D. Long, Z. Fang, T. C. Su and Q. Yang, *Appl. Energy*, 2014, **113**, 1819-1825.

19. G. Y. Chen, R. Shana, J. F. Shi and B. B. Yan, *Fuel Process. Technol.*, 2015, **133**, 8-13.

20. F. A. Moustaffa, N. A. Ghoneim, Z. A. El-Hadi, F. M. E. El-Din and N. A. Hasan, *CGCRI Bull* 32:1, 1985.

21. I. Halasz, M. Agarwal, R. Li and N. Miller, *Catal. Lett.*, 2007, **117**, 34-42.

22. M. T. Tognonvi, J. Soro and S. Rossignol, *J. Non-Cryst. Solids*, 2012, **358**, 81-87.

23. A. Gharzouni, E. Joussein, B. Samet, S. Baklouti, S. Pronier, I. Sobrados, J. Sanz and S. Rossignol, *J. Sol-Gel Sci. Technol.*, 2014, **73**, 250-259.

24. W. Guang, Y. Zifeng, S. Marianne, Z. Peng and W. Ben, *Fuel*, 2010, **89**, 2163-2165.

25. P. Guo, C. Zheng, M. Zheng, F. Huang, W. Li and Q. Huang, *Energy*, 2013, **53,** 377-383.

26. R. W. G. Wyckoff. *Am. J Sci.*, 1925, **9,** 448-459.

27. Y. Liu, T. Liu, X. Wang, L. Xu and Y. Yan, *Energy Fuels*, 2011, **25**, 1206-1212.

28. W. Boyang, L. Shufen, T. Songjian, F. Rihua and M. Yonglu, *Fuel*, 2013, **104**, 698-703.

29. M. Takase, M. Zhang, W. Feng, Y. Chen, T. Zhao, S. J. Cobbina, L. Yang and X. Wu, *Energy Convers. Manage.*, 2014, **80**, 117-125.

30. I. M. Atadashi, M. K. Aroua, A. R. A. Aziz and N. M. N. Sulaiman, *Renewable Sustainable Energy Rev.*, 2012, **16,** 3456-3470.

31. M. Canakci, *Bioresour. Technol.*, 2007, **98**, 183-190.

32. D. Y. C. Leung, X. Wu and M. K. H. Leung, *Appl. Energy*, 2010, **87**, 1083-1095.

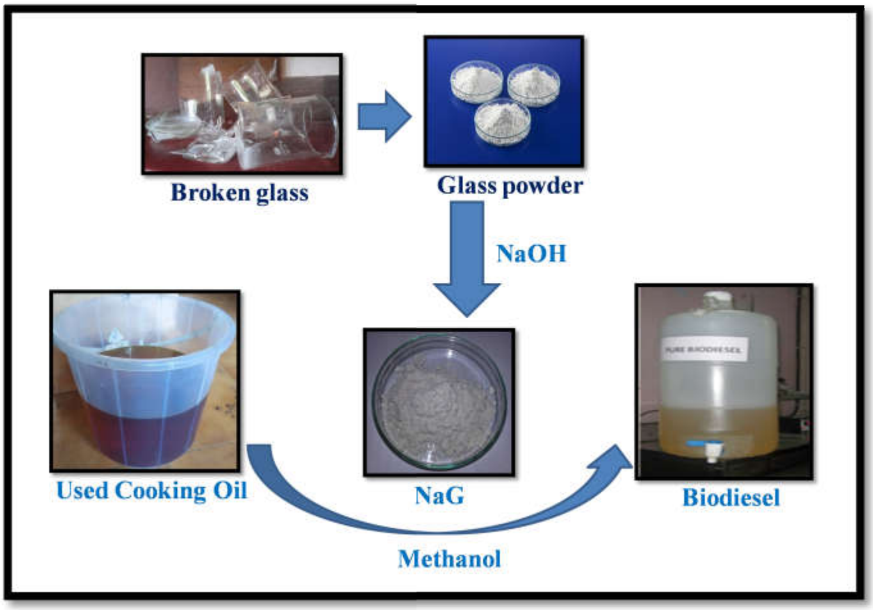
33. M. Saifuddin, P. E. Goh, W. S. Ho, K. M. MonEruzzaMan and A.Fatima, *BJAS*, 2014, **20**, 186-92.

34. C. Y. M. Ang, L. KeShun and W. H. Yao, *Asian foods: Science and Technology*, Technomic Publishing Co., Lancaster, Pennsylvania, 1999.

35. G. Knothe, *Fuel Process. Technol.*, 2005, 86, 1059-1070.

CHAPTER 5

BIODIESEL PRODUCTION OVER HETEROGENEOUS CATALYST DERIVED FROM WASTE GLASS MATERIALS



Sodium silicate based catalyst prepared by sodium impregnation to waste glass powder is effectively employed in the bulk scale production of biodiesel from triglyceride oils

5.1. Introduction

Glass, a noncrystalline amorphous solid has been in use for centuries in extensive domestic, technological and decorative purposes [1]. Depending on the applications, varieties of glasses are available which are different in chemical composition [2]. The pioneer and the most familiar one is the silicate glass which is composed of silica [3]. Soda lime glass, having the composition of silica (75%), sodium oxide, calcium oxide and several minor additives is used to make ordinary glazing and container glasses [4]. The property of optical transparency of the glass makes its use in the preparation of window pans, optical lenses, prisms, optical fibers etc [5]. The properties of glass can be tuned by chemical modifications. Glass can be formed or molded into any shape and it can be used for making vessels, bowls, vases, bottles, beakers, jars, drinking glasses etc [6]. In chemical laboratories, glasswares are necessary materials and ordinary glasses are not adequate for the laboratory usage. By the demanding conditions of maximum chemical inertness, thermal stability and optical transparency, borosilicate glass is ideal for the laboratory purposes [7]. Borosilicate glass is resistant to chemical corrosion and handles even the most volatile chemicals, making it perfectly suitable for laboratory experiments. The borosilicate glass can sustain corrosive environment for a long duration [8]. The heat resistance and affordability makes the use of the borosilicate glass in a variety of technological applications, ranging from scientific apparatus to regular kitchenware. Borosilicate glass composed of SiO_2 (80.6%), B_2O_3 (13.0%), Na_2O (4.0%) and Al_2O_3 (2.3%) [9].

In laboratories, lot of damaged or broken borosilicate glasswares are generated as waste. Disposal is the responsibility of the laboratory and in most of the cases, it is dumped into the land. Waste glass is not biodegradable, so landfilling is an unsustainable option. Recycling or converting the waste glass into useful purposes is the only way to reduce the environmental impact [10].

In addition, the abundance and density make the broken or damaged glasses as large household and industrial waste. Broken bottles, glasswares, light bulbs, window glass etc were considered as the municipal wastes. Many of these waste glasses are currently disposed of at the landfills. There are no much effective ways in waste glass disposal; only a minor amount is used in recycling for useful purposes. Some innovative approaches like making use of waste glass as cullet in glass production [11], as precursor material in geopolymer production [12], as raw material for the production of abrasives [13], as an aggregate substitute in concrete [14], in road construction [15], for preparing mortars [16], in building applications (glass tiles and bricks, wall panels, etc) etc are already available [17]. But still, mostly, the waste glass materials are dumped in bulk [18].

Keawthun et al prepared commercially important sodium silicate solution from waste glass bottles by hydrothermal and fusion methods [19]. Kouassi and coworkers studied the dissolution of glass with different particle size distributions in alkaline solution at different temperatures and alkali concentrations [20]. It was observed that the dissolution rate was greatly influenced by the temperature, glass composition, and the particle size distribution as well as fairly on the alkali concentration. Carrasco also prepared silicate solution by the dissolution of different waste glass types having smaller particle sizes in the alkaline solutions at different temperature conditions of solubility [21]. The sodium silicate solution is used in the preparation of alkaline cement and concretes [22]; it also has industrial applications in sealants, binders, deflocculants, emulsifiers and buffers [19].

Here, we introduce a highly effective and useful means of waste glass disposal via its use for catalyst development in the production of biodiesel. A solid base catalyst was prepared by the reaction between NaOH and waste borosilicate glass by impregnation method. The catalytically active phase of the highly efficient waste glass derived material was found to be Na_2SiO_3 which is distributed on cristobalite silica, as evident from the various characterization results. Very high FAME content was obtained in a range of reaction conditions and the prepared biodiesel was found to meet the international standard fuel specifications. Moreover, the catalyst was found to be effectively reusable for 4 repeated cycles, making the process further economical. We have also upgraded the biodiesel production process in the pilot scale unit aiming the industrial scale-up straightforward and cost-effective. The most important aspect of this work is the maximum incorporation of the precursor material in the finally developed heterogeneous catalyst.

5.2. Experimental

5.2.1 Preparation of catalyst from waste glass

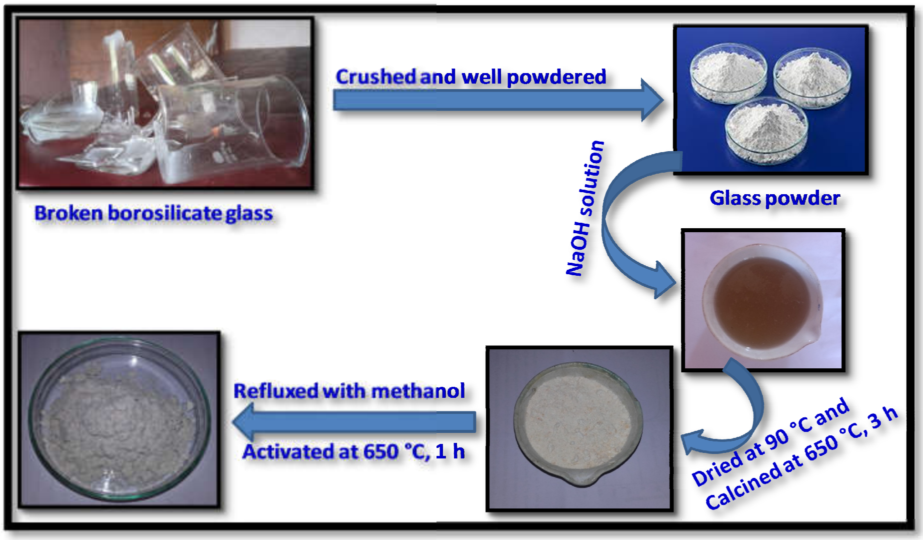


Fig 5.1 Scheme for the preparation of catalyst

The broken borosil® glass pieces were washed thoroughly with deionized water and dried. The glass pieces were then pulverized using a mixer grinder and finely powdered. The catalyst was prepared by impregnating NaOH to glass powder (using 1 M NaOH) so as to achieve a 2:1 Na/Si molar ratio. The contents were thoroughly mixed and water is evaporated. The dried material (at 90 °C for 12 hours in a hot air oven) was calcined at 650 °C for 3 h. It was then powdered and refluxed with methanol under stirring for 1 h and the methanol soluble fraction was removed to ensure heterogeneity of the catalytic reaction in methanol medium and the catalyst was further activated at 650 °C for 1 h. 650 °C is chosen as the calcination temperature since the sodium silicate based catalyst described in the chapter 4 is found to be highly active at this temperature. The catalyst was analyzed using various characterization techniques so as to investigate its structural and textural properties. Catalyst preparation is narrated in figure 5.1.

The catalytic activity of the glass derived solid catalysts is studied in the transesterification reaction of used cooking oil (UCO) with methanol. The detailed procedures for the initial laboratory scale studies conducted by varying the reaction parameters in the transesterification reaction of used cooking oil, up-gradation of the reaction at one of the selected reaction conditions in the pilot scale unit, biodiesel analysis, and the determination of fuel properties are well explained in chapter 2 in the sections 2.5, 2.12.2, 2.7 and 2.13 respectively.

5.3 Results and Discussion

Here, chemically modified waste glass powder is used as a catalyst for biodiesel production. As mentioned, a simple method of impregnation was used to develop the solid catalyst from the waste material, which makes the entire process green and economical. Methanol soluble fraction is removed from the catalyst so as to ensure heterogeneity in the catalytic reaction. The developed catalyst material is characterized in order to investigate the active phase of catalysis.

The performance of the glass derived solid catalyst in the transesterification of used cooking oil was studied at various reaction conditions. The catalyst dosage, methanol to oil molar ratio, catalyst reusability and the influence of FFA as well as water content in the oil on the activity of the waste glass derived base catalyst was investigated in the initial laboratory scale experiments. One of the best suited conditions was scaled up in the pilot plant. The entire process is eco-friendly and economical so that it can be effectively escalated into industrial scale production process.

5.3.1 Catalyst characterization

5.3.1.1 FTIR spectral analysis

The FTIR spectrum of the waste glass derived catalyst is depicted in figure 5.2. In the spectra, the absorption peak at 1040 cm^{-1} is due to asymmetric stretching vibrations of Si-O-Si bond [24]. Peak at 968 cm^{-1} corresponds to the vibrations of Si-O-Na [24]. Si-O-H stretching vibration is observed around 874 cm^{-1} [25]. The H-O-H bending vibration is observed around 1640 cm^{-1} and a broad band around 3400 cm^{-1} is due to the -OH stretching vibrations caused by the water molecules adsorbed on the catalyst surface [26]. The peak for adsorbed CO_2 is observed at 1450 cm^{-1} [27]. A band at 712 cm^{-1} indicates the Si-O-Si symmetric stretching vibration [28]. FTIR spectral analysis thus indicates the formation of sodium silicates [28]. Peak observed below 600 cm^{-1} corresponds to O-Si-O as well as Si-O-Si bending vibrations [29].

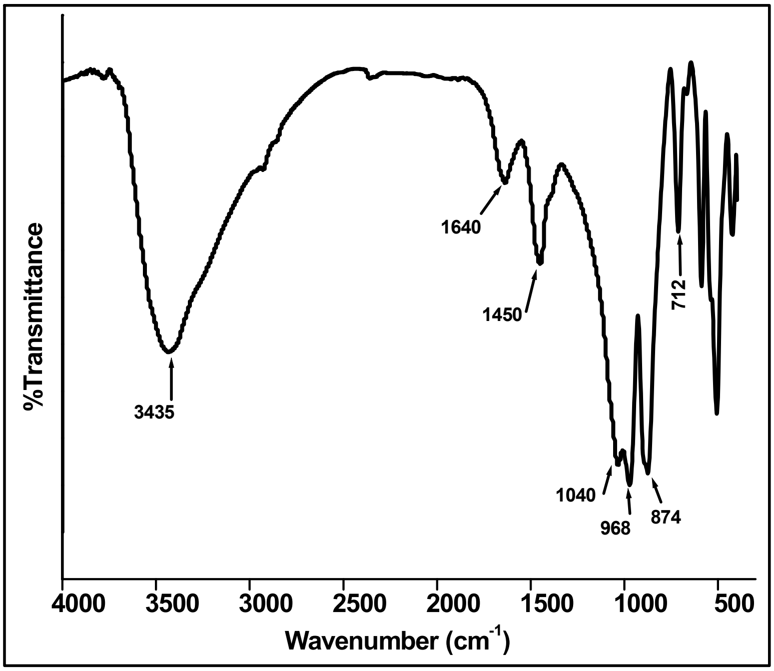


Fig.5.2 FTIR of glass derived catalyst

5.3.1.2 XRD analysis

The XRD pattern (figure 5.3) of glass powder showed a broad band at 22°, characteristics of amorphous silica. From the XRD pattern of the catalyst, it is revealed that NaOH incorporation transformed the glass powder into crystalline sodium silicate since the sample exhibited the characteristic peaks of Na_2SiO_3. The diffraction peaks appeared at 2θ values of 17.0°, 25.2°, 29.6°, 35.1°, 37.5°, 45.8°, 48.4°, 49.8°, 52.3°, 64.5°, and 66.0° corresponds to the (200), (111), (310), (311), (002), (510), (312), (511), (600), (621) and (602) planes respectively of base centered orthorhombic crystal lattice of Na_2SiO_3 (JCPDS-PDF No.01-072-0079) [29]. In addition, diffraction patterns of cristobalite

SiO_2 (JCPDS-PDF No. 01-082-1235) at 2θ values of 29.0°, 39.2° and 60.5° corresponding to lattice planes (111), (201) and (222) are also displayed by the material [30]. It is reported that in comparison with amorphous SiO2, presence of cristobalite SiO_2 leads to the formation of a selective and efficient catalyst [31].

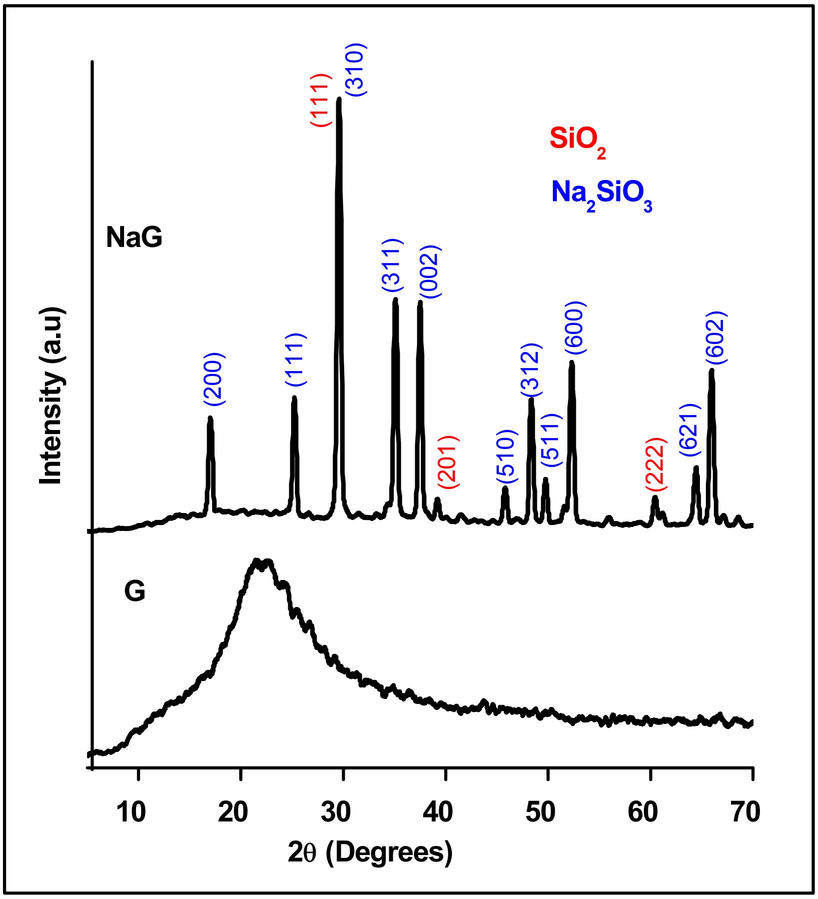


Fig 5.3 XRD pattern of Glass powder (G) and NaG catalyst

5.3.1.3 Elemental analysis

The percentage composition analysis revealed that the sodium impregnated glass catalyst possesses a Na/Si molar ratio of ~1.4:1. This confirmed the presence of SiO_2 in the sample in addition to Na_2SiO_3. The results indicate that Na_2SiO_3 supported over cristobalite SiO_2 is the active catalyst of the present study. A trace amount of boron is also found to be present in the catalyst. The results are shown in table 5.1.

Table 5.1 Elemental composition of waste borosilicate glass derived catalyst

Elements	Concentration (ppm)
B	0.740
Na	63.37
Si	53.10

5.3.1.4 SEM analysis

From the SEM image (figure 5.4), randomly oriented particle aggregates are observed.

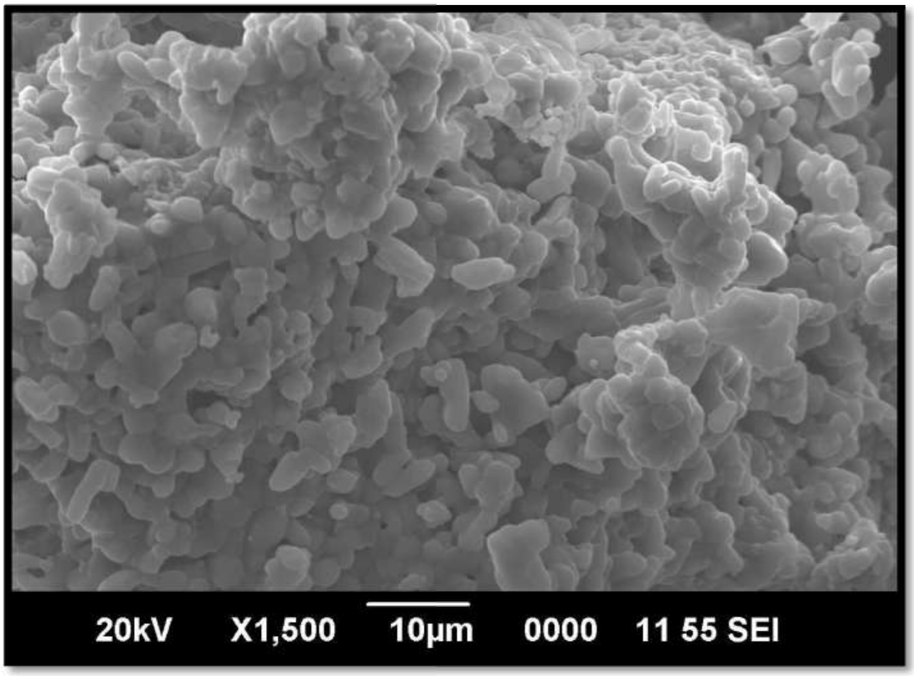


Fig 5.4 SEM image of glass derived catalyst

5.3.1.5 TEM analysis

TEM images of the sample shown in figure 5.5 indicate the sheet-like morphology of the catalyst [32].

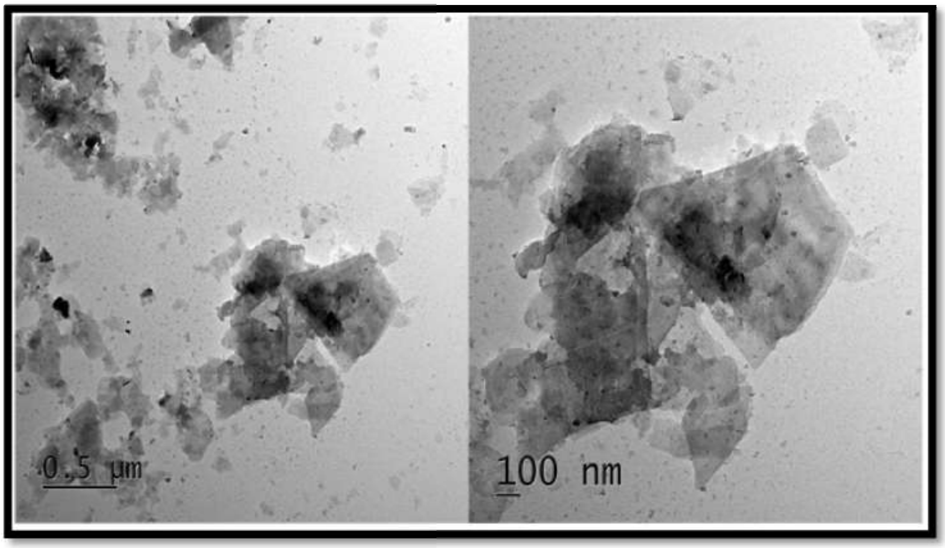


Fig 5.5 TEM images of glass derived catalyst

5.3.1.6 Temperature Programmed Desorption of CO_2 analysis

The sodium impregnated glass catalyst showed (figure 5.6) five desorption peaks centered at the temperatures of 158 °C, 451 °C, 509 °C, 599 °C and 804 °C in the TPD profile. The amount of CO_2 desorbed is a measure of basicity and the desorption temperature indicates the strength of basic sites [33]. The peak centered at 158 °C corresponds to desorption of CO_2 from weak basic sites and that centered at 451 °C can be assigned to CO_2 desorbed from moderately strong basic sites. The peaks centered at 509 °C, 599 °C and 804 °C corresponds to CO_2 desorbed from strong basic sites. A total basicity of 0.168 $mmolg^{-1}$ (sum of weak (0.0383 $mmolg^{-1}$), moderate (0.0312 $mmolg^{-1}$) and strong (0.0985 $mmolg^{-1}$) basic sites is shown by the catalyst.

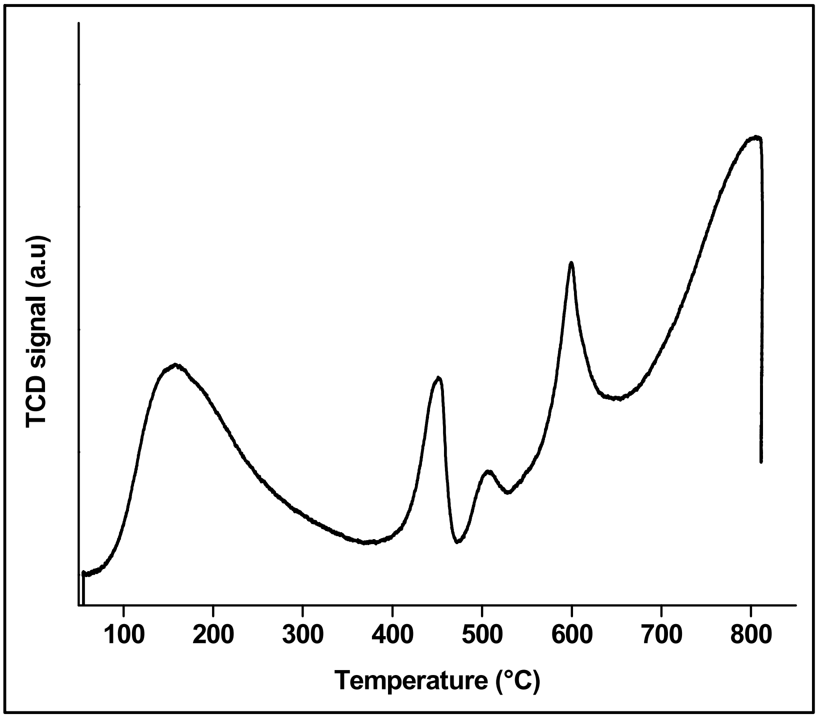


Fig 5.6 TPD of CO_2 of glass derived catalyst

5.3.2 Activity studies of glass derived catalyst

The activity of the waste borosilicate glass derived catalyst was analyzed by conducting laboratory scale experiments with UCO. The reaction parameters like reaction temperature, catalyst weight and methanol/oil molar ratio is varied and one of the best suited conditions was employed for the pilot scale production of biodiesel. The results obtained are discussed below.

5.3.2.1 Effect of catalyst weight on transesterification reaction

In order to study the effect of catalyst weight on the transesterification reaction, the catalyst to oil weight percentage was varied from 1 to 5 wt% at a fixed methanol/oil molar ratio of 15:1 at a temperature of 65 °C for 90 minutes reaction. Complete conversion of oil to FAME is achieved at higher weight percentages of the catalyst, i.e., from 4 wt% onwards. Results are shown in figure 5.7. More than 99% of FAME content is attained even at a low catalyst weight of 2 wt%, indicating the high efficiency of the present catalyst in the transesterification reaction of oil when compared to most of the reported heterogeneous catalysts in biodiesel production [34].

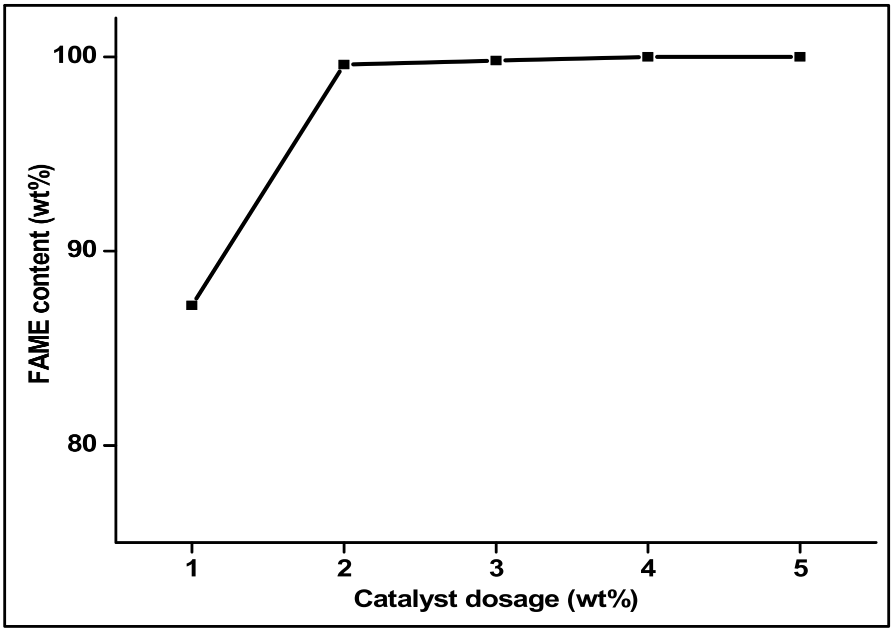


Fig 5.7 Effect of catalyst dosage on FAME content under the reaction conditions of methanol to oil molar ratio of 15:1 at a reaction temperature of 65 °C for 90 minutes

5.3.2.2 Effect of methanol on transesterification reaction

The most important variable affecting the methyl ester yield in the transesterification reaction is the methanol to oil molar ratio. Transesterification is a reversible reaction and more methyl ester could be produced by shifting the reaction equilibrium towards the right by increasing the amount of methanol in the reaction [35]. Additionally, methanol acts as a solvent in the reaction [36]. The molar ratio of methanol to oil was varied from 3:1 to 15:1 keeping the reaction at a temperature of 65 °C for 90 minutes using 5 wt% of the catalyst. The FAME content met the EN 14214 specifications from a methanol/oil molar ratio of 6:1 onwards. The result is highly promising in commercial point of view since it will reduce the cost of methanol recovery after the reaction.

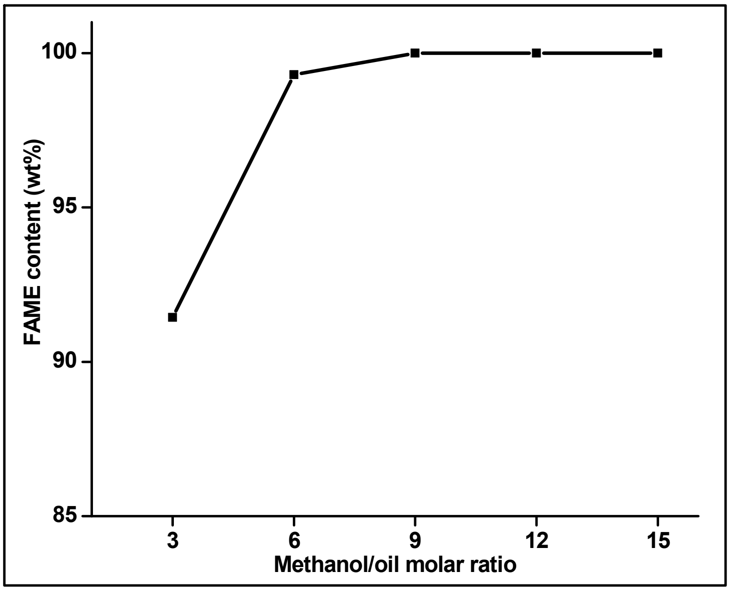


Fig 5.8 Effect of methanol/oil molar ratio on FAME content under the conditions of catalyst weight 5 wt%, at a reaction temperature of 65 °C for 90 minutes reaction

5.3.2.3 Effect of reaction time on transesterification reaction

The time taken for the complete conversion of the triglyceride oil into its corresponding methyl ester was investigated by conducting the transesterification reactions at different time intervals. The reaction was carried out at a methanol/oil molar ratio of 12:1 using 5 wt % of the catalyst at 65 °C. It is found that FAME content higher than 96.5% (fuel grade) is obtained for 60 minutes reaction and the FAME content reached 100% for 90 minutes reaction. The results are shown in figure 5.9.

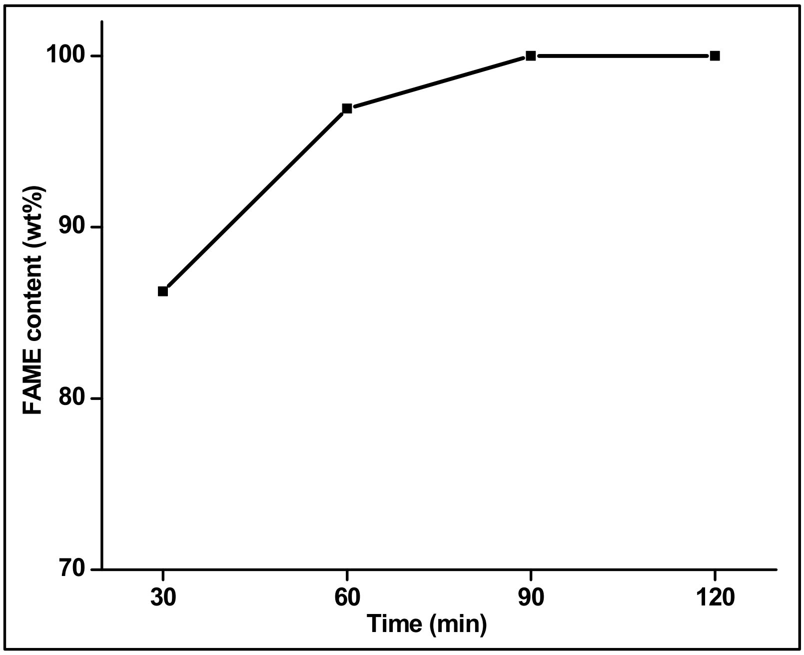


Fig 5.9 Effect of reaction time on FAME content under the conditions of catalyst dosage of 5 wt%, at a temperature of 65 °C with methanol/oil molar ratio of 12:1

5.3.2.4 Effect of reaction temperature on the transesterification reaction

The effect of reaction temperature on the transesterification reaction was investigated by conducting the reaction at various temperatures including room temperature (RT). The maximum FAME content of 100% is obtained at the reflux temperature of methanol (65 °C) for 90 minutes of the reaction (figure 5.10). A reaction temperature of 65 °C is the best suited temperature for the present transesterification reaction.

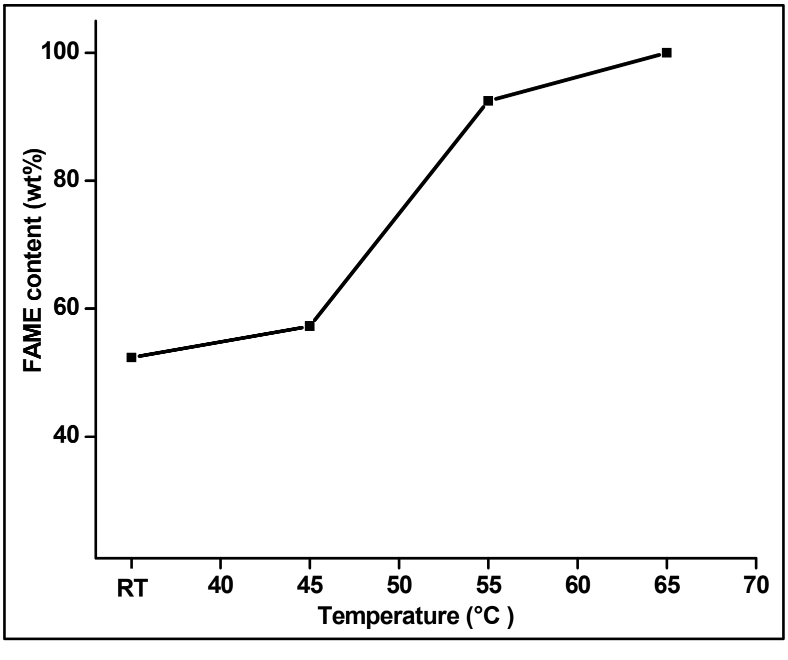


Fig 5.10 Effect of reaction temperature on the FAME content under the conditions of catalyst weight 5 wt%, 12:1 methanol/oil molar ratio for 90 minutes reaction

5.3.2.5 Effect of free fatty acid

Presence of free fatty acids (FFA) in the raw oil is a major hurdle in the biodiesel production in the base catalyzed transesterification reactions due to the formation of saponified products which causes reduction in biodiesel yield [37]. In order to analyze the activity of the catalyst in the presence of FFA, a series of experiments were conducted by varying the amount of free fatty acid (oleic acid) in the oil from 1-9 wt%. The FAME yield remained unaffected up to 5 wt% of FFA content. The yield was low thereafter as a result of soap formation, which made difficulties in biodiesel purification. The results are shown in figure 5.12.

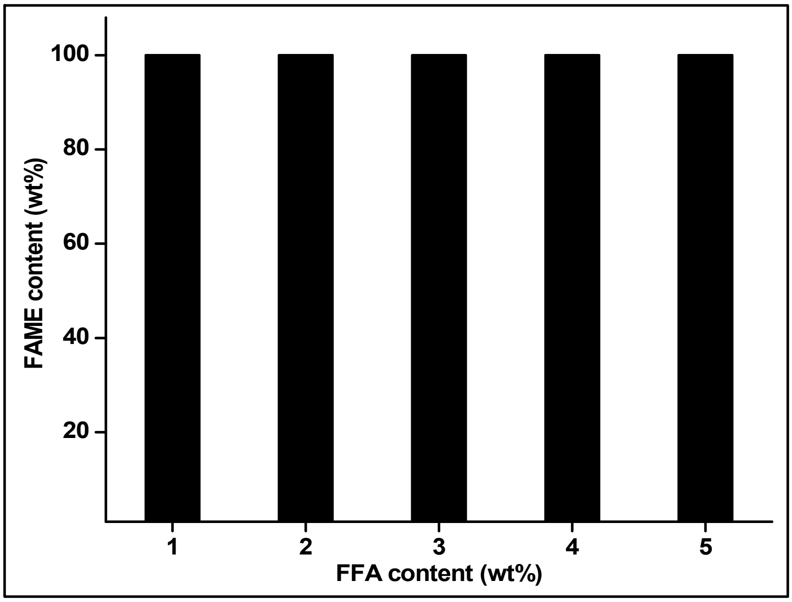


Fig 5.12 Effect of FFA content on the FAME content under the selected conditions of catalyst weight 5 wt%, 12:1 methanol/oil at 65 °C for 90 minutes reactions

5.3.2.6 Effect of water content

Water content has a negative effect on the biodiesel yield and hence it is a major concern in the transesterification reaction [38]. In this experiment, 1-3 wt% of water/oil is purposely added to the reaction mixture. The catalyst retained its activity of 100% up to 2 wt% of water in the UCO. Introduction of 3 wt% water content onwards lead to the formation of emulsions and it made difficulties in biodiesel separation. In most of the studies, presence of more than 0.5 wt% of water in the feedstock adversely affects the biodiesel production and thus the present catalyst is comparatively highly water tolerant [39].

5.3.3 Catalyst reusability

The reusability of the catalyst was investigated by recycling the catalyst after each reaction. The reaction was conducted for 90 minutes over 5 wt% of the waste glass derived catalyst at a temperature of 65 °C with a methanol to oil molar ratio of 12:1. The used catalyst was washed with methanol to remove the impurities and dried. The catalyst was then activated at its calcination temperature of 650 °C for 1 h before its repeated use. The FAME content of 100% is retained till 4 consecutive cycles. In the fifth cycle, the conversion dropped to 96.2%. The results are depicted in figure 5.11.

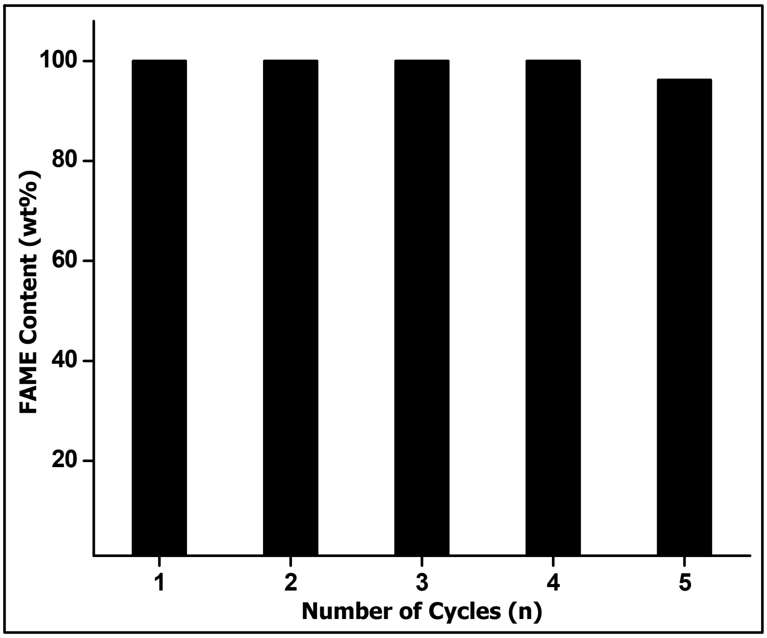


Fig 5.11 Reusability result of the catalyst

5.3.4 Production of biodiesel in the pilot plant

After the initial laboratory scale studies, one of the reaction conditions was extended for the pilot scale production of biodiesel. The reaction was performed at a methanol to oil molar ratio of 12:1 over 5 wt% of the catalyst at a temperature of 65 °C for 90 minutes duration. The details of biodiesel production are given in the experimental section described in chapter 2 in the section 2.9.4. Biodiesel is efficiently prepared over the present catalysts in the pilot plant and 99.94% FAME content is achieved. The biodiesel composition is analyzed using GCMS and the results are shown in the table 5.2.

Table 5.2 Chemical composition of biodiesel prepared from UCO

Fatty Acid Methyl Ester	Molecular formula	Area %
Methyl tetradecanoate	$C_{15}H_{30}O_2$	1.34
Tetradecanoic acid, 12-methyl-, methyl ester	$C_{16}H_{32}O_2$	0.60
Hexadecanoic acid, methyl ester	$C_{17}H_{34}O_2$	33.90
9,12-Octadecadienoic acid, methyl ester	$C_{19}H_{34}O_2$	2.04
12-Octadecenoic acid, methyl ester	$C_{19}H_{36}O_2$	22.65
15-Octadecenoic acid, methyl ester	$C_{19}H_{36}O_2$	38.20
Heptadecanoic acid, 16-methyl-, methyl ester	$C_{19}H_{38}O_2$	1.27

The results show the presence of seven fatty acid methyl esters as the components of biodiesel and it mainly contained 15-octadecenoic acid methyl ester, hexadecanoic acid methyl ester and 12-octadecenoic acid methyl ester in large quantities indicating palm oil as the major constituent in the present UCO [40].

5.3.5 Fuel properties of UCO biodiesel

Some of the fuel properties of the biodiesel made in the pilot plant from UCO were analyzed with standard test procedures to ensure its suitability as an alternative to petrodiesel [41, 42]. The results are tabulated (Table 5.3).

Table 5.3 Fuel properties of UCO biodiesel

Parameters	Unit	Limits	Standards	Biodiesel
Ester content	% m/m	96.5 min	EN 14214	99.94
Monoglyceride	% m/m	1.00max	D 6751	0.00
Triglyceride	% m/m	0.25max	D 6751	0.06
Free glycerol	% m/m	0.02 max	D 6751	0.00
Total glycerol	% m/m	0.38 max	D 6751	0.01
Acid value	mg KOH/g	0.80 max	D 6751	0.28
Water content	Vol.%	0.050 max	D 6751	0.00
Iodine value	mg I/100 g	120 max	D 6751	35
Viscosity	mm2/s	1.96-6.0	D 6751	2.6
Density	kg/ m3	860-890	D 6751	866
Flash point	°C	> 130 min	D 6751	152
Fire point	°C	>145 min	D 6751	160

From the results, it can be seen that the biodiesel met both ASTM D6751 as well as EN 14214 standard specifications of fuel where the ester content was more than 99.94 % and the total glycerin was only 0.01 %. The FAME content of the biodiesel produced in the pilot scale unit was almost same as that in lab scale operation indicating the efficiency of the catalyst for the bulk production of biodiesel and thus the entire process is effective for scale up.

5.4 Conclusions

In this study, waste glass material was effectively used to prepare a cost-effective catalyst by sodium incorporation and is highly active in a range of reaction conditions for biodiesel production. The active phase of the catalyst was found to be Na_2SiO_3 supported over SiO_2 and is evidently revealed from the XRD and FTIR spectral analysis. The catalyst was effectively reusable till 4 repeated cycles of reactions. The additional merit of the present heterogeneous catalyst is its FFA and water tolerance, which is highly desirable in commercial view point. The reaction was further extended to the pilot scale unit, which offers a lot of promise for an easy and economical industrial scale up. The advantage of the present process is the use of a cheap catalyst when compared to the commercially available heterogeneous catalysts in biodiesel production. Most of the contents of the precursors are effectively incorporated in the catalyst resulting in high yield of the catalyst in its preparation. The reaction was performed under mild conditions and the procedure is greener compared to most of the existing methods of heterogeneous catalyzed industrial scale biodiesel production processes. The biodiesel produced met the international standard specifications (EN 14214 as well as ASTM D 6751) for fuel.

References

1. Phillips, *The Encyclopedia of Glass*. New York: Crown Publishers, 1981.
2. R Brockner, *J.Non-Cryst. Solids*, 1970, **5**, 123-175.
3. S. Fearn, D. S. McPhail, R. J. H Morris and M. G. Dowsett, *Appl. Surf. Sci*., 2006, **252**, 7070-7073.
4. B. H. W. De Jong, *"Glass"; in "Ullmann's Encyclopedia of Industrial Chemistry*, VCH Publishers, Weinheim, Germany, 1989.
5. Barsoum and W. Michael, *Fundamentals of ceramics* (2 ed.), Bristol, 2003.
6. http://www.chemistryexplained.com/Ge-Hy/Glass.html#ixzz52rJy45St.
7. "Borosilicate glass vs. Soda Lime Glass? - Rayotek News". Rayotek.com. 23rd April 2017.
8. http://www.iitk.ac.in/centralstores/data/price/2015-16/Borosil_Glasswares.pdf
9. M. F. Ashby, K. Johnson, *Materials and Design: The Art and Science of Material Selection in Product Design*, Elsevier Science Technology, United Kingdom, 2014.
10. I. Hauwa, Sci. Res. Essays, 2008, **3**, 276-279.
11. R. F. Cook, *Comervatior & Recycling*, 1978, **2**, 59-69.
12. S. Zhang, A. Keulen, K. Arbi, and Y. Guang, *Geopolymers*, 2015 - An ECI Conference.
13. C. Guohua and L. Harry, *Waste Manage.*, 2002, **22**, 747-753.
14. S. Yixin, L. Thibaut, M. Shylesh and R. Damian, *Cem. Concr. Res*., 2000, **30**, 91-100.

15. T. Watson, When the tire hits the glasphalt. Resource Recycling, 1988.

16. V. Corinaldesi, G. Gnappi, G. Moriconi, A. Montenero, *Waste Manage.*, 2005, **25**, 197–201.

17. V. A. Leshina, A. L. Pivnev, *Glass Ceram.*, 2002, **59**, 9-10.

18. B. C. Bunker, D. R. Tallant, T. J. Headley, G. L. Turner and R. J. Kirkpatrick, *Chem. Glasses*, 1988, **29**, 106-120.

19. M. Keawthun, S. Krachodnok and A. Chaisena, *Int. J. Chem. Sci.*, 2014, **12**, 83-91.

20. S. S. Kouassi, J. Andji, J. P. Bonnet and S. Rossignol, *Ceramics – silikaty*, 2010, **54**, 235-240.

21. A. Paul, *Chemistry of glass, 2nd ed.*, Chapman and Hall, New York, 1990.

22. M. T. Carrascoa, J. G. Palomob and F. Puertas, *Materiales de Construccion*, 2014, **64**, 1-14.

23. H. S. Shankar and R. B. Khadiranaikar, IJRET: Conference Issue Nov-2013, Available @ http://www.ijret.org

24. H. X. Shuang, X. Hao, P Hang, C. L. Qi, L. S. Bao and Y. F.Zheng, *RSC Adv.*, 2015, **5**, 71844-71848.

25. I. Halasz, M. Agarwal, R. Li and N. Miller, *Catal. Lett.*, 2007, **117**, 34-42.

26. W. Guang, Y. Zifeng, S. Marianne, Z. peng and W. Ben, *Fuel*, 2010, **89**, 2163-2165.

27. W. Roschat, T. Siritanon, B. Yoosuk and V. Promarak, *Energy Convers. Manage.*, 2016, **119**, 453-462.

28. N. Lazarev, *Vibrational Spectra and Structure of Silicates*, Consultants Bureau, New York, 1972.

29. F. Guo, N. N. Wei, Z. L. Xiu and Z. Fang, *Fuel*, 2012, **93**, 468-472.

30. R. W. G. Wyckoff, *Am. J. Sci.*, 1925, **9**, 448-459.

31. A. Palermo, J. P. H. Vazquez, A. F. Lee, M. S. Tikhov and R. M. Lambertz, *J. Catal.,* 1998, **177,** 259-266.

32. X. Cai, R. Y. Hong, L. S. Wang, X. Y. Wang, H. Z. Li, Y. Zheng and D. G. Wei, *Chem. Eng. J.*, 2009, **151**, 380-386.

33. M. D. Serio, M. Ledda, M. Cozzolino, G. Minutillo, R. Tesser and E. Santacesaria, *Ind. Eng. Chem. Res.*, 2006, **45**, 3009-3014.

34. N. S. Talha and S. Sulaiman, *ARPN J. Eng. Appl. Sci.*, 2016, **11**, 439-448.

35. W. Boyang, L. Shufen, T. Songjian, F. Rihua and M. Yonglu, *Fuel*, 2013, **104**, 698-703.

36. M. Takase, M. Zhang, W. Feng, Y. Chen, T. Zhao, S. J. Cobbina, L. Yang and X. Wu, *Energy Convers. Manage.*, 2014, **80**, 117-125.

37. M. Canakci, *Bioresour. Technol.*, 2007, **98**, 183-190.

38. I. M. Atadashi, M. K. Aroua, A. R.A. Aziz and N. M.N. Sulaiman, *Renewable Sustainable Energy Rev.*, 2012, **16**, 3456-3470.

39. D. Y. C. Leung, X. Wu and M. K. H. Leung. *Appl. Energy*, 2010, **87**, 1083-1095.

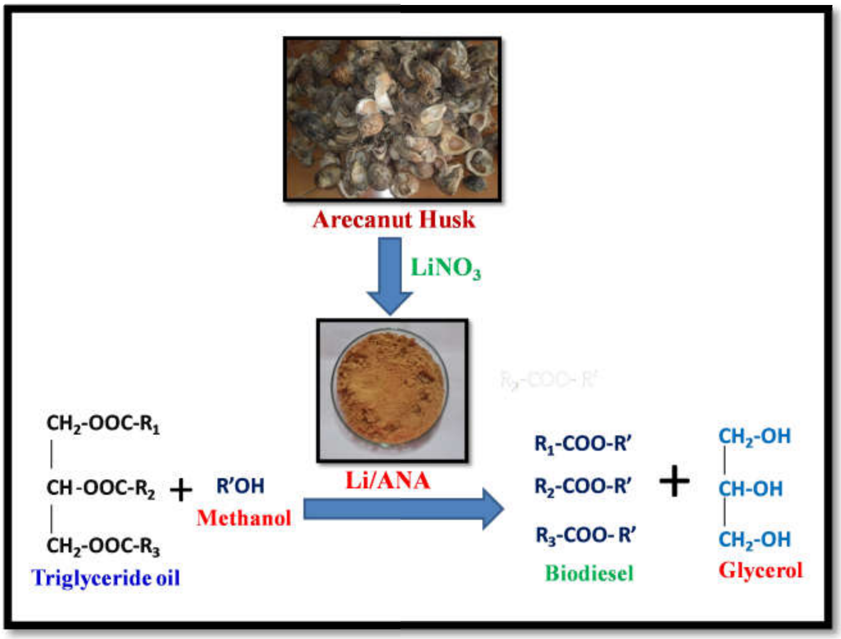
40. C.Y.M. Ang, L. KeShun and W. H. Yao, *Asian foods: Science and Technology*, Technomic Publishing Co., Lancaster, Pennsylvania, 1999.

41. S. P. Singh and D. Singh, *Renewable Sustainable Energy Rev.*, 2010, **14**, 200-216.

42. G. Knothe, *Fuel Process. Technol.*, 2005, **86**, 1059-1070.

CHAPTER 6

BIODIESEL PRODUCTION OVER Li LOADED ON ARECANUT HUSK ASH CATALYST



Lithium loaded arecanut husk ash catalyst is prepared by a facile method which showed excellent activity in the transesterification reaction of used cooking oil

6.1 Introduction

Arecanut is the seed of areca palm (*Areca catechu*), which grows in tropical Pacific, Asia, and parts of east Africa. In India, Karnataka and Kerala are the leading states in the production of areca. The term areca is originated from the Malayalam word adakka [1]. Arecanut husk is an agricultural by-product of arecanut. It is a widely available biomass in our country, especially in the southern parts of India [2]. The husk of the fruit is removed and it has no traditional use and left in the land. The husk is fibrous (hard and soft fibres) and predominantly composed of cellulose with varying proportions of hemicellulose, lignin, pectin and protopectin [3]. India ranks first in the areca nut production in the world, having a contribution of 49.74% as per the 2013 statistics for food and agricultural organization (FAO) of United Nations, Rome [4].

The husk has been utilized as a fuel for the processing of the nut. This produces husk ash residue that has limited applications. Use of areca nut husk ash as a supplementary cementitious material has been evaluated [5]. Akhila and co workers have used areca nut husk as a support substrate for the production of manganese peroxidases from *Phanerocheate* species by solid state fermentation technique [6]. The activated carbon from arecanut husk has been used for the adsorption of malachite green dye from aqueous solutions [7] Mohammad investigated the ability of areca nut peel in the removal of Cr, Cd and Pb from aqueous solutions [8]. In Karnataka district, rural areas of dakshina kannada use arecanut husk as traditional tooth brush (chewing sticks) instead of plastic for maintaining their oral health and hygiene [9]. Arecanut husk ash has been used as an additive with water hyacinth stem ash for improving the plasticity index of the soil [10]. Sathish and coworkers produced biodiesel from arecanut shell oil by two step reaction, pre-esterification followed by transesterification since the oil have high amount of FFA [11]. Biochar production from arecanut husk is reported and it may be useful to add to the soil for improving the soil functions [12]. Activated carbon produced from arecanut husk by chemical activation method using phosphoric acid acts as an effective dye adsorbent [13]. Tannin extracted from arecanut waste is used as a rust deactivator [14].

Table 6.1. Chemical composition of areca nut husk ash

Compound	Percentage (wt%)
SiO_2	28.44
Al_2O_3	3.64
Fe_2O_3	1.91
CaO	2.71
MgO	3.87
SO_3	7.80
Na_2O	0.24
K_2O	26.52
Total loss on ignition	23.50

The chemical composition of areca nut husk ash is given in table 6.1. It can be seen that the ash contains silica as the major compound. In addition, it also contains alumina, magnesium oxide and significant amount of alkali metal oxide (K_2O) [5, 10]. In the present chapter, the use of areca nut husk ash for the development of heterogeneous catalyst for biodiesel production is described. There are no other reports mentioning the use of arecanut husk as a source of catalyst. Since the availability is plenty, its use as a heterogeneous catalyst is economical. So as to improve the alkali content in the ash, $LiNO_3$ was impregnated to the areca nut husk ash in the presence of a suitable surfactant citric acid. The developed catalyst upon characterization indicated the formation of a mixture of lithium silicates that is responsible for the high basicity and activity of the catalyst in the transesterification reaction of used cooking oil (UCO). Even at a low catalyst loading, better conversion to fatty acid methyl ester (FAME) higher than the fuel grade biodiesel (96.5%) is obtained under mild reaction conditions. The catalyst is feasible for the large scale biodiesel production and the biodiesel produced in the pilot plant gave the same results with the lab scale preparation and the fuel quality met the international standard specifications.

6.2 Experimental

6.2.1 Preparation of catalyst from arecanut husk

Fig 6.1 Scheme for the preparation of catalyst from areca nut husk

Cleaned and dried areca nut husk was burned in air, the char obtained was powdered and calcined at 750 °C for 3 h. Dirty white colored hard ash obtained was powdered and lithium was incorporated by means of impregnation method with the aid of citric acid as a surfactant. Lithium nitrate, arecanut husk ash and citric acid were mixed thoroughly in a weight ratio of 2:1:1 respectively. In a typical procedure, citric acid was added to a 0.25 N solution of lithium nitrate. To this solution, arecanut husk ash (calcined at 750 for 3 h) was added with stirring and the contents were evaporated to dryness. The lithium inserted ash was then dried in a hot air oven at 90 °C for overnight and calcined at 650 °C for 3 h. The resultant material was powdered and refluxed with methanol at 65 °C for 1 h to separate the unbound components from the catalyst. The contents were filtered, dried and the catalyst was then activated at 650 °C for 1 h before its use for biodiesel preparation. The catalyst prepared without citric acid was not uniform and leaching of lithium species was observed in the reaction and this was not investigated for further studies.

The catalytic activity of the lithium loaded arecanut husk ash derived solid catalyst is investigated in the transesterification reaction of UCO with methanol. The detailed procedures for the initial laboratory scale studies conducted by varying the reaction parameters in the transesterification reaction of UCO, up-gradation of the reaction at one of the selected reaction conditions in the pilot scale unit, biodiesel analysis, and the determination of fuel properties are well explained in chapter 2 in the sections 2.5, 2.12.2, 2.7 and 2.13 respectively.

6.3 Results and Discussion

In the present study, arecanut husk ash after chemical modification with lithium is used as a catalyst for biodiesel production. Catalyst preparation was done by a simple method of impregnation with the aid of citric acid. To ensure the heterogeneity of the catalyst in the reaction, the unbound methanol soluble fraction is removed from the catalyst. The developed catalyst material was characterized using various techniques in order to investigate the active phase responsible for catalysis. The activity of the arecanut husk ash derived catalyst in the transesterification of UCO was studied at various reaction conditions. Effect of reaction parameters, catalyst reusability, influence of FFA and moisture content etc on the catalytic activity were investigated in the initial laboratory scale experiments. Reaction was also carried out in the pilot plant under one of the best suited conditions. The catalyst has the potential for industrial scale biodiesel production.

6.3.1 Catalyst characterization

6.3.1.1 FTIR spectral analysis

The FTIR spectrum of the arecanut husk ash derived catalyst is depicted in figure 6.2. In the spectra, the broad band centered at 3433 cm^{-1} corresponds to the stretching vibration of -OH groups from adsorbed water [15]. The stretching vibration for Si-O-Si is found at 1060 cm^{-1} and the band centered at 947 cm^{-1} is due to the Si-O-Li stretching vibration [16]. The peak at 866 cm^{-1} is attributed by the

O-Si-O stretching vibration [17]. The absorption peaks in the spectra at 741 cm^{-1} corresponds to the Si-O-Si symmetric stretching vibration [18]. The absorption band at around 1450 cm^{-1} corresponds to the carbonate stretching mode [19]. The peaks observed at 523 cm^{-1} is attributed to the Si-O-Li deformations and that at 423 cm^{-1} is attributed to the bending vibrations of Si-O-Si bond [18, 20]. The spectral data indicate the formation of lithium silicate.

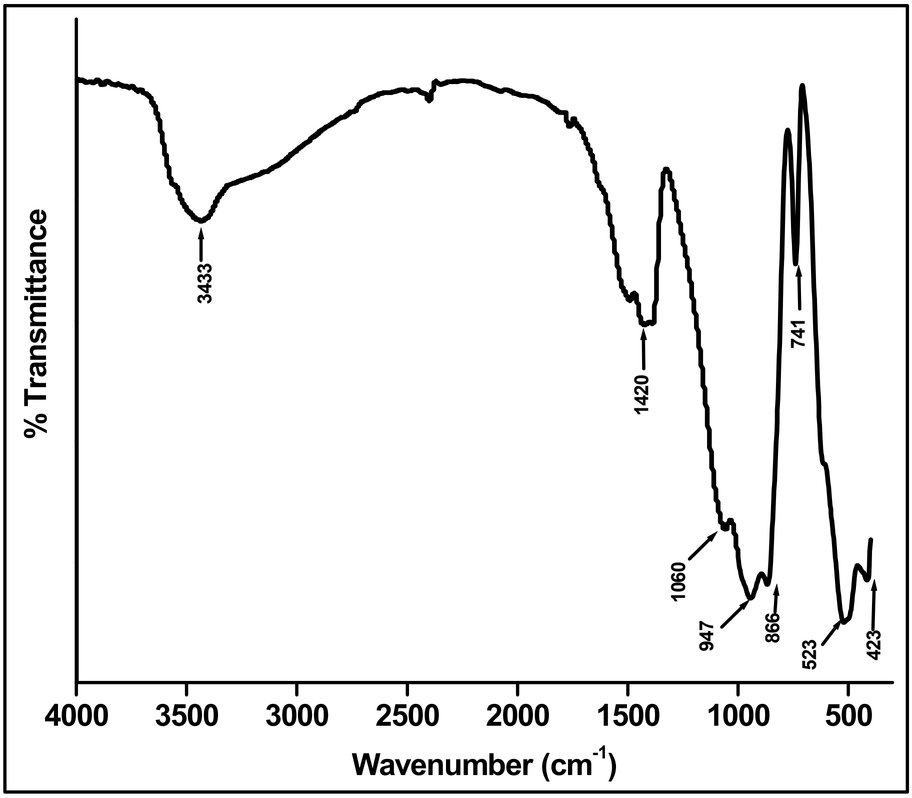


Fig.6.2 FTIR of arecanut husk ash derived catalyst

6.3.1.2 XRD analysis

The XRD pattern (figure 6.3) of lithium impregnated arecanut husk ash catalyst shows that the catalyst is a combination of different lithium silicates. The diffraction peaks are in good agreement with the JCPDS data of Li_2SiO_3 (JCPDS-29-0829) [21], Li_4SiO_4 (JCPDS-37-1472) [22, 23] and $Li_2Si_2O_5$ (JCPDS-04-0436) [24, 25] accompanied with the diffraction patterns of α-cristobalite SiO_2 (JCPDS-39-1425) [26]. SiO_2 may act as a support for various lithium silicates providing high activity as well as heterogeneity to the catalytic reaction.

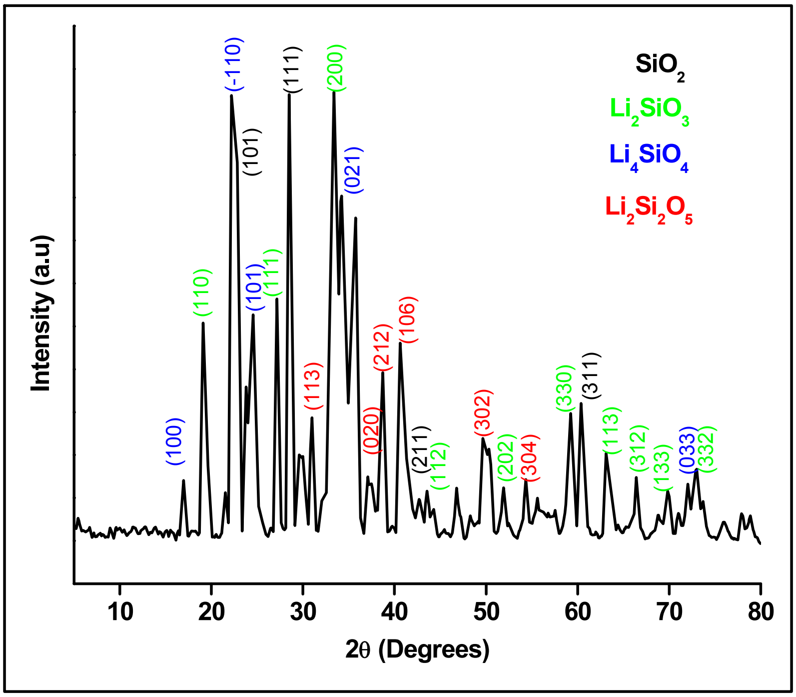


Fig.6.3 XRD of arecanut husk ash derived catalyst

6.3.1.3 Temperature Programmed Desorption of CO_2 analysis

Lithium impregnated arecanut husk ash catalyst showed (figure 6.4) three desorption peaks of CO_2, two of them centered at moderate basic sites in the temperature range of 300 °C to 500 °C, and one at strong basic sites in the range of 600 °C to 800 °C in the TPD profile. A total basicity of 0.8797 $mmolg^{-1}$ is shown from the sum of both moderate (0.3216 $mmolg^{-1}$) and strong (0.5581 $mmolg^{-1}$) basic sites.

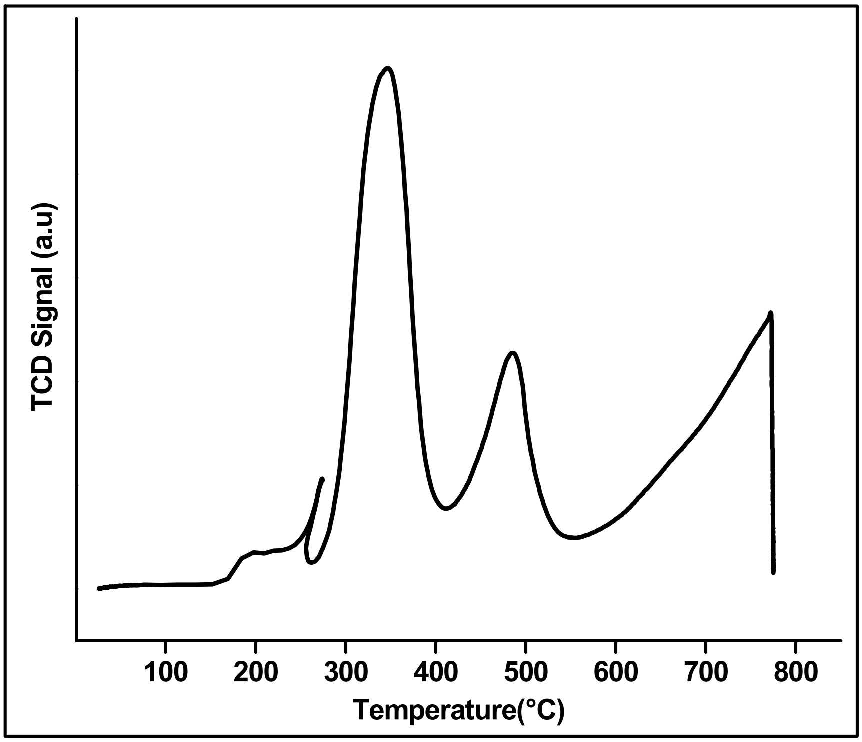


Fig.6.4 TPD of CO_2 of arecanut husk ash derived catalyst

6.3.1.4 SEM analysis

In the SEM analysis (figure 6.5), agglomeration of particles with macroporous morphology is observed.

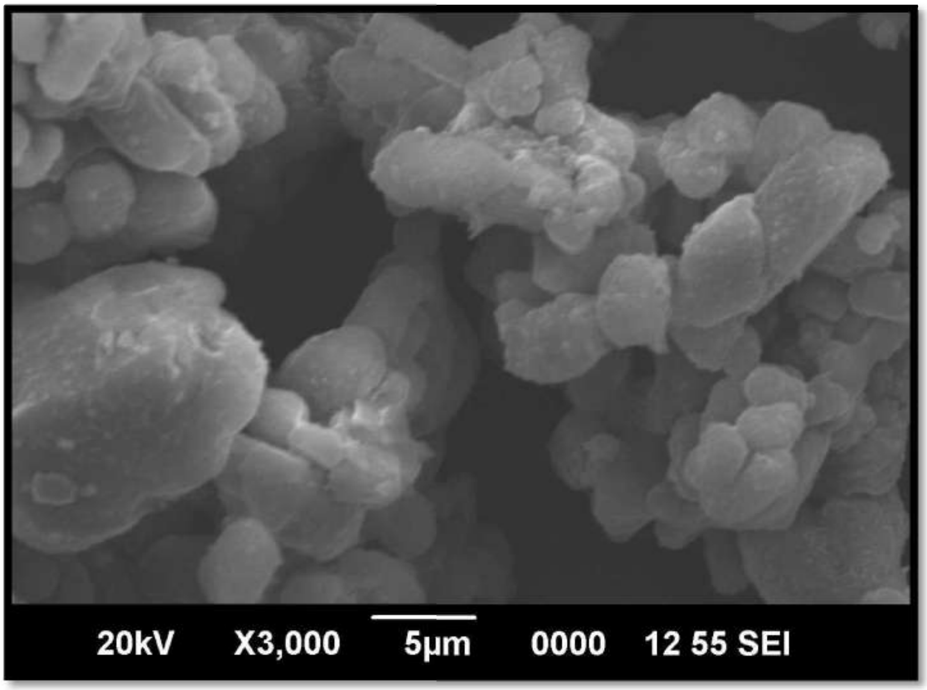


Fig.6.5 SEM arecanut husk ash derived catalyst

6.3.2 Catalytic activity studies in the laboratory scale

The activity of arecanut husk ash derived catalyst was investigated in the laboratory scale transesterification experiments with UCO. One of the best suited conditions was employed for the pilot scale production of biodiesel. The catalytic activity results are discussed in the following sections.

6.3.2.1 Effect of catalyst weight on the transesterification reaction

The activity of lithium loaded arecanut husk ash catalyst on the transesterification reaction of UCO was investigated by varying the catalyst to oil weight percentage from 1 wt% to 5 wt% by fixing the methanol/oil molar ratio at 15:1 at a temperature of 65 °C for 120 minutes reaction. Even with the use of 1 wt% of the catalyst, fuel grade biodiesel (FAME content above 96.5%) is obtained. By increasing the catalyst dosage, more than 99% FAME content is resulted and maintained. Results are shown in figure 6.6. The major highlight of the present catalyst is that even at a low catalyst concentration of 1 wt% of oil, high conversion of triglycerides to FAME is achieved.

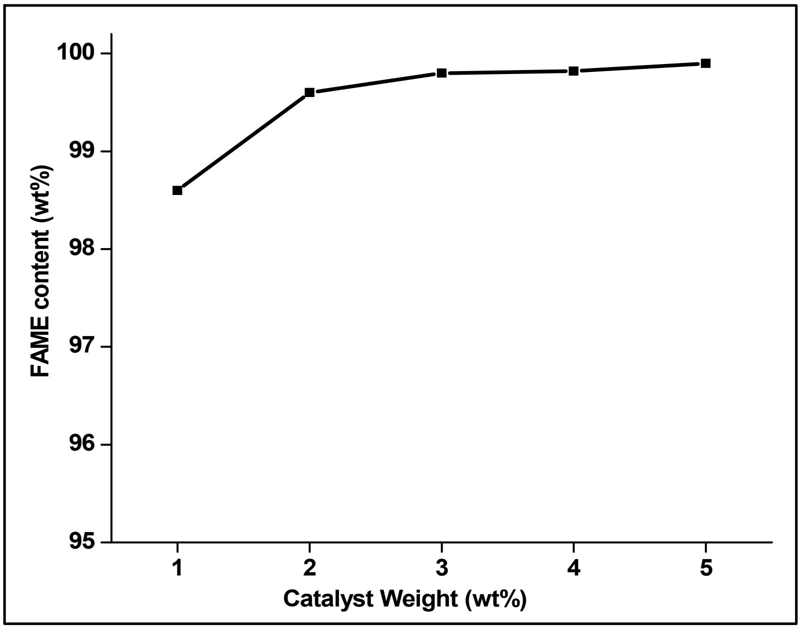


Fig 6.6 Effect of catalyst dosage on FAME content under the reaction conditions of methanol to oil molar ratio of 15:1 at a reaction temperature of 65 °C for 120 minutes

6.3.2.2 Effect of methanol on the transesterification reaction

The molar ratio of methanol to oil was varied from 3:1 to 15:1, keeping the reaction at a temperature of 65 °C for 120 minutes using 1 wt% of the catalyst. The FAME content met the EN14214 specifications at a higher methanol/oil molar ratio of 12:1 that increased on further addition of methanol. The results are shown in the figure 6.7. The methanol to oil molar ratio of 15:1 is chosen for further investigations.

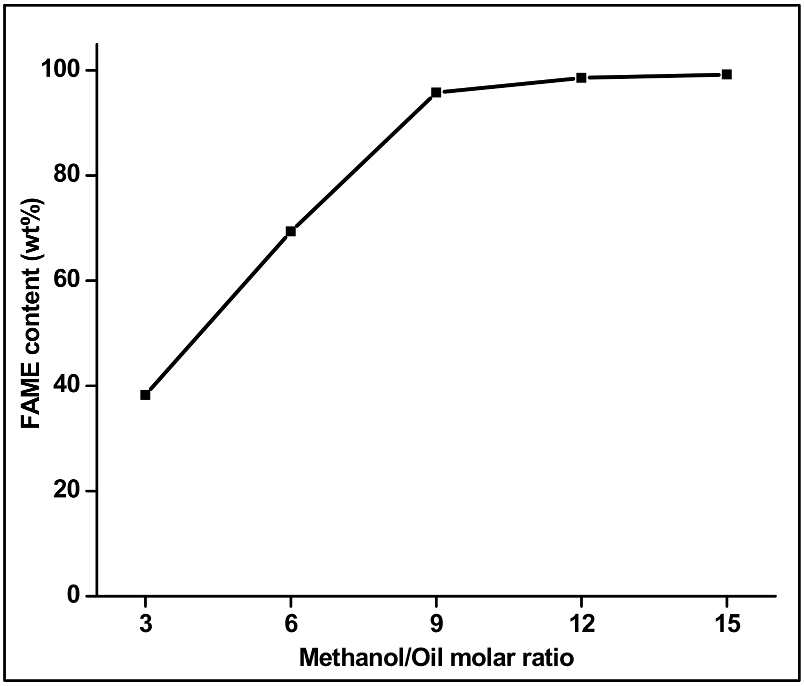


Fig 6.7 Effect of methanol/oil molar ratio on FAME content under the reaction conditions of 1 wt% catalyst at a reaction temperature of 65 °C for 120 minutes

6.3.2.3 Effect of reaction time on transesterification reaction

In order to study the time taken for the complete conversion of the UCO into its corresponding methyl ester, the transesterification reactions was conducted at different time intervals. The reaction was carried out at 65 °C with a methanol/oil molar ratio of 15:1 using 1 wt% of the catalyst. It is found that 120 minutes is required for achieving FAME content higher than 96.5% (fuel grade). Further increase in time increased the conversion to 99.89%. The results are shown in figure 6.8.

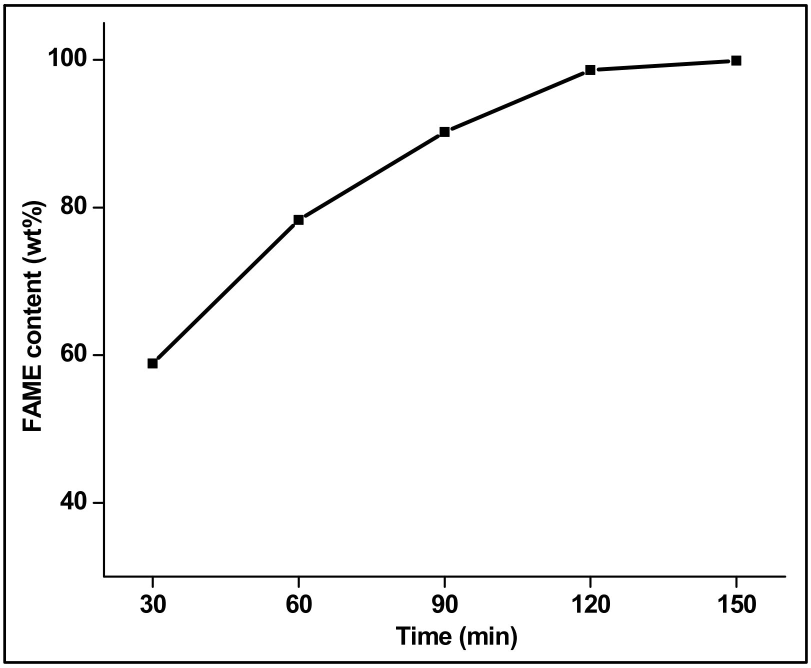


Fig 6.8 Effect of reaction time on FAME content under the conditions of catalyst dosage of 1 wt%, at a temperature of 65 °C at a methanol/ oil molar ratio of 15:1

6.3.2.4 Effect of reaction temperature in the transesterification reaction

From the reactions carried out at different temperatures including room temperature (RT), it is found that high conversion of oil is obtained only at the reflux temperature of methanol. The reaction is not so effective at lower reaction temperatures. The results are in shown in figure 6.9.

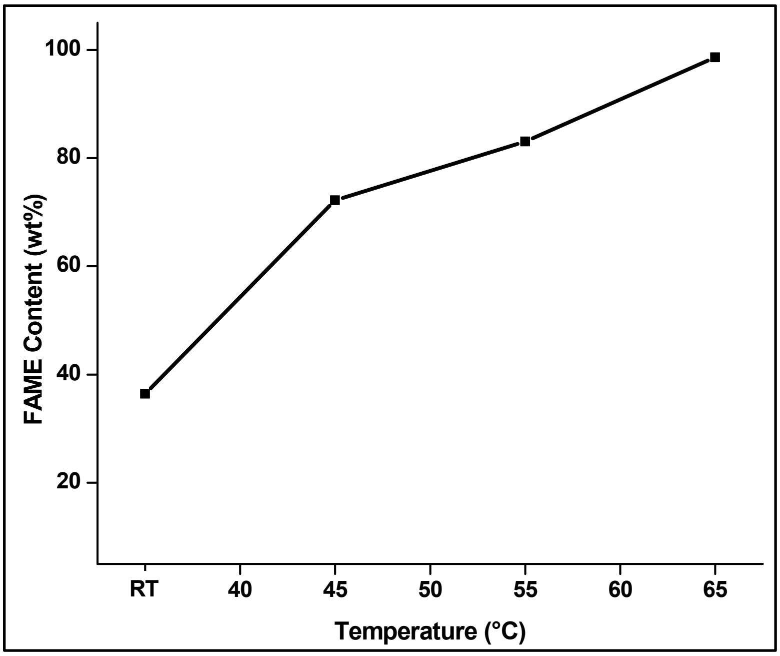


Fig 6.9 Effect of reaction temperature on the FAME content under the conditions of catalyst weight 1 wt%, 15:1 methanol/oil molar ratio for 120 minutes reaction

6.3.2.5 Effect of free fatty acid

A series of experiments were conducted by adding oleic acid as the free fatty acid (FFA), into the reaction medium in order to analyze the activity of the catalyst in the presence of FFA. The reaction was carried out with the added FFA in the oil, under the conditions of 3 wt% catalyst dosage, at 65 °C with a methanol/oil molar ratio of 15:1 for 120 minutes reaction. FAME content of above 99% was attained till 3 wt% of FFA in the oil. The results are shown in table 6.2. Thereafter, soap formation was the resultant of the reaction creating loss of biodiesel yield.

Table 6.2 Effect of FFA on FAME content over Li/ANA catalyst

FFA content (wt%)	FAME content (wt%)
1	99.90
2	99.89
3	99.80

Reaction conditions: 3 wt% catalyst dosage/oil, at 65 °C with a methanol/oil molar ratio of 15:1 for 120 minutes reaction

6.3.2.6 Effect of water content

Water is added directly to the UCO with varying amounts of 1-3 wt% of oil to study the effect of water in the transesterification reaction. From the reaction carried out using 15:1 methanol/oil molar ratio at 65 °C over a catalyst weight of 3 wt% for 120 minutes reaction, it is seen that the water content has a detrimental effect on the biodiesel yield and is found that the catalyst was tolerant only to 1 wt% of water content in the oil feedstock. Further increase in the amount of water lead to the formation of soap.

6.3.3 Catalyst reusability

The reusability of the arecanut husk ash derived catalyst was investigated under the reaction conditions of 5 wt% of the catalyst at a temperature of 65 °C with a methanol to oil molar ratio of 15:1 for 120 minutes reaction. The procedure for reusability studies are explained in chapter 2 in the section 2.6. The conversion of above 99% is retained till 3 consecutive cycles. The results are depicted in figure 6.10.

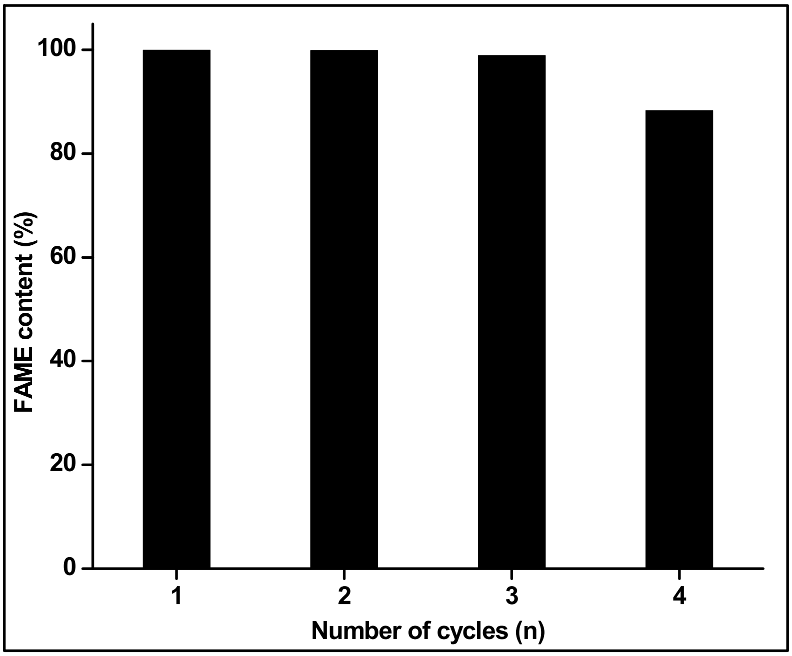


Fig 6.10 Reusability result of the catalyst

6.3.4 Production of biodiesel in the pilot plant

At one of the best suited reaction conditions obtained from the laboratory scale experiments, pilot scale production of biodiesel was conducted. The reaction was performed at a methanol to oil molar ratio of 15:1 over 3 wt% of the catalyst at a temperature of 65 °C for 120 minutes duration. The details of biodiesel production are given in the experimental section described in chapter 2 in the section 2.9.4. FAME content of 99.92% is achieved and the fuel properties of the produced biodiesel were analyzed which is matching with the standard fuel specifications [27, 28]. The results are tabulated in the table 6.

Table 6.3 Fuel properties of UCO biodiesel

Parameters	Unit	Limits	Standards	Biodiesel
Ester content	% m/m	96.5 min	EN 14214	99.92
Monoglyceride	% m/m	1.00 max	D 6751	0.00
Triglyceride	% m/m	0.25 max	D 6751	0.08
Free glycerol	% m/m	0.02 max	D 6751	0.00
Total glycerol	% m/m	0.38 max	D 6751	0.01
Acid value	mg KOH/g	0.80 max	D 6751	0.45
Water content	Vol.%	0.050 max	D 6751	0.00
Iodine value	mg I/100 g	120 max	D 6751	58
Viscosity	mm^2/s	1.96-6.0	D 6751	5.1
Density	kg/ m^3	860-890	D 6751	868

6.4 Conclusions

In this study, arecanut husk ash is employed effectively in the preparation of a solid catalyst by lithium incorporation with the aid of a surfactant, citric acid. The catalyst showed high activity in the transesterification of UCO even at low catalyst concentrations. The active phase of the catalyst is found to be a mixture of lithium silicates supported over α-cristobalite SiO_2 and is evidently revealed from the XRD and FTIR spectral analyses. The catalyst is heterogeneous in nature and showed reusability till 3 repeated cycles of reactions. The catalyst showed tolerance towards low amount of FFA and water content in the oil feedstock. The feasibility of the catalyst in the large scale production is verified by conducting the reaction in the pilot scale unit. The highlights of the present process are the first time use of arecanut husk for the solid catalyst preparation and the requirement of low amount of catalyst in the reaction. The biodiesel produced met the international standard specifications (EN 14214 as well as ASTM D 6571) for fuel.

References

1. https://apaelo.com/know/view_html.php?sq=&language=&q=Areca_nut.
2. P. Rethinam and K. Sivaraman, *Indian J. Arecanut, Species Med. Plants*, 2001, 3, 35-50.
3. T.V. Ramachandra, G. Kamakshi and B.V. Shruthi, *Renewable Sustainable Energy Rev.*, 2004, 8, 1-47.
4. http://www.kscst.iisc.ernet.in/spp/41_series/40S_awarded_&_selected_projs_further_devpt/40S_BE_1160.pdf.
5. N. Das and S. Singh, *Concr. Res. Lett.*, 2015, **6**, 126-135.
6. R. Akhila, J.G. Kurup and T. E. Abraham, *Braz. Arch. Biol. Technol.*, 2010, **53**, 555-562.
7. A. Basker, P. S. S. Shabudeen, S. Daniel and P. V. Kumar, *RASAYAN J. chem.*, 2014, **7**, 1-15.
8. M. A. Rahman, M. A. Hasan, M. A. Salam, A. Salam, N. Siddique and A. M. S. Alam, *Pak. J. Anal. Environ. Chem.*, 2012, **13**, 137-147.
9. M. B. Cyriac, V. Pai, I. Varghese, M. Shantaram and M. Jose, *IJRAP*, 2012, **3**, 81-84.
10. N. Das and S. K. Singh, *AJET*, 2016, **4**, 149-151.
11. B.Y. S. Kumar, *IJESC*, 2016, **6**, 2242-2247.
12. C. Vijayanand, S. Kamaraj, S. Sriramajayam and D. Ramesh, *Int. J. Farm Sci.*, 2016, **6**, 43-48.
13. A. S. Jadhav and G. T. Mohanraj, *Carbon Sci. Tech.*, 2016, **8**, 32-39.
14. K. Rathod, M. Shivaprasad and Rajshekhar, Int. J. Sci. Eng. Technol., 2015, **3**, 366-372.

15. W. J. Xun, C. K. Tung, W. J. Syuan, W. P. Hsiang, H. S. Tsuena and C. C. Chang, *Fuel Process. Technol.*, 2012, **104**, 167-73.

16. N. Hindryawati, G. P. Maniam, M. R. Karim and K. F. Chong, *Eng. Sci. Technol.*, 2014, **17**, 1-9.

17. A. N. Lazarev, *Vibration Spectra and Structure of Silicates*, Consultants Bureau, New York, 1972.

18. B. Zhang, M. Nieuwoudt and A.J. Easteal, *J. Am. Ceram. Soc.*, 2008, **91**, 1927-1932.

19. J. O. Landerosa, L. M. Cruz, C. G. Yanez and H. Pfeiffer, *Thermochim. Acta*, 2011, **515**, 73-78.

20. B. Zhang, A. J. Easteal, and N. R. Edmonds, *J. Am. Ceram. Soc.*, 2007, **90**, 1592-1596.

21. K.F. Hesse, *Acta. Cryst.*, 1977, **33**, 901-902.

22. H. Peiffer, P. Bosch and S. Bulbulian, *J. Nucl. Mater.*, 1998, **257**, 309-317.

23. P. V. Subha , B. N. Nair, A. P. Mohamed, G. M. Anilkumar, K. G. K. Warrier, T. Yamaguchi and U. S. Hareesh, *J. Mater. Chem. A*, 2016, **4**, 16928-16935.

24. T. Fuss, A. M. Milankovic, C.S. Ray, C.E. Lesher, R. Youngman and D.E. Day, *J. Non-Cryst. Solids*, 2006, **352**, 4101-4111.

25. X. Li and H. Yang, *Cryst. Eng. Comm.*, 2014, **16**, 4501-4523.

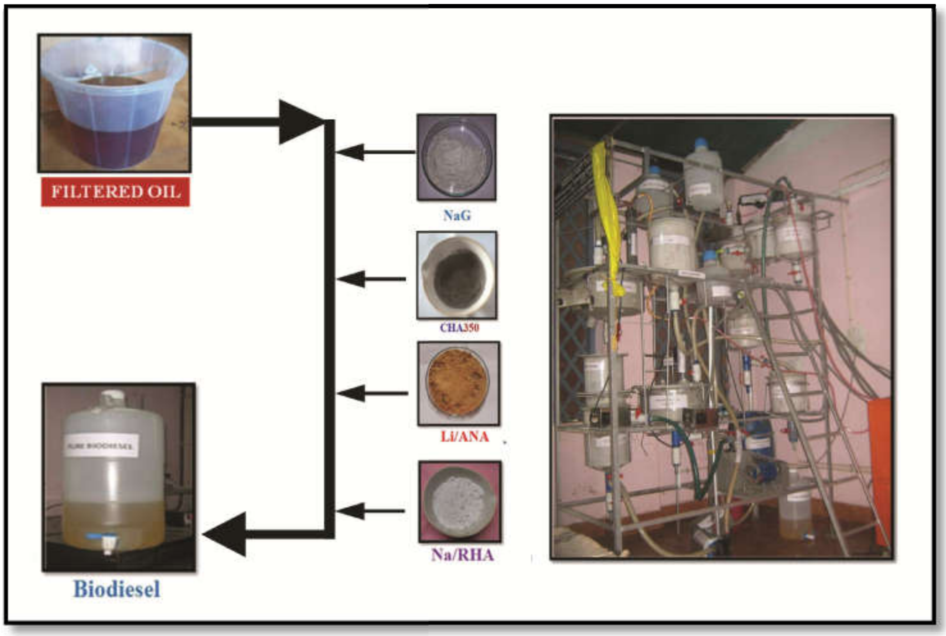
26. A. Honglin, Y. Tang, M. Pam and S. Fleming, *Opt. Express*, 2004, **12**, 1055-1060.

27. S. P. Singh, D. Singh, *Renewable Sustainable Energy Rev.*, 2010, **14**, 200-216.

28. G. Knothe, *Fuel Process. Technol.*, 2005, 86, 1059-1070.

CHAPTER 7

SUMMARY AND CONCLUSIONS



7.1 Introduction

Commercial biodiesel production is still carried out by the corrosive homogeneous base catalyzed transesterification process. This process have some bottleneck; possibility for operational difficulties such as soap formation, catalysts consumption, neutralization and washing requirements after the reaction, emulsion formation leading to loss of biodiesel yield etc. It is not suited for the biodiesel production from low cost feedstocks (especially *Jatropha curcas* oil and used cooking oils having high FFA) and requires additional pre-esterification step with concentrated acids. The uses of corrosive alkali/acid catalysts make the entire process environmentally unfavorable. The best remedy for this situation is heterogeneous (solid) catalyzed biodiesel production, which has the advantage of catalyst regeneration; additionally it avoids extra efforts for the neutralization and washing steps as well as results in high yield of biodiesel and high purity glycerol byproduct. Thus the entire heterogeneous catalyzed biodiesel production process is eco-friendly and cost effective. However, the commercial biodiesel production over solid catalyzed route is not well established yet and majority of the solid catalysts reported are not used beyond laboratory scale. Relatively high cost or extra care required in the catalyst production process is the problem in a commercial point of view. Here, we have developed 4 different sets of solid catalysts from waste materials for biodiesel production and among them 3 sets are prepared by alkali metal treatment. Preparation from renewable/waste materials by simple methods makes the heterogeneous catalysts low cost and thus has the potential of easy industrial scale up.

One of the serious issues in biodiesel production is the high cost of the feedstocks. Triglycerides derived from vegetable oils or animal fats are the raw materials for biodiesel production. In the current scenario, vegetable oil price is increasing and it reached more than 3 times when compared to the conventional diesel fuel, which diminishes the possibility of using biodiesel as a substitute for diesel fuel. So, nowadays, low cost feedstocks such as used cooking oils (UCO) and non-edible oils are getting more attention. Use of UCO for biodiesel production is an alternative solution for the waste oil disposal and reduces the health hazards associated with the repeated use of frying oil. Among the wide variety of non-edible oils, *Jatropha curcas* oil (JCO) is the broadly used one for biodiesel production. It can be cultivated even in barren lands at harsh climate conditions and thus is not causing any competition with agricultural land. Here, we used both UCO and JCO for the production of biodiesel by their transesterification with methanol using 4 different sets of solid catalysts derived from waste materials. Alkali metal incorporation is the preferred method of catalyst preparation aiming the development of highly basic heterogeneous catalysts. The activity of the 4 different sets of catalysts in the transesterification reaction is investigated under varying reaction conditions.

We have designed and assembled a pilot plant in our laboratory aiming the industrial scale up of the present biodiesel production process easy and cost effective. Pilot plant is made of polypropylene (PP) vessels with a production capacity of 15 L biodiesel/run. At one of the best suited conditions, the biodiesel production was scaled up in the pilot plant using selected catalyst from each set. Here, we could produce biodiesel in the pilot plant with the same yield obtained in the laboratory scale experiments and the fuel properties of the produced biodiesel sample were found to satisfy the international standard fuel specifications.

7.2 Summary

In summary, present study deals the preparation of solid catalysts from waste materials, characterization of the catalysts using various techniques to find out the active sites responsible for the activity, laboratory scale studies on the transesterification reaction of UCO as well as JCO over different catalysts, investigation of the reusability of the catalysts, design and assembly of biodiesel pilot plant, up-gradation of biodiesel production in the pilot plant under the selected reaction conditions and analysis of the produced biodiesel to check its suitability as fuel. The thesis is structured into 7 chapters including the summary and conclusions chapter. The summary of each chapter and the conclusions obtained are mentioned in brief in the following sections.

7.2.1 Chapter 1: Biodiesel and biodiesel production strategies

The 1st chapter describes about biodiesel, its need and importance among the renewable alternate fuels. The biodiesel production process, feedstocks, fuel properties and its use as an alternate for petrodiesel are briefly explained here. The main emphasis is on the catalysts used in the transesterification of triglycerides for biodiesel production. The demerits of homogeneous base catalyzed commercial biodiesel production and the superiority of heterogeneous catalysts over homogeneous catalysts is clearly mentioned in this chapter. A review of literature of solid catalysts in the laboratory as well as pilot scale production of biodiesel is also provided. Use of solid catalysts derived from waste materials in the transesterification and the importance and need of such catalysts for the commercial biodiesel production is also explained. Some of the heterogeneous catalysts commercialized for the industrial scale biodiesel production is mentioned in this chapter to inspire the studies on the development of efficient solid catalyst from renewable/waste materials.

7.2.2 Chapter 2: Materials and methods

The 2nd chapter deals the experimental section. This chapter includes the materials used throughout the study and their supplier/manufacturer etc. Various characterization techniques used and its working principles are briefly mentioned in the chapter. Details of the instruments used for the catalyst characterization as well as biodiesel analysis are also given here. The general procedure for the purification of biodiesel feedstock, preparation of biodiesel in the laboratory scale and reusability studies of the catalysts as well as design and assembling of pilot plant, different operational parts of the pilot plant and its working, production of biodiesel in the pilot plant etc are narrated in the chapter. The fuel quality analysis of biodiesel using standard test procedures is well explained towards the end.

7.2.3 Chapter3: Production of biodiesel using coconut husk ash catalyst

The 3rd chapter discusses the preparation and characterization of coconut husk derived catalysts and their effective use in the transesterification reaction for biodiesel production. The catalyst preparation is straight forward and simple combustion was found to be highly effective in the catalyst development. The preparation of the catalytic systems is also described in this chapter. Results of catalyst characterization revealed information about the active components responsible for catalysis, the surface morphology and composition of the catalysts. The prepared catalysts were found to be complex aggregates of minerals and displayed macroporous morphology. The SEM-EDS analysis revealed that potassium is the major component in the catalyst, which is responsible for the high activity of the catalyst. The catalytic activity studies of the catalyst in the transesterification reaction are monitored well and the reaction parameters are varied to find out the suitable condition to produce maximum fatty acid methyl ester (FAME) content. The transesterification of JCO was carried out under mild reaction conditions. Even at room temperature, FAME content reached fuel grade (above 96.5% for 3 h reaction) and at 45 °C more than 99% FAME content is obtained for 1 h reaction at a lower methanol/oil ratio of 12:1. The feasibility of the catalyst for large scale biodiesel production is verified by up-grading the reaction in the pilot plant with JCO as well as UCO. The fuel properties of the produced biodiesel are analyzed and found that it meets the standard fuel specifications.

7.2.4 Chapter 4: Single step biodiesel production over Na loaded rice husk ash catalyst

This chapter narrates the use of rice husk ash (RHA) as the precursor for the development of highly active catalyst in biodiesel production. Since alkaline materials are found to be highly effective in biodiesel production and RHA is mainly composed of silica (~18%), we have done the incorporation of Na into RHA via sol gel method. The preparation was found to be highly effective in producing biodiesel catalyst where the active phase of the material was found to be Na_2SiO_3 supported over cristobalite SiO_2 as revealed from material characterization. The catalyst was found to be macroporous in nature, which is very much beneficial in biodiesel synthesis. The catalyst is found to be active under mild conditions yielding fuel grade biodiesel even up to eight repeated runs. Excellent reusability, high free fatty acid (FFA) and water tolerance makes it superior to any reported heterogeneous catalysts in biodiesel production. The biodiesel production process is also up-graded in the pilot plant resulting in similar performance with the lab scale operation yielding high quality biodiesel. Another feasibility of the process is the absence of pre-esterification step before transesterification, reducing the overall cost and effort in large scale biodiesel production process.

7.2.5 Chapter 5: Biodiesel production over heterogeneous catalyst derived from waste glass materials

Chapter 5 describes the preparation of highly active catalyst for biodiesel production by the use of waste borosilicate glass beakers. When compared to any other waste material of the present study, the advantage of the present waste precursor material is that majority of the contents of the precursor material is incorporated to the finally developed catalyst material. Here also, alkali metal incorporation is the effective route of catalyst development where simple means of impregnation is performed in material preparation. The active phase of the catalyst was analyzed by means of various characterization techniques and its basic nature is also revealed from the analysis. Mild reaction conditions, FFA and water tolerance and effective reusability are the major factors promoting the catalyst for industrial scale up. A very low amount of the catalyst, even 2 wt% of the oil, is found to be effective in producing fuel grade FAME in the biodiesel sample. The results indicate the suitability of the present glass derived catalyst in the single step production of biodiesel without the pre-esterification step. The process is successfully up-graded in the pilot scale unit and the fuel qualities met the standard specifications of biodiesel fuel.

7.2.6 Chapter 6: Biodiesel production over Li loaded areca nut husk ash catalyst

In this chapter, arecanut husk ash is effectively used for the first time in the preparation of a solid catalyst by lithium incorporation with the aid of a suitable surfactant, citric acid. XRD and FTIR spectral analyses revealed that the active phase of the catalyst is a mixture of lithium silicates supported over cristobalite SiO_2. The main highlight of the present catalyst is that it showed high activity in the transesterification of UCO even at low catalyst dosage. Biodiesel produced over lithium loaded arecanut husk ash catalyst met the standard fuel specifications and the catalyst showed reusability for 3 repeated reactions. The feasibility of the catalyst in the large scale production is verified by conducting the reaction in the pilot scale unit.

7.2.7 Chapter 7: Summary and conclusion

The 7th chapter summarizes results of the present work on the development of solid catalysts from waste materials, its characterization and use in biodiesel production, design and assembly of biodiesel pilot plant, biodiesel production process up-gradation in the pilot plant and fuel property analysis of the biodiesel.

7.3 Conclusion

In the present study, we have developed 4 different sets of highly active solid catalysts from waste materials and alkali metal precursors. The developed catalysts are characterized by using different analytical techniques in order to investigate the structure, morphology as well as the active phases that are responsible for catalytic activity. The activity of the prepared heterogeneous catalysts in the transesterification reaction of UCO as well as JCO feedstocks for the production of biodiesel was investigated. A pilot plant is designed and assembled on a skid mount unit for the pilot scale production of biodiesel over the prepared catalysts. Pilot plant is made of PP vessels and has the capacity of 15 L biodiesel production per run. Pilot scale production of biodiesel had done with the representative catalysts prepared from each waste material at one of the best suited reaction conditions. The fuel properties of the biodiesel produced in the pilot plant were analyzed by different procedures and it is found that all the tested fuel properties lies in the range of values mentioned by ASTM D 6751 and EN 14214 standard specifications for biodiesel fuel. All the catalysts except coconut husk derived one, shows excellent reusability, FFA tolerance and water tolerance.

7.4 Future outlook

The depleting nature of fossil fuels makes attention to the use of renewable alternate fuels, among which biodiesel is a perfect substitute fuel in diesel engines. Today, most of the countries are giving attention to the use of biodiesel. In biodiesel production, heterogeneous catalysts have got predominance over homogeneous catalysts considering its various advantages. Here, in the present work, we have established green and economical route for the pilot scale biodiesel production over low cost heterogeneous catalysts by the transesterification of non-edible oils as well as used cooking oil. The solid catalysts for the pilot scale production of biodiesel are developed using waste materials; in most cases by their treatment with alkali metal sources. Present strategy has the promise of easy and economical industrial scale up, since we could demonstrate the production in a small unit having the facilities of a large plant for biodiesel production.

The design and assembly of the biodiesel pilot plant made the advantage of the use of polypropylene vessels which is light weight, non corrosive and stable to the reactants as well as products of the transesterification reaction. We could offer competent route for the industrial biodiesel production processes in terms of production cost as well as eco-friendly nature of the entire process.