PROCESS OPTIMIZATION FOR BIODIESEL PREPARATION FROM VEGETABLE OILS USING HETEROGENEOUS CATALYSTS

By

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Dedicated……

…to my mummy & papa

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DECLARATION CERTIFICATE

I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no materials previously published or written by another person nor material which has been accepted for the award of any other degree or diploma of the University or other institute of higher learning, except where due acknowledgment has been made in the text.

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THESIS COMPLETION CERTIFICATE

This is to certify that the thesis entitled **“PROCESS OPTIMIZATION FOR BIODIESEL PREPARATION FROM VEGETABLE OILS USING HETEROGENEOUS CATALYSTS”** submitted by **Ms. Surbhi Semwal** to University of Petroleum and Energy Studies, Dehradun for the award of the degree of Doctor of Philosophy is a bona fide record of the research work carried out by her under my supervision and guidance. The content of the thesis, in full or parts have not been submitted to any other Institute or University for the award of any other degree or diploma.

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(Surbhi Semwal)

EXECUTIVE SUMMARY

Rapid fossil fuel depletion and increasing environmental awareness have been the main reasons for development of alternate fuels. Among the different possible sources, fatty acid methyl esters, known as biodiesel derived from triglycerides (vegetable oils and animal fats) by transesterification present the promising alternative substitute to diesel fuels and have received the most attention. The main advantages of using biodiesel are its renewability, lower exhaust gas emission, biodegradability and also its ability to mitigate green house gas (GHG) emission.

Application of biodiesel as a blending component with petroleum diesel in transport fuels is now well accepted. Biodiesel lowers the sulphur content of the blends, imparts desirable properties of lubrication apart from providing a mean to substitute the fossil fuel. Though biodiesel has been approved for use in automotives as a blend with normal petro-diesel, there are very stringent quality norms viz. ASTM, IS, DIN and EN etc prescribed by several countries. Therefore, it is imperative for biodiesel to meet the specifications for its use in IC engines.

Several commercial plants have been established for manufacture of biodiesel and most of these employ base catalyzed homogeneous transesterification process of oil and fats using KOH or NaOH as the homogeneous catalyst. Methanol being cheaper is commonly used alcohol during transesterification reaction. The advantage of this process is production of methyl esters at very high yields under mild reaction conditions and reaction generally takes about an hour for completion. However, major quality related problems were encountered. Production costs were rather high as the process involved number of washing and purification steps in order to meet the stipulated quality. It was quite difficult to remove the traces of K/Na remaining in the product and separation of glycerin also posed technical challenges. The higher amount of water used in washing and consequent treatment of the resulting effluent added to the overall process cost. As it is generally difficult to meet the target specifications of transport fuels, therefore alternate methods of transesterification have been researched.

Additionally any commercial biodiesel plant must have the inbuilt capability to handle a variety of different feedstocks which may differ widely in quality. The vegetable oils may be from edible sources, non-edible sources, waste cooking oils, animal fats, algae, fungi etc. In Europe and US, the primary sources for producing biodiesel are edible oils like rapeseed, sunflower, and soybean. In countries like India, non-edible oils like jatropha and karanja are being promoted on a very large scale, as these can be grown on marginal and waste lands. The conventional biodiesel production process of base catalyzed homogeneous transesterification encounters difficulties to handle multiple feed stocks. Nonedible oils with higher fatty acid content lead to formation of soap and consequent loss of oil and problems of product separation.

Due to these issues a large number of alternative methods were developed. These include heterogeneous catalysis, supercritical process and enzymatic process. However most of these could not be adopted on industrial scale as either they required extreme conditions or the catalyst had short life time.

Biodiesel synthesis using solid catalysts instead of homogeneous liquid catalyst could potentially lead to economical production costs because of reuse of the catalyst and offer the possibility for carrying out both transesterification and esterification simultaneously. It is become imperative to use heterogeneous catalysis as they are non-corrosive, environmentally benign as there is no need for acid or water treatment in the separation step and present fewer disposal problems. They are also much easier to separate from liquid products and they can be designed to give higher activity, selectivity and longer catalyst life times and thus help reduce biodiesel production cost and help making it competitive with diesel. However, these catalysts are much milder and take long for completion of reaction.

For a successful commercial catalyst, catalyst life, recyclability or retention of activity and lower cost is extremely important as these have a direct effect on overall cost of the process.

In order to understand the mechanism of heterogeneous catalysis and to have an insight of the prior work in this area, complete literature was scanned. **The state- of- the- art review on all aspects of heterogeneous transesterification of vegetable oil has been published in Bioresource Technology 2011, volume 102, page no. 2151-2161.**

The various types of heterogeneous catalysts have been investigated for transesterification of vegetable oils for biodiesel production. The common problems encountered while using heterogeneous catalysts for transesterification of triglycerides are higher catalyst cost, lower recyclability and elaborate procedures for catalyst preparation. Since, biodiesel has to be cost competitive with normal diesel, the production process has to be simple and cost effective. It was realized that, the cost can be reduced by production of solid catalysts from cheap natural resources. The natural resource has to be carefully selected with major criteria of abundance, activity, overall ease of preparation and lower costs. These aspects have been the main motivation for the present work. The present invention involves the selection and identification of natural waste materials capable of giving catalytic properties for transesterification of jatropha oil to produce biodiesel. The natural waste materials include natural waste or fresh natural seashell and eggshells which are available in plenty and are very economic.

The catalysts i.e. $CaTiO_3$ and $Ca_2Fe_2O_5$ are A-B-O type metal oxides (where A is an alkaline earth metal, alkaline metal or rare earth metal and B is transition metals) are developed for transesterification of jatropha oil in which calcium part is derived from natural waste raw material such as egg shell/sea shell. The catalysts has shown better catalytic activity due to porous structure of $CaCO_3$ obtained from egg shell (calcined at 550^oC) which after combination with TiO_2 and Fe_2O_3 to give $CaTiO_3$ and $Ca_2Fe_2O_5$ after calcined at 1050^oC at 3 h. The catalyst was then extruded at cylindrical shaped by mixing with pseudoboehmite using nitric acid as peptizing reagent. During the process of extrusion of $Ca_2Fe_2O_5$, one of the types of fullers earth i.e. palygorskite $[(Mg,Al)_2Si_4O_{10}(OH).4(H_2O)]$ is additionally mixed due to brittle nature of iron and clay is the tendency to easily molded to any shape.

The synthesized catalysts has been characterized by different techniques viz. X-ray Diffraction (XRD), thermogravimetric analysis (TGA), BET surface area, Average pore size , Total pore volume, Fourier transform infra red spectroscopy (FTIR), Scanning electron microscope (SEM) and Basic strength by Hammett indicator method. For benchmarking the catalysts which were prepared from egg shells/sea shells derived $CaCO_3$ were also compared with $CaTiO_3$ and $Ca_2Fe_2O_5$ which were prepared from normal $CaCO_3$.

The catalysts activity of $CaTiO_3$ and $Ca_2Fe_2O_5$ obtained from abundant waste egg shells/ sea shells showed good catalytic activity than prepared from normal $CaCO_3$. The porous structure of $CaCO_3$ and also very large surface area and high basicity (approximately more than 10 times) of the catalysts (from natural waste) enhanced the transesterification of vegetable oil.

After having prepared the suitable catalyst, extensive experiments were performed in a pressure autoclave to optimize the catalyst concentration, methanol amount and reaction time. The effect of variation of catalyst concentration of 3 to 12% (w/w), methanol to oil ratio of 5:1 to 30:1 and reaction time was studied to arrive at optimum condition for maximum biodiesel yield/conversion. Catalysts activity and recyclability were performed by carrying out repeated transesterification reaction of jatropha oil using recovered catalyst under optimized conditions. The catalyst structures of repeated cycles were checked by XRD.

In order to check the efficiency of catalyst is presence of free fatty acid or water, synthetic mixture of jatropha oil were prepared and studied for transesterification. The developed catalyst was effective in transesterification of high FFA jatropha oil and also in presence of moisture. The performance of reaction was primarily monitored by thin layer chromatography (TLC) and analytical techniques viz. gas chromatography (GC), gel permeation chromatography (GPC) and nuclear magnetic resonance (^{1}HNMR). The synthesized biodiesel was also evaluated for various physico-chemical characteristics viz. viscosity, density, acid value, cloud point, flash point, total glycerin etc as per ASTM/ IS standards.

The transesterification of jatropha oil using calcium titanate was optimized at 170 ^oC temperature, 80 bar pressure, 20:1 molar ratio of methanol to oil, 10% (w/w) catalyst concentration and 3 h reaction time and 94.2%

biodiesel conversion was achieved. The developed catalyst could be recycled for 12 times without much loss in its activity.

In another set of experiments, Calcium ferrite was prepared by fusion of calcined egg shells with Fe_2O_3. This catalyst was also fully characterized by XRD, FTIR, SEM, basicity etc. Similar set of experiments in high pressure autoclave were performed with this catalyst as in the case of $CaTiO_3$. The optimized set of conditions for temperature, catalyst concentration, methanol ratio and reaction time were arrived at for maximum conversion for biodiesel.

The optimum reaction conditions were almost same for calcium ferrite except that this catalyst was active at lower concentration and 5% (w/w) catalyst concentration gave 96.9% conversion. This catalyst was also found to be active even after 8 cycles of use.

After successful optimization of developed catalysts in autoclave (high pressure reactor), the catalysts performance were also evaluated in fixed bed pilot plant of continuous conversion of biodiesel for commercial scale operation. The pilot plant had maximum biodiesel production capacity of 540 ml/h. The fixed bed pilot plant consisted of five sections i.e. feed section, reactor section, distillation section, separation section and drying section. The catalyst was loaded (80-100 g each) in two identical tube reactors. The advantage of the fixed bed operation is that catalyst to feed ratio in reactor is very high compared with pressurized autoclave. Thus, the transesterification reaction proceeds very fast and reaction can be completed in a residence time of few minutes. The catalyst is generally used as extruded form rather than powder form in a fixed bed reactor, which prevent the blockage and excessive back pressure of the reactor.

The reactor was fed with vegetable oil and methanol through a calibrated pump and first pumped into a pre heater having static mixture before charging it into a reactor due to limited miscibility of the reactants. The reaction conditions of transesterification of jatropha oil by using Ca/Ti extruded catalyst in the pilot plant at temperature range of 170- 200 ^{o}C, 50- 80 bar pressure, 12:1 to 107:1 methanol to oil ratio and 0.23-0.36 h^{-1} liquid hourly space velocity (LHSV). The maximum biodiesel conversion of 88.6% was obtained by using $CaTiO_3$ at optimized reaction condition of 190 ^{o}C

temperature, 80 bar pressure, 107:1 molar ratio of methanol to oil and 0.3 h^{-1} LHSV. While for $Ca_2Fe_2O_5$, the reaction condition of transesterification of jatropha oil in pilot plant at temperature range of 170- 190 ^oC, 50-80 bar pressure, 12:1-21:1 methanol to oil ratio and 0.23-0.36 h^{-1} LHSV. It was observed that both titanium and iron based metal oxides were robust and have potential for use in industrial preparation of biodiesel with Ca/Fe based catalyst being better in performance than Ca/Ti based catalyst.

Nano sized catalysts offer advantages of much larger surface area/g of the catalyst which translates into higher conversion efficiency. The synthesis of fatty acid methyl ester (FAME) from jatropha oil has been also developed using nanosized $CaTiO_3$ catalyst. Methoxy coated nanosized $CaTiO_3$ catalyst has been prepared from low value abundant natural waste egg shells/ sea shells and through top down approach and also characterized by various analytical techniques. The catalyst activity was evaluated in transesterification of jatropha oil and compared with micron sized $CaTiO_3$ in various parameters. It was found that nano sized catalysts is effective in lower catalyst concentration and is shorter time. The catalyst activity and durability over repeated cycles was also evaluated.

The maximum biodiesel conversion of 97.5% was obtained by using nanosized $CaTiO_3$ at optimized reaction condition of 170 ^oC temperature, 80 bar pressure, 20:1 molar ratio of methanol to oil and 5% (w/w) catalyst concentration in 2 h reaction time.

The present study also investigated the pretreatment of jatropha oil prior to transformation for biodiesel production. The crude vegetable oils needs pretreatment because it contains a number of impurities such as free fatty acids, hydrocarbons, ketones, tocopherols, glycolipids, phytosterols, phospholipids, proteins, pigments, resins and metal contents as these can deposits on the reactor column having the catalyst and it have negative effects on catalyst life as well as on the quality of biodiesel. Therefore, these impurities should be removed from vegetable oils by chemical or physical refining process. Hydratable phospholipids (HPL) are removed from oil by water degumming but nonhydratable (NHPL) are removed by the phosphoric acid or citric acid treatment.

Removal of phosphorous and metal from oil involves the decomposition of their salts by a degumming acid capable of binding the alkaline earth ions and subsequent dissociation of the phosphatidic acid, which is separated by raising the pH by addition of dilute alkali solution i.e. NaOH. For this purpose two numbers of jatropha blends- I and II (crude and partially refined) were used. The first blend was that very crude jatropha oils having P content of 174 ppm, other metals at 235 ppm and total acid value of 23.58 mgKOH/g. The second blend was refined jatropha oil having P content of 49 ppm, metal /P content of 81 ppm and total acid value of 8.2 mgKOH/g. The experiments were carrying out of jatropha oils with the concentration of 0.05 to 0.1 % of phosphoric acid, citric acids and in combination of both phosphoric and citric acid at 70 ^{o}C temperature for 3 h. It was observed that metal contents were reduced below 1 ppm for refined and below 5 ppm for crude jatropha oil respectively and total acid value were reduced upto 2 mgKOH/g. The mixture of 0.05% (w/w) H_3PO_4 and 0.02% (w/w) citric acid is the optimized concentration for maximum reducing the metal /P content from jatropha oils. These purified oils can be easing taken for transesterification of heterogeneous catalyst in continuous pilot plant without any adverse effect on catalyst. Moreover, these purified oils were also found suitable for hydrotreatment to produce green diesel/ATF.

In conclusion the present investigation describes the following:

- Complete prior-art on use of heterogeneous catalyst for transesterification of vegetable oil to biodiesel.
- Preparation, characterization and evaluation of $CaTiO_3$ derived for waste natural material.
- Preparation, characterization and evaluation of $Ca_2Fe_2O_5$ derived for waste natural material.
- Preparation, characterization and evaluation of nano sized $CaTiO_3$ derived for waste natural material.
- Method of jatropha oil purification to removed P and metals.
- Pilot scale evaluation of developed catalyst for continuous production of biodiesel from jatropha oil.

LIST OF SYMBOLS

Å	Angstrom (unit of length)
Btu/gal	British Thermal Unit/ Gallons
CI	Cetane Index
cSt	Centistokes
g	Gram
g/cc	Gram/cubic centimeter
h	Hour
H_	Basic strength
H_Z	Hertz
Hβ	Spectral line made by hydrogen with transition
K	Temperature in Kelvin scale
Kcal/mol	Kilocalorie/mol
kDG	Rate constants for diglycerides
kMG	Rate constants for monoglycerides
kTG	Rate constants for triglycerides
Lit	Litre
MJ/kg	Megajoules/ kilograms
MJ/L	Megajoules/ litre
n	Number of moles
v/v	Volume/volume
w/w	Weight/weight

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
ATF	Aviation Turbine Fuel
BD	Biodiesel
BET	Brunauer Emmett Teller (method of determining surface area)
BIS	Bureau of Indian Standards
CCR	Conradson Carbon Residue
CII	Confederation of Indian Industry
CNT	Carbon Nano Tubes
CTAB	Cetyltrimethyl Ammonium Bromide
DG	Diglyceride
DIN	Deutsche Industrienorm (German Industry Standard)
EN	European Norm
EPA	Energy Policy Act
GHG	Green House Gases
GPC	Gel Permeation Chromatograph
HFRR	High Frequency Reciprocating Rig Testing
HPR	High Pressure Reactor
HSD	High Speed Diesel
ICAP	Inductively Coupled Argon Plasma
IEA	International Energy Agency
IS	Indian Standard
LHSV	Liquid Hourly Space Velocity
MMT	Million Metric Tones
MT	Million Ton
PUFA	Polyunsaturated Fatty Acid
SEM	Scanning Electron Microscopy
TAN	Total Acid Number
TGA	Thermogravimetric Analysis

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INTRODUCTION AND LITERATURE REVIEW

1.1. ENERGY SCENE IN INDIA

Energy has been the main factor for global economic growth and its contribution to better standard of living has increased with each passing year. Fossil sources are most important for generation of primary energy. Fossil fuels account about 89% of the primary energy consumption with oil, coal and natural gas having a share of 33.6, 29.6 and 25.3% respectively. Whereas, nuclear energy, hydroelectricity and renewable energy accounted for 4.4%, 5.3% and 1.8% of the total primary energy consumption respectively [1].

The consumption of crude oil in India was about 184.68 MT in the year 2007-2008 and approx. 80% was met by imports [2]. Petroleum oil reserves are diminishing day by day, however, the rate of energy consumption is rising at the rate of 4-6% per annum. India's share of crude oil production is about 1% of total world crude oil production while in consumption, its share is about 3.1% of total world consumption [3]. The import of crude oil has increased from 63% in 1971 to 80% in 2007-2008 and trend is likely for continue in future. The demand of high-speed diesel (HSD) has grown from 39.81 MT in 2000–2001 to 52.32 MT in 2007–2008 at the rate of 5.6% per annum [2,4] and the growth trend continues. The dependence of world on fossil fuels has increased to an extent that it cannot be a sustainable proposition. Recent estimates suggest that at current rate of usage, we will run out of oil in 40 years, gas by 60 years and eventually coal in about 100 years. Because of these alarming future predictions, alternative energy sources have gained a great attention. Increased environmental concerns are yet another reason to look for carbon neutral or low carbon fuels. Therefore, developing alternative energy is an urgent need for sustainable economic growth in human society [5].

1.2. BIODIESEL AS AN ALTERNATE TRANSPORT FUEL

Several alternative energy options have been explored which include biomass based fuels, solar, wind etc. However, for application as transportation fuels, liquid fuels are desired and preferred alternate sources. Transport fuels are important as about 26% crude oil is used for transportation purpose. Transport fuels are mainly gasoline (petrol), diesel and jet fuel. Unlike US where gasoline usage is much more than diesel, Indian transport sector is based on diesel. We consume diesel which is more than 6 times the consumption of petrol. Therefore, Indian situation necessitates focus on development of alternate fuel which could part replace diesel.

Biodiesel is the name of a clean burning alternative fuel, produced from renewable resources which are mainly vegetable oils or fats. It is defined as mono-alkyl esters (usually methyl ester) of long chain fatty acids derived from edible/ nonedible oils or animal fat with the addition of methanol and catalyst through a chemical process called transesterification. It can be used in conventional compression ignitions engines, which need almost no or very slight modifications. Biodiesel is a legally registered fuel and fuel additive with the U.S. Environmental Protection Agency. Biodiesel is also a recognized alternative fuel under the Energy Policy Act of 1992 (EPAct) as amended in 1996 and 1998, and thus qualifies under the alternative fuel vehicle purchase provisions of EPAct (provided a B20 or higher blend is used). American Standard testing Materials (ASTM) has specified biodiesel for use in IC engines according to ASTM D 6751.

Biodiesel i.e. the liquid which has combustion properties like petrodiesel, but it is derived from renewable bio-resources. Biodiesel can be easily blended into petrodiesel in any proportions and most vehicle manufactures allows up to 20% biodiesel blended diesel to be used in the existing vehicles and that too without any modifications in the engine. Biodiesel has better burning properties than conventional fossil-based fuels. It has similar physical and chemical properties with petro-diesel. In fact, biodiesel properties can sometimes be superior to that of petro-diesel fuel because it has higher flash point, ultra low sulphur content, better lubricating efficiency and better cetane number. The major physical properties for biodiesel and petroleum based diesel are depicted in Table 1.1 for the comparison [6].

Table 1.1: Comparison of the properties of petrodiesel and biodiesel based on American Society for Testing and Materials (ASTM) [6]

Property	Diesel	Biodiesel
Standard Number	ASTM D 975	ASTM D6751
Composition	Hydrocarbon (C_{10}-C_{21})	Fatty acid methyl ester (C_{12}-C_{22})
Specific gravity (g/ml)	0.85	0.88
Flash point (^oC)	60 to 80	100 to 170
Cloud point (^oC)	-15 to 5	-3 to 12
Pour point (^oC)	-35 to -15	-15 to 16
Water (vol%)	0.05	0.05
Carbon (wt%)	87	77
Hydrogen (wt%)	13	12
Oxygen (wt%)	0	11
Sulphur (wt%)	0.05	0.05
Cetane number	40 to 55	48 to 60
Lower heating value (Btu/gal)	131,295	117,093
Boiling point (^oC)	188-343	182-338
Stoichiometric Air/ Fuel ratio (w/w)	15	13.8

Based upon the advantages of biodiesel its use has seen rapid developments. The report of International Energy Agency's (IEA) on biodiesel production that surveyed the several leading biofuel producing countries [7]. Each country has its own set of goals for development of biodiesel. The key driving force behind the government policies to develop biodiesel can be the following three:

- As the global energy crisis are approaching, biodiesel fuel will play a more important role in strengthening a **nation's energy security.**
- **Reduction of greenhouse gas (GHG) emissions** when replacing fossil oil is one of the major factors.

- It adds to the income of farmers, specially the one which have only marginal lands and hence **seen as support to farmers**.

One of major reason for interest in biodiesel is positive environmental effects associated with its use. Biodiesel produced from biomass is consisted to be ‘‘carbon-neutral” or low carbon over its life cycles as their combustion returns to the atmosphere the CO_2 absorbed from the air by feedstock crops through photosynthesis. Whereas, unlike fossil fuels which have taken millions of years to form under the earth’s surface, biofuels are renewable. Therefore, biofuels are considered good choice to replace fossil-based fuels and contribute to the mitigation of green house gases emissions [8, 9]. Biodiesel from soya oil on average result in a 57% reduction in GHG compared to fossil diesel, and biodiesel produced from waste kitchen grease results in an 86% reduction of GHG, according to the EPA’s Renewable Fuel Standards Program Regulatory Impact Analysis, released in February 2010 [10].

Considering the advantages of biodiesel in terms of lower green house gas emission and energy security, several countries have drawn up plans for its commercial application. The aim of Europe is to cut GHG emission by 20% by 2020, with a target of 10% vehicles being fueled by biofuels. USA announced that the Federal Government will reduce its GHG emissions by 28% by 2020. Likewise, the Chinese government announced the action to control greenhouse gas emissions reduction targets. The Japanese government has a GHG emission reduction target of 60-80% by 2050 from its current level [11]. India, Brazil, South Africa and other countries have also set their GHG reduction target and development program of renewable alternate energy. All of these provide biodiesel industry exceptional opportunities of development. Table 1.2 shows that by the year 2020, against a total requirement of diesel of 162.67 MT, the 32.53 MT biodiesel (B_{20}) shall be required. For achieving this target a land area of about 54.22 Mha shall be required for the cultivation of jatropha and other oil seed crops.

Table 1.2: The biodiesel and land requirement in India for future [12]

Year	Diesel demand (MT)	Biodiesel requirement (MT)			Seed requirement (MT)*			Area requirement (Mha)**		
		BD_5	BD_{10}	BD_{20}	BD_5	BD_{10}	BD_{20}	BD_5	BD_{10}	BD_{20}
2007-2008	60.18	3.01	3.01	3.01	10.0	20.0	40.1	5.01	10.0	21.0
2008-2009	90.27	4.51	4.51	4.51	15.0	30.1	60.1	7.52	15.0	30.0
2009-2010	95.23	4.76	4.76	4.76	15.8	31.7	63.5	7.94	15.8	31.7
2010-2011	100.47	5.02	5.02	5.02	16.7	33.5	66.9	8.37	16.7	33.5
2011-2012	106.00	5.30	5.30	5.30	17.6	35.3	70.6	8.83	17.6	35.3
2012-2013	111.83	5.59	5.59	5.59	18.6	37.2	74.5	9.32	18.6	37.2
2013-2014	117.98	5.90	5.90	5.90	19.6	39.3	78.6	9.93	19.6	39.3
2014-2015	124.47	6.22	6.22	6.22	20.7	41.5	82.9	10.3	20.7	41.5
2015-2016	131.31	6.57	6.57	6.57	21.9	43.7	87.5	10.9	21.9	43.7
2016-2017	138.54	6.93	6.93	6.93	23.1	46.1	92.6	11.5	23.1	46.1
2017-2018	146.16	7.31	7.31	7.31	24.3	48.7	97.4	12.1	24.3	48.7
2018-2019	154.19	7.71	7.71	7.71	25.7	51.4	102	12.8	25.7	51.4
2019-2020	162.67	8.13	8.13	8.13	27.1	54.2	108	13.5	21.1	54.2

*Assuming 30% conversion of seed to biodiesel

** Assuming seed yield of 2Tons/ha

Biodiesel blended diesel fuel is often referred to by the percentage of biodiesel in the fuel. For example, B20 is a blended fuel that contains 20% biodiesel and 80% conventional diesel. B20 is a common blend because it provides a good balance between costs, performance, and environmental benefits. As a result, the emission profile of biodiesel and biodiesel-diesel blends, compared to petroleum based diesel, is much cleaner and has substantially lower sulfur emissions (Table 1.3) [13].

Table 1.3: Average B100 and B20 emissions compared to normal diesel taken as the base case [14]

Emission	B100	B20
Carbon monoxide (%)	-48	-12
Carbon dioxide (%)	-48	-12
Total unburned hydrocarbons (%)	-67	-20
Particulate matter (%)	-47	-12
Nitrogen oxides (%)	+10	+2
Sulfates (%)	-100	-20
Air toxics (%)	-60 to -90	-12 to -20
Mutagenicity (%)	-80 to -90	-20

B100 Quality Specifications

The ASTM specification for biodiesel (B100) is ASTM D6751 and it is summarized in Table 1.4 [14].

Table 1.4: ASTM D6751 specification for B100 biodiesel

Property	Test method	Limits	Units
Calcium and Magnesium combined	EN14538	5 max.	ppm
Flash point	D93	93 min.	^oC
Methanol content	EN14110	0.2 max.	vol%
Water and sediment	D2709	0.050 max	vol%
Kinematic viscosity, 40^oC	D445	1.9-6.0	mm^2/s
Sulfated Ash	D874	0.020 max.	% mass
Sulfur	D5453	0.0015 max.(S15) 0.05 max. (S500)	% mass
Copper Strip Corrosion	D130	No. 3 max.	-
Cetane Number	D613	47 min.	-
Cloud Point	D2500	Report to customer	^oC
Carbon residue[a]	D4530	0.050 max.	% mass
Acid number	D664	0.50 max.	mgKOH/g
Free glycerin	D6584	0.020 max.	% mass
Total glycerin	D6584	0.240 max.	% mass
Phosphorus content	D4951	0.001 max.	% max.
Distillation temperature, 90% recovered (T90)[b]	D1160	360 max.	^oC
Na and K combined	EN14538	5 max.	ppm
Oxidation stability	EN14112	3 min.	h

[a] Carbon residue shall be run on the 100% sample

[b] Atmospheric equivalent temperature

Bureau of Indian standards (BIS) has also adopted biodiesel standards. The Indian specifications for biodiesel are given in Table 1.5.

Table 1.5: IS 15607 specifications for B100 biodiesel

Properties	Test method	Limits	Units
Kinematic Viscosity at 40 °C	IS 1448 P:25	2.5-6.0	cSt
Density at 15 °C	EN 14103	0.8-0.9	g/cm^3
Acid value	IS 1448 P:1/Sec.1	0.50 max.	mgKOH/g
Flash Point	IS 1448 P:21	120 min.	°C
Cloud Point	IS 1448 P:10	NA	°C
Sulphated ash	IS 14448 P:4	0.02 max.	% mass
Water and sediment (vol. %)	D-2709	0.05 max.	vol %
Cetane number	IS 1448 P:9	51 min.	-
Carbon residue (mass %)	D- 4530	0.05 max.	% mass
Copper corrosion	IS 1448 P:15	1 max.	-
Free Glycerol, (mass %)	D- 6584	0.02 max.	% mass
Total Glycerol, (mass %)	D- 6584	0.25 max.	% mass
Phosphorus (mass %)	D-4951	0.001 max.	% mass
Distillation temperature	Not under spec.	-	°C
Oxidation stability, h	EN 14112	6 h max.	h

Biodiesel was promoted in the United States during 1992 by the National Soya diesel Development Board (presently National biodiesel board) which has pioneered the commercialization of biodiesel in United States. The major motivation was to find an alternate use of soya, as US had excess soya production.

Advantages of Biodiesel

- Biodiesel is non-toxic.
- Biodiesel degrades four times faster than diesel (99.6% bio-degradability within 21 days).
- Blending of biodiesel with diesel fuel increases engine efficiency.
- The higher flash point makes the storage safer.
- 90% reduction in cancer risks, according to Ames mutagenicity tests.
- Provides a domestic, renewable energy supply.

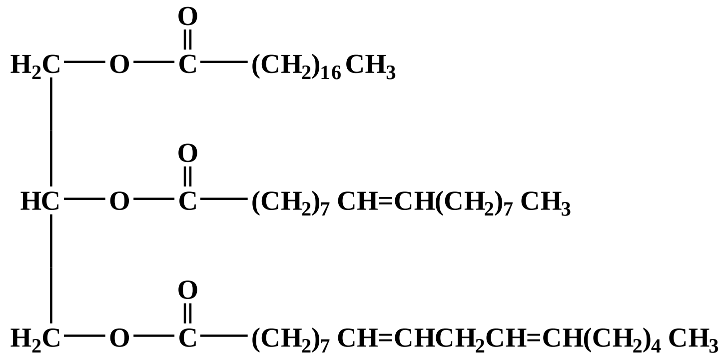
- Biodiesel produce much lower greenhouse effects, because it maintain balance between the amount of CO_2 emitted and amount of CO_2 absorbed by plants producing vegetable oil.
- Biodiesel can be used directly (upto 20%) in compression ignition engines with no or little modifications of the engine.
- Biodiesel contains no sulphur, no aromatics and is generally suitable to match the future European regulations which limit the sulphur content to 0.05% in 1996 and even lower in recent years.
- The emissions of polycyclic aromatic hydrocarbons (PAH) and nitro PAH compounds were substantially lower with biodiesel as compared to conventional diesel fuel.

Disadvantages of Biodiesel

- Low calorific value than diesel.
- Higher pour and cloud point.
- Higher NO_X emission.
- Corrosive nature against copper and brass.
- Less volatile than petroleum diesel.
- Water content present in biodiesel may reduce the heat of combustion.
- Degrades rubber.

1.3. PREFERRED FEEDSTOCK FOR BIODIESEL PRODUCTION: VEGETABLE OILS AND FATS

Vegetable oils both edible and non edible contain fatty acid triglycerides, free fatty acids (generally 1-5%), phospholipids, phosphatides, carotenes, tocopherols and traces of water [15]. Vegetable oil contains triglycerides as the major component and its chemical structure has given in Fig. 1.1. Mainly oils are water-insoluble, hydrophobic substances and comprise upto 98% triglycerides and small amounts of mono- and diglycerides [16,17]. The fatty acids differ in their carbon chain length and in the number of double bonds [18]. Different types of vegetable oils have varying fatty acid composition.



$$\begin{array}{l} H_2C-O-\overset{O}{\overset{\|}{C}}-(CH_2)_{16}CH_3 \\ HC-O-\overset{O}{\overset{\|}{C}}-(CH_2)_7CH{=}CH(CH_2)_7CH_3 \\ H_2C-O-\overset{O}{\overset{\|}{C}}-(CH_2)_7CH{=}CHCH_2CH{=}CH(CH_2)_4CH_3 \end{array}$$

Fig. 1.1: Chemical structure of a typical triglyceride

Table 1.6 shows the empirical formula and structure of various fatty acids present in vegetable oils [19].

Commonly found fatty acids in vegetable oils are stearic, palmitic, oleic, linoleic and linolenic. Table 1.7 summarizes the fatty acid composition of some vegetable oils [20,21, 22]. Molecular weight of triglyceride molecules vary between 800 and 900 and are thus it is nearly four times greater than typical diesel fuel (molecular wt. ~230) molecules [23]. Fuel related properties of vegetable oil or fat used for biodiesel production are given in Table 1.8 [20].

Petroleum derived diesel is composed of about 75% saturated hydrocarbons (primarily paraffins including normal, iso, and cycloparaffins), and 25% aromatic hydrocarbons (including naphthalenes and alkylbenzenes) [24]. The average chemical formula for common diesel fuel is $C_{12}H_{23}$, ranging from approximately $C_{10}H_{20}$ to $C_{15}H_{28}$.

Table 1.6: The chemical structures of fatty acids commonly found in vegetable oils

Fatty acid	Structure	Chemical structure	Systematic name
Lauric	12:0	$C_{12}H_{24}O_2$ $[CH_3(CH_2)_{10}COOH]$	Dodecanoic acid
Myristic	14:0	$C_{14}H_{28}O_2$ $[CH_3(CH_2)_{12}COOH]$	Tetradecanoic acid
Palmitic	16:0	$C_{16}H_{32}O_2$ $[CH_3(CH_2)_{14}COOH]$	Hexadecanoic acid
Palmitolileic	16:1	$C_{16}H_{30}O_2$ $[CH_3(CH_2)_5CH{=}CH\text{-}(CH_2)_7\text{-}COOH]$	Cis-9-hexadecnoic acid
Stearic	18:0	$C_{18}H_{38}O_2$ $[CH_3(CH_2)_{16}COOH]$	Octadecanoic acid
Oleic	18:1	$C_{18}H_{34}O_2$ $[CH_3(CH_2)_7\text{-}CH{=}CH\text{-}(CH_2)_7COOH]$	Cis-9-Octadecanoic acid
Linoleic	18:2	$C_{18}H_{32}O_2$ $[CH_3(CH_2)_4CH{=}CH{=}CH_2\text{-}CH{=}CH\text{-}(CH_2)_7COOH]$	Cis-9-cis-12-Octadecadeneoic acid
Linolenic	18:3	$C_{18}H_{30}O_2$ $[CH_3(CH_2)_4CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_4COOH]$	Cis-6-cis-9-cis-12-octadecatrienoic acid
Arachidic	20:0	$C_{20}H_{40}O_2$ $[CH_3\text{-}(CH_2)_{18}COOH]$	Eicosanoic acid
Gadolic	20:1	$C_{20}H_{38}O_2$ $[CH_3(CH_2)_9CH{=}CH\text{-}(CH_2)_7\text{-}COOH]$	9-eicosenoic acid
Behenic	22:0	$C_{22}H_{44}O_2$ $[CH_3(CH_2)_{20}COOH]$	Docosanoic acid
Erucic	22:1	$C_{22}H_{42}O_2$ $[CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOH]$	Cis-13-docosaenoic
Lignoceric	24:0	$C_{24}H_{48}O_2$ $[CH_3(CH_2)_{22}COOH]$	Tetracosanoic acid

Table 1.7: The fatty acid composition of some biodiesel feedstocks

Vegetable Oil	Fatty acid composition (% weight)												
	12:0	**14:0**	**16:0**	**16:1**	**18:0**	**18:1**	**18:2**	**18:3**	**20:0**	**20:1**	**22:0**	**22:1**	**24:0**
Corn	-	-	11.67	-	1.85	25.16	60.60	0.48	0.24	-	-	-	-
Cottonseed	-	-	28.33	-	0.89	13.27	57.51	-	-	-	-	-	-
Crambe	-	-	20.7	-	0.70	18.86	9.00	6.85	2.09	-	0.80	58.51	1.12
Peanut	-	-	11.38	-	2.39	48.28	31.95	0.93	1.32	-	2.52	-	1.23
Rapeseed	-	-	3.49	-	0.85	64.4	22.30	8.23	-	-	-	-	-
Soybean	-	-	11.75	-	3.15	23.26	55.53	6.31	-	-	-	-	-
Sunflower	-	-	6.08	-	3.26	16.93	73.73	-	-	-	-	-	-
Palm	-	-	10.2	-	3.7	22.8	53.7	8.6	-	-	-	-	-
Coconut	46.5	19.2	9.8	-	3.0	6.9	2.2	-	-	-	-	-	-
Used frying oil	-	-	12.0	-	-	53.0	33.0	1.0	-	-	-	-	-
Tallow	-	3-6	24-32	-	20-25	37-43	2-3	-	-	-	-	-	-
Lard	-	1-2	28-30	-	12-18	4-50	7-13	-	-	-	-	-	-
Castor	-	-	-	-	-	87.0	0.00	11.2	-	-	-	-	-
Jatropha	-	-	14.1	0.5	6.8	38.6	36.0	0.2	0.2	-	-	-	3.6
Karanja	-	-	10.6	-	6.8	49.4	19.0	-	4.1	2.4	5.3	-	2.4

Table 1.8: Fuel properties of vegetable oil [25]

Vegetable oils	Kinematic viscosity at 38 ^oC (cSt)	Cetane number	Heating value (MJ/kg)	Cloud point (^oC)	Pour point (^oC)	Flash point (^oC)	Specific gravity at 15 ^oC
Corn	34.9	37.6	39.5	-1.1	-40.0	277	0.9095
Cottonseed	33.5	41.8	39.5	1.7	-15.0	234	0.9148
Rapeseed	37.0	37.6	39.7	-3.9	-31.7	246	0.9115
Peanut	39.6	41.8	39.8	12.8	-6.7	271	0.9026
Soybean	32.6	37.9	39.6	-3.9	-12.2	254	0.9138
Sunflower	33.9	37.1	39.6	7.2	-15.0	274	0.9161
Palm	39.6	42.0	39.5	31.0	-	267	0.9180
jatropha	55 at 30 ^oC	40-45	39-40	2.0	-3.0	240	0.912
linseed	27.2	34.6	39.3	1.7	-15.0	241	0.9236

There are some reports of application of vegetable oil as such i.e without transesterification, in diesel engines. Though these vegetable oils contains no or the least sulphur element [19,26] but their application in diesel engines has several drawbacks. The most prominent problems arise due to their high viscosity, low volatility and poor cold flow properties [27]. The other drawbacks of use of neat vegetable oil in engines are:

- High viscosity of vegetable oil interferes with the injection process and leads to poor fuel atomization leading to incomplete combustion and excessive smoke.
- The high flash point attributes to lower volatility characteristics and diesel engine design does not allow use of low-volatiles fuels.
- High carbon deposits as the fuel does not burn fully.
- Ring sticking and scuffing of the engine liner
- Injection nozzle failure due to higher deposits.
- Both cloud and pour points are significantly higher than that of diesel fuel. These high values may cause problems during cold weather.

Blending of vegetable oils with diesel and transesterification are used for reduce the high viscosity of vegetable oils to enable their use in conventional compression ignitions engines.

Raw materials used for biodiesel are mainly rapeseed oil, canola oil, soybean oil, sunflower oil, jatropha, karanja and palm oil. Beef and sheep tallow and poultry oil from animal sources and waste cooking oil are also used for preparing biodiesel. Recently algae and fungi have also been investigated as an oil sources [28,29]. Besides, vegetable oils and animal fats, other materials such as spent frying oils have been used for biodiesel production. Some important fuel properties of biodiesel (methyl ester) produced from different feedstocks is shown in Table 1.9 and for comparison properties of B 20 and conventional diesel are also included.

Table 1.9: Physical properties of biodiesel

Vegetable oil methyl ester	Kinematic viscosity at 40 ^oC (cSt)	Cetane number	Heating value (MJ/kg)	Cloud point (^oC)	Pour point (^oC)	Flash point (^oC)	Density (g/cm^3)	Oxidation stability (h)
Soybean	4.08	50.9	33.5	4	-4	131	0.884	3.80
Sunflower	4.60	49.0	33.5	4	-7	183	0.880	1.73
Rapeseed	4.83	52.9	32.8	-4	-10.8	155	0.882	6.3
Palm	4.71	57.3	33.5	16	12	135	0.864	13.37
Jatropha	4.40	57.1	-	4	-6 to 2	163	0.875	3.23
Karanja	4.16	55.1	35.8	6	3	141	0.882	2.35
Tallow	5.0	58.8	-	12	9	150	0.877	0.4
Diesel	3.06	50	43.8	-	-16	76	0.855	22 up to >33
20% BD blend	3.2	51	43.2	-	-16	128	0.859	17.30 h up to 2.30

It is estimated that approx 75% of biodiesel cost is due to the feedstock cost [30]. Therefore, it is imperative that for a successful biodiesel programme, the vegetable oils should be available at low cost. However, since lower cost of seeds would translate into low income to farmers, the best way is to increase yield/hectare. Presently, several research programmes have been initiated to improve the yield of jatropha and some of these include genetic modification and tissue culture [31-38].

Jatropha Curcas

Most of the work reported in this thesis is carried out on jatropha oil which is obtained from jatropha curcas. Jatropha curcas is a drought-resistant, photo-insensitive perennial plant, growing well in marginal/ poor soil and belongs to the Euphorbiaceae family [39]. It grows almost everywhere-even on gravely, sandy, acidic and alkaline soils with pH ranging from 5.5 to 8.5. Jatropha curcas is a small tree or shrub with smooth gray bark, which exudes whitish colored, watery, latex when cut. Normal growth is between three and five meters in height, but can attain a height of up to eight or ten meters under favorable conditions. It's easy to establish grows relatively quickly and have seed producing life span of 50 years with 25 to 35% oil content for seeds [40].

The seeds mature within 3-4 months after flowering when capsule changes from green to yellow. The seeds are black and have weight of 727 g per 1000; there is approx. 1375 seeds/kg on an average [41]. Fig. 1.2 shows the physical appearance of seed and kernel of jatropha curcas.

Fig. 1.2: Fruit and Kernel of Jatropha curcas

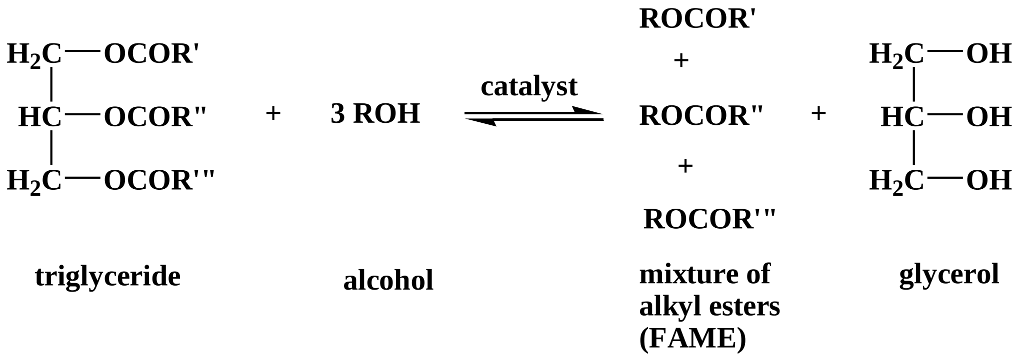
The Jatropha oil contains 21% saturated fatty acids and 79% unsaturated fatty acids. Jatropha seeds contain approximately 18-25% of crude protein, 35-42% of crude fat and 5-7% of moisture [42]. Some of the chemical elements in the seed like cursin and phorbol esters are poisonous and render the oil not fit for human consumption. Oil has very high saponification value and therefore used for making soap in some countries. Jatropha oil is used as an illuminant in lamps as it burns without emitting much smoke. Jatropha curcus oil cake is rich in nitrogen, phosphorous and potassium and can be used as organic manure. The nitrogen content ranges from 3.2 to 3.8%, depending on the source. Analysis of jatropha curcus seed shows the following chemical compositions:

Moisture: 6.20%
Protein: 18.00%
Fat: 38.00%
Carbohydrates: 17.00%
Fiber: 15.50%
Ash: 5.30%

1.4. TRANSESTERIFICATION

Transesterification is also known as alcoholysis of a vegetable oil and was invented as early as 1853 by scientists E. Duffy and J. Patrick, many years before the first diesel engine became functional. Transesterification can lower the viscosity of vegetable oil/animal fat to a large extent and also lowers the volatility. The transesterification converts the vegetable oils or fat (edible, nonedible) to their alkyl esters using alcohol, in presence of an acid or a basic catalyst and reduce the viscosity to diesel fuel level and produce biodiesel with properties that were similar to petroleum-based diesel fuel [43].

The alcohol used for transesterification is usually methanol. The general scheme of the transesterification reaction is presented in Fig. 1.3, where R’, R” and R”’ represents alkyl chain of various fatty acids.



R',R'',R''' = Hydrocaron chain ranging from 15 to 21 carbon atoms

Fig. 1.3: Transesterification of vegetable oil

1.4.1. Reaction Chemistry

Transesterification of triglyceride with lower alcohols is a reversible reaction. Therefore, an excess of alcohol is usually employed to force reaction towards the product side. The stoichiometry need of the reaction is a 3:1 molar ratio of alcohol to oil, to produce 3 mol of biodiesel and 1 mol of glycerol. However, in practice the molar ratio is increased from 6:1 to 50:1 to favor the formation of products. Though higher molar ratio of alcohol favors the reaction and lower the completion time, but a large amount of energy is required to recover the excess alcohol and for its purification for use in subsequent reactions. Complete conversion of the triglyceride involves three consecutive reactions, first triglyceride (TG) are converted to diglyceride (DG), monoglyceride (MG) and finally to biodiesel (BD) and glycerol (GL). A mole of ester is librated in each step (Fig. 1.4) [44,45].

In presence of excess alcohol, the forward reaction is pseudo-first order and the reverse reaction is found to be second order [46].

$$\text{Triglyceride} + \text{R'OH} \underset{k_4}{\overset{k_1}{\rightleftharpoons}} \text{Diglyceride} + \text{RCOOR'}$$

$$\text{Diglyceride} + \text{R'OH'} \underset{k_5}{\overset{k_2}{\rightleftharpoons}} \text{Monoglyceride} + \text{RCOOR'}$$

$$\text{Monoglyceride} + \text{R'OH} \underset{k_6}{\overset{k_3}{\rightleftharpoons}} \text{Glycerol} + \text{RCOOR'}$$

Fig. 1.4: General mechanism of transesterification of triglycerides

While transesterification is an equilibrium reaction between esters and alcohols, the reaction may be under kinetic control before thermodynamic equilibrium is achieved, and this would favor the formation of monoalkyl esters [47]. Two liquid phases i.e. alkyl esters and crude glycerol are produced in transesterification reaction. After some time of settling, glycerol is collected at the bottom because it is heavier than biodiesel. When the reaction is carried out at laboratory scale, phase separation can be observed within short time (~ 10 min) and can be complete on large scale within 2 to 20 h [48].

Primary or secondary monohydric aliphatic alcohols having from 1 to 8 carbon atoms can be used, however the rate of reaction decreases with increasing molecular weight of alcohol. Methanol, ethanol, propanol, isopropanol, butanol, pentanol and amyl alcohol have been used for biodiesel production with addition of catalyst [47-49]. Among all, the use of methanol is advantageous because it is most reactive and comparatively inexpensive.

Use of ethanol as a alcohol is becoming more popular because this alcohol is derived from renewable resource and does not raise the same toxicity concerns than methanol [47,48,50]. However it is difficult to get anhydrous ethanol. In the case of methanol, mild reaction temperature (~ 60°C) can be employed, whereas for the ethanol and other alcohols such as butanol (similar molar ratios) higher temperatures (75 and 114°C, respectively) are required for optimum conversions [50].

Generally, biodiesel is prepared in the presence of homogeneous base or acid catalysts. With homogenous base catalysts (mainly, sodium and potassium hydroxides, carbonates, sodium and potassium alkoxides) the reaction is faster than with acid catalysts (mainly, sulfuric acid, phosphoric acid, hydrochloric and sulfonic acid) [49,51].

1.4.2. Reaction Mechanism

The mechanism of the base-catalyzed transesterification of vegetable oils is shown in Fig. 1.5. The first step (Eq. 1) is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate (Eq. 2), from which the alkyl ester and the corresponding anion of the diglyceride are formed (Eq. 3). The latter deprotonates the catalyst, thus regenerating the active species (Eq. 4), which is now able to react with a second molecule of the alcohol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol [52].

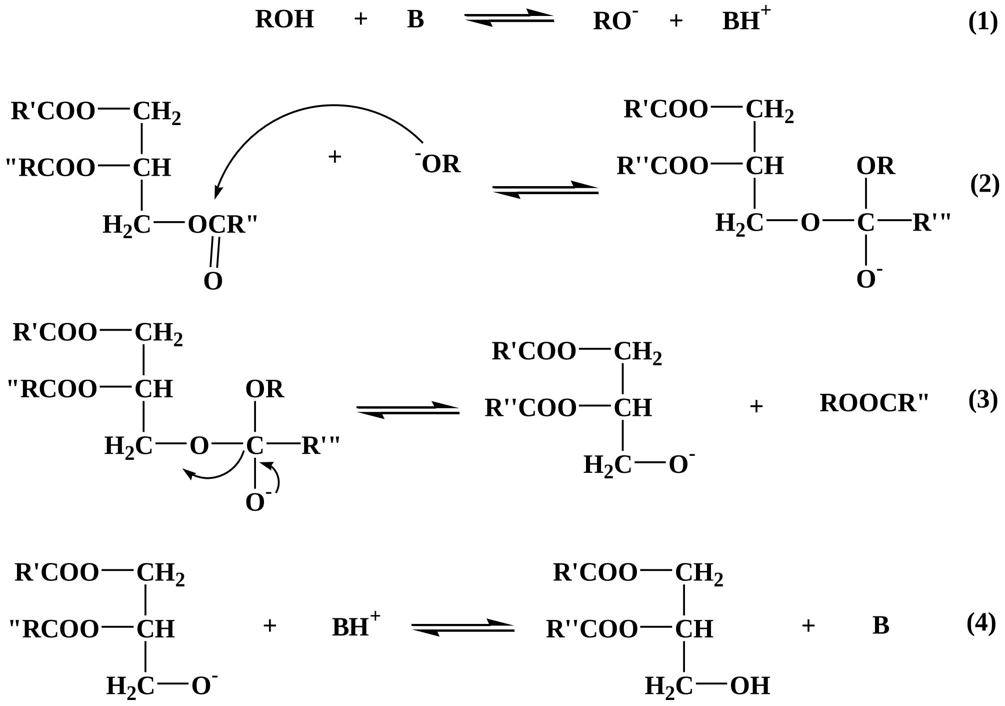
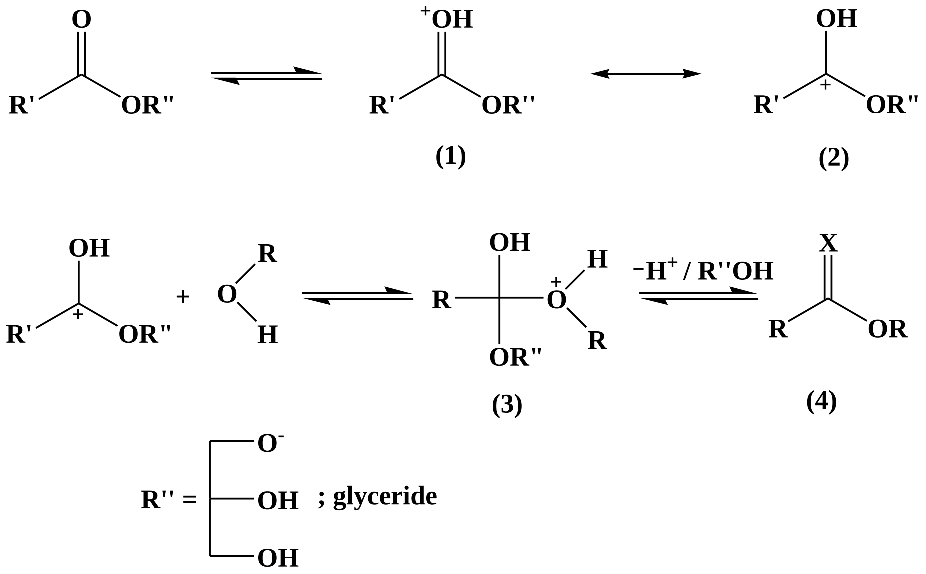


Fig. 1.5: Mechanism of base catalyzed transesterification

The transesterification process is catalyzed by Bronsted acids, preferably by sulfonic and sulfuric acids. These catalysts give very high yields in alkyl esters, but the reaction is slow, requiring, typically, temperatures above 100°C and more than 3 h to reach complete conversion. The mechanism of the acid-catalyzed transesterification of vegetable oils is shown in Fig. 1.6, for a monoglyceride. However, it can be extended to di- and triglycerides. The protonation of the carbonyl group of the ester leads to the carbocation (2) which, after a nucleophilic attack of the alcohol, produces the tetrahedral intermediate (3), which eliminates glycerol to form the new ester (4), and to regenerate the catalyst H+. According to this mechanism, carboxylic acids can be formed by reaction of the carbocation (2) with water present in the reaction mixture. Thus, acid-catalyzed transesterification should be carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids which reduce the yields of alkyl esters [52].



R' = carbon chain of the fatty acid
R'' = alkyl group of the alcohol

Fig. 1.6: Mechanism of acid catalyzed transesterification

Major quality related problems were encountered which are main hindrance for large scale industrial production of biodiesel by homogeneously catalyzed transesterification. Production costs are rather high as the process involves number of washing and purification steps in order to meet the stipulated quality [51]. It was quite difficult to remove the traces the K/Na remaining in the product and separation of glycerin also posed technical challenges and also undesirable production of both, soap and glycerol. The higher amount of water used in washing and consequent treatment of the resulting effluent added to the overall process cost.

Due to these issues a large number of alternative methods were developed. These include supercritical process [53] and enzymatic process [54]. Alternatively, heterogeneous catalysts could improve the synthesis methods by eliminating the need for water washing and therefore the number of separation steps can be reduced [55]. Also, heterogeneous catalysts exhibit a less corrosive character and can be used in a fixed-bed reactor, leading to safer, cheaper (because of reuse of the catalyst) [30], environment-friendly [56] and also offer the possibility for carrying out both transesterification and esterification simultaneously [57].

Other than the type of catalyst, important parameters of the transesterification reaction are the molar ratio of alcohol, type of alcohol, temperature, reaction time and degree of refinement of the vegetable oil [49-51, 58-62]. In addition, stirring is of significance in the efficiency of the process, higher stirring is recommended to create a homogeneous phase [61]. The significance of different catalysts in the production of biodiesel is shown in Table 1.10.

Table 1.10: Comparison of the different technologies to produce biodiesel

Variable	**Base Catalyst**	**Acid Catalyst**	**Lipase catalyst**	**Supercritical alcohol**	**Heterogeneous catalyst**
Reaction temperature (^oC)	60-70	55-80	30-40	239-385	180-220
Free fatty acid in raw materials	Saponified products	Esters	Methyl esters	Esters	Not sensitive
Water in raw materials	Interfere with reaction	Interfere with reaction	No influence	-	Not sensitive
Yields of methyl esters	Normal	Normal	Higher	Good	Normal
Recovery of glycerol	Difficult	Difficult	Easy	-	Easy
Purification of methyl esters	Repeated washing	Repeated washing	None	-	Easy
Production cost of catalyst	Cheap	Cheap	Relatively expensive	Medium	Potentially Cheaper

1.5. HETEROGENEOUS CATALYSTS: THE NEW GENERATION MATERIALS FOR TRANSESTERIFICATION OF VEGETABLE OIL

Development of heterogeneous catalyst has been found promising by some of the researchers [1-4] for the transesterification of vegetable oils/fats suitable for biodiesel production. It has been was observed that both acidic and basic heterogeneous catalysts have been investigated and are to found to be suitable for transesterification. However, for a commercial catalyst, catalyst life, recyclability, stability and lower cost are extremely important as these have a direct effect on overall cost of a process. Therefore, reducing cost of a catalyst by selecting cheap and abundantly available natural materials (like egg and sea shells) became the main motivation for the work described in the thesis. The use of acid, base and acid–base solid catalysts such as metal oxides, supported catalysts and zeolites etc. has been reviewed as under for biodiesel synthesis.

1.5.1. Basic Solid Catalysts

Various basic metal oxide type catalysts have been reported in literature for biodiesel synthesis. Some of the high performing catalyst preparations and their application in biodiesel synthesis are summarized here.

Liu et al. [63] studied SrO metal oxide for transesterification of soybean oil. Catalyst preparation was carried out by calcinations of $SrCO_3$ at 1200 ^oC for 5 h. SrO has strong basicity H_-=26.5 and have BET surface area of 1.05 m^2/g. The conversion obtained was 95% at temperature of 65 ^oC, catalyst content of 3 wt%, molar ratio of methanol to oil of 12:1 and reaction time of 30 min. Further, biodiesel yield was only slightly lower when the SrO catalyst is subsequently reused for 10 cycles. Mechanism given by authors is as described in Fig. 1.7. The main step is formation of ionic complex by SrO with methanol.

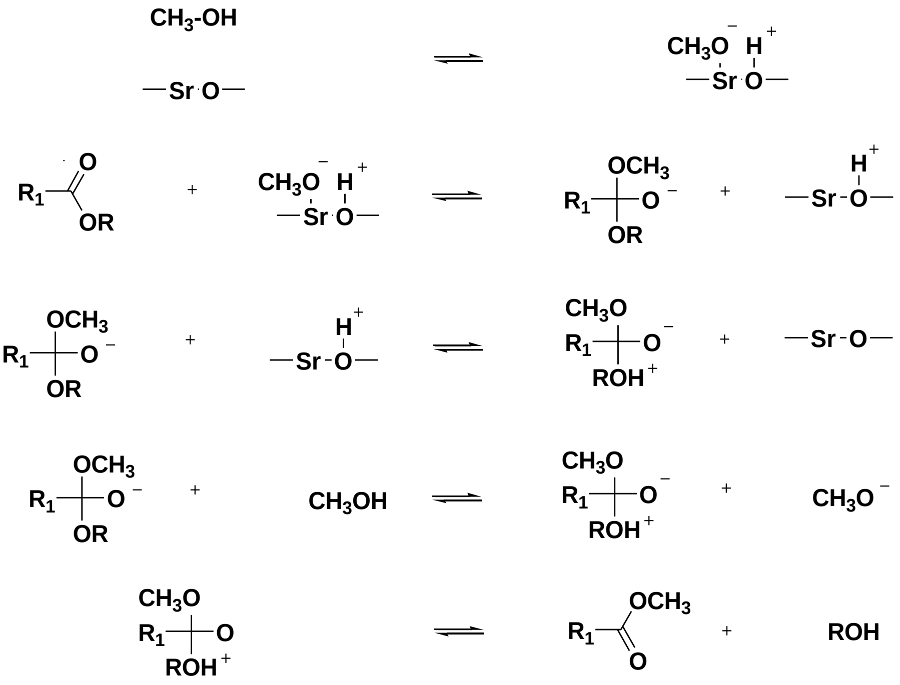


Fig. 1.7: Mechanism of SrO catalyst transesterification

Liu et al. [64] studied transesterification of soybean oil to biodiesel using CaO as a solid catalyst. The BET surface area of the catalyst was 0.56 m^2/g. The reaction was carried out using 12:1 molar ratio of methanol to oil, 8 wt% catalyst concentration at 65 ^oC. 95% biodiesel yield was obtained when reaction was carried out for 3 h. The authors also reported comparative activity of CaO with $K_2CO_3/\gamma Al_2O_3$ and $KF/\gamma Al_2O_3$ catalysts. It was observed that CaO maintained sustained activity for longer time (20 cycles) after repeated use and biodiesel yield was also not affected, while $K_2CO_3/\gamma Al_2O_3$ and $KF/\gamma Al_2O_3$ catalysts were not able to maintain activity and biodiesel yield also got affected after every use. This was because that the alkali metal compounds dissolved in methanol, which reduced the active ingredients and thereby decreasing biodiesel yield in the subsequent experiments. It was also observed in this study that the presence of water, if in small amount of about 2.8 by wt% of soybean oil, act as promoter, but if amount of water increases (more than 2.8 by wt% of soybean oil) it hydrolyzed FAME under basic conditions and also induced soap formation.

The catalytic activity of activated calcium oxide was also evaluated by Granados et al. [65] for production of biodiesel by transesterification of sunflower oil in batch reactor. The reaction was complete in 100 min giving 94% conversion. The specific surface area of catalyst was 32 m^2/g and mean pore size diameter (MPS) was approx ~ 25-30 nm. The authors observed poisoning of active surface site of CaO by the atmospheric H_2O and CO_2. Therefore, to improve catalytic activity of CaO, it was subjected to an activation treatment at high temperature ($\geq$ 700 ^oC) before the reaction and as a result of this, the main poisoning species (the carbonate group) from the surface was removed.

Veljkovic et al. [66] described the kinetics of CaO heterogeneously catalyzed methanolysis of sunflower oil. The optimal CaO calcination temperature was 550 ^oC. They observed 98% yield in the transesterification with 6:1 molar ratio of sunflower oil to methanol, 1wt% catalyst content (based on oil wt.) at 60 ^oC within 2 h reaction time**.**

Sarin et al. [67] reported use of seashell and eggshells as a catalyst for production of biodiesel from various feed stocks such as jatropha, castor, sunflower, soybean, rapeseed, cotton, corn, coconut oils etc in a batch and continuous reactor. The reaction was performed using 1 mole of vegetable oil and 6 mole of methanol and 4 wt% of catalyst composition. 98% conversion was achieved within 2 h.

Kawashima et al. [68] studied catalytic activity of calcium oxide (CaO) as a heterogeneous catalyst for biodiesel production by the transesterification of rapeseed oil. The author pretreated CaO with methanol for activation. CaO was activated with methanol at 25 ^oC for 1.5 h so that small amount of CaO could be converted into $Ca(OCH_3)_2$, which exhibits a higher catalytic activity than non-activated CaO. Rapeseed oil was thus transesterified using $Ca(OCH_3)_2$ to produce FAME and glycerin. During the transesterification reaction, the produced glycerin reacted with CaO at 60 ^oC, and a CaO-glycerin complex was formed as secondary catalyst, which then accelerated the transesterification reaction. To determine the exact pattern of catalytic activity, XRD measurements of activated CaO, non-activated CaO, $Ca(OH)_2$, and $Ca(OCH_3)_2$ were performed and it was observed that XRD spectrum of activated CaO was similar to that of non-activated CaO but exhibiting small diffraction peak attributed to $Ca(OCH_3)_2$ and $Ca(OH)_2$. This was responsible for the observed differences in the catalytic activity and the basic strengths of nonactivated CaO, $Ca(OH)_2$. The activated CaO has basic strength in the range of 10.1 to 11.1. While $Ca(OCH_3)_2$ had a high basic strength in the range of 11.1 to 15.0 and these results explained the reasons why $Ca(OCH_3)_2$ exhibited a higher catalytic activity for the transesterification reaction than CaO and $Ca(OH)_2$.

Catalytic activity of calcium based metal oxides such as $CaTiO_3$, $CaMnO_3$, $Ca_2Fe_2O_5$, $CaZrO_3$ and CaO-CeO_2 in the methanolysis of rapeseed oil was studied by Kawashima et al. [69]. The authors also studied the change of activity on replacement of Ca with barium, magnesium, or lanthanum. The reaction was carried out in a batch reactor at 60 ^oC with 6:1 molar ratio of methanol to rapeseed oil for 10 h, resulting in yield of 79–92%. It was found that $CaZrO_3$ and CaO–CeO_2 show high durability, ester yields greater than 80% and has the potential to be used in biodiesel production processes as heterogeneous base catalysts. For synthesis of $CaTiO_3$, an equimolar mixture of TiO_2 and $CaCO_3$ was milled in an agate mortar then mixture calcined in air to 500 ^oC and subsequently at 1050 ^oC for 2 h. For preparing $Ca_2Fe_2O_5$, Fe_2O_3 and $CaCO_3$ were milled with molar ratio of 1:2 and calcined in air to 900 ^oC and then at 1050 ^oC for 4 h. Due to calcination step at high temperature, the surface area of each of the catalysts was small and varied from 7.7 m^2/g for $MgCeO_3$ to 0.71 m^2/g for $Ca_2Fe_2O_5$. The basic strengths of $CaTiO_3$ were in the range of 6.8–7.2. $CaMnO_3$, $Ca_2Fe_2O_5$, $CaZrO_3$, and $CaCeO_3$ showed the highest basic strength, while Ba, Mg, and La series catalysts had weaker basic strength. Hence, Ca series catalysts exhibit the high catalytic activity for the transesterification reaction.

MgO-catalyzed transesterification reaction, at industrially relevant conditions was reported by Dossin et al. [70] in batch and continuous stirred tank reactors. A kinetic model based on the three steps ‘Eley-Rideal’ type mechanism assuming methanol adsorption as rate-determining step was proposed.

K_2CO_3 supported on MgO catalyst was prepared by mixing K_2CO_3 and MgO as carrier in a mortar. The mixture calcined at 600 ^oC for 3 h, thus forming catalyst for synthesis of biodiesel from soybean oil with the yield of 99.5% [71]. These results indicate that carriers increased the reaction yield and basic carriers have higher activities than acidic carriers. The catalytic activity of the K_2CO_3/MgO was higher than that of K_2CO_3 due to the interaction between K_2CO_3 and MgO and because of the high degree of dispersion of the active sites on the surface of MgO. The maximum activity of catalyst was obtained when the loading ratio was 0.7 and after 2 h reaction time the maximum conversion was achieved in transesterification. The MgO supported K_2CO_3 catalyst was most efficient among all the catalyst from different carriers. After six cycles, the catalytic activity decreased minutely but activity was regained after calcination. The loss of the active sites on the catalyst was also investigated.

Transesterification of different edible and non-edible oils (such as sunflower, soybean, ricebran and jatropha) using Mg/Zr catalyst (catalyst ratio 2:1 wt/wt%) have been reported by Sree et al. [72]. Mg/Zr was prepared by co-precipitation method by dissolving $Mg(NO_3)_2$ and $ZrO(NO_3)_2$ in deionised water. The XRD results indicated that ZrO_2 was in tetragonal phase, while MgO was in rocksalt form. The catalyst showed small Zr and large Mg crystallite sites, making Zr strongly interacted with MgO. However the high transesterification activity of Mg/Zr catalyst might be due to the presence of higher number of total basic sites. Total basicity of catalyst was 1204 μmol/g while surface area was 47 m^2/g.

Samart et al. [73] utilized 15 wt% KI loaded on mesoporous silica as a solid base catalyst for transesterification of soybean oil with optimum reaction conditions of 16:1 methanol to oil ratio, 5 wt% catalyst at 70 ^oC in 8 h. Conversions of 90% were obtained. The maximum activity of catalyst was obtained when KI solution got impregnated on mesoporous silica by incipient wetness impregnation with concentration of 15 wt%.

Alumina-supported potassium iodide catalyst was applied for biodiesel synthesis from soybean oil. The catalyst was prepared by impregnation of powdered alumina with an aqueous solution of KI, 35 wt% KI loaded on

Al_2O_3 and calcined at 500 ^oC for 3 h has best catalytic activity and highest basicity (1.5607 mmol/g). The catalyst activity was dependent on strength of basic sites as well as upon their amount. On comparison of alumina loaded with KI, KF, KOH, K_2CO_3, KBr and KNO_3, the order of conversion reported by the authors was $KI/Al_2O_3 > KF/Al_2O_3 > KOH/Al_2O_3 > KNO_3/Al_2O_3 > K_2CO_3/Al_2O_3 > KBr/Al_2O_3$ [74].

NaX zeolite loaded with 10% KOH (KOH/NaX) was reported as a base catalyst in soybean oil transesterification performed by Xie et al. [75]. NaX zeolite was first dried at 110 ^oC for 2 h then impregnated with aqueous solution of KOH for 24 h followed by drying and by heating at 120 ^oC for 3 h. 85.6% conversion was achieved within 8 h. The results obtained by X-ray diffraction analysis showed striking similarity in XRD pattern between KOH/NaX samples and parent zeolites. Further, it was observed by SEM results that NaX zeolite and KOH/NaX catalysts have nearly spherical shape crystal with size of 2–4 μm. The basic strengths of the catalyst as observed was $15.0 < H\_ < 18.4$ and it’s very likely that higher percentage of KOH (>10%) resulted in agglomeration of active sites and hence lowering the surface areas for active components and resulting lower the catalytic activity. The regenerated catalyst provides the conversion rate of 84.3%.

Faria et al. [76] utilized tetramethylguanidine, which is covalently bonded on to silica gel surface (SiG), as solid catalyst for transesterification of soybean oil with methanol. SiG catalyst was prepared by suspending activated silica gel in dry xylene and the new agent silylant (Silylant was prepared by reacted SiCl with triethylamine). The SEM image showed that SiG catalyst particles had spherical morphology with average size of about 1μm.

Georgogianni et al. [77] studied conversion of used soybean frying oil over Mg MCM-41, Mg-Al hydrotalcite and K^+ impregnated zirconia catalysts and found that the Mg-Al hydrotalcite has the greater activity due to higher basicity. Georgogionni et al. [78] also tested Mg MCM-41, Mg-Al hydrotalcite and K^+ impregnated zirconia catalysts and found that Mg-Al hydrotalcite was more active catalyst due to its highly basic nature for transesterification of rapeseed oil giving quantitative yield. MCM-41 also gave high yields of methyl esters in the transesterification reaction (conversion 87%).

KF/ZnO catalyst has been reported as solid base catalyst for the transesterification of palm oil with methanol to produce biodiesel. The KF/ZnO was synthesized by impregnation of the ZnO support with aqueous of $KF.2H_2O$ followed by overnight drying at 110 ^oC and calcination at 600 ^oC for 5 h. A loading of 35 wt% of KF was done on ZnO and good conversions were achieved [79].

Yan et al. [80] studied the $ZnO-La_2O_3$ catalyst for transesterification of unrefined and waste oil. $ZnO-La_2O_3$ was prepared by homogeneous coprecipitation method where 2M $Zn(NO_3)_2$ and 1M $La(NO_3)$ solutions were prepared in distilled water. These solutions, with various Zn-La ratios, were mixed with a 2M urea solution and the resulting mixture calcined at 450 ^oC for 8 h. The catalyst with 3:1 ratio of Zinc to lanthanum was found to exhibit highest activity in the transesterification of unrefined or waste oil. A strong interaction between Zn and La species was observed with enhanced catalytic activities. The catalyst was active in both transesterification and esterification reactions, and with no hydrolytic activity. $Sr(NO_3)_2/ZnO$ catalyst has been reported by Yang and Xie [81] for soybean oil transesterification with methanol at 65 ^oC. $Sr(NO_3)_2/ZnO$ was prepared by an impregnation method with an aqueous solution of an alkaline earth metal nitrate and calcined at 600 ^oC for 5 h.

The activity and selectivity of $NaOH/\gamma-Al_2O_3$ catalyst for the transesterification of sunflower oil with methanol was investigated by Arzamendi et al. [82]. $NaOH/\gamma Al_2O_3$ was synthesized by incipient wetness impregnation of the 212-300 µm size fraction of alumina. Prior to use alumina support was calcined at 500 ^oC for 12 h. Subsequently, the required amount of NaOH solution were slowly added to the support, dried for 12 h at 120 ^oC followed by calcination at 400 ^oC for 12 h. NaOH contents of the final solids were 10.7 and 19.3 wt% and this was referred as 10-Al and 19-Al respectively. XRD analysis revealed that a calcined and non-calcined 19-Al catalyst was very similar with the presence of NaOH and Na_2O_2 diffraction peaks, both as hydrated compounds, as well as sodium aluminate ($NaAlO_2$). These results indicate that NaOH has reacted with the support giving rise to the formation of aluminate. For calcined sample, the reaction was performed at 50 ^oC, 12:1 molar ratio of methanol/oil with 19-Al at 0.4 wt% of NaOH which gave the conversion rate of about 86% for 24 h. While the conversion for the non-calcined 19-Al sample increased up to 99%. Thus the result indicated that calcination of $NaOH/\gamma Al_2O_3$ catalyst had a negative effect on their activity.

Benjapornkulaphong et al. [83] compared the catalytic performance of Al_2O_3-supported alkali, alkali earth metal oxides and effect of calcination temperature on activity of different catalyst for transesterification of palm kernel oil and crude coconut oil with methanol. They found that $Ca(NO_3)_2/Al_2O_3$ calcined at 450 ^oC was the most suitable catalyst giving 94.3% conversion, however when the calcination temperature was increased the methyl ester formation dropped due to the formation of inactive metal aluminates. Kumar et al. [84] reported an effective catalyst composition which contained major amount of nickel zinc aluminate supported on clay and alumina. On a continuous reactor system, this catalyst gave conversion in the range of 40-60% at 200 ^oC and 40 bar pressure.

Abdullah et al. [85] reported use of SBA-15 as a neutral material made up of Si-O-Si network as a catalyst for biodiesel production. The incorporation of potassium in to mesoporous SBA-15 (K/SBA-15) imparted basicity to make it suitable for base catalyzed reaction like transesterification of palm oil. The authors used a composite experimental design for optimization of biodiesel yield so that this mathematical model could predict the biodiesel yield at any point of time in the experimental domain as well as the determination of the optimal biodiesel conditions with sufficient degree of accuracy.

1.5.2. Acidic Solid Catalysts

Di Serio et al. [86] investigated application of vanadyl phosphate (VOP) as catalyst in the transesterification of soybean oil. They found that the catalyst was active in transesterification reaction with 80% methyl ester yield obtained only after 1 h reaction time even though the specific surface area of catalyst was low (2-4 m^2/g). Vanadyl phosphate was prepared from the suspension of V_2O_5 in diluted phosphoric acid and then calcined at 500 ^oC for

2 h. The catalytic activity was increased by the increasing the calcination temperature, which helped in removing the hydration water of the sample and thus, increasing the concentration of the coordinatively unsaturated VO group and resulted in increased Lewis acidity of solids.

Shu et al. [87] studied carbon based solid acid catalyst for transesterification of cottonseed oil with methanol. The carbon based solid acid catalyst was prepared by the sulfonation of carbonized vegetable oil asphalt. The catalyst was prepared from carbonized vegetable oil asphalt and concentrated H_2SO_4 solution. Both these ingredients were heated at 210 ^oC in an oil bath for 10 h. Sulfated zirconia solid acid catalyst was studied for transesterification reaction of soybean oil and simultaneous esterification of oleic acid with methanol and ethanol in a high pressure reactor by Garcia et al. [88]. Carma et al. [89] studied the Al-MCM-41 mesoporous molecular sieves with Si/Al ratio of 8 for esterification of palmitic acid with methanol, ethanol and isopropanol. The catalyst Al-MCM-41 with ratio of 8 of Si/Al, produced the highest conversion at 130 ^oC, 0.6 wt% catalysts with alcohol to acid molar ratio of 60 and reaction time of 2 h.

Zeolite beta modified with La (La/zeolite beta) had been tested as a solid acid catalyst for methanolysis of soybean oil. Zeolite beta has a high silica zeolite, containing an intersecting three dimensional structure of 12 member ring channels. Due to this relatively voluminous channel structure, it is possible to carry out numerous acid catalyzed reactions effectively [90]. Karmee and Chadha [91] used Hβ-zeolite, montmorillonite K-10 and ZnO catalysts for transesterification of non-edible oil of crude Pongammia Pinnata with 1:10 molar ratio of oil/methanol, 0.575 g (0.115 wt% of oil) catalyst in 5 g oil at 120 ^oC. They found that ZnO gave the highest conversion rate of 83%, while Hβ-zeolite, montmorillonite K-10 catalyst gave low conversion rates of 59% and 47% respectively after 24 h of reaction time.

Jitputti et al. [92] compared the catalyst activities of several acidic and basic solids catalysts such as ZrO_2, ZnO, SO_4^{2-}/SnO_2, SO_4^{2-}/ZrO_2, KNO_3/KL zeolite and KNO_3/ZrO_2 for transesterification of crude palm kernel oil (PKO) and crude coconut oil (CCO) with methanol. Application of sodium molybdate (Na_2MoO_4) was reported by Nakagaki et al. [93] for the methanolysis of different types of lipids derived from soybean oil such as refined soybean oil, degummed soybean oil and used frying oil.

Furuta et al. [94] studied solid superacid catalysts such as sulfated tin oxide (STO), tungstated zirconia-alumina (WZA) and sulfated zirconium-alumina (SZA) for transesterification of soybean oil with methanol at 300 ^{o}C with 4.0 g of catalyst: molar ratio of methanol to oil was 40:1. Peng et al. [95] prepared $SO_4^{2-}/TiO_2–SiO_2$ solid for the production of biodiesel from low cost feedstocks (50% oleic acid + 50% refined cotton seed oil) with high FFAs in autoclave reactor at 200 ^{o}C, with molar ratio of methanol to oil 9:1 and 3 wt% catalyst concentration. The 92% conversion was obtained within 70 min reaction time.

Zirconia supported tungsten oxide (WO_3/ZrO_2) has been tested as a solid acid catalyst for esterification of palmitic acid with methanol [96]. Lopez et al. [97] studied tungstated zirconia (ZrO_2/WO_3^{2-}) as strong solid acid catalyst for both esterification and transesterification with methanol as a reactant. The authors evaluated the effect of calcination temperature (400-900 ^{o}C) on the catalytic properties of tungusted zirconia. Catalytic activities of esterification and transesterification were increased with the formation of polymeric W species in the presence of the tetragonal phase of the ZrO_2 support.

Sreeprasanth et al. [98] reported Fe-Zn double–metal cyanide (DMC) complex as a solid acid catalyst for esterification/transesterification of sunflower oil. Double-metal cyanide complexes have zeolite- like cage structures [99].

1.5.3. Acid-Base Solid Catalysts

Cheaper feedstocks like waste oils, animal fats cannot be converted to biodiesel using the conventional base mediated process, as the FFA of oils creates the problems of saponification. Acids can esterify free fatty acid (FFA) but the slow rates and limitation of using expensive metallurgy makes it less accepted. Heterogeneous catalysts having both acidic and basic sites have been investigated which could esterify FFA and at the same time transesterify triglycerides to biodiesel.

Lin et al. [100] reported synthesis of mixed metal oxide mesoporous silica material for TG transesterification and simultaneous esterification of FFA. They prepared these mesoporous calcium silicate mixed metal catalysts having different amount of calcium oxide. A co-condensation method was used for preparation in which cetyltrimethyl ammonium bromide (CTAB) provided the micelles template in a NaOH catalyzed reaction of tetraethylorthosilicate (TEOS) and the metal oxide.

Lin et al. [101] obtained a patent for preparation of mesoporous calcium, magnesium silicate and barium silicate by co-condensation method. By forming a mixed oxide from strongly basic metal oxide and a weakly acidic silica, the acidity of silica was significantly enhanced. In calcium silicates mixed oxide, silica sites were lewis acidic, Ca sites as basic and hydroxyl group on surface acted as Bronsted acids. The co-condensation procedure adopted were similar to the one reported by authors earlier.

Very recently Macario et al. [102] reported a biodiesel production process by homogeneous/ heterogeneous catalyst system of acid-base type. First the acid catalyst, both strong acid type USY, BEA and weak acid catalyst of the type MCM-41 were prepared by hydrothermal synthesis procedures. Later, for preparation of acid-base type catalyst, potassium (K) was loaded on different materials by ionic exchange methods. It was observed that strong acid catalysts like USY, BEA were not good for triglyceride conversion and commercial potassium silicate was found to be much better. The K loading of MCM-41 increased the conversion of triglyceride to a great extent but biodiesel production was low as the main products were FFA (32%), mono-glycerides (42%).

1.6. REFERENCES

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PREPARATION OF FEEDSTOCK

2.1. INTRODUCTION

For transesterification of vegetable oils using heterogeneous catalyst, the oil should be made free of metals and phospholipids as these will deposits on the catalyst in the reactor column. This deposit will reduce the efficiency of heterogeneous catalyst by blocking pores and chocking of column.

Crude vegetable oils contain a number of impurities like seed fragments and meal fines which are insoluble in oil and can easily be removed by filtration. However free fatty acids, hydrocarbons, ketones, tocopherols, glycolipids, phytosterols, phospholipids, proteins, pigments and resins, which are oil soluble and have negative effects on quality of biodiesel and therefore need to be removed from the vegetable oils by chemical or physical refining processes [1].

The Table 2.1 describes various methods reported in literature [2] for the removal of major impurities which are generally present in the feedstock.

Table 2.1: Basic steps of the refining process

Alkali or Chemical Refining	**Main groups of compounds removed**	**Physical Refining**
Degumming	Phospholipids	Degumming
Neutralization	Free fatty acids	-
Bleaching	Pigments/metals/soaps	Bleaching
Winterization	Waxes/saturated triacylglycerols	Winterization
Deodorization	Volatiles/Free fatty acids	Deodorization/ Deacidification

Bleaching is common to both physical and alkali refining. It is used for removal of colour bodies, trace metals and oxidation products as well as residual soaps and phospholipids. Mainly acid activated clays, active carbon and synthetic silicas are used as adsorbent. Active carbons are used for elimination of polycyclic aromatic hydrocarbon (PAH) [3] while, silicas have been reported for adsorbing secondary oxidation products, phospholipids and soaps.

Winterization is also called dewaxing and is only applied when the oil is not clear at room temperature because of the presence of waxes or saturated triacylglycerols. These oils are generally cooled and filtered to separate the waxes.

Deodorization process is used to remove volatile compounds (mainly ketones and aldehydes) which contribute to oil odour. Neutralization process is used for the removal of free fatty acids, residual phospholipids in degummed oils or all the phospholipids in the crude oils by caustic soda (NaOH) where free fatty acids are converted into insoluble soaps, which can be easily separated by centrifugation.

Degumming and Demetalation

The oilseeds such as jatropha, soybean, cottonseed, sunflower etc are rich in phospholipids [4,5] which create many problems during storage and processing of crude vegetable oil. Free fatty acids, hydrocarbons, ketones, tocopherols, glycolipids, phytosterols and metal contain such as Na, K, Ca, Mg, Ni, Cu, Zn etc also pose problem as some of these can be transferred to biodiesel. To remove these impurities degumming [6] and demetallization process [7] are used. Metals (Na, K, Ca, Mg, Cu and Fe etc) and P are present in vegetable oils and animal fats in the range of about 50-800 ppm. They originate from contamination by soil and fertilizers in crude vegetable oil. Metals are removed by either physical methods like distillation, solvent extraction and filtration [8-10] or chemical methods like treatment with HCl, H_3PO_4, H_2SO_4, EDTA, HF etc. [11-14].

Many gums such as phospholipids are present in crude vegetable oil and it was found that phospholipids can possibly deactivate the alkaline catalyst used in biodiesel production process [15]. Gerpen et al. [16] reported that presence of 50 ppm phosphorus in oil led to the reduction of yield of methyl esters by 3-5%. Performance of the catalytic converters used in modern vehicles degrades is the presence of higher phosphorus content leading to premature failure and thus leading to higher particulate emissions [17].

According to their level of hydration, two types of phospholipids are present, i.e. Hydratable phospholipids (HPL) and Non hydratable phospholipids (NHPL). Hydratable phospholipids are hydrated and insoluble in oil. They are removed by water degumming processes [18]. The hydrated compounds can be efficiently separated by filtration or centrifugation. Nonhydratable phospholipids are mainly present as calcium and/or magnesium salts of phosphatidic acid (PA) and phosphatidyl ethanolamine (PE) and method of their decomposition is by addition of acid or complexing agent, followed by hydration of phospholipids by water. Partial neutralization of acid is applied to avoid migration of phosphatides back to the oil phase [19]. For the elimination of the non-hydratable fraction, the oil is usually treated with phosphoric acid (0.05 to 1%), citric acid and other degumming substances which chelates the Ca and Mg converting the phosphatides into the hydratable forms (the acid treatment has the additional function of chelating trace pro-oxidant metals). Due to the variable content of phospholipids in crude oils, analysis of phosphorous prior to acid treatment is necessary to ensure that the acid dosage is correct, especially when the content of Ca and Mg salts is high.

A process for the reduction of non-hydrable gums and wax content in edible oils was patented by Rohdenburg et al. [20]. The process involves treatement of oil with 0.01 to 0.08% acid (in the form 10-15% aqueous solution), followed by treatment with 1-5% base solution and finally slow mixing for 1-4 h, leading to the separation of gums and water washing of oil. This process involves water washing and neutralization steps and thus suffers drawbacks due to this. Refining methods for vegetable oils are reported by Copeland and Belcher [21]. Their method involved subjecting oil and aqueous organic acid to high and low shear followed by centrifuge to remove gums.

Phospholipids and metals can be removed by hydrofluoric acid but it suffers from a number of disadvantages, including extensive side reactions and product contamination [22]. Aqueous solution of HCl or HNO_3 containing a demulsifying agent which transferred the metal to aqueous phase [23], phosphoric acid (H_3PO_4) [24, 13], sulfuric acid (H_2SO_4) [25] are also used for demetalation of vegetable oil. Haldara et al. [26] studied the degumming process by phosphoric acid in three non-edible oils karanja, putranjiva and jatropha to remove the impurities and improvement of viscosity.

Membrane techniques are the one of the modern technologies for removal of phospholipids from vegetable oils [27]. Recently soft degumming and enzymatic degumming process were reported for degumming and demetallization of vegetable oil. Soft degumming process involves a complete elimination of phospholipids by a chelating agent, such as ethylenediaminetetraacetic acid (EDTA), in the presence of emulsifying agent. Different kind of crude oils were degummed by soft degumming method; the content of phospholipids in the treated samples of the oils studied was lowered approximately to 5 mg kg^{-1}. However, the high cost of EDTA discourages its use in industry [28].

The process for the elemination of metals from fatty substances and gums associated with these metals was developed by Deffense [29]. The developed method comprised the mixing of vegetable oil with aqueous solution of salt of polycarboxylic acid (Sodium salt of ethylenediaminetetraacetic acid, EDTA) in the droplets or micelles in the weight ratio above 3. Centrifugation or ultra filtration is then employed to seperate aqueous phase from oil.

Zullaikah et al. 2005 [30] reported that rice bran stored at room temperature was hydrolyzed and free fatty acid (FFA) content was raised up to 76% in six months. A two-step acid-catalyzed methanolysis process was employed for the efficient conversion of rice bran oil into fatty acid methyl ester (FAME). The pre-esterification process was carried out at 60 ^{o}C by H_2SO_4 (2 wt%) for 2 h.

There have been several efforts to convert vegetable oils in to green diesel by the process of hydrotreating. By adopting catalytic hydrotreatment process, which is common in petroleum refineries, vegetable oils can be converted to hydrocarbons which are in the diesel range. This solves the problem of oxidative stability as the unsaturation is removed by hydrogen treatment. This process has been commercialized by UOP of USA and few other companies. However, for the purpose of hydrotreatment the vegetable oil has to be essentially free of metals and phospholipids, as these have damaging effect on the catalyst used in hydroprocessing. Refiners can co-process vegetable oils with petroleum fraction in existing hydroprocessing unit only if the oil is almost free of metals and phospholipids. Therefore, methods to remove metals and gums from vegetable oil become very vital. The method of removal must be easy involving low cost materials so that it does not add large additional costs.

2.2. AIM OF THE PRESENT WORK

Present work is aimed at developing an effective composition of reagents to remove metals and P from crude jatropha and karanja oils. Another objective was to derive the optimum concentration of these reagents for:

- Removal of phospholipids of crude Jatropha oil.
- Removal of metal contents (Ca, Mg, Fe, Cu etc) from vegetable oils.
- Reduction of total acid number (TAN) and free fatty acid (FFA) of Jatropha oil.
- To propose the cost effective, easy and efficient method for industrial scale application.
- To optimize the dose of degumming agent and to arrive at optimum reaction conditions.

The degumming and demetalation method developed herein can not only meet the requirement of transesterification process but also prepare a suitable feedstock for production of green diesel or green ATF by hydroprocessing of vegetable oils.

2.3. EXPERIMENTAL

2.3.1. Reagents and Materials

Commercial non-edible grade crude jatropha oil having typical acid value of 8.0 to 23.0 mgKOH/g, viscosity of 37.18 at 40 ^{o}C and total metal content of 80-500 ppm was procured from the Surendra Nagar, Gujarat, India (jatropha plantation carried out by Indian oil Corporation, R&D Centre). Citric acid, phosphoric acid, sodium hydroxide, anhydrous sodium sulphate and hexane were of laboratory grade.

The metal content was determined by inductively coupled plasma (ICP) emission spectroscopy (Perkin Elmer, Optima 5300 V).

2.3.2. Studies on the Removal of Impurities Present in Jatropha Oil

Jatropha and karanja oil quality varies with the source of production and also with the method of extraction of oil from the seeds. In present experiments, two types of jatropha oils have been taken for treatment. First oil termed as raw jatropha oil (RJO) was rather impure and contained large amount of phospholipids (P-174 ppm) and metals (200 ppm). The second jatropha oil was little refined, by cooling and filtration and had lower P (49 ppm) and metals (upto 50 ppm). This oil is referred as jatropha oil partially refined (JPR).

Experiment 1

100 g of crude jatropha oil containing 409 ppm of metals and P were taken in a 500 mL four necked RB flask equipped with a thermometer, stirrer, dropping funnel. The oil was heated to 40 ^{o}C followed by addition of 0.05% w/w phosphoric acid (H_3PO_4). The reaction mixture was stirred with mechanical stirrer. The temperature was increased to 70 ^{o}C and mixing was continued for 30 min. Then 2% solution of sodium hydroxide (50 ml) was added to reaction. The temperature was maintained at 70 ^{o}C for 3 h. Transferred the reaction mixture to separating funnel and allowed it to settle for 2-3 h and lower aqueous layer removed. The upper layer was filtered

through G2 crucible using filter aid and anhydrous sodium sulphate. The metal content of crude jatropha oil and treated oil are given in Table 2.2.

Table 2.2: Removal of metals and P from raw jatropha oil (RJO)

Metal	Metal content in ppm	
	Jatropha oil (RJO)	Treated jatropha oil
P	174	23
Na	4	2
K	-	-
Mg	83	8
Cr	<1	-
Cu	<1	-
Fe	43	-
Ca	101	7
Mo	<1	-
Si	<1	-
Zn	1	-
Mn	3	-
Total	409	40

While P content reduced from 174 to 23 ppm, the metals were reduced from 235 to 17 ppm by use of 0.05% w/w of phosphoric acid.

Experiment 2

In this experiment (Table 2.3) jatropha oil used was of better quality and had only 49 ppm P and 32 ppm metals. By adopting the procedure as given in experiment 1, this oil was further refined.

Table 2.3: Removal of metals and P from partially refined jatropha oil (JPR)

Metal	Metal content in ppm	
	Jatropha oil (JPR)	Treated jatropha oil
P	49	3
Na	-	<1
K	-	<1
Mg	12	<1
Cr	<1	-
Cu	<1	-
Fe	5	<1
Ca	12	<1
Mo	<1	-
Si	<1	-
Zn	3	-
Mn	-	-
Total	81	4

While P content was reduced from 49 to 3 ppm, almost all the metals were removed by use of 0.05% w/w of phosphoric acid.

Experiment 3

In this experiment the concentration of phosphoric acid was increased from 0.05 to 0.1 % w/w. The metal content of crude jatropha oil and treated oil estimated by ICAP is given below in Table 2.4. It can be seen that increased concentration of phosphoric acid resulted in further lowering of P content while other metals were in the same range as in experiment 1.

Table 2.4: Removal of metals and P from raw jatropha oil (RJO)

Metal	Metal content in ppm	
	Jatropha oil (RJO)	Treated jatropha oil
P	174	19
Na	4	2
K	-	-
Mg	83	8
Cr	<1	-
Cu	<1	-
Fe	43	4
Ca	101	7
Mo	<1	-
Si	<1	-
Zn	1	-
Mn	3	-
Total	409	40

Experiment 4

Better quality of jatropha oil having P (49 ppm) and metals 32 ppm was treated with 0.1% phosphoric acid as in experiment 2. The metal content of crude jatropha oil and treated oil estimated by ICAP is given below in Table 2.5 and it can be seen that no beneficial effect was noticed by increased the concentration of phosphoric acid.

Table 2.5: Removal of metals and P from partially refined jatropha oil (JPR)

Metal	Metal content in ppm	
	Jatropha oil (JPR)	**Treated jatropha oil**
P	49	3
Na	-	<1
K	-	<1
Mg	12	<1
Cr	<1	-
Cu	<1	-
Fe	5	<1
Ca	12	<1
Mo	<1	-
Si	<1	-
Zn	3	-
Mn	-	-
Total	81	3

Experiment 5

In this experiment (Table 2.6), the demetalation was carried out by citric acid. 100 g of crude jatropha oil containing 409 ppm of metals and P were taken in a 500 mL four necked RB flask equipped with a thermometer, stirrer, dropping funnel. The oil was heated to 40 ^{o}C followed by addition of 0.05% w/w citric acid ($C_6H_8O_7$). The reaction mixture was stirred with mechanical stirrer. The temperature was increased to 70 ^{o}C and mixing was continued for 30 min. Then 2% solution of sodium hydroxide (50 ml) was added to reaction. The temperature was maintained at 70 ^{o}C for 3 h and separation of layers done as per earlier experiments.

Table 2.6: Removal of metals and P from raw jatropha oil (RJO)

Metal	Metal content in ppm	
	Jatropha oil (RJO)	Treated jatropha oil
P	174	17
Na	4	-
K	-	-
Mg	83	4
Cr	<1	-
Cu	<1	-
Fe	43	6
Ca	101	7
Mo	<1	-
Si	<1	-
Zn	1	-
Mn	3	-
Total	409	34

Citric acid was observed to be slightly better than phosphoric acid at the same concentration level for removal of P and metals.

Experiment 6

In this experiment, the concentration of citric acid was increased to 0.1 % w/w. As seen from Table 2.7, the lowering of concentration of citric acid had very little effect on removal of P and metals.

Table 2.7: Removal of metals and P from raw jatropha oil (RJO)

Metal	Metal content in ppm	
	Jatropha oil (RJO)	Treated jatropha oil
P	174	11
Na	4	1
K	-	-
Mg	83	4
Cr	<1	-
Cu	<1	-
Fe	43	3
Ca	101	8
Mo	<1	-
Si	<1	-
Zn	1	-
Mn	3	-
Total	409	27

Experiment 7

Earlier experiments had shown that 0.05% phosphoric acid and 0.05% citric acid could affect good removal of P and metals. In order to see the combined effect of phosphoric acid and citric acid, in this experiment, the crude jatropha oil was treated with a mixture of 0.05% citric acid and phosphoric acid.

The metal content of crude jatropha oil and treated oil estimated by ICAP is given below in Table 2.8. It is observed that combination of citric acid and phosphoric acid at 0.05% w/w which has a synergistic effect. This combination could effectively remove almost complete P, which was not possible when these acids were used individually.

Table 2.8: Removal of metals and P from raw jatropha oil (RJO)

Metal	Metal content in ppm	
	Jatropha oil (RJO)	Treated jatropha oil
P	174	2
Na	4	3
K	-	-
Mg	83	4
Cr	<1	-
Cu	<1	-
Fe	43	-
Ca	101	2
Mo	<1	-
Si	<1	-
Zn	1	-
Mn	3	-
Total	409	11

Experiment 8

This experiment was conducted to optimize the minimum dosage of phosphoric acid and citric acid which could do effective demetalation and degumming to reduce P and total metals. Crude jatropha oil having P and metals at 409 ppm was treated with a mixture of 0.1% phosphoric acid and 0.02% w/w citric acid. The results are shown in Table 2.9. This combination was extremely effective and reduced P from 174 to 3 ppm while metals came down from 235 to just 2 ppm.

Table: 2.9: Removal of metals and P from raw jatropha oil (RJO)

Metal	**Metal content in ppm**	
	Jatropha oil (RJO)	**Treated jatropha oil**
P	174	3
Na	4	-
K	-	-
Mg	83	-
Cr	<1	-
Cu	<1	-
Fe	43	-
Ca	101	2
Mo	<1	-
Si	<1	-
Zn	1	-
Mn	3	-
Total	409	5

Experiment 9

With a better quality of jatropha oil having P of 49 ppm and metals of 32 ppm, the mixture of 0.05% phosphoric acid and 0.02% citric acid was very effective. While almost total P was removed, metals were also reduced to just 1 ppm. This treatment gives clean oil which can be hydrotreated for obtaining green diesel. The metal content of crude jatropha oil and treated oil estimated by ICAP is given below in Table 2.10.

Table 2.10: Removal of metals and P from partially refined jatropha oil (PRJ)

Metal	Metal content in ppm	
	Jatropha oil (PRJ)	Treated jatropha oil
P	49	<1
Na		<1
K	-	<1
Mg	12	<1
Cr	<1	-
Cu	<1	-
Fe	5	<1
Ca	12	1
Mo	<1	-
Si	<1	-
Zn	3	-
Mn	-	-
Total	81	1

Experiment 10:

In this experiment the amount of citric acid was further reduced, as this is the expensive component. Crude jatropha oil having P + metals at 409 ppm was treated with a mixture containing 0.05% phosphoric acid and 0.01% citric acid. The results are shown in Table 2.11. Reduction of citric acid had a negative effect on the combining of this mixture for demetalation and for P removal. The treated oil contained 5 ppm P and 9 ppm total metals and this oil may just meet the need of hydrotreatment.

Table 2.11: Removal of metals and P from raw jatropha oil (RJO)

Metal	Metal content in ppm	
	Jatropha oil (RJO)	Treated jatropha oil
P	174	5
Na	4	-
K	-	-
Mg	83	2
Cr	<1	-
Cu	<1	-
Fe	43	4
Ca	101	3
Mo	<1	-
Si	<1	-
Zn	1	-
Mn	3	-
Total	409	14

However at this concentration of metals and P, the resulting oil is good enough to be taken up for biodiesel conversion by heterogeneous catalysis.

Experiment 11:

When a jatropha of better quality was treated with the acid mixture having 0.01% citric acid and 0.05% phosphoric acid, a very good reduction in P and total metals was achieved. This treated oil having almost 2 ppm P and 1 ppm metals was good base material for both catalytic process and hydrotreating process. The metal content of crude jatropha oil and treated oil estimated by ICAP is given below in Table 2.12.

Table 2.12: Removal of metals and P from partially refined jatropha oil (PRJ)

Metal	Metal content in ppm	
	Jatropha oil (PRJ)	Treated jatropha oil
P	49	2
Na		<1
K	-	<1
Mg	12	<1
Cr	<1	-
Cu	<1	-
Fe	5	<1
Ca	12	1
Mo	<1	-
Si	<1	-
Zn	3	-
Mn	-	-
Total	81	3

2.4. RESULTS AND DISCUSSIONS

A critical review of the chemistry involved in the degumming process shows that non-hydratable phosphatides (NHP) consists of alkaline earth salts of the phosphatidic acid and some free phosphatidyl ethanolamine (PE). Their removals from oil involves the decomposition of these salts by a degumming acid capable of binding the alkaline earth ions and subsequent dissociation of the phosphatidic acid, which is separated by raising the pH by addition of dilute alkali solution. The phophatidate ion thus formed is hydratable and is capable of getting PE in to a separable gum phase. To remove NHP and PE, only water degumming is not sufficient and acid treatment is essentially required. However, the chosen acid treatment process should be economically justifiable. Therefore, the precise concentration of acids and optimized conditions are necessary to develop a low cost industrially acceptable degumming process.

Jatropha and karanja from different sources available in market and these oils have varied amount of gums and metals. In our laboratories oils from different sources were analyzed for metal, P and metals content. It was observed that there are variations in the metal, P and TAN values of oils from different sources. The values of P varied from 100-210 ppm and the metals varied from 120-850 ppm.

In the present study phosphoric acid, citric acids individually and in combination were used. The efficiency of these acids probably is due to their tribasic nature. After acid treatment, the pH of solution was raised by addition of dilute NaOH in order to make sodium salts of phosphatidic acids, which can be gummed out. Economic concentration of phosphoric acid at 0.05% to 0.1% w/w and citric acid at similar range was employed. Effect of combination of both acids at 0.05% w/w was also seen. As the combinations of acids showed synergetic effect, the citric acid content was gradually brought down from 0.05% w/w to 0.01% w/w. This exercise was primarily aimed at discovering a most economic composition of phosphoric and citric acid which could give maximum removal of P and metals. Table 2.13 summarizes the 14 different experiments conducted in the study.

Table 2.13: Effect of different acid concentrations in jatropha oil

Experiment	**Acid Conc. % w/w**			**Total Metal/ P content of crude oil**	**Total Metal/ P content after treatment**
	H_3PO_4	**Citric**	**H_3PO_4+Citric**		
1	0.05	-	-	409/ 174	40/ 23
2	0.05	-	-	81/ 49	3/ 3
3	0.1	-	-	409/ 174	47/ 19
4	0.1	-	-	81/ 49	3/ 3
5	-	0.05	-	409/ 174	34/ 17
6	-	0.05	-	81/ 49	4/ 3
7	-	0.1	-	409/ 174	27/ 11
8	-	0.1	-	81/ 49	3/ 3
9	-	-	0.05 + 0.05	409/ 174	11/ 2

Experiment	Acid Conc. % w/w			Total Metal/ P content of crude oil	Total Metal/ P content after treatment
	H_3PO_4	Citric	H_3PO_4+Citric		
10	-	-	0.05 + 0.05	81/ 49	2/<1
11	-	-	0.05 + 0.02	409/ 174	5/ 3
12	-	-	0.05 + 0.02	81/ 49	1/<1
13	-	-	0.05 + 0.01	409/ 174	14/ 5
14	-	-	0.05 + 0.01	81/ 49	3/ 2

Table 2.14 describes the % removal of metals/ P in different acid concentration.

Table 2.14: Removal of total metal/ P in different acid concentration

Experiment	Acid Conc. % w/w			% P removal	% Metal removal
	H_3PO_4	Citric	H_3PO_4+Citric		
1	0.05	-	-	86.78	92.76
2	0.05	-	-	93.87	100
3	0.1	-	-	89.08	88.08
4	0.1	-	-	93.0	100
5	-	0.05	-	90.22	92.76
6	-	0.05	-	93.87	96.87
7	-	0.1	-	93.67	93.19
8	-	0.1	-	93.87	100
9	-	-	0.05 + 0.05	98.85	95.31
10	-	-	0.05 + 0.05	100	93.75
11	-	-	0.05 + 0.02	98.27	99.14
12	-	-	0.05 + 0.02	100	96.87
13	-	-	0.05 + 0.01	97.12	96.17
14	-	-	0.05+ 0.01	95.91	96.87

As can be seen from the above tables removal of P can be affected by both phosphoric acid and citric acid and individually and in combination. The combination of 0.05% H_3PO_4 and 0.05%-0.02% citric acid gives oils which are almost free of phosphorous.

For demetallization, increase of H_3PO_4 acid concentration from 0.05 to 0.01% w/w has shown no improvement. There for subsequent experiments H_3PO_4 acid concentration was kept at 0.05% w/w level. Similarly, for citric acid doubling of concentration from 0.05 to 0.1% w/w, the removal of metals though improved but was not propositional.

Combination of lower concentration of H_3PO_4 and citric acid (0.05 % w/w each), showed a clear synergistic effect and enhanced metal and P removal was observed.

The next sets of experiments were conducted by reducing the concentration of citric acid (expensive part) in the acid mixture. When citric acid content in the mixture was reduced by 2.5 times i.e H_3PO_4 0.05% w/w: citric 0.02% w/w, the removal of metals of P was excellent. Attempts were made to further reduce the citric acid content to 0.01% w/w, while keeping H_3PO_4 acid at 0.05% w/w.

2.5. CONCLUSIONS

The optimum concentration of reagents for maximum removal of both P and metal was 0.05% H_3PO_4 w/w: 0.02% citric acid w/w. This lower concentration combination of H_3PO_4 acid and citric acid is the most cost effective solution for preparing P and metal free vegetable oils which are good both for transesterification to produce biodiesel and also for preparation of green diesel/ ATF by hydroprocessing. At this concentration and mild conditions P and metals can be removed in cost effective manner. The treated oils after transesterification produced biodiesel which had no difficulties in meeting the stringent ASTM/ IS/ DIN specifications for P and metals.

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PREPARATION, CHARACTERIZATION AND EVALUATION OF Ca-Ti BASED CATALYST

3.1. INTRODUCTION

Heterogeneous catalysts have been basically classified as solid acid and base catalysts. Use of solid base catalyst is preferred over acid catalyst specially for preparation of biodiesel by transesterification of triglycerides due to advantage of shorter reaction time. Heterogeneous catalysts for biodiesel synthesis have been widely reported in literature. Wide group of materials in the category of alkaline earth metal hydroxides, hydrotalcites/layered double hydroxides and alumina loaded with various compounds, zeolites, and various other compounds showing high basicity coupled with active basic sites, pore size, and other parameters are included reported in literature. High conversion rates and higher yields of biodiesel obtained are key factors for success of solid base catalysts [1]. The common problems encountered while using heterogeneous catalysts for transesterification of triglycerides are higher catalyst cost, lower recyclability and elaborate procedures for catalyst preparation. Since, biodiesel has to be cost competitive with normal diesel, the production process has to be simple and cost effective. Furthermore, the cost can also be reduced by production of solid catalysts from natural resources [2]. The natural resource has to be carefully selected with major criteria of abundance, activity, overall ease of preparation and lower costs. These aspects have been the main motivation for the present work.

Among the heterogeneous catalysts that are being used CaO has a promising place in transesterification reaction and many reports have been published on CaO catalyzed transesterification [3-5].

Utilization of CaO from waste egg and sea shells has been of recent interest so as to make the reaction more sustainable and attractive for low cost biodiesel production. Liu et al. [5] studied transesterification of soybean oil to biodiesel using CaO as a solid catalyst. The BET surface area of the catalyst was 0.56 m^2/g. The mechanism and activity of this has been discussed in chapter I. The catalytic activity of activated calcium oxide was also evaluated by Granados et al. [3] and by Veljkovic et al. [6] for production of biodiesel by transesterification of sunflower oil in batch reactor at 13:1 methanol to oil molar ratio, 3% catalyst content at 60 ^oC. Under these conditions, reaction was complete in 100 min giving 94% conversion.

Kouzu et al. [4] studied CaO catalyst for transesterification of soybean oil at 12:1 molar ratio of methanol to oil at reflux temperature for 2 h in glass batch reactor and achieved 93% biodiesel yield.

Calcium titanate $CaTiO_3$ is mineral perovskite which links it to the large and very important family of ABO_3 compounds. The mineral perovskite ($CaTiO_3$) was discovered by Gustav Rose (1839) in the Ural mountains of Russia, and later named after L.A. Perovski a Russian mineralogist, who first characterized its structure [7]. Helen Dick McGaw was first to publish the crystal structure of a $CaTiO_3$ type orthorhombic perovskite in 1945 [8]. The general chemical formula for perovskite compounds is ABX_3, where ‘A’ and ‘B’ are two cations of very different sizes, and X is an anion that bonds to both. The ‘A’ atoms are larger than the ‘B’ atoms. The ideal cubic-symmetry structure has the ‘B’ cation in 6-fold coordination, surrounded by an octahedron of anions and the ‘A’ cation in 12-fold cuboctahedral coordination.

Perovskite are stable under extremely wide range of conditions, and have unique chemical and physical properties that make it an ideal material for many technological applications. The importance of these materials is not only for their technical applications but also for fundamental research. Perovskite have a wide range of applications in technology, especially in solid-state ionics. Perovskite are currently used in sensors, memory devices (RAM), amplifiers, fuel cells, superconductors, electroptical devices, catalyst and nuclear application [9-11]

Various methods have been reported in the literature for the synthesis of $CaTiO_3$. These include (i) conventional ceramic technique [12,13], (ii) organometallic [14], (iii) liquid mix method [15,16], (iv) chemical co-precipitation method [17], (v) combustion method [18,19] and (vi) organic-inorganic solution technique [20], sol-gel method [21], solid state reaction [22] and hydrothermal process [23].

Moreira et al. [24] have also reported preparation of $CaTiO_3$ using $TiCl_4$, $CaCl_2.2H_2O$ and KOH which are reacted using microwave assisted hydrothermal method. Kawashima et al. [22] have prepared $CaTiO_3$ catalyst by solid state reaction using pure TiO_2 and $CaCO_3$ as key raw material and then used it for biodiesel preparation. They have reported maximum biodiesel yield of 85% using $CaTiO_3$ catalyst from edible grade rapeseed oil.

Balachandran et al. [15] synthesized the $CaTiO_3$ powder by a liquid mix technique. For preparation of $CaTiO_3$, calcium carbonate and tetraisopropyl titanate solution were dissolved in an ethylene glycol-citric acid solution and then evaporated to form a rigid, transparent, uniformly-colored polymeric glassy state. The synthesized glassy sample was then calcined at 800 ^oC in air for 12 h.

Kutty et al. [25] prepared $CaTiO_3$ (0.1- 0.5 μm size) by the hydrothermal method with molar ratio of Ca/Ti at 0.98-1.02. For preparation of $CaTiO_3$ (0.1-0.5 μm size), hydrated titania gel (prepared by precipitating from aqueous $TiOCl_2$ solution) and reactive calcium oxide (prepared by the decomposition of Ca-acetate around 700 ^oC) suspended as an aqueous slurry in autoclave and heated at 150-200 ^oC for 5-8 h. The product obtained were filtered and washed with very dilute acetic acid to remove any excess $Ca(OH)_2$ followed by air drying. X-ray diffractogram studied revealed that the hydrothermally prepared and heat treated (at 1300 ^oC) $CaTiO_3$ were more pure with absence of CaO and TiO_2. However, commercial sample which was prepared by solid-state reaction between $CaCO_3$ and TiO_2 showed presence of unreacted CaO and TiO_2 (rutile).

Calcium titanate was prepared from calcium titanyl oxalate hexahydrate [$CaTiO(C_2O_4)_2 \cdot 6H_2O$] (CTO) by heating it in a microwave heating system as well as in silicon carbide furnace at temperatures of 500 °C and 700 °C for 1 h. CTO was synthesized by chemical co-precipitation method, where $CaCO_3$ was dissolved in equimolar aqueous solution of $TiOCl_2$. This mixture was added to aqueous solution of oxalic acid to maintain the mole ratio Ca : Ti : oxalic acid as 1 : 1 : 2. The aqueous solution was kept over sodium hydroxide pellet in a desiccator for 4 to 5 days when a white precipitate was obtained. The precipitate was filtered followed by washing with distilled water and then with acetone and dried in air. It was observed that CTO heated in microwave system at 500 ^oC for 1 h gave a perovskite $CaTiO_3$ and at 700 °C for the same duration, it was found to be much more crystalline compound compared to that obtained at 500 ^oC. On the other hand, calcination of CTO in silicon carbide furnace at 500 ^oC for 1 h could not form the $CaTiO_3$ and calcined at 700 ^oC for 1 h was found to yield $CaTiO_3$ which was as crystalline as the product obtained by microwave heating at 500 ^oC for the same duration. So it was observed that the microwave heating facilitates the formation of $CaTiO_3$ from CTO precursor at much lower temperatures [26].

$CaTiO_3$ powder was prepared by the polymeric precursor method [27] and processed in different furnaces such as CF (conventional furnace) and microwave oven (MO). For synthesis of $CaTiO_3$, isopropoxide $[Ti(OC_3H_7)_4]$ was added in aqueous citric acid solution under constant stirring at 80 ^oC for several hours to get homogenous titanium citrate. Then $CaCO_3$ was dissolved into the Ti citrate. After solution homogenization, ethylene glycol was added to promote citrate polymerization by the poly esterification reaction with fixed citric acid/ethylene glycol mass ratio at 60:40. The solution was slowly heated at 100 ^oC under constant stirring to allow the evaporation of water and formation of the polymeric resin. The obtained polymeric resin was then placed in a conventional furnace and heated at 350 ^oC or 240 min, promoting the pulverization of the polymeric resin and formation of the precursor powders.

Luxova et al. [28] synthesized the $CaTiO_3$ by solid state reaction followed by calcination at 1000-1200 °C for the 3 h duration. The X-ray diffraction analysis results confirmed that higher calcining temperature (1200 °C) is essential for preparation of one-phase perovskite compound.

3.2. AIM OF THE PRESENT WORK

The aim of present research work is to develop a process for preparation of novel, cost effective and recyclable catalyst from natural waste for production of biodiesel from non-edible oils viz. jatropha oil, karanja and others. The catalyst composition $CaTiO_3$ has been developed using eggshell in combination with transition metal oxide TiO_2 to form A-B-O type metal oxide complex, where A is alkaline metal, B is transition metal. The catalyst composition developed has been evaluated and a robust cost effective method for biodiesel production is proposed. The outline of work methodology is as follows:

- Preparation of novel, cost effective, recyclable catalyst which has major ingredient of waste eggshell.
- Extrusion of synthesized catalyst.
- Characterization of the synthesized catalyst using techniques such as TGA, XRD, IR, surface area, pore size, pore volume, SEM and basic strength.
- Study of synthesis and kinetic properties of biodiesel preparation such as catalyst concentration, molar ratio of methanol to oil, temperature and effect of time etc. using novel $CaTiO_3$ heterogeneous catalysts in high pressure reactor.
- Evaluation of catalyst activity over repeated cycles to validate catalyst recyclability.
- Detailed physico-chemical characteristics of synthesized biodiesel as per IS/ASTM standards.

3.3. EXPERIMENTAL

3.3.1. Reagents and Materials

Commercial non-edible-grade jatropha oil was taken from the Surendra Nagar, Gujarat, India (jatropha plantation carried out by Indian Oil Corporation) and used without further purification. Other chemicals viz. titanium oxide (72%) (from Renkem, India) and pseudoboehmite, nitric acid

(85%) (from CDH, India), methanol, hexane analysis grade solvents (Merck, India) were of commercial/ lab grade.

Eggshell weighs approximately 10% of the total mass (ca. 60 g) of hen egg, and eggshell is the significant solid waste produced from food processing and manufacturing plants. Eggshell has a little developed porosity and contains pure $CaCO_3$ as an important constituent. The chemical composition (by weight) of eggshell has been reported as follows: calcium carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%) and organic matter (4%) [29]. Due to its intrinsic pore structure in the calcified form, higher content of $CaCO_3$ and the availability in abundance, it is possible to prepare active heterogeneous catalyst from eggshell.

Eggshells are collected from local market. The eggshells were cleaned to remove protein and other interference substances by washing several times with warm water. Washed shells were dried overnight in oven at 110 ^{o}C to remove traces of water.

3.3.2. Catalyst Preparation

The catalyst sample was prepared from waste egg shell by the conventional solid-state reaction, which involves mixing the metal oxides in desired proportions followed by calcination. The shells are grounded to fine powder than calcined in muffle furnace at 550 ^{o}C for 3 h to obtain a black solid in 94.75% yield.

For preparation of $CaTiO_3$ catalyst, calcined eggshell ($CaCO_3$) and TiO_2 in molar ratio of 1:1.2 (25 g $CaCO_3$ and 24 g TiO_2) were milled in mortar for 15- 20 min. The mixture was calcined at 550 ^{o}C for 3 h and then at 1050 ^{o}C for 3.5 h to obtain $CaTiO_3$ as white solid (77%) which was stored in dry container and kept in desiccator.

The formed catalyst is extruded by mixing with pseudoboehmite in ratio of 3:1 by weight and using 2.5% (v/v) solution of nitric acid as peptizing reagent. The final mixture was extruded on an extruder (Collin E 30 P) (Fig.3.1) to obtain cylindrical shaped 1/10 inch diameter catalyst.

Fig. 3.1: Extrusion Instrument

Pseudoboehmite (AlO(OH)) was selected as a binder for the preparation of extruded catalyst because it imparts

- Higher catalytic activity,
- Improvement in the mechanical strength,
- Improved the hydrothermal stability of the catalyst [30].

The block diagram of development of Ca/Ti based catalyst is summarized in Fig. 3.2.

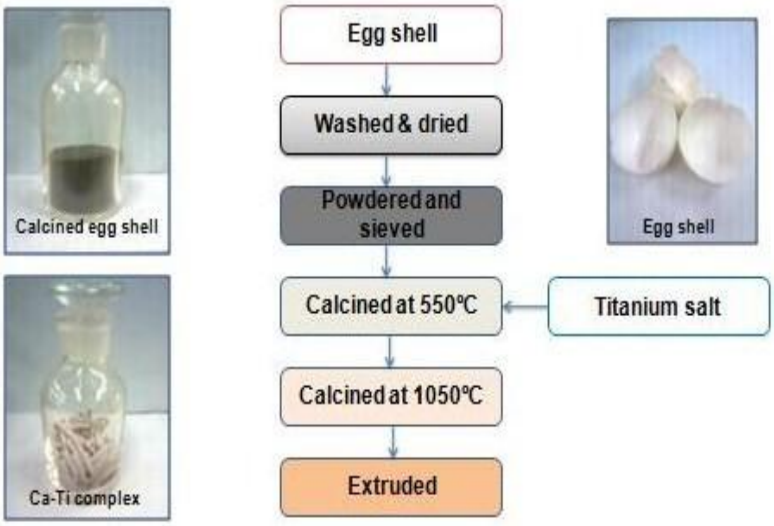


Fig. 3.2: Block diagram for preparation of Ca-Ti based catalyst

3.3.3. Catalyst Characterization

The catalyst was characterized using following state of the art tools.

X-ray Diffraction (XRD)

XRD studies were carried out in a 18 KW X-ray dffractometer (Rigaku, Japan) having copper rotating anode. XRD patterns were recorded at 50 KV and 250 mA, at a scan rate of 2^o/min with a step size of 0.01^o in the temperature range of 2 to 75^o 2θ. The XRD patterns were processed and peak search was conducted by search match to find out different phases present in the sample.

Fourier Transform Infra Red Spectroscopy (FTIR)

FTIR studies were conducted using a Perkin Elmer FT-IR spectrometer by normal procedure and samples are recorded as KBr pellets. 1-3 mg of the dried samples are mixed with ~ 100 mg dried KBr powder and pressed in to thin wafers using hydraulic press.

Thermogravimetric Analysis (TGA)

The thermal stability of the catalyst was measured using TGA model 2960 thermal analyzing machine (TA Instruments, USA) under a flow of nitrogen. Nearly 5-10 mg of the sample was taken in the Platinum pan and heated in air at the heating rate of 10^o/ min up to 800 ºC.

Surface Area

BET surface area was estimated from the N_2-adsorption/ desorption isotherm, measured at 77K (NOVA 2200 Quanta Chrome equipment).

Average Pore Size and Total Pore Volume

Pore size and Average pore volume were measured on Micrometrics instrument as per ASAP- 2010 method.

Scanning Electron Microscopy (SEM)

SEM micrographs were taken and analysis performed to view textural structure changes in catalyst complex with change in calcination temperature during formation using a Hitachi S3400N scanning electron microscope. The S3400N SEM utilizes an electron beam accelerated at 300V to 30 KV.

Basic Strength

The basic strength of the catalyst was obtained by application of Hammett indicators. The following Hammett indicators were used: neutral red (H_-= 6.8), bromothymol blue (H_-=7.2), phenolphthalein (H_-=9.3), 2, 4-dinitroanoline (H_-= 15.0) and 4-nitroanoline (H_-= 18.4). About 0.025 g (25 mg) of catalyst was shaken with 5.0 mL of solution of Hammett indicators and left to equilibrate for 2 hrs. After equilibraton, the color on the catalyst was noticed. If the indicator exhibits a colour change, then the catalyst is labeled as stronger than the indicator and if not, then the catalyst was said to be weaker than the indicator.

3.3.4. High Pressure and Temperature Reactor (HPR) Used for Catalyst Evaluation

High pressure and temperature reactor (Fig.3.3) (equipment of 1 lit and 700 ml capacity) purchased from Amar equipment Pvt. Ltd., India is made up of stainless steel and it consists of one nitrogen pressure inlet and outlet, sample outlet, water inlet and outlet and stirrer with PID temperature controller and digital pressure control system. The reactor is controlled by auto cooling system with the help of water. The maximum working pressure, temperature and stirrer are 200 kg/cm^2, 350 ^{o}C and 1450 revolution per minutes (rpm) respectively.

Fig. 3.3: High pressure Reactor

The transesterification reactions of jatropha oil were carried in 1 lit and 700 ml high pressure and temperature reactors as shown in Fig. 3.3. The reactor was loaded with jatropha oil and methanol and thereafter catalyst was added. The reaction mixture was heated up to 170 ^{o}C and 80 bar pressure with stirring at 350 rpm. The reaction progress was monitored with thin layer chromatography using mixture of petroleum ether, diethyl ether and glacial acetic acid (85:13.5:1.5) as eluent. The product formed was evaluated by analytical techniques like GC, GPC and ^{1}H NMR.

The reactions were carried out using jatropha oil (having total acid number of 8 mg-KOH/g) with varying catalyst concentration with range of 3 to12 % w/w with respect to vegetable oil and methanol: oil ratio of 5:1 to 30:1. Catalyst durability tests were performed by carrying out repeated transesterification reaction of jatropha oil using recovered catalyst under optimized conditions. The effect of variation in acid value and in moisture content of jatropha oil was also studied with respect to conversion efficiency to biodiesel.

After the reaction, the catalyst was separated by filtration. The filtrate was allowed to equilibrate which resulted in separation of two phases. The upper layer consisted of fatty acid methyl ester in methanol and lower layer consisted of glycerol and excess methanol. After separating the upper layer, it was passed through the column of acidic alumina followed by alcohol recovery by rotavapour to yield biodiesel. Biodiesel produced was evaluated for various physico-chemical characteristics as per IS/ASTM standards as given in Table 3.6. Catalyst recovered was washed with methanol and dried at 100 °C before reuse. The block diagram of transesterification reaction procedure in high pressure reactor is shown in Fig. 3.4.

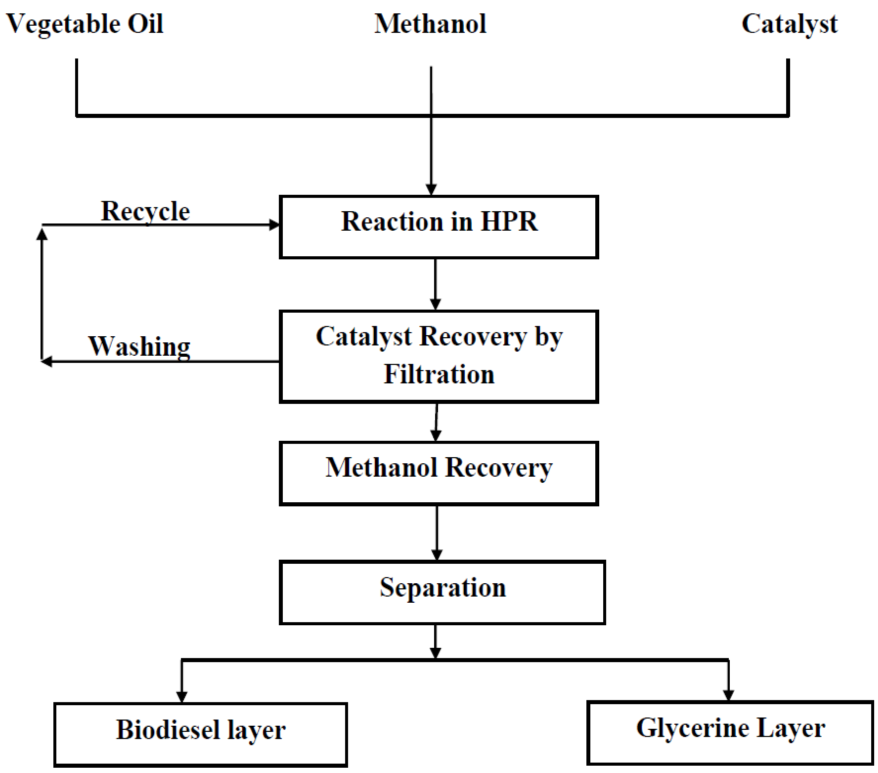


Fig. 3.4: Block Diagram of transesterification reaction procedure

The yield of methyl esters was calculated as follow [31].

$$\textbf{Yield of methyl esters (\%)} = \frac{\text{Methyl ester produced (g)}}{\text{Oil used in reaction (g)}} \times 100$$

3.3.5. Investigation of the Reaction Product (for Conversion and Selectivity Determination)

The following techniques were used for the analysis of reaction products. **The significance of these properties for use of biodiesel as transportation fuel is also given.** Biodiesel must meet all the listed properties before it is certified for use in IC engines.

Gel Permeation Chromatograph (GPC)

Gel Permeation Chromatograph (GPC) analysis of biodiesel samples was carried out on Waters 515 HPLC equipment fitted with a UV and RI detector. A styragel stainless steel column of 60 cm x 7.5 mm having pore size of $100A^0$ was used with tetrahydrofuran as the mobile phase at a flow rate of 1ml/minute. The sample was introduced through Rheodyne injector using 20µl loop. The chromatographic data was processed through Millennium 32 HPLC software. The basic principle of separation in GPC is fractionation according to molecular size. The molecules with higher molecular weight/size are excluded first followed by one with lower molecular size. Hence the order of elution in GPC is triglyceride followed by diglyceride and monoglyceride and FAME.

Gas Chromatography (GC)

Biodiesel was characterized by Gas Chromatography (Perkin Elmer Clarus-500). Gas chromatograph equipped with split/splitless injector and flame ionization detector. For ester content, split ratio 1:50 and injector and FID detector temperature 300^0C was used for helium carrier (ultra high pure grade). A fused silica capillary column CP-Wax 52 BD (30m × 0.32 mm id × 0.25 µm) procured from M/S Varin was used.

For glycerin content by ASTM Method 6584, a Carlo Erbo model HRGC 5300 equipped with split/splitless injector and flame ionization detector (FID) was used. Split ratio-20:1 and injection temperature 350 ^{o}C and detector temperature 380 ^{o}C was used. A non polar capillary with a 5%phenol 95% polymethyle siloxane (15m ×0.32 mm id ×0.1 µm film thickness) procured from M/S Restek USA was used.

Nuclear Magnetic Resonance (^{1}HNMR)

The ^{1}HNMR spectrum of the biodiesel was recorded on Bruker ACP-300 MHz NMR spectrometer. The concentration of the sample used was 5-10% w/w in $CDCl_3$ for ^{1}H-NMR containing tetramethylsilane (TMS) as internal reference. All the ^{1}HNMR spectra were integrated after base line correction and a mean of three integration values has been taken for each calculation. The integral intensities of the biodiesel to oil /fat signal were used to estimate biodiesel purity.

3.3.6. Physico-Chemical Properties Determination of Reaction Products

Biodiesel synthesized was tested for its physico-chemical properties as per ASTM D 6751 and IS 15607 test specifications. The acid value and moisture content were measured by ASTM D 974 and ASTM D 2709 method respectively. While kinematic viscosity was determined with Cannon-Fenske viscometers following standard methods ASTM D 445. All viscosity data reported are mean of triplicate determinations. Oxidation stability was determined by Rancimat apparatus by following EN14112 method and density at 15 ^{o}C was determined by using EN14103 method. Biodiesel for transesterification purposes must meet the specification [IS 15607 for India]. Some of the major important specifications and their significance are listed below:

Viscosity

Required viscosity levels are important to protect against power loss due to fuel injection pump and injector leakage. The test is usually conducted by measuring the time required for a volume of liquid to flow under gravity through a calibrated glass capillary tube. The kinematic viscosity is then equal to the product of flow time and a calibration constant for the tube. Cannon-Fenske style glass capillary tube is commonly used for kinematic viscosity ASTM D 445. Depending on feedstock and the amount of oxidation, biodiesel’s viscosity will vary between 1.9 to 6.0 cSt at 40 ^{o}C which is very close to petrodiesel indicating its suitability in IC engines.

Density

Density is defined as mass per unit volume and is expressed mathematically as $\rho = m/V$ (ρ is density, m is mass, and V is volume). The specific gravity of conventional diesel fuel is about 0.85 while a typical density of biodiesel is 0.88, which means that biodiesel is denser than conventional diesel fuel. ASTM D 4052 test method is used for determination of density of biodiesel.

Acid Value/Neutralization Number

Acid Value is the milligram of potassium hydroxide necessary to neutralize the free fatty acids in 1 g of sample. Acid number is used to determine the level of free fatty acids or processing acids that may be present in biodiesel. Biodiesel with a high acid number has been shown to increase fuel system deposits and may increase the likelihood for corrosion. It also reflects the degradation of biodiesel due to thermal effects. ASTM D 664 test method is used for determination of acid number of petroleum products by potentiometric titration and maximum limit of acid value of biodiesel is 0.8 mg KOH/g. In this test, the sample is dissolved in a mixture of toluene and isopropyl alcohol containing a small amount of water and titrated potentiometrically with alcoholic KOH.

Flash Point

The flash point is the lowest temperature at which given sample ignites when exposed to a flame or spark. The flash point of biodiesel is higher than that of petroleum based diesel fuel. The flash point is determined by heating a sample of the fuel in a stirred container and passing a flame over the surface of the liquid. If the temperature is at or above the flash point, the vapor will ignite and an easily detectable flash can be observed. The lower flash point for biodiesel indicates presence of residual alcohol. The flash point is also of importance in connection with legal requirements and a safety precaution involved in fuel handling and storage and is normally specified to meet insurance and fire regulations. The limit for biodiesel flash point has been set at 130 ^{o}C minimum. ASTM D 93, test method for determination of flash point should be used employing Pensky-Martins Closed Cup apparatus.

Cloud Point

Cloud point of any petroleum fuel is the temperature at which a cloud of wax crystals first appears in the fuel when it is cooled down at a specific rate. Biodiesel generally has a higher cloud point than petroleum based diesel. To ensure trouble free operation in cold climates, the cloud point of biodiesel and is impact on cold flow properties should be monitored. ASTM D 2500, test methods for determination of cloud point should be use. However, the precision and bias of these test methods for biodiesel are not known and are currently under investigation.

Sulfated Ash

Sulfated ash content is a measure of the concentration of ash forming compounds in the unused fuel. Ash- forming materials may be present in biodiesel as abrasive solids, soluble metallic soaps and unremoved catalysts. Abrasive solids and unremoved catalysts can contribute to fuel injector coking, fuel pump failure, piston and ring were as well as engine deposits. Soluble metallic soaps have little effect on were but may contribute to filter plugging and engine deposits.

The method involves evaporating 50-100 ml of the biodiesel product until only ash and carbon remains. After cooling the residue is treated with concentrated sulfuric acid and heated to 775 ^{o}C in a muffle furnace until all of the carbon is oxidized to CO_2. The residual ash is cooled, retreated with H_2SO_4, and heated again to 775 ^{o}C until a constant weight is obtained. The maximum limit of sulfated ash in biodiesel is 0.02%.

Water and Sediment

Water and sediment in a fuel oil tend to cause fouling of the fuel handling facilities and to give trouble in the fuel system of engine. An accumulation of sediment in storage tanks and on filter screens can obstruct the flow of oil from the tank to combustor. Water can cause corrosion of tanks and equipment and if detergent is present, the water can cause emulsions or hazy appearance. Water and sediment in diesel fuel are measured using ASTM D 2709. It uses a centrifuge to separate small water droplets and particles to be sure they do not exceed 0.05% (500 ppm). This test is particularly important when working with biodiesel because biodiesel is usually water-washed to remove traces of soap and free glycerol. Vacuum drying is usually needed to remove residual water following the washing process.

Cetane Number

Cetane number is a measure of the ignition quality of the fuel and influences white smoke and combustion roughness. It is not directly related to the energy content of the fuel. Higher the cetane number, better it is in its ignition properties. Cetane number affects a number of engine performance parameters like combustion, stability, drive ability, white smoke, noise and emissions of carbon monoxide and hydrocarbons. Biodiesel has higher cetane number than conventional diesel fuel. This results in higher combustion efficiency and smoother combustion. ASTM D 613 test method is used for determination of cetane number.

Conradson Carbon Residue (CCR)

This method involves the measurement of the carbon residue formed after evaporation and heating to 500 ^{o}C in an inert (nitrogen) atmosphere. Conradson Carbon Residue (CCR) for biodiesel is more important than that in diesel fuel because it show a high correlation with presence of free fatty acids, glycerides, soaps, polymers, higher unsaturated fatty acids, inorganic impurities and even on the additives used for pour point depression. ASTM D 4530 test method is used for determination of carbon residue and maximum limit of CCR as 0.05%.

Copper Strip Corrosion

The presence of acids or sulfur containing compounds can tarnish the copper strip, thus indicating the possibility for corrosion. ASTM D 130 test method for detection of copper corrosion of biodiesel and the maximum limit of copper strip corrosion is 3.

Free Glycerin

Free glycerin is a measure of the amount of glycerin remaining in the fuel. High levels of free glycerin can cause injector deposits, as well as clogged fuel systems and result in a buildup of free glycerin in bottom of storage and fuel system. ASTM D 6584 test method for determination of free and total glycerin in B100 biodiesel methyl esters by Gas Chromatography determines free glycerin. The maximum limit of free glycerides is 0.02%.

Total Glycerin

Total glycerin is the sum of the free glycerin and the glycerin portion of any unreacted or partially reacted oil or fat. Low levels of total glycerin ensure that high conversion of the oil or fat into its mono-alkyl ester has taken place. High levels of mono-, di-, and triglycerides can cause injector deposits and may adversely affect cold weather operation and filter plugging. ASTM D 6584 test method for determination of free and total glycerin in B100 biodiesel methyl esters by Gas Chromatography, determines total glycerin. The maximum limit of total glycerides is 0.24%.

Phosphorus Content

Presence of phosphorus can damage catalytic converters used in emission control systems that are becoming more common on diesel powered vehicles. It is necessary to keep the level of phosphorus in fuel low. Usually biodiesel have < 1 ppm phosphorus. The specification (ASTM D 4951) of minimum 10 ppm phosphorus content is intended to ensure compatibility with catalytic converters irrespective of the source of biodiesel. Inductively Coupled plasma Atomic Emission Spectrometry (ICAP) shall be used for measuring phosphorus content.

Oxidation Stability

Biodiesel age more quickly than fossil diesel fuel due to the chemical structure and presence of unsaturation in fatty acids methyl esters. The stability of biodiesel fuel is affected by the proportion of individual esters present in it. Saturated fatty acid methyl esters (C14:0, C16:0, C18:0) increase cloud point, cetane number and improve stability whereas more poly-unsaturated (C18:2, C18:3) reduce cloud point, cetane number and stability. Oxidation stability of biodiesel is the important issue because fatty acid derivatives are more sensitive to oxidative degradation than mineral fuel [32]. Poor oxidation stability can cause fuel thickening, formation of gums and sediments, which lead to filter clogging and injector fouling. The oil/fat/fatty acid derivatives undergo a chemical process called autoxidation causing rancidity when the material is stored for long time. Autoxidation converts the R-H group to an ROOH group called hydroperoxide. These hydroperoxides degrade and rearrange to other compounds including carboxylic acids and carbonyls.

The oxidation stability is determined with the Rancimat apparatus. The biodiesel samples are aged at a constant temperature of 110 ^{o}C with an airflow passing through at the rate of 10 L/h. The air flow is passed through a measuring cell filled with distilled water. The conductivity is determined continuously and recorded automatically. During the oxidation process, volatile acids are formed. At the end of the ageing period the conductivity increases rapidly. The period up to this point is called induction period [33]. In the Indian and European specifications for biodiesel, a minimum value of 6 h Rancimat induction period at 110 ^{o}C is specified.

3.4. RESULTS AND DISCUSSIONS

3.4.1. Catalyst Characterization

XRD Studies

XRD results revealed that the composition of calcined eggshell mainly consisted of calcite-calcium carbonate (Fig. 3.5). The intense peaks at 2θ~

29.4, 39.4, 43.2, 47.4 and 48.5 Å correspond to the d-value of 3.03, 2.28, 2.09, 1.91 and 1.87 respectively of calcium carbonate (Fig. 3.5).

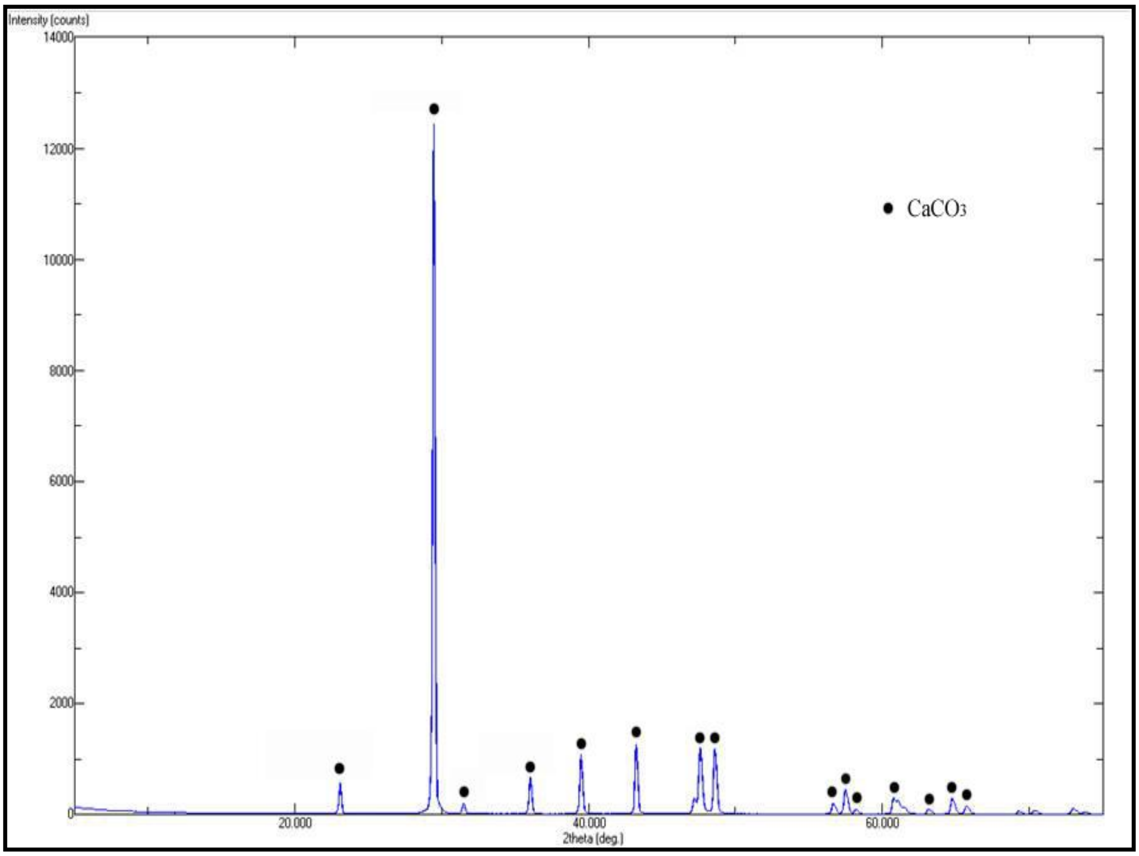


Fig. 3.5: XRD patterns of calcined eggshell

Fig. 3.6 depicts the XRD patterns of $CaTiO_3$ (extruded) calcined at 1050 °C. XRD of the catalyst sample showed characteristic peak of $CaTiO_3$ and minor peak of TiO_2 (rutile) indicating conversion of calcium carbonate to calcium oxide and its subsequent reaction with TiO_2 to form desired $CaTiO_3$ complex. However some traces of calcium dialuminate; Grossite ($CaAl_4O_7$) was also observed by XRD (Fig. 3.6).

The intense peaks at 2θ~ 33.1, 47.4, 32.9, 33.3, 59.4 and 69.5 to the d value of 2.71, 1.91, 2.70, 2.69, 1.56 and 1.35 respectively of calcium titanate. The titanium oxide peaks were observed at 2θ~ 27.4, 54.3 and 36.1 to the d value of 3.25, 1.68 and 2.48 respectively (Fig. 3.6.).

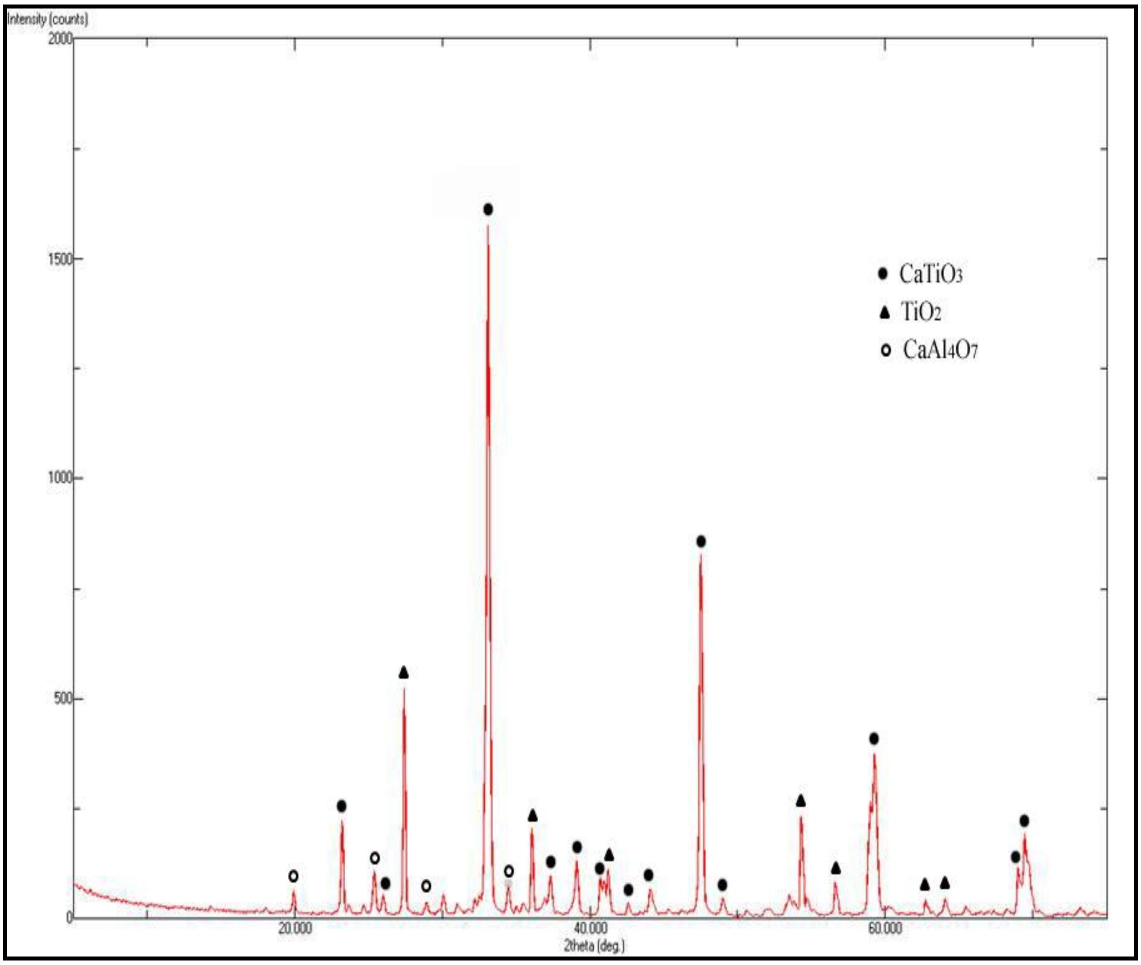


Fig. 3.6: XRD patterns of Ca-Ti based catalyst

Effect of calcination on extruded Ca/Ti catalyst was also observed by XRD (Fig. 3.7). These results showed that calcined at 1050 ^{o}C (indicated as 'c') mainly consisted of active ingredient, $CaTiO_3$ and minor peak of TiO_2 with the absence of $Ca(OH)_2$ peak, while in the case of uncalcined but dry (a) and calcined at 550 ^{o}C (b) extruded catalyst have a major peak of TiO_2 and minor peak of $CaTiO_3$ and $Ca(OH)_2$.

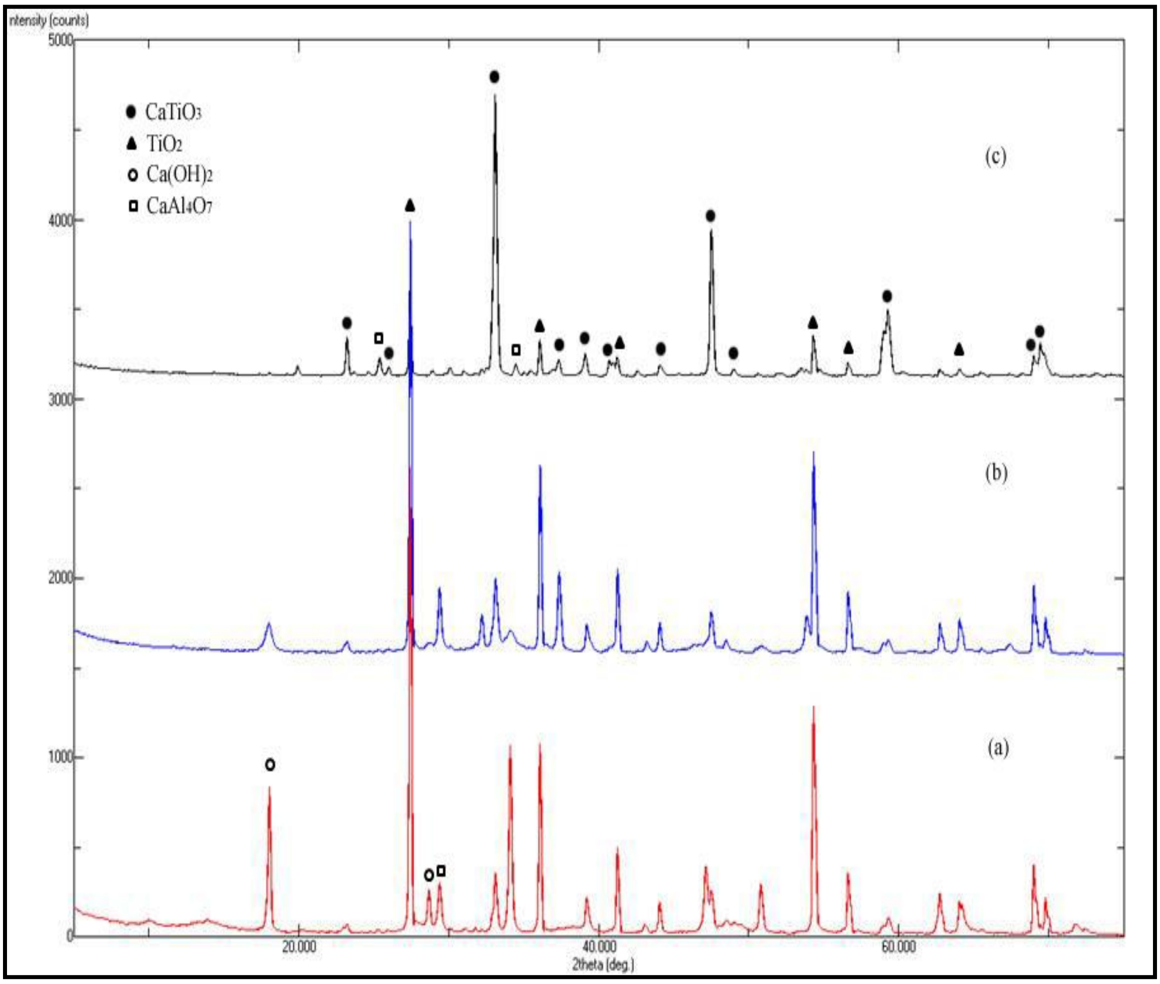


Fig. 3.7: XRD patterns of Ca-Ti based extruded catalyst. (a) without calcination; (b) calcined at 550 °C; (c) calcined at 1050 °C

Fourier Transform Infra Red Spectroscopy (FTIR)

FTIR spectra of $CaTiO_3$ (Fig. 3.8) calcined at 1050 °C temperature revealed the formation of $CaTiO_3$ phase in the region 400- 600 cm^{-1}. The two peaks at ~ 576 and ~ 447 cm^{-1} are the representative peaks of $CaTiO_3$, where the former peak is due to Ti-O stretch and the later to Ti-O_3 torsion, respectively [34].

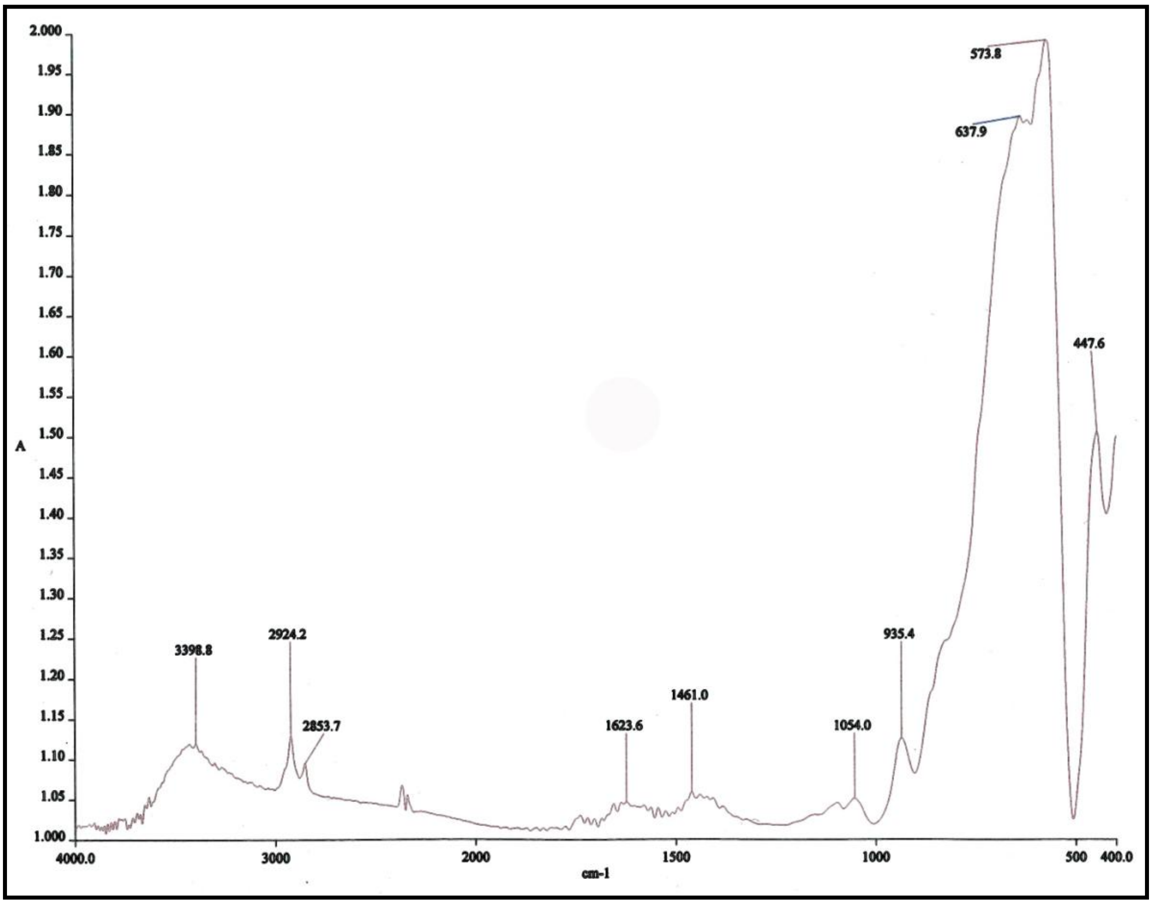


Fig. 3.8: IR spectra of Ca-Ti based catalyst

Thermal Studies

Thermo gravimetric analysis (Fig. 3.9) of synthesized $CaTiO_3$ depicted two stages of weight loss. First stage of weight loss was possibly due to initial decomposition at temperature 100 to 200 ^{o}C involving loss of water. At about 650-800 ^{o}C the plot shows a plateau. The weight loss was indicating thermal decomposition of $CaCO_3$ to form CaO with loss of carbon dioxide. The CaO phase can react with the other active ingredient TiO_2 to form $CaTiO_3$.

$$CaCO_3 \longrightarrow CaO + CO_2 \uparrow$$

$$CaO + TiO_2 \longrightarrow CaTiO_3$$

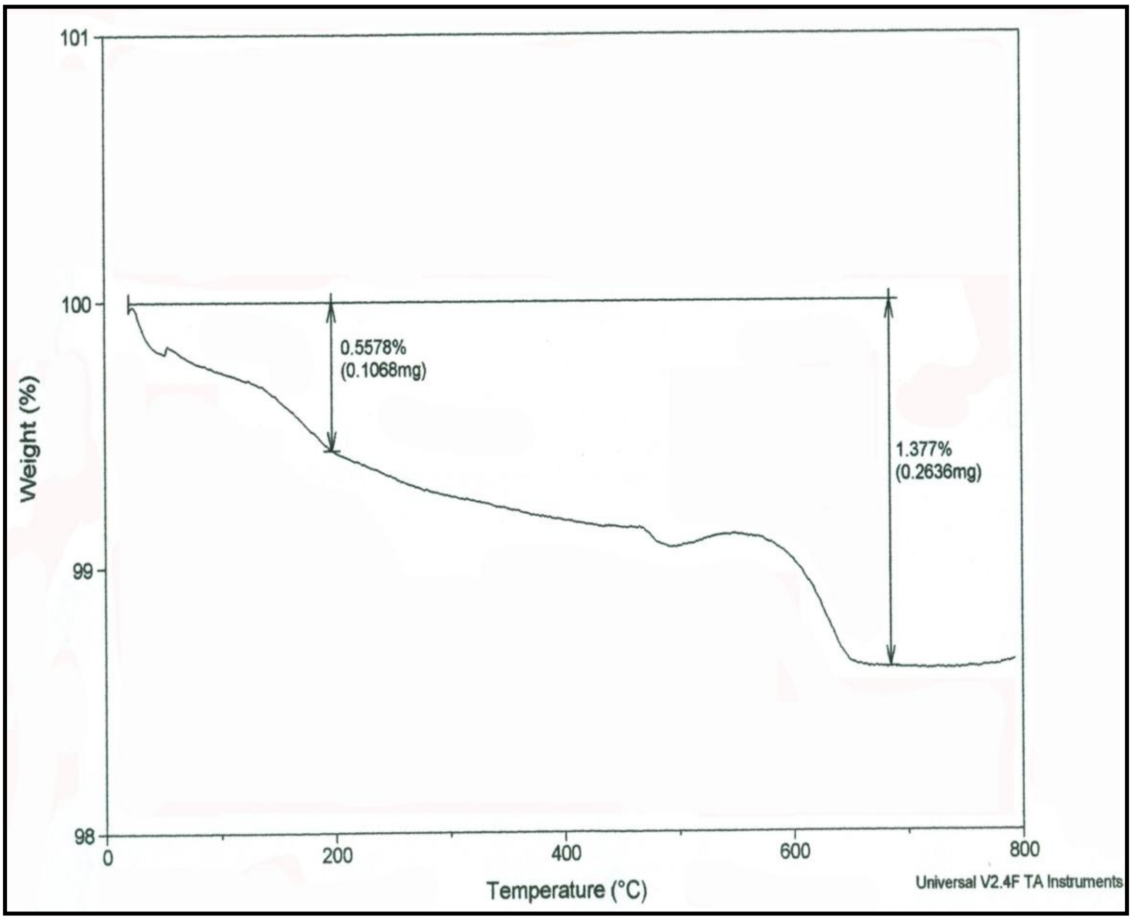


Fig. 3.9: TGA of Ca-Ti Catalyst

The thermal gravimetric results of Ca/Ti based catalyst is depicted in Fig.3.9. The thermal analysis temperature range (°C) and the percentage weight loss are presented in Table 3.1.

Table 3.1: Thermal gravimetric analysis of Ca-Ti based catalyst

	Thermal analysis, Temperature range (°C)	
Weight loss (%)	Up to 200	200-650
	0.5578	1.377

Surface Studies

The average pore size of catalyst was found to be 70 Å, BET surface area 7.59 m^2/g and 0.01 cm^3/g as the total pore volume. Surface area and total pore volume of $CaTiO_3$ are small due to its high calcination temperature [22, 35].

Scanning Electron Microscope Studies

The Scanning electron micrograph of $CaTiO_3$ is depicted in Fig.3.10. The agglomerates are spherical in shape and having uniform distribution. The average particle size of $CaTiO_3$ is found to be around 218-266 μm.

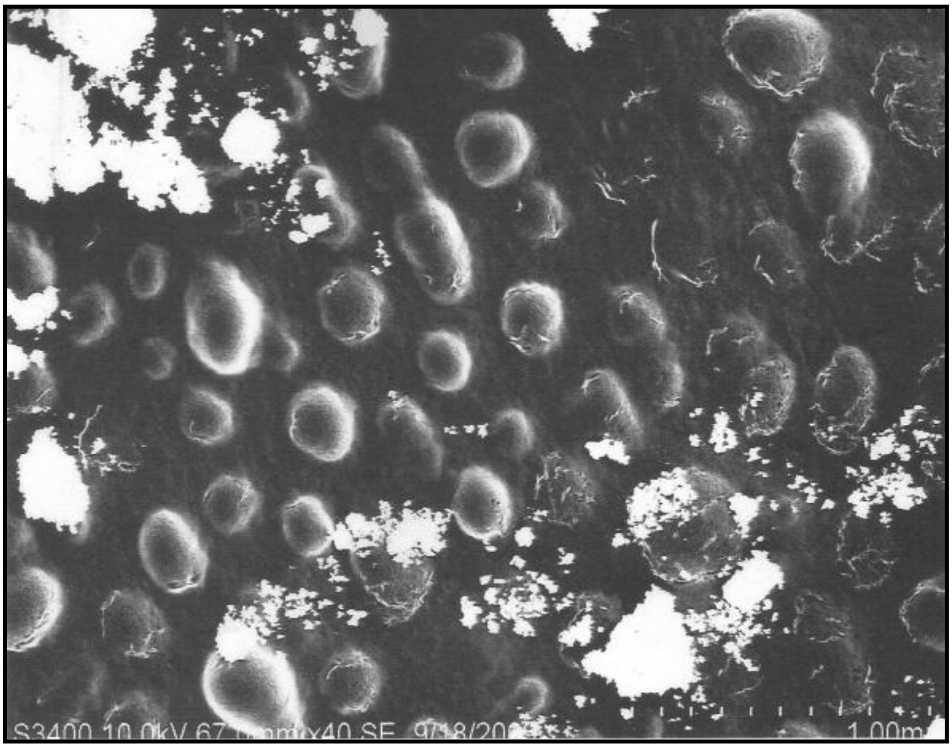


Fig. 3.10: SEM of Ca-Ti Catalyst

Basic Strength Studies

The catalyst changed the colour of bromothymol blue (H_= 7.2) from green to blue but failed to change the colour of phenolphthalein (H_= 9.3). So that, the catalyst basic strength was designated as 7.2< H_<9.3 and it was considered as a strong base for transesterification reaction. Table 3.2 summarizes the surface area, pore size, pore volume and basic strength of synthesized Ca-Ti catalyst.

Table 3.2: Characteristics of Ca-Ti based catalyst

Catalyst characterization	$CaTiO_3$ (extruded)
BET Surface Area (m^2/g)	7.59
Pore Size (Å)	70
Pore Volume (cm^3/g)	0.01
Basic strength	$7.2 < H\_ < 9.3$

3.4.2. Optimization of Reaction Parameters

Effect of Catalyst Concentration

In this study, effect of catalyst concentration on biodiesel yield was evaluated at methanol to oil molar ratio of 20:1, reaction temperature 170 °C and pressure of 80 bar. The catalyst concentration was varied from 3 to 12% w/w with respect to vegetable oils at identical reaction conditions. The overall conversion of jatropha oil to biodiesel was evaluated in terms of % yield in reaction time of 3 h. Biodiesel yield obtained by varying the catalyst concentration is depicted by plot (Fig. 3.11). The maximum biodiesel yield (94%) was obtained at catalyst concentration of 10 % (w/w) in reaction time of 3 h. At higher concentration than 10%, no significant increase in biodiesel yield was observed.

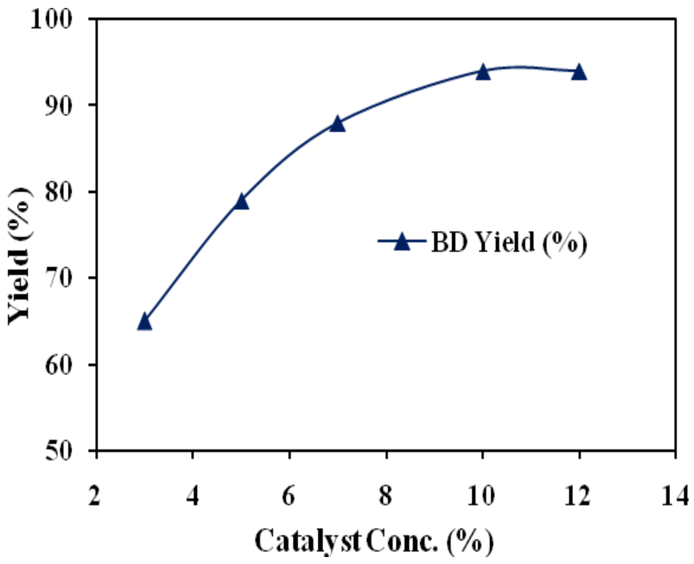


Fig. 3.11: Effect of catalyst concentration

Optimization of Reaction Time

In this study catalyst activity was evaluated for the transesterification of jatropha oil at various concentrations in range of 3 to 12% w/w of vegetable oil, methanol to oil ratio of 20:1 with temperature 170 ^{o}C and pressure 80 bar in terms of reaction time. At 3 % catalyst composition, completion of reaction took 7 hrs and with increase in catalyst concentration reaction becomes quicker. It can be observed that with catalyst concentration at 10%, reaction completion was observed in minimum time of 3 h (Fig. 3.12). 94% of biodiesel yield was obtained after 3 h of reaction time.

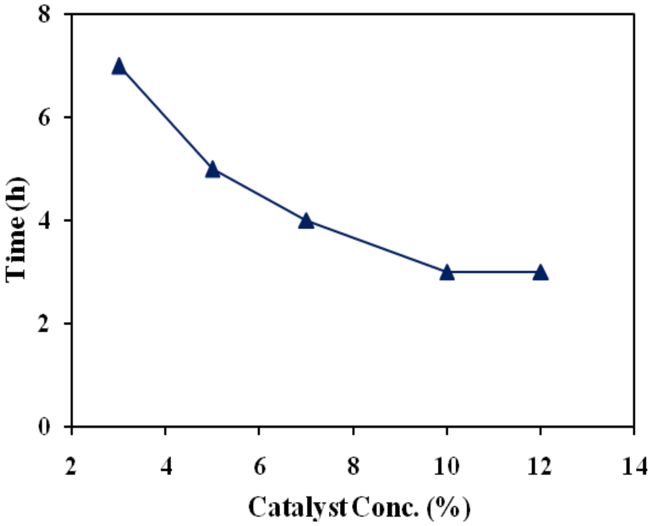


Fig. 3.12: Effect of catalyst concentration on reaction time

Biodiesel formed at various catalyst concentrations was analyzed for % biodiesel/oil content by GPC and other physico-chemical properties. The results are depicted in Table 3.3. The result show that at 170 ^{o}C, 10% catalyst concentration and 80 bar pressure, maximum yield of 94% is obtained.

Table 3.3: Transesterification of jatropha oil using different catalyst concentration

Catalyst conc. (%)	GPC (%)		Viscosity (cSt)	Density g/cm^3	Total acid number (mgKOH/g)	Duration (h)
	BD	Fat				
3	91.6	8.4	4.669	0.87	0.270	7
5	91.0	9.0	5.097	0.82	0.437	5
7	92.6	7.4	4.516	0.83	0.465	4
10	94.2	5.8	4.394	0.85	0.421	3
12	91.3	8.7	4.666	0.81	0.437	3

Variation of Methanol to Oil

Results of study on effect of different molar ratio of methanol to oil on reaction time were depicted by plot (Fig. 3.13). Experiments were carried out with molar ratio of 5:1, 10:1, 15:1, 20:1, 25:1 and 30:1 of methanol to oil with catalyst concentration of 10% w/w of oil, temperature of 170 °C and pressure of 80 bar.

The result indicated that the transesterification reaction was not complete even in 10 h with methanol to oil ratio of 5:1 (Fig. 3.13). The reaction time decreases to 3 h at molar ratio of 20:1. Thereafter, no change in reaction time was observed on increasing methanol ratio.

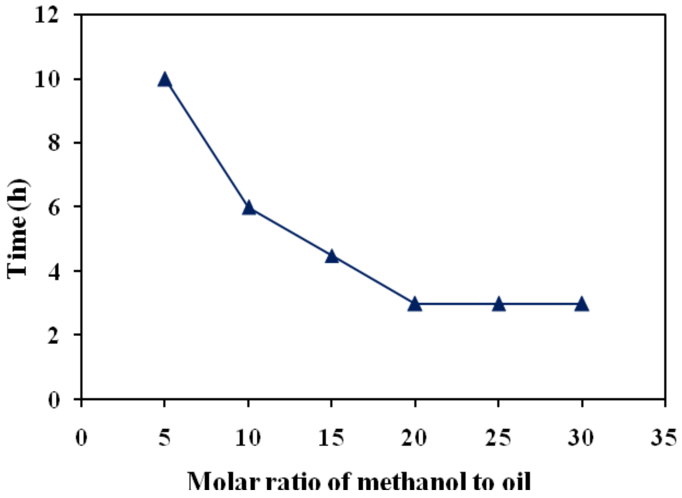


Fig. 3.13: Effect of molar ratio of methanol to oil on reaction time

The biodiesel samples using different methanol to oil ratio were analyzed for critical parameters such as viscosity, density, TAN, GPC. The results are depicted in Table 3.4.

Table 3.4 Transesterification of jatropha oil using different methanol to oil molar ratio

MeOH: Oil	GPC (%)		Viscosity (cSt)	Density g/cm^3	Total acid number (mgKOH/g)	Duration (h)
	BD	Fat				
5:1	69.2	30.8	8.448	0.82	4.682	10
10:1	83.8	16.2	5.102	0.80	0.565	6
15:1	91.1	8.9	4.910	0.86	0.224	4.5
20:1	94.2	5.8	4.394	0.85	0.421	3
25:1	91.0	9.0	5.098	0.82	0.467	3
30:1	93.4	6.6	4.820	0.80	0.410	3

Effect of Acidity and Moisture

The acid value of jatropha oil having initial acid value of 8 was varied by adding 2, 5 and 10% wt of oleic acid to obtain samples having acid value of 16.09, 25.76 and 40.92 mg-KOH/g. Reaction were carried out in high pressure reactor at T= 170 ^{o}C, P=80 bar, methanol to oil molar ratio of 20:1 and 10 wt% of catalyst. The results indicate that when acid value of oil was increased, methyl ester yield was also increased and same is indicated by Fig 3.14. However due to higher amount of acid, reaction time for completion of methyl ester yield was also higher. It was observed that methyl ester yield of esterification of oleic acid was much higher (97.2 wt%) than the transesterification (94 wt%) of jatropha oil due to more solubility of methanol in acid value/FFA’s than jatropha oil. So it can be concluded that Ca/Ti based catalyst is very well suited for vegetable oils having high acid value. It can be concluded from this study that Ca/Ti based catalyst was effective to convert vegetable oils of acidity upto 25 mg-KOH/g to biodiesel.

The experiment was also conducted in presence of water and it was observed that transesterification activity of catalyst was retarded by presence of even 2% water. Apart from reducing the ester yields and there was considerable difficulty in the recovery of the glycerol due to the formation of emulsions (Fig. 3.14).

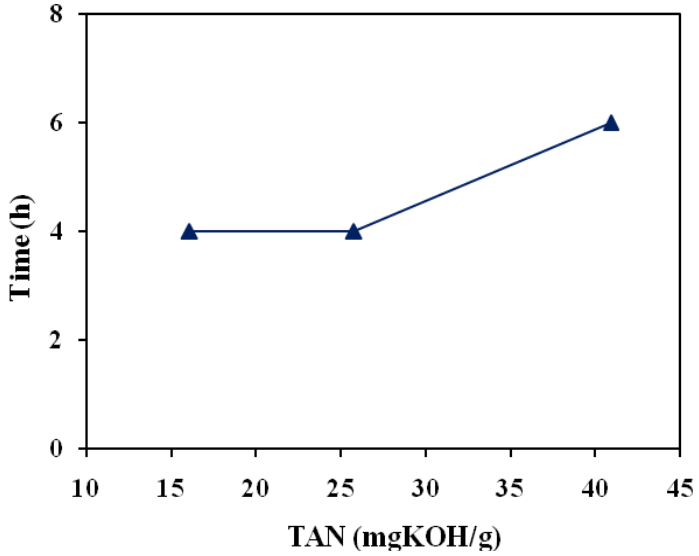


Fig. 3.14: Effect of acid value on reaction time

Effect of oleic acid and moisture content in jatropha oil for biodiesel synthesis and its properties were given in Table 3.5.

Table 3.5: Transesterification of jatropha oil using different concentration of water and oleic acid in reactants

Oleic acid (%) in jatropha oil	Water (%) in jatropha oil	Biodiesel yield (%)	Viscosity (cSt)	Density (g/cm^3)	Total acid number (mgKOH/g)	Duration (h)
2	-	84.5	5.623	0.86	0.538	4
5	-	92.7	4.786	0.87	0.513	4
10	-	97.2	5.507	0.85	0.583	6
10	2	93.0	6.102	0.86	0.874	7
10	5	88.2	6.474	0.87	5.448	8
-	2	77.8	13.767	0.88	12.773	7

Catalyst Stability and Reusability

Catalyst durability was evaluated by repeating the transesterification reaction of jatropha oil under optimized conditions of T=170 °C, P=80 bar, methanol: oil ratio of 20:1, catalyst concentration of 10 wt% and reaction time of 3 h. Catalyst was filtered after every use, washed with methanol and dried at 100 °C for 1 h. XRD patterns showed no change in catalyst structure after repeated use of 4 times establishing the durability of $CaTiO_3$ catalyst (Fig. 3.15).

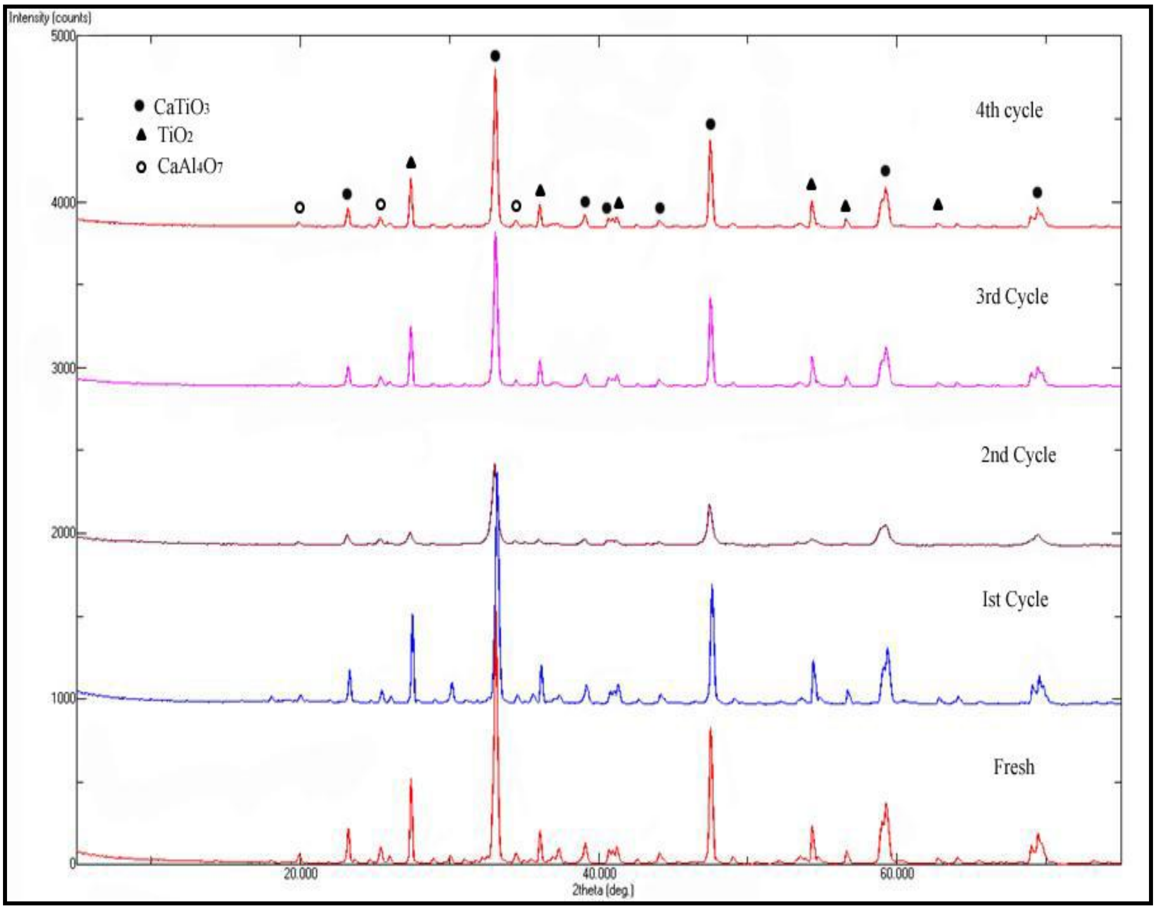


Fig. 3.15: XRD patterns of recycle catalysts

3.4.3. Quantification of Methyl Ester

Nuclear Magnetic Resonance (^{1}HNMR)

As described in literature [36-38], the peaks of methyl ester moiety (3.6–3.7 ppm), the clusters of peaks (0.8–3.0 ppm) from methylene and terminal methyl protons of the hydrocarbon moieties in biodiesel and the olefin protons (5.3–5.4 ppm) in biodiesel were used.

The percentage of methyl esters were quantified by proton NMR method depicts as Fig. 3.16. The strong singlet at 3.6 ppm indicates methyl ester (–CO_2CH_3) formation. The signal due to methylene protons adjacent to the ester group in triglycerides (–$CH_2CO_2CH_3$ for methyl esters) appears at 2.3 ppm. The signals at 0.8 ppm related to terminal methyl hydrogens, a strong signal at 1.2 ppm from the methylenes of carbon chain, a signal at 1.6 ppm from the b-carbonyl methylenes, and signals associated to unsaturation at 2.0, 2.8 and 5.3 ppm, assigned to allylic, bis-allylic and olefinic hydrogens, respectively. The ^{1}HNMR of synthesized biodiesel confirms the biodiesel purity of 94%.

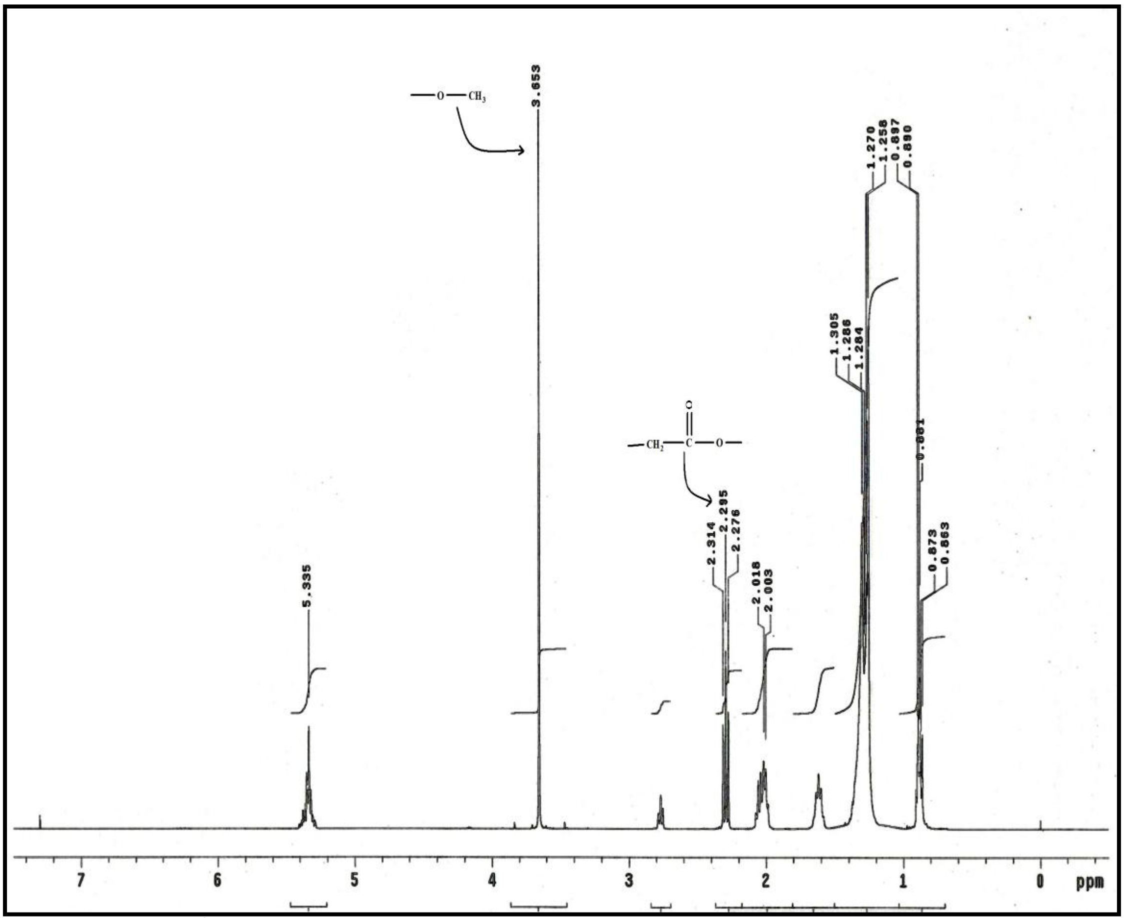
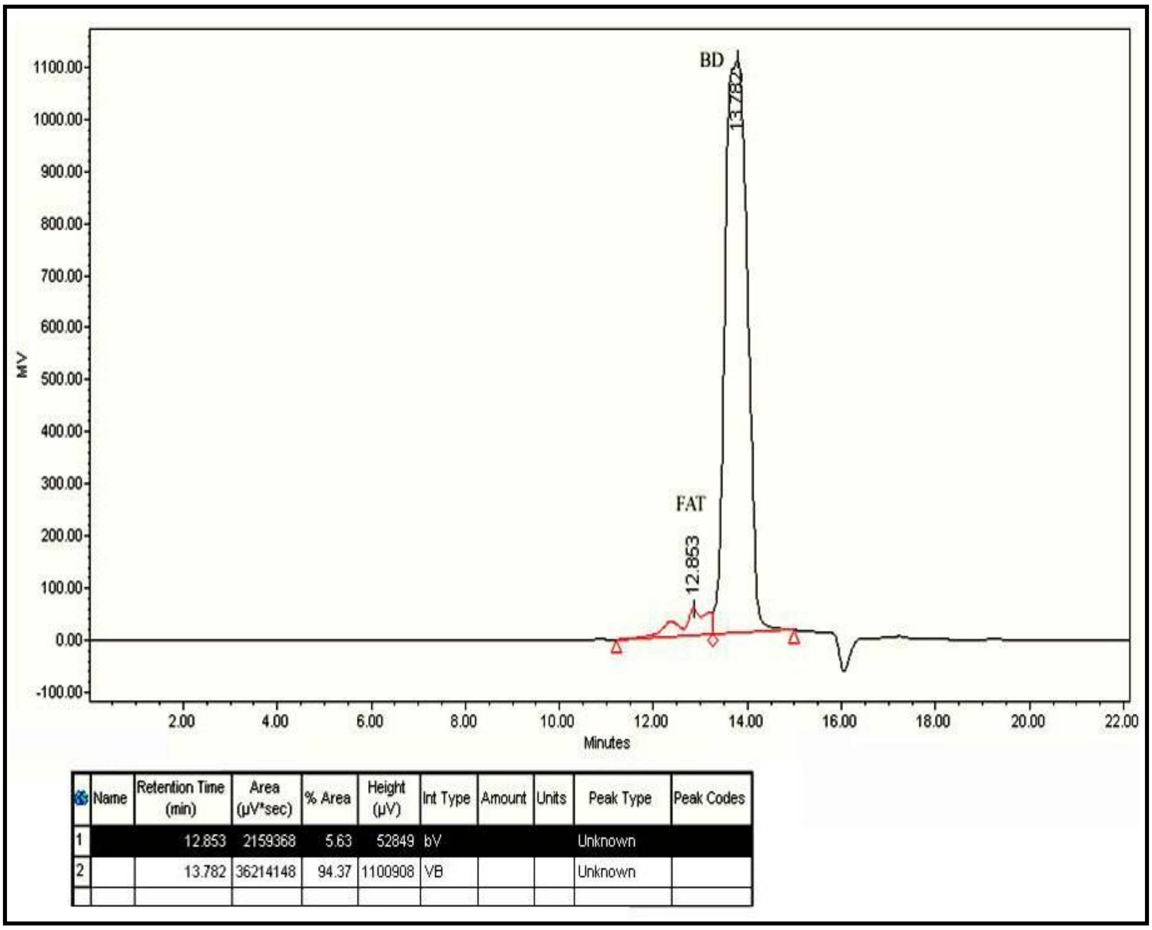


Fig. 3.16: ^{1}HNMR of biodiesel prepared by using $CaTiO_3$ (E) catalyst

Gel Permeation Chromatography (GPC)

The quantification of methyl esters (ME), monoglycerides (MG), diglycerides (DG) and triglycerides (TG) and glycerol has detected by Gel permeation chromatography using a refractive index detector and tetrahydrofuran (THF) as mobile phase [39]. TG, DG, MG, ME and glycerol were eluted in order of their decreasing molecular weight and quantified by comparing the peak area of their respective standards. A typical GPC chromatogram is illustrate in Fig. 3.17. GPC confirmed the conversion rate of 94.2 % for jatropha to biodiesel.



	Name	Retention Time (min)	Area (µV*sec)	% Area	Height (µV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		12.853	2159368	5.63	52849	bV			Unknown	
2		13.782	36214148	94.37	1100908	VB			Unknown	

Fig. 3.17: GPC of product obtained by using $CaTiO_3$ (E) catalyst

Gas Chromatography (GC)

ASTM 6584 standard is the prescribed method for measuring free and total glycerol for biodiesel. It determines the amount of glycerol (in derivatized form), mono- and diacylglycerols (both also in derivatized form), triacylglycerols and methyl esters in a biodiesel sample [40]. The derivatized glycerol is the first material to elute, followed sequentially by the methyl esters and the derivatized monoacylglycerols, diacylglycerols and triacylglycerols. The chromatogram of methyl ester is shown in Fig.3.18. The free glycerine, mono glyceride and total glycerides of synthesized biodiesel were 78 ppm, 862 ppm and 940 ppm respectively. Whereas, ester content of biodiesel was obtained 96.6 wt %.

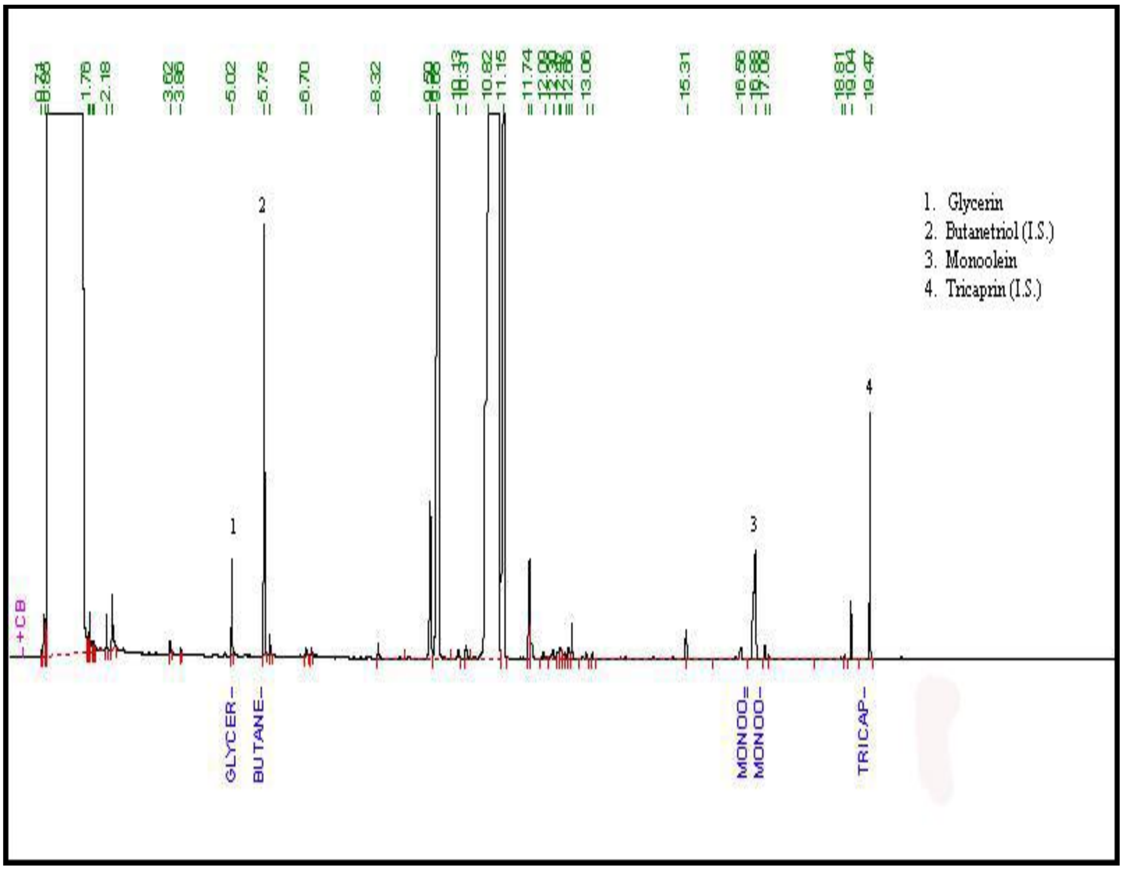


Fig. 3.18: GC of product obtained by using $CaTiO_3$ (E) catalyst

3.4.4. Evaluation of Synthesized Biodiesel

Table 3.6 depicts the ASTM D 6751 and IS 15607 test methods and limits for biodiesel. In respect of synthesized biodiesel, it is observed that it meets all the specification of American Society for Testing and Materials (ASTM) and Indian Standards except oxidation stability. However oxidation stability of jatropha biodiesel further increased by using stabilizer or antioxidants.

Table 3.6: Physico-chemical properties of synthesized biodiesel

Properties	ASTM D6751	ASTM D6751 limits	IS 16507 test method	IS 15607 limits	Jatropha oil methyl ester
Kinematic Viscosity at 40 ^{o}C (cSt)	D-445	1.9-6.0	IS 1448 P:25	2.5-6.0	4.394
Density at 15 ^{o}C (g/cm^{3})	D-4052	0.8-0.9	EN 14103	0.8-0.9	0.852
Acid value (mgKOH/g)	D- 664	Max. 0.80	IS 1448 P:1/Sec.1	Max. 0.50	0.421
Flash Point (^{o}C)	D-93	Min. 130	IS 1448 P:21	Min. 120	161
Cloud Point (^{o}C)	D-2500	NA	IS 1448 P:10	NA	4
Sulphated ash (mass %)	D-874	Max. 0.02	IS 14448 P:4	Max 0.02	0.002
Water and sediment (vol. %)	D-2709	Max. 0.05	D-2709	Max. 0.05	0.04
Cetane number	D-613	Min.47	IS 1448 P:9	Min. 51	51.5
Carbon residue (mass %)	D-4530	Max. 0.05	D- 4530	Max. 0.05	0.022
Copper corrosion	D-130	Max. 3	IS 1448 P:15	Max. 1	1
Free Glycerol, (mass %)	D-6584	Max. 0.02	D- 6584	Max. 0.02	0.0078
Total Glycerol, (mass %)	D-6584	Max. 0.24	D- 6584	Max. 0.25	0.094
Phosphorus (mass %)	D-4951	Max. 0.001	D-4951	Max. 0.001	<0.001
Distillation temperature	D-1160	90% at 360 ^{o}C	Not under spec.	-	90%
Oxidation stability, h	NA	NA	EN 14112	Min. 6h	3.27

3.5. CONCLUSIONS

In the present study we report development of a heterogeneous catalyst that is easy to prepare, uses low value abundant natural raw material and is recyclable. The catalyst is suitable for transesterification of non edible vegetable oil to produce biodiesel meeting IS/ASTM specifications and with excellent yield. The Ti based perovskite type catalyst made from egg shell has exhibited high catalyst activity and durability over repeated cycles and it was easily recovered and also easily separated, without loss of yield. Optimum reaction conditions were determined by varying catalyst amount, reaction time, TAN and water content. The results indicate the possibility of using this catalyst for continuous commercial production of biodiesel.

3.6. REFERENCES

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PREPARATION, CHARACTERIZATION AND EVALUATION OF $Ca_2Fe_2O_5$ CATALYST

4.1. INTRODUCTION

Various types of heterogeneous catalysts which are used for transesterification of vegetable oils have been described in first chapter of the thesis. Among these catalysts the predominantly evaluated heterogeneous catalysts are of A-B-O type metal oxides, where A is an alkaline earth metal, alkaline metal or rare earth metal and B is selected from transition metals. These A-B-O types of catalyst are reported to be stable for several transesterification cycles. Additionally these catalysts are easy to prepare from commonly available raw materials. Kawashima et al. [1] explored the basic catalytic activity of thirteen different kinds of metal oxides containing calcium, barium, magnesium, or lanthanum. They described a common method of preparation of these catalysts. Generally oxides of rare earth metal or their carbonate were mixed with corresponding oxide of transition metal and resulting mixture calcined at higher temperatures to get A-B-O type catalyst. Thus they evaluated $CaTiO_3$, $CaMnO_3$, $Ca_2Fe_2O_5$, $CaZrO_3$, and mixed oxide of Ba-Ti, Ba-Zr, Mg-Ti, Mg-Zr, Mg-Ce, La-Ce etc. These studies concluded that catalysts containing calcium was found to have high basicity and good activity for transesterification. They also observed that mixed metal oxide containing Ba, Mg, La were ineffective or slow in transesterification as these metal oxides have low basicity. Furthermore, it was observed that out of all catalysts studied only $CaZrO_3$ and CaO-CeO_2 showed catalytic activity after five cycles of use.

Viriya-empikul et al. [2] studied the solid oxide catalyst derived from waste shells of eggs, golden apple snail and meretrix venus shells. Though all these shells are predominantly $CaCO_3$, which after calcination gives CaO, their reactivity for biodiesel synthesis was significantly different. All shell derived catalysts are considered to be less porous material due to their trace pore volume and it was found that all these shells after calcination at 800 ^oC for 4 h showed wide variations in BET surface area.

In catalysis, the solid catalyst with higher BET surface area and having smaller size particles always provide higher reactions conversions. This has been seen in case of CaO for transesterification of vegetable oils. Transesterification activity depends upon the availability of basic sites, which intern is dependent on surface area. It was also noted by same author that calcination of less than one hour was not enough to give highly active catalyst. The calcined samples for two to four hours exhibited good catalytic activity for transesterification. However, any further increase in calcination time suppressed the catalytic activity of the catalyst due to sintering of the catalyst which resulted in lower surface area.

Wei et al. [3] investigated waste egg shells for triglyceride transesterification of vegetable oils for biodiesel synthesis. A large number of XRD studies were carried out at different calcination temperatures. It was found that uncalcined egg shells were mainly $CaCO_3$ which did not decompose upto 600 ^oC. From 700 ^oC onwards, the calcined egg shells exhibited CaO peaks and at 1000 ^oC, it was completely present as CaO. The TGA results showed that the water and organics were removed below 600 ^oC and CaO was lost between 700-800 ^oC. It was also observed by SEM that natural egg shells have micropores of irregular crystal structure. However, above 800 ^oC the size of particles decreased and particle shape became more regular.

Boey et al. [4] used crab shell after calcination as heterogeneous catalyst for transesterification. Though they reported activity of catalyst for up to 11 times of reuse, however each time the recovered catalyst was calcined at 900 ^oC for 2 h for subsequent use.

Several workers have prepared $Ca_2Fe_2O_5$ catalyst which is named after Ivanovich Srebrodolskii (1927), Russian-Ukrainian mineralogist and it is related to the perovskite (ABO_3) structure by the introduction of an ordered array of oxygen vacancies and the creation of an alternate layer structure of octahedrally (FeO_6) and tetrahedrally (FeO_4) coordinated transition metal cations [5].

These ferrite of catalyst have been used in the field of catalysis [1,6-8] and for the application of radio, television, microwave and satellite communication, bubble devices, audio-video, digital recording and as permanent magnets and Li-ion batteries [9,10]. Ferrite material is also applied for microwave application due to excellent combination of electrical and magnetic characteristics apart from the appreciable.

Hirabayashi et al. [7] prepared $Ca_2Fe_2O_5$ catalyst by ceramic route by physical mixing of CaO and Fe_2O_3. They prepared several catalyst compositions by varying the Ca/Fe ratio from point 3.3 to 3. They observed maximum $Ca_2Fe_2O_5$ formation (by XRD) at Ca/Fe ratio of 1 and at lower ratios, $CaFe_2O_4$ was also seen in appreciable amounts.

Smith et al. [11] used $CaCO_3$ and Fe_2O_3 for preparation of $Ca_2Fe_2O_5$ by mixing the ingredients in isopropanol and followed by calcination at 1100 ^{o}C

The $Ca_2Fe_2O_5$ prepared by our method, that is by reaction of waste egg shell /sea shell with Fe_2O_3, showed different properties then the $Ca_2Fe_2O_5$ reported by Kawashima et al. [1]. They reported the preparation of $Ca_2Fe_2O_5$ by physically mixing $CaCO_3$ and Fe_2O_3 in 1:2 molar ratio followed by calcination at 1050 ^{o}C for 4 h. The XRD pattern of the $Ca_2Fe_2O_5$ prepared by Kawashima et al. [1] showed appreciable peaks associated with CaO. They reported surface area as 0.71 m^2/g and basic strength between $7.2 < H\_ < 9.3$. They investigated the catalyst activity at 10% catalyst level and about 92% methyl ester yield was reported. However, during catalyst durability test it was discovered that $Ca_2Fe_2O_5$ showed poor performance as compared to other catalyst. Residual amount of CaO which eventually get converted to $Ca(OH)_2$ may be one of the reason for poor recyclability.

4.2. AIM OF THE PRESENT WORK

The objective of the present work is to prepare A-B-O type of metal oxides and most specially $Ca_2Fe_2O_5$ and its evaluation as catalyst for transesterification of vegetable oils. The major innovative steps which differentiates the present work from the past reports is selection of naturally available waste materials as one of the component for catalyst preparation. The calcium ferrite type of catalyst has been synthesized by reaction of Fe_2O_3 with Ca component derived from eggshells and or sea shells. The synthesized catalyst has been fully characterized by XRD, TGA, and particle size analysis. Extensive experimentations were carried out so as to optimize the variables like temperature, pressure, catalyst concentration and methanol to oil ratio so as to maximize biodiesel yield. The catalyst activity was also evaluated over repeated cycles to validate catalyst recyclability. The produced biodiesel has been evaluated for various physico-chemical characteristics as per IS/ASTM standards. The work methodology adopted is as follows:

- Preparation of cost effective, recyclable catalyst which has major ingredient of waste eggshells/ seashells.
- Characterization of the synthesized catalyst using techniques such as TGA, XRD, surface area, pore size, pore volume, SEM and Hamment indicators.
- Study of kinetic properties of biodiesel preparation such as catalyst concentration, molar ratio of methanol to oil temperature and effect of time etc. using novel $Ca_2Fe_2O_5$ heterogeneous catalysts in high pressure reactor.
- The catalyst activity was evaluated over repeated cycles to validate catalyst recyclability.
- Physico-chemical characteristics of synthesized biodiesel as per IS/ASTM standards.

4.3. EXPERIMENTAL

4.3.1. Reagents and Materials

Commercial non-edible grade Jatropha oil having total acid number of 8.2 was taken from Surendra Nagar, Gujarat and used without further purification. Methanol (>98%) and Ferric Oxide (>98%) were procured in LR grade from CDH, India.

Eggshells are collected from local market. The eggshells were cleaned to remove protein and other interference substances by washing several times with warm water. Washed shells were dried overnight in oven at 110 ^{o}C to remove traces of water.

4.3.2. Catalyst Preparation

For the formation of $Ca_2Fe_2O_5$, one of the reactant viz. egg shells are grounded to fine powder than calcined in muffle furnace at 550 ^{o}C for 3 h. After calcined, it was obtained as black solid in 94.75% yield. The calcined egg shell and ferric oxide (Fe_2O_3) were milled in molar ratio of 2:1 (25 g $CaCO_3$ and 20 g Fe_2O_3) in mortar for 15 min (solid-state reaction). The mixture was calcined at 900 ^{o}C for 3 h and then at 1050 ^{o}C for 3.5 h to obtain $Ca_2Fe_2O_5$ as red brown solid (74.66%), which was stored in a dry container and kept in desiccators. XRD results confirmed that the composition of calcined eggshell mainly consisted of calcite-calcium carbonate.

4.3.3. Catalyst Characterization

The physico-chemical property of the prepared catalyst was determined by various analytical tools such as XRD, TGA, SEM and IR etc. The make and specifications of these instruments is already given in chapter 3 and interpretation of result for the prepared catalyst is given in the section 4.3.1.

4.4. RESULTS AND DISCUSSIONS

4.4.1. Catalyst Characterization

The catalyst prepared by us is significantly better than one reported by Kawashima et al. [1]. As compared to their reported surface area of 0.71 m^2/g, our catalyst showed surface area of 6.02 m^2/g and pore size of 29 Å. This large surface area is responsible for higher basic strength of our catalyst which is far superior to the one reported. Addionally, the average particle size of $Ca_2Fe_2O_5$ prepared by us was smaller in the range of 170-240 µm. Our catalyst was free of CaO and that explains why we had no difficulty in recycling this catalyst.

Because of the higher activity of our catalyst then the one prepared by Kawashima et al. [1], we could get appreciable yield even at 1% concentration of catalyst, whereas literature reported minimum is 10%. The catalyst was characterized by the following analytical techniques.

X-ray Diffraction (XRD)

XRD was performed under conditions described earlier. X-ray diffraction pattern exhibits $Ca_2Fe_2O_5$ formation on calcination at temperature 1050 ^{o}C. XRD of the catalyst sample showed characteristic peak of $Ca_2Fe_2O_5$ (Srebrodolskite phase) and minor peak of CaO and $CaFe_2O_4$ indicating conversion of calcium carbonate to calcium oxide and its subsequent reaction with Fe_2O_3 to form desired $Ca_2Fe_2O_5$ complex (Fig. 4.1).

XRD spectra show intense peaks at $2\theta \sim 11.9$, 22.8, 24.1, 31.9, 32.9, 33.4, 43.5, 46.6, 49.4 and 57.9 to the d value of 7.39, 3.90, 3.70, 2.80, 2.72, 2.69, 2.08, 1.95, 1.85 and 1.60 respectively of calcium ferrite ($Ca_2Fe_2O_5$). The calcium iron oxide ($CaFe_2O_4$) peaks were observed at $2\theta\sim$ 19.3, 25.5, 30.8, 33.5, 33.6, 35.5 and 61.5 to the d value of 4.61, 3.49, 2.90, 2.68, 2.67, 2.53 and 1.51 respectively. The calcium oxide (CaO) peaks were observed at $2\ \theta\sim$ 32.2, 37.7 and 53.9 to the d value of 2.78, 2.41 and 1.71 respectively (Fig. 4.1).

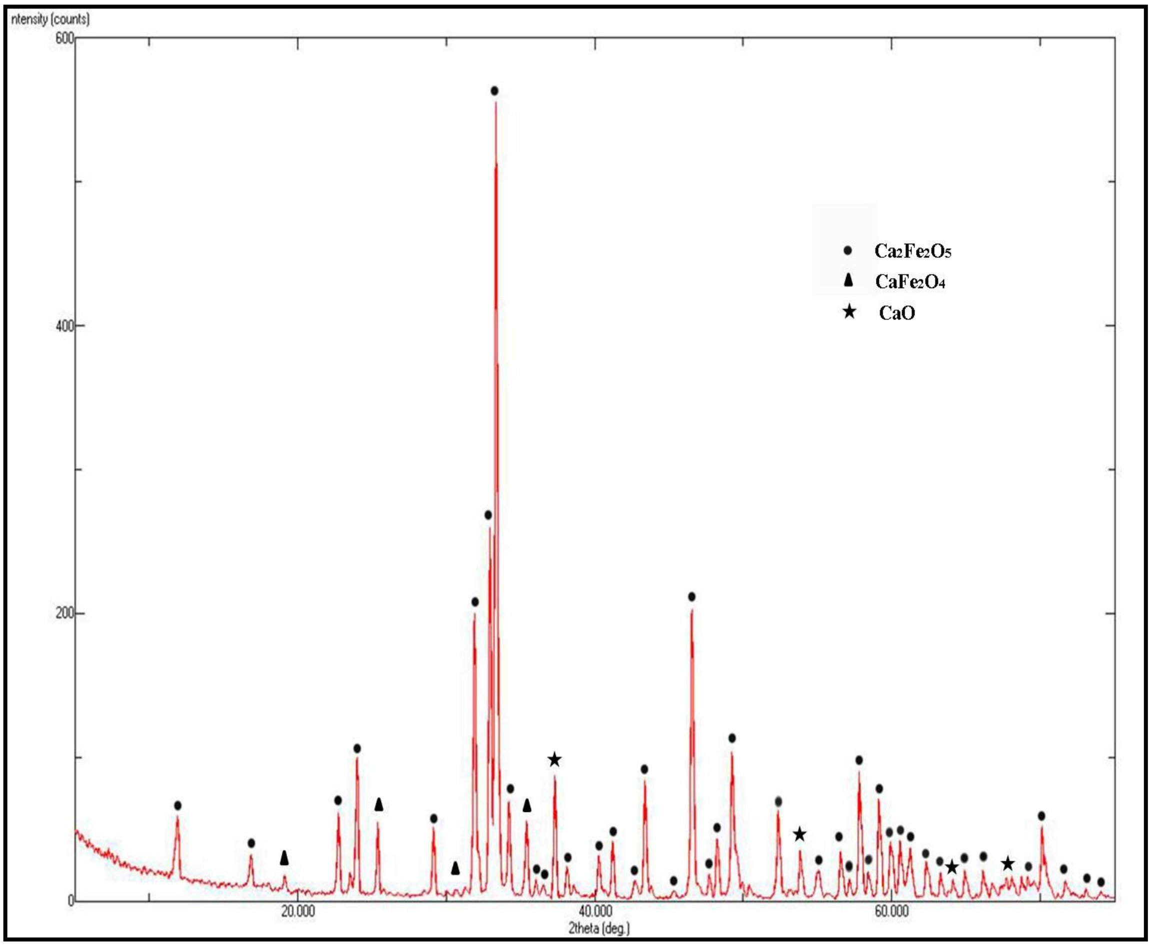


Fig. 4.1: XRD of $Ca_2Fe_2O_5$ catalyst

Thermogravimetric Analysis (TGA)

Three stages of weight loss of synthesized $Ca_2Fe_2O_5$ were depicted by Thermo gravimetric analysis (Fig. 4.2). First stage shows the weight loss of 0.640% due to initial decomposition involving loss of water at 100 to 200 ºC temperature. Then, at temperature of 380-550 ºC weight loss observed is 2.285% which can be attributed to the decomposition of $Ca(OH)_2$. Further when temperature is increased to about 600-800 ºC, the weight loss (0.8331%) due to thermal decomposition of $CaCO_3$ to form CaO with loss of carbon dioxide. The CaO phase reacts with the other active ingredient Fe_2O_3 to form $Ca_2Fe_2O_5$. The thermal gravimetric results of Ca/Fe based catalyst is illustrated in Fig. 4.2.

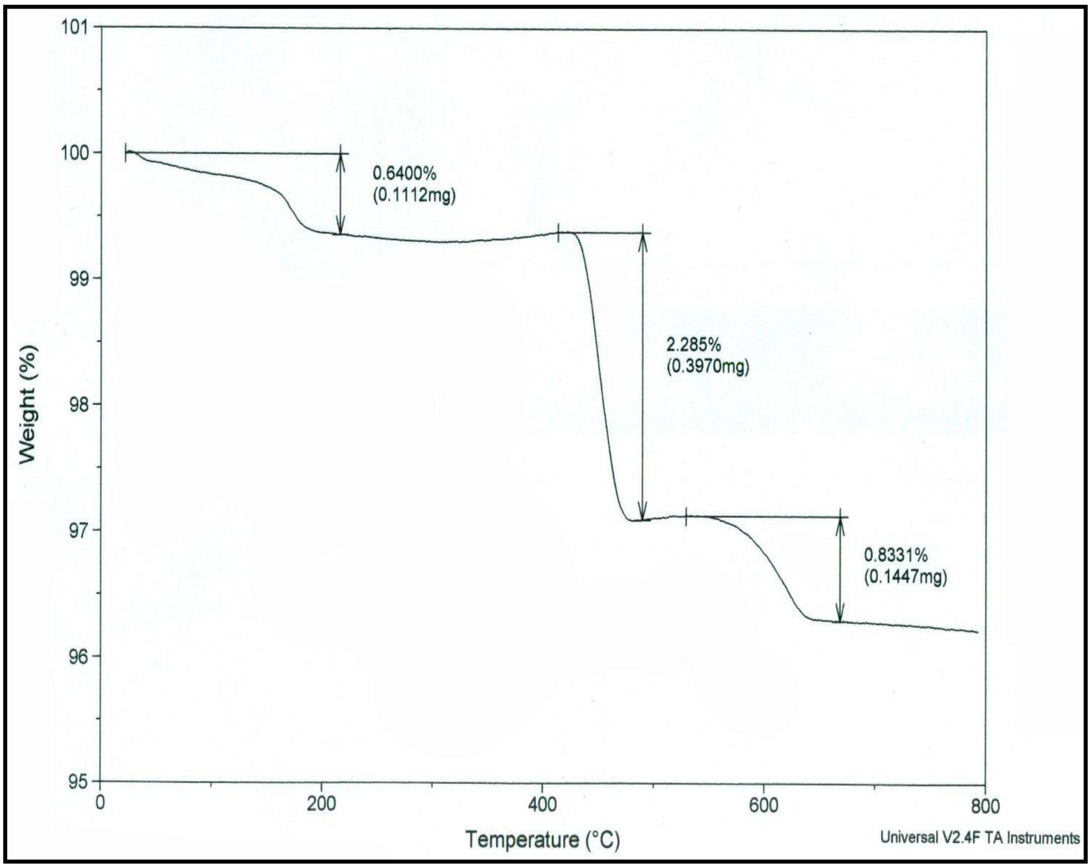


Fig. 4.2: TGA of $Ca_2Fe_2O_5$ catalyst

Surface Area, Average Pore Size and Total Pore Volume

The average pore size, BET surface area and total pore volume of catalyst were found to be 29 Å, 6.02 m^2/g and 0.02 cm^3/g respectively. Surface area and total pore volume of $Ca_2Fe_2O_5$ are small due to its high calcination temperature and preparation method of catalyst (physical mixing), however possibility of reactivity of the reacting moieties enhances due to large pore size.

Scanning Electron Microscopy (SEM)

Under the experimental conditions described earlier, SEM images (Fig. 4.3) show that agglomerates are spherical in shape became more regular at 1050 ^{o}C. The average particle size of $Ca_2Fe_2O_5$ is found to be around 173-239 μm.

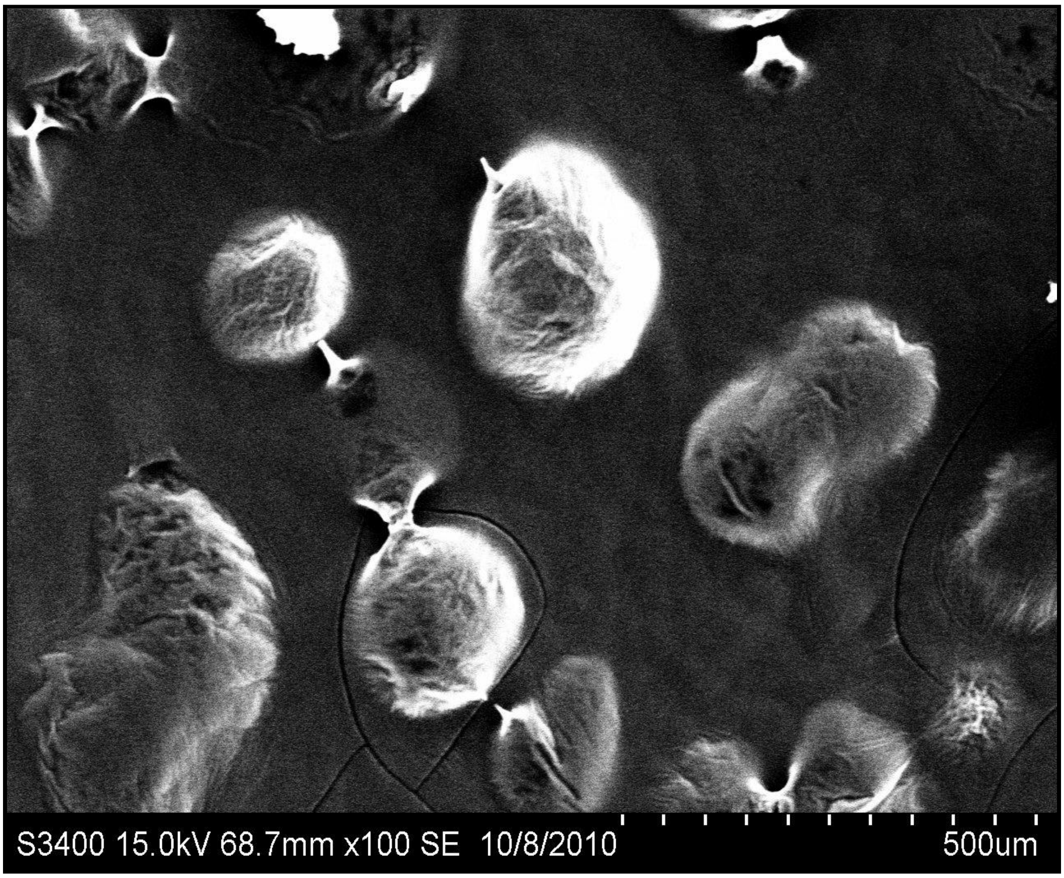


Fig. 4.3: SEM of $Ca_2Fe_2O_5$ Catalyst

Basic Strength

Basic strength was determined by titration as described earlier. Table 4.1 summarizes the surface area, pore size, pore volume and basic strength of synthesized Ca-Fe based catalyst.

Table 4.1: Characteristics of $Ca_2Fe_2O_5$ catalyst

Catalyst characterization	$Ca_2Fe_2O_5$ (powder)
BET Surface Area (m^2/g)	6.02
Pore Size (Å)	29
Pore Volume (cm^3/g)	0.02
Basic strength	$9.3 < H\_ < 15.0$

4.4.2. Process Optimization Studies and Kinetics Parameters Determination for Transesterification Reaction

To optimize and maximize yield of biodiesel in transesterification of jatropha oil by $Ca_2Fe_2O_5$, several systematic experiments were planned and performed. In these experiments effect of catalyst concentration, molar ratio of reactants, impurities like acidity and moisture were studied. After optimization the catalyst was evaluated for its stability and recyclability. The details of these experiments are given below:

Effect of Catalyst Concentration

In this study the concentration of $Ca_2Fe_2O_5$ with respect to jatropha oil was varied with in the range of 1 to 10%. All other reaction conditions were kept constant i.e. 170 ^{o}C temperature, 80 bar pressure, 20:1 ratio of methanol to oil and reaction time of 3 h. As can be seen in Fig. 4.4, the catalyst was reasonably active even at 1% level giving biodiesel yield of 89%. However, catalyst at 3% and 5% yielded 93.3 and 96% conversion. The conversion remained almost constant at 7% catalyst concentration but the conversion dropped when the catalyst concentration was increased to 10%. The probable reason could be formation of thick emulsion at higher concentration level which resulted in lower intermixing.

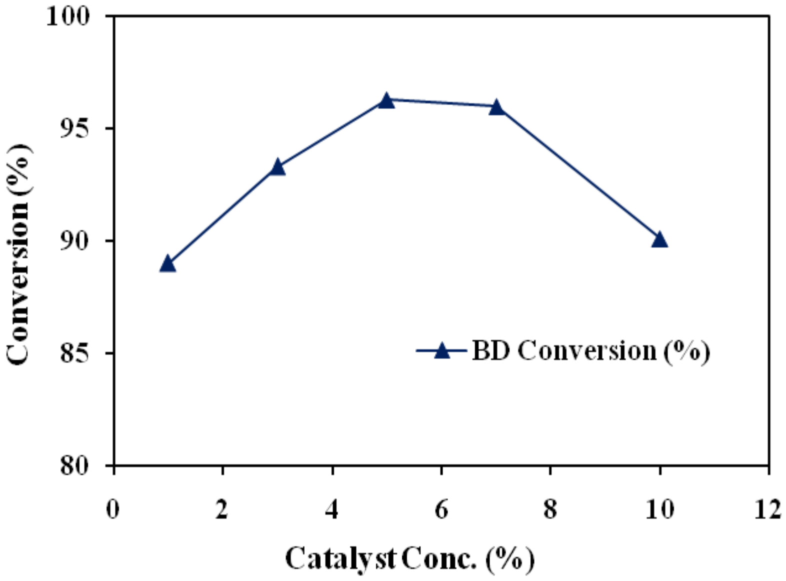


Fig. 4.4: Effect of catalyst concentration

For all practical purposes catalyst 3-5% (w/w) with respect to oil could be taken as the appropriate catalyst concentration for maximum conversion to biodiesel.

Effect of Methanol to Oil Ratio

In this study the molar ratio of methanol to jatropha oil was varied from 5:1 to 30:1 in various steps. In order to evaluated effect of molar ratio all other experimental parameter were kept constant i.e. 170 ^{o}C temperature, 80 bar pressure, 5% catalyst concentration and 3 h reaction time. As in shown in Fig. 4.5, it was observed that biodiesel yield increased from 75.9% (5:1) to 96.9% at molar ratio of 20:1. Thereafter, on increasing the molar ratio to 25:1 or 30:1, no benefit was obtained and rather a small decrease at 30:1 (93.3%) was observed.

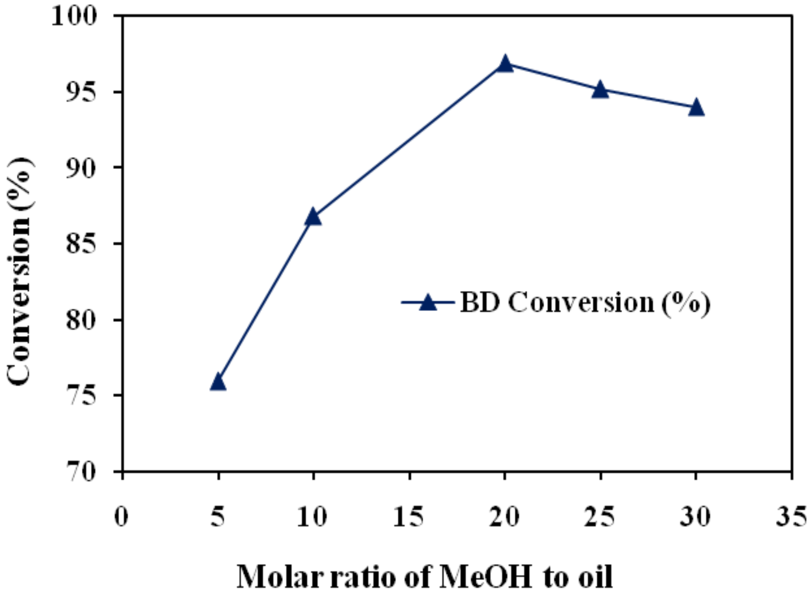


Fig. 4.5: Effect of methanol to oil ratio

For all practical purposes in order to get pure biodiesel (FAME), methanol to oil ratio 20:1 is most appropriate. Transesterification of jatropha oil using different catalyst concentration and methanol to oil ratio are depicted in Table 4.2.

Table 4.2: Transesterification of jatropha oil using different catalyst content and methanol to oil molar ratio

S.No.	Catalyst conc. (% w/w of oil)	MeOH/ oil ratio	Biodiesel conversion (%)*
1	1	20:1	89.0
2	3	20:1	93.3
3	5	20:1	96.3
4	7	20:1	96.0
5	10	20:1	90.1
6	5	5:1	75.9
7	5	10:1	86.8
8	5	20:1	96.9
9	5	25:1	95.2
10	5	30:1	94.0

*Temperature 170 ^{o}C, pressure 80 bar and reaction time 3 h

Effect of Impurities in Jatropha Oil

Natural jatropha oil does contain some free fatty acids (FFA) and amount of these FFA may vary with the source of jatropha oil and the method by which oil is extracted. It is seen that jatropha oil on storage get rancid giving more free fatty acid and the solvent extraction from the seed, also gives more free fatty acid as compared to mechanical pressing.

Presence of FFA has been the major constraint in homogeneously catalyze (by NaOH or KOH) transesterification and its leads to excessive catalyst consumption, formation of soap and loss of vegetable oil. Heterogeneous catalysts are particularly preferred as higher free fatty acid, vegetable oil can also be transesterified and heterogeneous catalyst generally converts FFA into corresponding methyl esters.

To obtained sample having higher acid value, jatropha oil having initial acid value of 8 was fortified with 2, 5, 10 and 15% by wt. of oleic acid. These mixture resulted jatropha oil having TAN value of 12.59, 20.83, 30.29 and 38.44 mg-KOH/g respectively. To study the transesterification of these high TAN jatropha samples, reactions were carried out with all other parameters kept as constant. i.e. 170 °C temperature, 80 bar pressure, 20:1 ratio of methanol to oil, 5% wt. of catalyst with respect to oil and reaction time of 3 h.

As can be seen in Fig. 4.6, the synthesized catalyst $Ca_2Fe_2O_5$ could easily convert these high TAN jatropha to corresponding fatty acid methyl esters. Though the yields were little lower but no soap formation was seen. However, the sample having acidity more than 20 required additional time for completion of reaction. Thus, this ability from $Ca_2Fe_2O_5$ to convert high TAN jatropha in to fatty acid methyl ester is a noticeable improvement.

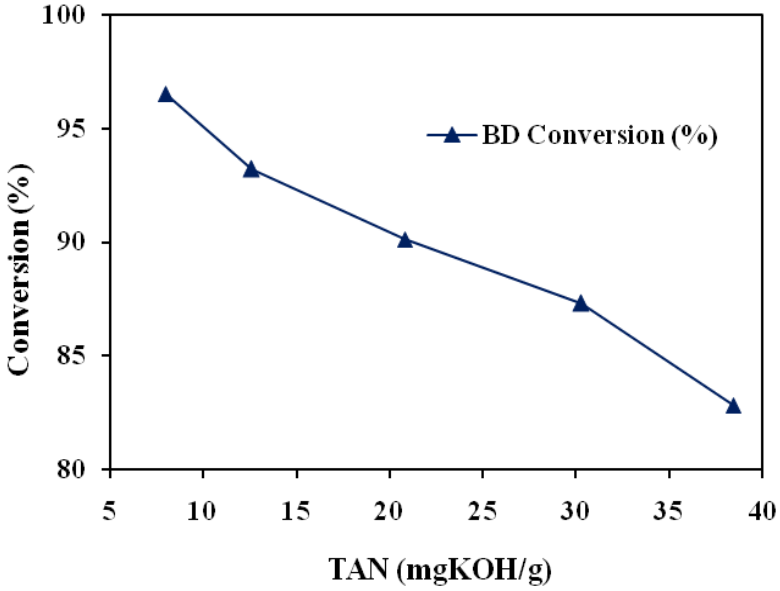


Fig. 4.6: Effect of impurities in jatropha oil

Jatropha oil may have some moisture which may vary from as low as 1000 ppm to as high 2%. Effect of presence of moisture/water of jatropha oil in transesterification by $Ca_2Fe_2O_5$ was studied by addition of 2% water in jatropha oil. Keeping all other reaction parameter were constant, the reaction was monitored and it was found that though the reaction yield was significantly lower at 73.8%, the reaction still went smoothly. Absorption of water on the active surface, blocking these sites may be the probable reason the drop in biodiesel yield. Effect of oleic acid and moisture content in jatropha oil for biodiesel synthesis are given in Table 4.3.

Table 4.3: Transesterification of jatropha oil using different concentration of water and oleic acid in reactants

S.No.	Jatropha oil (%)	Oleic acid (%)	TAN of initial jatropha oil	Addition of water (%)	Biodiesel conversion by GPC (%)*
1	100	-	8.0	-	96.5
2	98	2	12.59	-	93.2
3	95	5	20.83	-	90.1
4	90**	10	30.29	-	87.3
5	85**	15	38.44	-	82.8
6	100	-	8	2	73.8

**Catalyst concentration 5%, temperature 170 °C, pressure 80 bar, methanol to oil ratio 20:1, reaction time 3 h and moisture in jatropha oil 1000 ppm.
**5 h reaction time

Catalyst Recyclability and Reusability

To study the catalyst stability and reusability, catalyst after completion from first reaction was filtered, washed with methanol and dried at 100 °C for 1 h. Keeping the other reaction parameter constant i.e. 170 °C temperature, 80 bar pressure, 20:1 ratio of methanol to oil, 5% catalyst concentration and reaction time of 3 h. The catalyst was recovered upto 4 cycles and after drying at 100 °C for 1 h, its XRD was studied.

As shown in Fig. 4.7, they was hardly any change in XRD pattern except for little change in catalyst structure possibly because of some left over organic moieties. It was however observed that the catalyst could be safely used for up to 12 cycles and hence has a good stability and reusability.

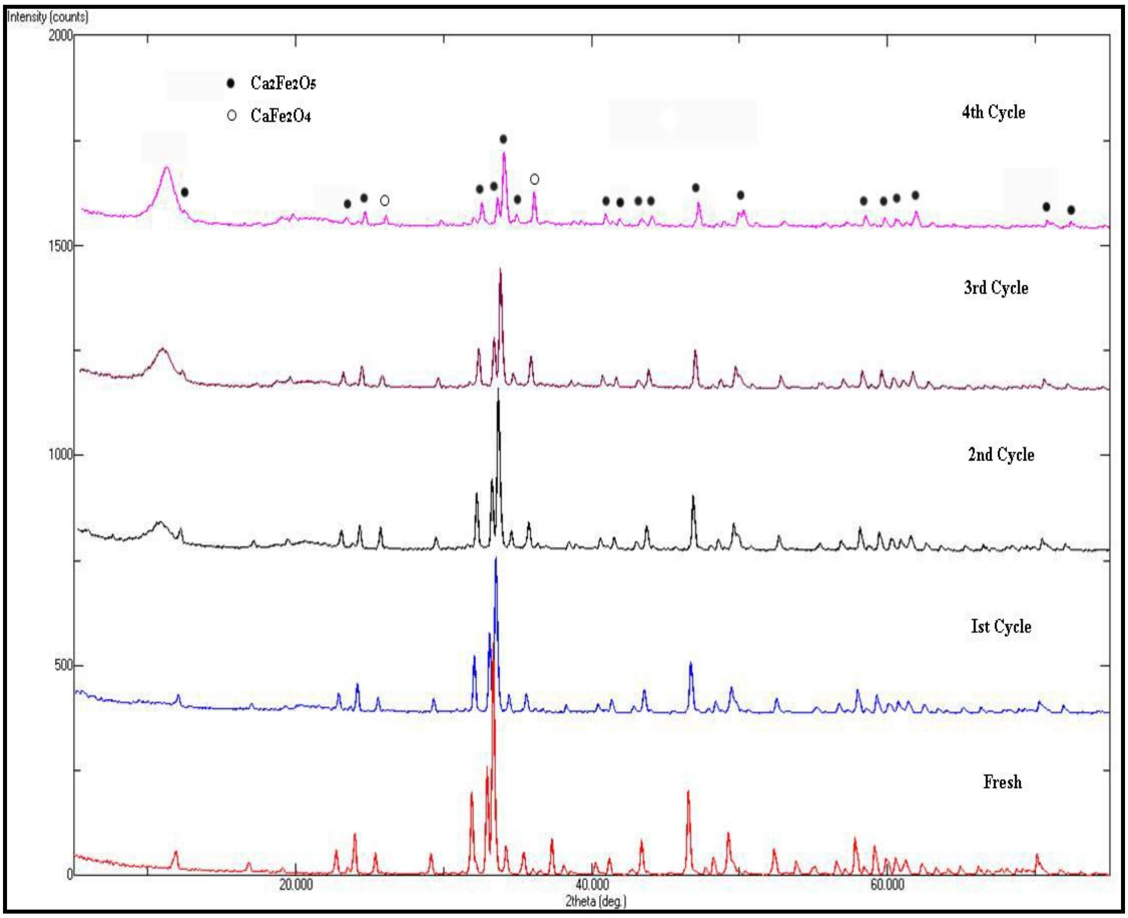


Fig. 4.7: Effect of recyclability on XRD of catalyst

The biodiesel obtained by transesterification of jatropha oil with methanol using $Ca_2Fe_2O_5$ catalyst was fully characterized by ^{1}HNMR, GPC and GC.

The peak assignment was carried out as explained in chapter IV. The NMR spectrum of Fig. 4.8, GPC curve is as shown in Fig. 4.9 and GC trace is shown in Fig. 4.10.

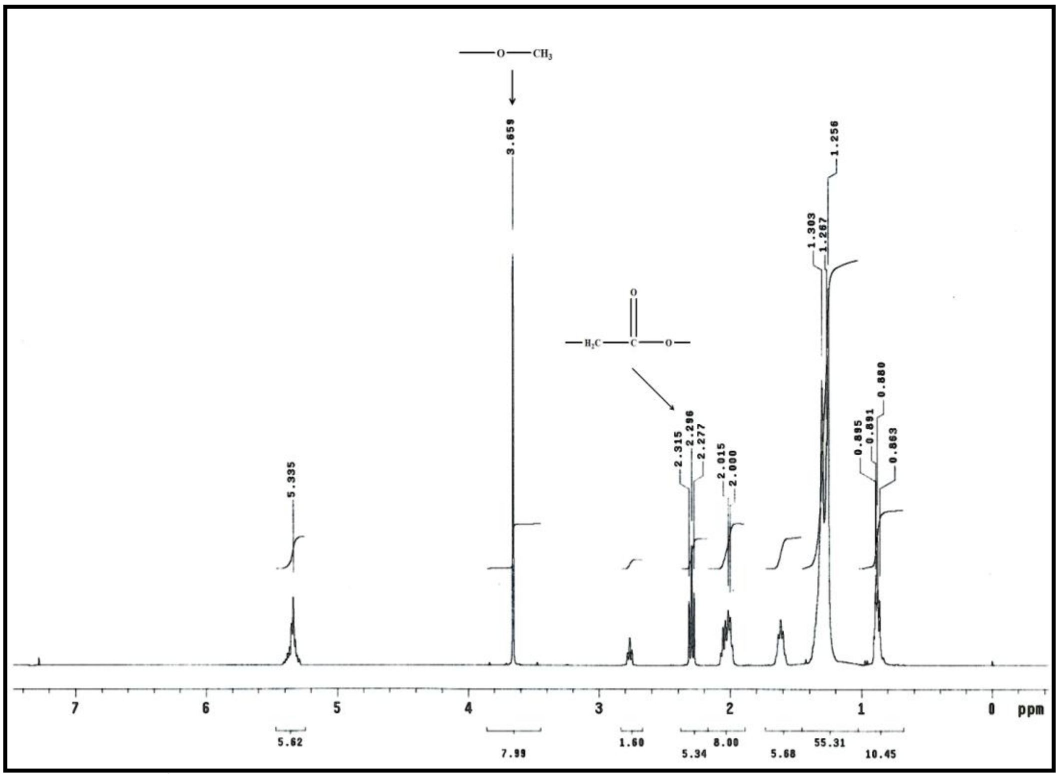
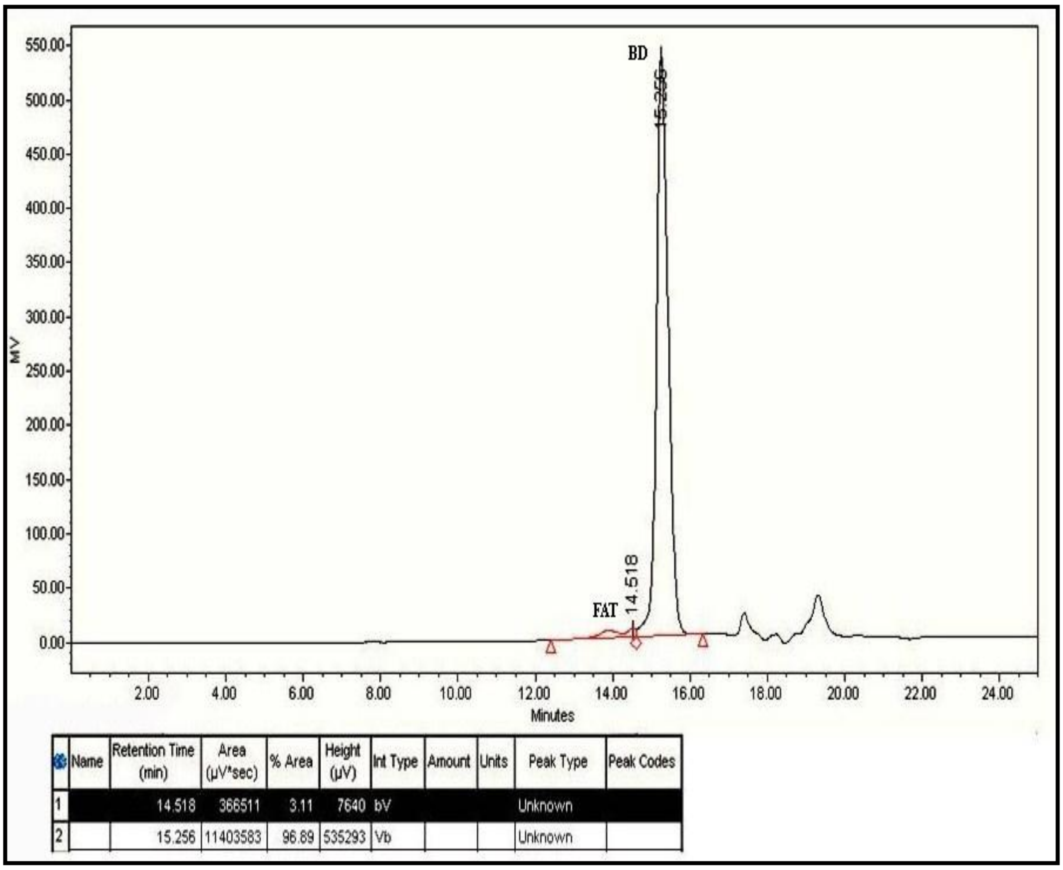


Fig. 4.8: ^{1}H NMR of biodiesel prepared by using $Ca_2Fe_2O_5$ catalyst



	Name	Retention Time (min)	Area (µV*sec)	% Area	Height (µV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		14.518	366511	3.11	7640	bV			Unknown	
2		15.256	11403583	96.89	535293	Vb			Unknown	

Fig. 4.9: GPC of product obtained by using $Ca_2Fe_2O_5$ catalyst

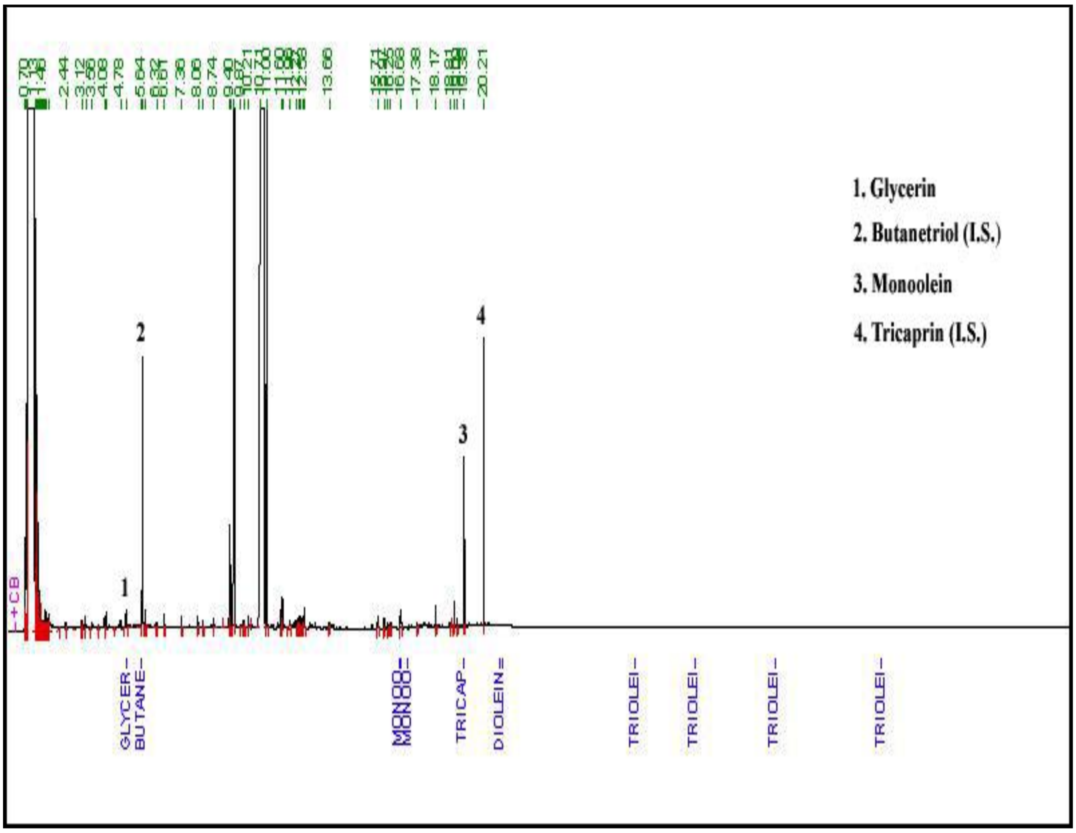


Fig. 4.10: GC of product obtained by using $Ca_2Fe_2O_5$ catalyst

4.4.3. Investigation of Synthesized the Reaction Products

Biodiesel synthesized was tested for its physico-chemical properties as per ASTM D 6751 and IS 15607 test specifications. The acid value and moisture content were measured by ASTM D 974 and ASTM D 2709 method respectively. While kinematic viscosity was determined with Cannon-Fenske viscometers following standard methods ASTM D 445. All viscosity data reported are mean of triplicate determinations. Oxidation stability was determined by Rancimat apparatus by following EN14112 method and density at 15 ^{o}C was determined by using EN14103 method.

It was observed that synthesized biodiesel meets all the specification of American Society for Testing and Materials (ASTM) and Indian Standards, except oxidation stability which can be increased by using stabilizer or antioxidants.

4.5. CONCLUSIONS

A new method of preparing $Ca_2Fe_2O_5$ catalyst for transesterification of jatropha /any other vegetable oil has been reported. The catalyst $Ca_2Fe_2O_5$ in which the calcium part is derived from natural waste raw material such as egg shells and sea shells has shown better catalytic activity than earlier reported $Ca_2Fe_2O_5$ which was prepared from pure $CaCO_3$. The reason of enhanced catalytic activity is because of porous structure of $CaCO_3$ obtained from egg shells which after fusion with Fe_2O_3 give $Ca_2Fe_2O_5$ having very large surface area. This enhancement of surface area by approximately 10 fold made available more surface and more basicity per g of the catalyst.

By conducting large number of experiments, the optimum reaction condition for maximization of conversion of jatropha oil to corresponding biodiesel was investigated. The optimized reaction conditions are 170 ^{o}C temperature, 80 bar pressure, 20:1 molar ratio of methanol to oil, 5% catalyst concentration and 3 h reaction time. Under these conditions catalyst after being used for repeated cycles of transesterification has shown excellent stability and durability. Since one of the raw material is naturally available waste its leads to lower cost and possibility to utilization of waste for preparation of catalyst which can evaluated for commercial bases in continuous production of biodiesel. The egg shells which generally spill over all the places are considered as health and environmental hazard. This new application can address this problem as well.

4.6. REFERENCES

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TRANSESTERIFICATION OF JATROPHA OIL USING Ca/Ti BASED NANOCATALYST

5.1. INTRODUCTION

Biodiesel is prepared by transesterification of triglyceride by homogeneous (acid or basic) and heterogeneous (acid, basic) catalysts using methanol as the lower alcohol. As described in earlier chapter, the heterogeneous catalysts are preferred over homogeneous catalyst for transesterification reaction. But at the same time, heterogeneous catalytic methods are usually mass transfer resistant, time consuming and inefficient. However, conversion of heterogeneous catalyst in to nanocatalysts has potential to solve the above problems due to higher specific surface areas and higher activities. The high specific surface area and large pore size are favorable for efficient contact between catalysts and substrate, which effectively improves efficiency of transesterification.

A nanocatalyst is a substance or material with catalytic properties that has at least one nanoscale dimension, either externally or in terms of internal structures [1]. Generally, catalysts that are able to function at atomic scale are in general called, nanocatalysts. Nanotechnology deals with structures sized between 1 to 100 nanometers in at least one dimension. One nanometer (nm) is one billionth or 10^{-9} of a meter.

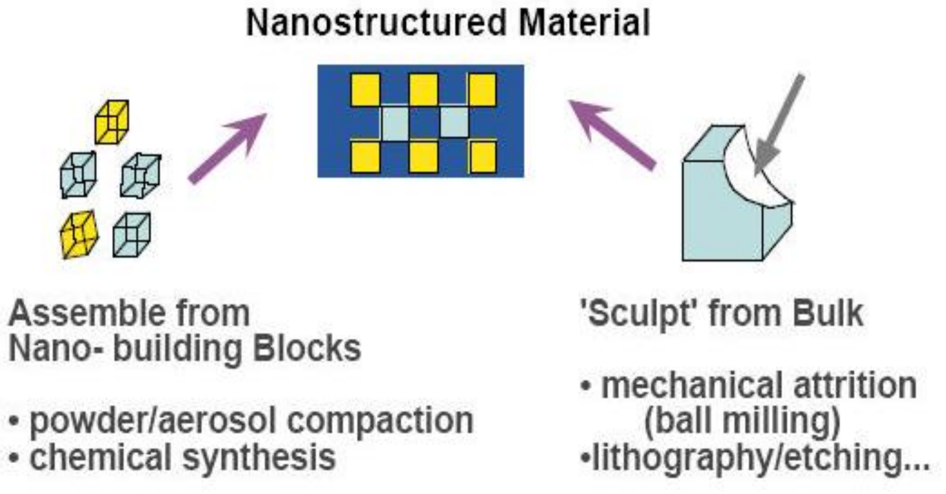
The basic role of nanocatalysts is to control catalytic reactions by optimizing the size, dimensionality, chemical composition and morphology of the active catalyst nanoparticles and requires a fundamental understanding of how catalyst particles are shaped, how they stay immobilized on metal-oxide surface, and how the nanoparticles respond to changes in the gas pressure and temperature, and finally how all these factors influence the catalytic activity.

Effectiveness of nano-particle can be gauged for their extremely small size (typically 10–80 nm) yields a tremendous surface area-to-volume ratio. At nano-scale they achieve properties not found within their macroscopic counterparts. Increasing demand of nanocatalysts are being found day by day in which involves the use of nanomaterials as catalysts for a variety of homogeneous and heterogeneous catalysis applications. Heterogeneous catalysis represents one of the oldest commercial practices of nanoscience i.e. nanoparticles of metals, semiconductors, oxides, and other compounds have been widely used for important chemical reactions.

The active sites of zeolites and other porous structures (mesoporous materials) are in nanoscale dimension (0.35-50 nm) and they are well-studied in prior to the emergence of modern nanotechnology and is itself a separate subject for discussion. The use of nanocatalysts in various fields is as depicted in Fig. 5.1.

Fig. 5.1: Benefits of nanocatalysts

Two general methodologies are adopted for generating particles of nano size. First approach is a "bottom–up" method, where the materials and catalysts are built atom-by-atom. The second, more commonly employed, approach is “top-down” where nano materials are synthesized by stripping bulk materials to nano size. Fig. 5.2 depicts the variety of techniques covering bottom up and top down approaches.



Bottom-up Methods **Top-down Methods**

Fig. 5.2: Bottom up and top down approaches

The “bottom-up” approach first forms the nano structured building blocks and then assembles them into the final material. An example of this approach is the formation of powder components through aerosol techniques and then the compaction of the components into the final material. These techniques have been used extensively in the formation of structural composite materials.

The “top-down” approach begins with a suitable starting material and then “sculpts” the functionality from the material. Mostly used top-down approach is “grinding” which is simply formation of nanostructure building blocks through controlled, mechanical attrition of the bulk starting material. These nano building blocks are then subsequently assembled into a new bulk material. High energy ball milling is one of the top-down approach for nanoparticle synthesis and has been used for the generation of magnetic, catalytic, and structural nanoparticles. The technique, which is already a commercial technology, has been considered dirty because of contamination problems from ball-milling processes. However, the availability of ceramic components and the use of inert atmosphere and or high vacuum processes have reduced impurities to acceptable levels for many industrial applications [2].

5.2. NANOCATALYSTS IN TRANSESTERIFICATION

Though there are many advantages of heterogeneous catalysts, the application of solid catalysts in transesterification reaction has been limited because of their low availability of active site for catalytic reaction where the reaction takes place [3-5]. The active surface area increases when the size of the catalysts is decreased: the smaller the catalyst particles, the greater the ratio of surface area to volume. The reaction efficiency increases with catalysts active surface area. One of the limitations with use of solid catalyst is the formation of three phases together with oil and alcohol in transesterification reaction which leads to diffusion limitations thus decreasing the rate of the reaction [6]. But at the same time, heterogeneous catalytic methods are usually mass transfer resistant, time consuming and inefficient. However conversion of heterogeneous catalyst in to nanocatalysts may solve the above problems due to its high specific surface area and high catalytic activities. The high specific surface area and large pore size are favorable for contact between catalysts and subtracts, which effectively improved efficiency of transesterification.

To overcome the limitation of diffusion controlled reaction, its essential to develop a catalyst with highly active surface with effective design and morphology. To achieve the aim, development of catalyst in submicron/nano range provides a good way because of large surface area and relatively smaller size. Due to enhanced physical [7] and chemical properties [8] nanosized materials have received much attention in chemical industry including energy sector. Some of the literatures for production of biodiesel from nanocatalysts are listed below:

Isahak et al. [9] compared the nanosized CaO over bulk CaO for transesterification of palm oil with methanol. Due to relatively greater surface area (85.0 m^2/g of nano CaO in comparison to 15.10 m^2/g of bulk CaO), having higher contact surface with reactants with nano CaO gave 94% conversion with in 2.5 h reaction time at 65 ^{o}C at 1:15 molar ratio of oil to methanol, 2.5 wt% catalyst, whereas 90% conversion for bulk CaO under same condition was obtained. Nano-CaO was less emulsion prone than bulk CaO in separation step of product and it is easily removed by addition of citric acid.

Reddy et al. [10] studied nanocrystalline CaO (NC-CaO) as catalyst for biodiesel production from soybean oil (SBO) and poultry fat with methanol at room temperature. The specific surface area of NC-CaO was 90 m^2/g whereas surface area of commercial CaO was 1 m^2/g. Deactivation was observed after 8 cycles with SBO and after 3 cycles with poultry fat. 99% conversion was obtained with 1:27 molar ratio of oil to methanol, 0.012 wt% nanocatalyst content in 24 h. Whereas, under same condition laboratory grade CaO gave only 2% conversion in the case of SBO and there was no observable reaction with poultry fat. Addition of co-solvent THF enhanced the transesterification reaction and reaction was complete with in 6 h under same reaction conditions with SBO.

Wen et al. [11] reported use of KF/CaO nano catalyst in Chinese tallow seed oil for biodiesel production. KF/CaO nano catalyst was prepared by using impregnation method and calcined at 600 ^{o}C for 4 h with 109 m^2/g specific surface area and 97 nm average pore size. Reaction was performed at 65 ^{o}C, 1:12 molar ratio of oil to methanol and 4 wt% catalysts content, in 2.5 h reaction time and 96.8% yield was obtained. The catalyst sustained its activity after 16 cycles and gave 91% yield. The effect of acid values on biodiesel yield was also studied and they found that KF/CaO catalyst had good anti-acidic ability and 80 % of biodiesel yield was achieved when the acid values of oil was less than 7 mg KOH/g oil. They also analyzed free Ca^{2+} concentration in biodiesel determined by atomic absorption spectroscopy and observed that KF/CaO catalyst is more stable than CaO in reaction system as concentration of dissolved Ca^{2+} from KF/CaO and CaO catalysts were 31.6 and 150 mgL^{-1}, respectively.

A mesoporous nanosized KF/CaO-MgO catalyst was studied by Wang et al. [12]. They prepared catalyst by used CaO and MgO as a complex carrier via coprecipitation method and compared the catalyst activity with CaO and KF/CaO catalyst. The catalyst performed the highest activity (95% biodiesel yield), when mass ratio of KF to CaO–MgO is 0.25, calcination temperature 600 ^oC for 3 h, under 3% catalyst amount, 1:12 molar ratio of rapeseed oil to methanol at 70 ^oC for 3 h. They studied leaching effect and observed that addition of MgO can block the leach of Ca ion in the transesterification, which would increases the catalytic activity of CaO. It was also found that KF/CaO-MgO catalysts resisted higher acidity compared with KF/CaO and CaO catalysts. KF/CaO-MgO catalyst gave biodiesel yields exceeding 80% when acid value was less than 10 mg KOH/g oil, while biodiesel yields were less than 80% when acid value was less than 7 mg KOH/g oil and 2 mg KOH/g oil for KF/CaO and CaO catalysts respectively. It was examined that 90% biodiesel yield obtained when KF/CaO-MgO catalyst was recycled six times.

Wang et al. [13] used nano-MgO catalyst for the transesterification of soybean oil with supercritical/subcritical methanol. Reaction was completed only in 10 min due to the lower activation energy (75.94 KJ/mol) at 250 ^oC temperature, 3 wt% catalyst, 1:36 oil to methanol ratio and 1000 rpm in cylindrical autoclave.

Qiu et al. [14] utilized ZrO_2 loaded with $C_4H_4O_6HK$ as a solid base nano catalyst for transesterification of soybean oil with methanol to biodiesel. The catalyst was prepared by impregnation method where zirconium dioxide was impregnated with potassium acid tartrate compound solution and standing 24 h. After impregnation, water was removed in a rotary evaporator at 100 ^oC and then calcined at 512 ^oC for 5 h. The BET surface area and pore volume of ZrO_2 decreased from 7.04 m^2/g and 0.07 cm^3/g to 3.73 m^2/g and 0.03 cm^3/g respectively when $C_4H_4O_6HK$ was loaded on to the support. The pore diameters of ZrO_2 and Zr-0.65–512 were 17.59 and 17.16 nm and the basic strength was stronger with $H\_$ in the range of 9.8–15.0. The reaction was carried out at 60 ^oC, 1:16 molar ratio of oil to methanol, 6.0% catalyst for 2 h and 98.03 % yield was obtained. It was found that the nanocatalyst had granular and porous structures with particle sizes of 10–40 nm which was confirmed by TEM. The catalyst was maintained its activity and reused 1-5 times and biodiesel yield slightly decreased from 98.03 % to 89.65 % in leached K from 15 to 4 ppm. It was due to leaching behavior generated the largest amount of methoxide potassium as the homogeneous catalyst, thus promoting biodiesel yield due to the superior mass transfer for this homogeneous catalyst.

Calcium oxide impregnated with 1.75 wt% of lithium has been reported as solid catalyst for the transesterification of karanja (3.4 wt% FFA) and jatropha oil (8.3 wt% FFA) with methanol to produce biodiesel. The catalyst (X-Li-CaO) was prepared by CaO suspended in deionized water and aqueous solution of $LiNO_3$ of desired concentration was added and then slurry was stirred for 2 h followed by evaporated to dryness, and heated at 120 ^oC for 24 h. 1.75-Li-CaO catalysts were prepared by impregnating 1.75 wt% of lithium using 1.739 g of $LiNO_3$. The Basic strength of the catalysts was $15.0 < H\_ < 18.4$. The SEM study revealed that the formation of catalyst in hexagonal and oval shaped particle and average sizes of particles found was 2 mm. The TEM image reveals that these particles are made up of further smaller rod shaped and hexagonal particles with an average size of 50-70 nm. The optimum reaction condition of transesterification of karanja and jatropha oils was achieved in 1 and 2 h, respectively at 65 ^oC with 1:12 molar ratio of oil to methanol and 5 wt% (catalyst/oil, w/w) of catalyst which results >99% conversion of oils to fatty acid methyl esters. It was found that the catalyst was non-recyclable, which was the major drawback of this catalyst [15].

Hsiao et al. [16] evaluated the catalytic efficiency of nano CaO (purchased from Aldrich Co. Ltd., USA) as a heterogeneous base catalyst in the transesterification of soybean oil to biodiesel, assisted by microwave irradiation. They were found that microwave irradiation is more efficient than the conventional bath for biodiesel production. The 96.6% conversion was achieved at 60 ^oC, 3.0 wt% of catalyst concentration with 1:7 oil/methanol molar ratio in 1 h reaction time.

Nano-magnetic catalyst $KF/CaO–Fe_3O_4$ was prepared by a convenient co-precipitation method and was investigated in the methanolysis of stillingia oil. For preparation of Nano-magnetic catalyst, Fe_3O_4 and MOs (MgO, CaO and SrO) was mixed and then the mixture was completely dipped in aqueous solution of KF with different mass in range of 5.0–45.0 g (ca. 5–45 wt% of KF loading) and subsequently dried at 105 ^oC for 24 h followed by calcined in temperature range of 300-800 ^oC. It was found that the nano-magnetic solid base catalyst with 25 wt% KF loading and 5 wt% Fe_3O_4, calcined at 600 ^oC for 3 h, shows the best activity. For KF/ CaO-Fe_3O_4, the biodiesel yield is improved from 78% to 95% when the KF loading increases from 15 wt% to 25 wt.%. When the KF loading is beyond 25 wt.%, however, the activity of catalyst is decreased with the increase of loading of KF, and the biodiesel yield is only 81.1% at 45 wt.% KF loading. This is probably due to the fact that the excessive KF covers the active sites of catalyst surface, resulting in the decrease of catalytic activity. The catalyst has a unique porous structure with an average particle diameter of ca. 50 nm and a ferromagnetic property with little remanence and coercive force. The BET surface area of catalyst was 20.8 m^2/g. The reaction was carried out at 65 ^oC with a oil to methanol molar ratio of 1:12 and a catalyst concentration of 4 wt.%, the biodiesel yield exceeds 95% at 3 h of reaction time. It was also found the catalyst was able to be reused up to 14 times without much deterioration in its activity. Furthermore, the catalyst recovery is more than 90% [17].

In another work, Deng et al. [18] used hydrotalcites nanocatalyst as a solid base catalyst for methanolysis of jatropha oil for conversion of biodiesel in the ultrasonic reactor. Hydrotalcite particles were prepared in an ultrasonic reactor by coprecipitation of aqueous nitrate solutions of Mg and Al using urea as precipitating agent, and subsequently with MHT (microwave-hydrothermal treatment) followed by calcined at 500 ^oC for 6 h. The catalyst was high surface area of 218 m^2/g with pore volume and pore diameter of 0.17 cm^3/g and 3.9 nm, respectively. The basic sites (H_) of catalyst with were in the range of 7.2-9.8 and the other sites with H_ were in the range of 9.8-15. Biodiesel yield increased from 77.7% to 94.5% as ultrasonic power rose from 180 to 210 W. However, as the ultrasonic power increased further from 210 to 270 W, biodiesel yield dropped from 94.5 to 76.9%. The possible reason was that methanol was vaporized that it was seen fog formed on the liquid surface at higher ultrasonic power. The optimum reaction conditions of transesterification of jatropha oil at 45 ^oC, 1.0 wt % catalyst concentration with oil to methanol ratio of 1:4 and ultrasonic power of 210 W. After 1.5 h reaction time, biodiesel yield of 95.2% was achieved. It was found that the catalyst was reused for 8 times.

5.3. PRESENT WORK

The aim of present research work is to prepare nanosized $CaTiO_3$ based heterogeneous catalyst from low value abundant natural raw material by top down approach. The catalyst activity was evaluated in transesterification of jatropha oil and compared with micron sized calcium titanate in various parameters such as catalyst concentration, methanol to oil molar ratio, temperature, pressure etc. The catalyst activity and durability over repeated cycles was also evaluated. The purpose of the development of nanosized catalyst is to increase the specific surface area as higher surface area of catalyst, increases the reaction rate.

In the experimental work, submicron sized calcium titanate was prepared and characterized. The synthesis of biodiesel from non-edible jatropha oil using methoxy coated nanosized calcium titanate ($CaTiO_3$) based heterogeneous catalysts was studied and its catalytic activity was compared with bulk $CaTiO_3$. Scanning electron microscopy, powder X-ray diffraction (XRD), dispersive Raman spectroscopy, BET surface area, pore size and average pore volume were employed to characterize the catalyst. The catalyst activity was also evaluated over repeated cycles to validate catalyst durability. The produced biodiesel has been evaluated for various physico-chemical characterization as per IS/ASTM standards. Our flow of work is detailed as below:

- Preparation of nanosized $CaTiO_3$ catalyst and then characterization of synthesized catalyst such as TGA, XRD, IR, surface area, average pore size, pore volume, SEM and basic strength.
- Synthesis and physico-chemical properties of biodiesel.
- Effect of catalyst concentration, molar ratio of oil to methanol, temperature and effect of time etc. using nano sized $CaTiO_3$ heterogeneous catalyst in high pressure reactor.
- Comparative catalytic activity evaluation of bulk $CaTiO_3$ and nanosized $CaTiO_3$ catalyst.

- Evaluation of catalyst activity over repeated cycles to validate catalyst recyclability.
- Physico-chemical characterization of synthesized biodiesel as per IS/ASTM standards.

5.3.1. Reagents and Materials

Commercial non-edible-grade jatropha oil having acid value (8.0 mgKOH/g) and viscosity at 40 ^{o}C (37.18 cSt) was taken from the Surendra Nagar, Gujarat (jatropha plantation carried out by Indian Oil Corporation) and used without further purification. Other chemicals viz. titanium oxide (99%) (SDS, India), pseudoboehmite, nitric acid (85%) (CDH, methanol (99.5%), hexane analysis grade solvents (Merck, India) were of commercial/ lab grade.

Eggshells are collected from local market. The eggshells were cleaned to remove protein and other interference substances by washing several times with warm water. Washed shells were dried overnight in oven at 110 ^{o}C to remove traces of water.

5.3.2. Catalyst Preparation

Preparation of Micron Sized $CaTiO_3$ Catalyst

The dried egg shells was grounded to fine powder and sieved through 150 micron mesh followed by calcined in muffle furnace at 550 °C for 3 h before use. After calcined, it was obtained as grey solid in 94.75% yield. XRD results confirmed that the composition of calcined eggshell mainly consisted of calcite-calcium carbonate (Fig. 3.5).

For preparation of $CaTiO_3$ catalyst, the calcined egg shell (source of $CaCO_3$) and TiO_2 in ratio of 1:1.2 (25 g $CaCO_3$ and 24 g TiO_2) were milled for 15-20 minutes. The mixture was calcined at 550 ^{o}C for 3 h and then at 1050 ^{o}C for 3.5 h to obtain $CaTiO_3$. The obtained catalyst composition was checked by XRD and stored in dry container in desiccator. The formed catalyst was extruded by mixing with alumina binder (pseudoboehmite) in ratio of 3:1 (w/w) and using 2.5% (v/v) solution of nitric acid as peptizing reagent. The final mixture was extruded on an extruder (Collin E 30 P) to obtain cylindrical shaped 1/10 inch diameter catalyst.

Preparation of Nano Sized $CaTiO_3$

Milling experiments were done using Retsch Planetary Ball Mill (Model: PM 200). In the milling studies, Tungsten carbide vessel and beads were used to minimize impurity to the product system.

In all the milling experiments, calcium titanate powder (without binder) was taken in the vessel and filled up to 1/3 of its volume along with excess methanol. The milling experiments were conducted in two steps as per the sequence detailed below.

- Milling with 1.6 mm tungsten carbide (TC) ball for 2 h at 1000 rpm followed by sieving.
- and further milling with 0.5 mm TC ball for 2 h at 1000 rpm and sieving.

After milling through planetary ball mill excess methanol was removed using vacuum at room temperature and dried. The prepared powder was washed several times with methanol and dried under vacuum. The prepared product was analyzed through surface and spectroscopic technique.

5.3.3. Catalyst Characterization Techniques

The catalyst was characterized by the following analytical techniques and by adopting the conditions as described earlier in this thesis.

- X-ray Diffraction (XRD)
- Fourier Transform Infrared Spectroscopy (FTIR)
- Dispersive Raman Studies
- Thermogravimetric Analysis (TGA)
- Particle Size Analysis
- Surface Area, Average Pore Size and Total Pore Volume
- Scanning Electron Microscopy (SEM)
- Basic Strength

5.3.4. Biodiesel Preparation Process

Transesterification reactions of Jatropha oil were carried out in high pressure reactor (HPR) of capacity 1 lit. This equipment was operated in a manner as described earlier. Catalyst durability test was performed by carrying out repeated transesterification reactions employed the recovered catalyst. Biodiesel synthesized was tested for its physico-chemical properties as per ASTM D-6751 test method.

5.4. RESULTS AND DISCUSSIONS

5.4.1. Catalyst Characterization

X-ray Diffraction (XRD)

For micronsized $CaTiO_3$, XRD showed characteristic peaks of $CaTiO_3$ and minor peak of TiO_2 (rutile) indicating conversion of calcium carbonate to calcium oxide and its subsequent reaction with TiO_2 to form desired $CaTiO_3$ complex. However some traces of calcium dialuminate; Grossite ($CaAl_4O_7$) was also observed by XRD (Fig. 5.3).

Whereas for nanosized $CaTiO_3$, XRD shows characteristic peak of $CaTiO_3$ and minor peak of TiO_2 indicating conversion to $CaTiO_3$ complex and very negligible amount of $CaAl_4O_7$ was observed. The XRD data of both the compounds are presented in Fig. 5.3.

The intense peaks of calcium titanate ($CaTiO_3$) at 2θ~23.2, 33.1, 39.1, 40.6, 40.9, 47.5, 58.9, 59.3 and 69.5 to the d value of 3.83, 2.70, 2.30, 2.21, 2.20, 1.91, 1.56, 1.55 and 1.35 respectively. The titanium oxide peaks were observed at 2θ~27.4, 36.1, 41.2, 54.3 and 54.6 to the d value of 3.25, 2.48, 2.18, 1.68 and 1.67 respectively. However, calcium dialuminate peak was observed at 2θ~25.4 to the d value of 3.51.

The XRD results revealed that the peak of $CaTiO_3$ which represents (121) plane was found highly crystalline, whereas in the case of nano sized $CaTiO_3$, the peak has been broadened and less intense suggesting amorphous nature of the power.

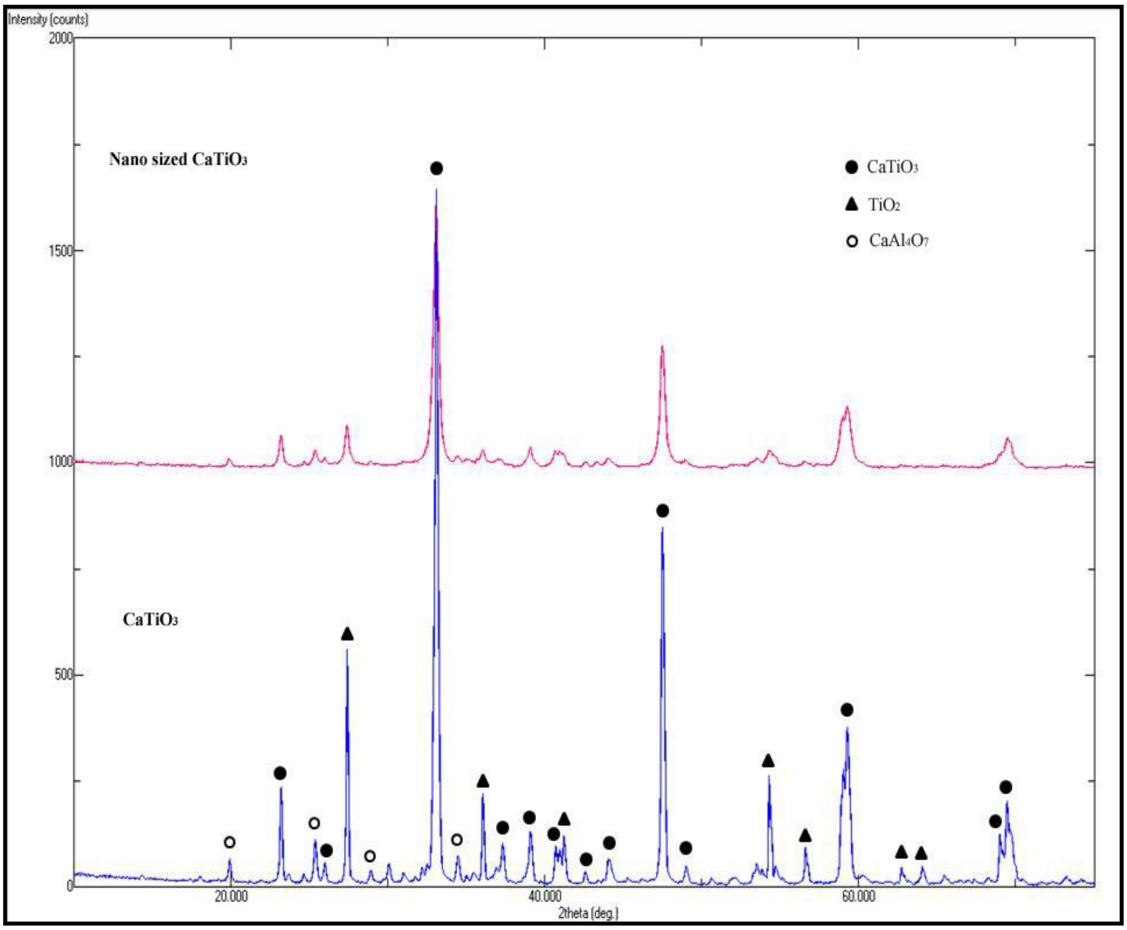


Fig. 5.3: XRD of micron and nanosized Ca-Ti catalyst

Fourier Transform Infrared Spectroscopy (FTIR)

In the FTIR spectra of micron sized $CaTiO_3$ and nano sized $CaTiO_3$ (Fig. 5.4), the band associated with Ti-O bond are detected in the range of 1050 cm^{-1}. The characteristic peaks for $CaTiO_3$ was found at 576 cm^{-1} and that of ideal cubic standard of $CaTiO_3$ was detected at 447 cm^{-1} and this matched well with reference literature [19].

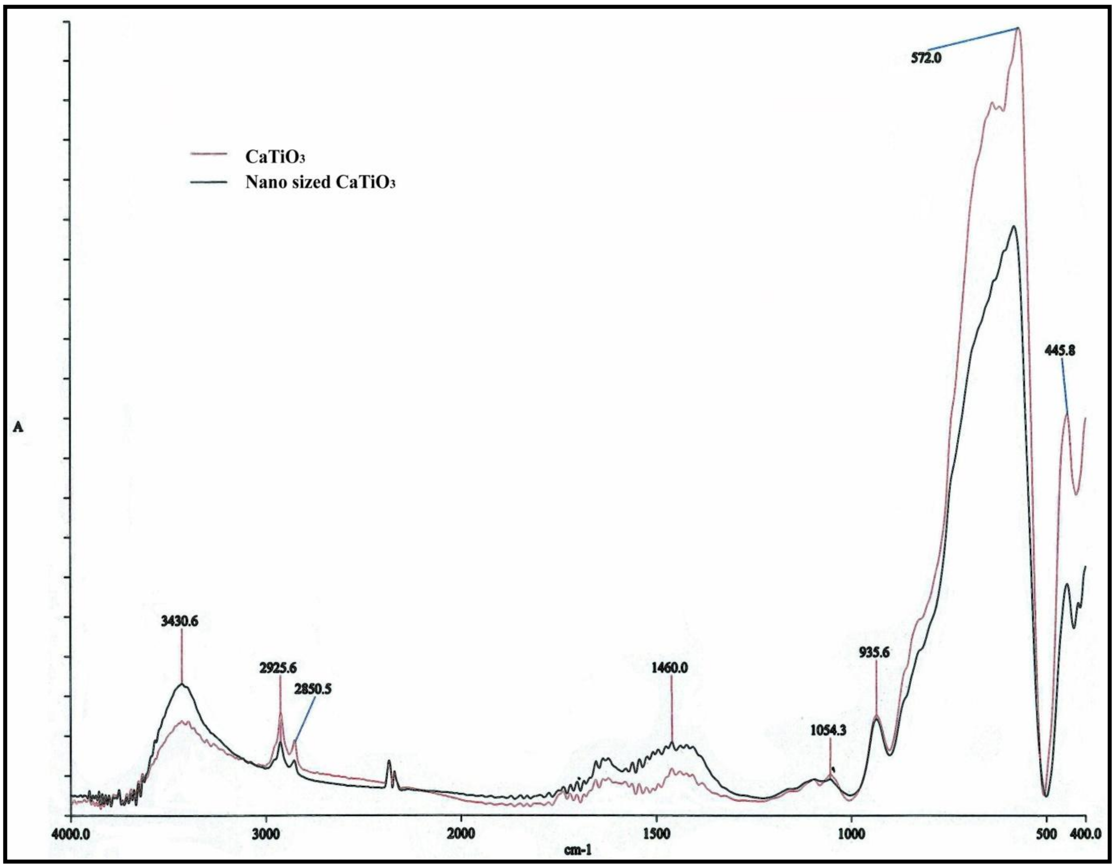


Fig. 5.4: IR Spectra of micron and nanosized Ca-Ti catalyst

Dispersive Raman Studies

Room temperature dispersive Raman spectrum of nanosized $CaTiO_3$ is shown in Fig. 5.5. The tentative band assignments for the sample are given in Table 5.1 and its comparison with the literature [20]. It is possible that many of the predicted bands are hidden behind intense bands, may overlap on the many modes having very low polarizabilities so as to prevent their bands from being seen in spectrum. The band assignments comparison was made empirically on the basis of available literature.

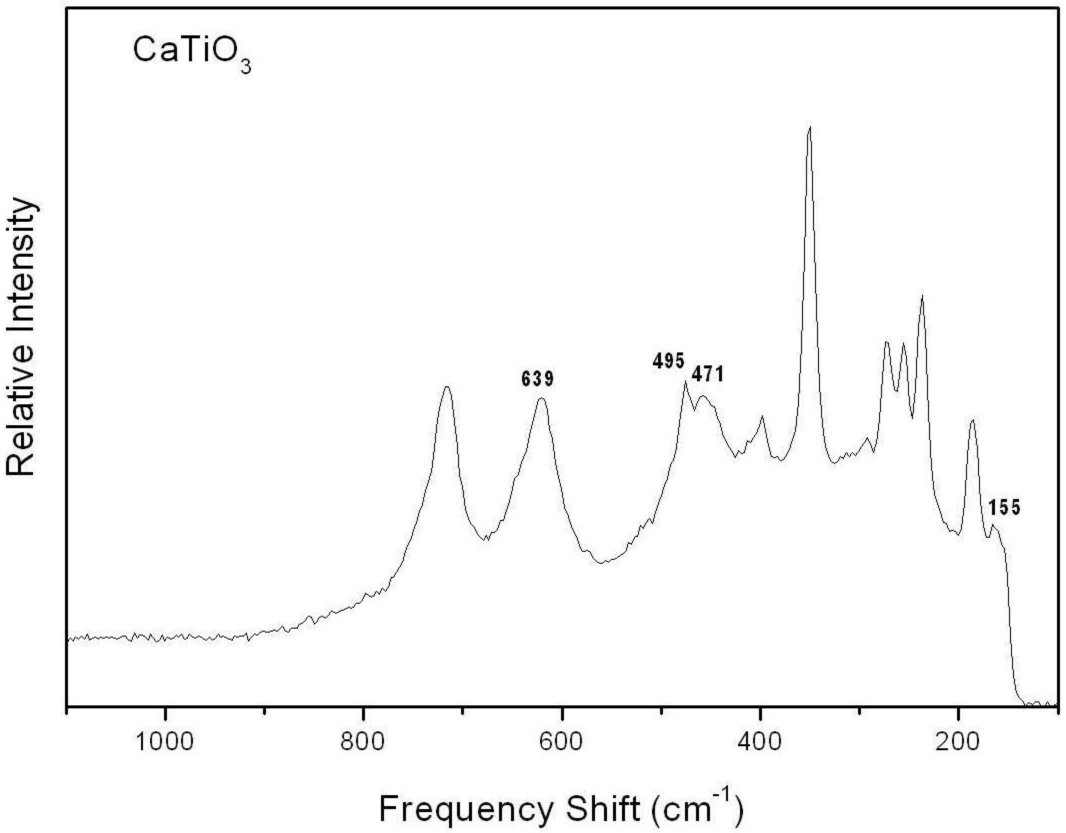


Fig. 5.5: Raman Spectra of nanosized Ca-Ti catalyst

Table 5.1: Tentative band assignments for CaTiO$_3$

Observed energy shift (cm^{-1})	Band assignments
639	Ti-O symmetric stretching
495	Ti-O$_3$ torsional mode
471	Ti-O$_3$ torsional mode
155	Ca-TiO$_3$ lattice mode

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis of synthesized micronsized CaTiO$_3$ depicts two stages of weight loss (Fig. 5.6). First stage of weight loss (<1%) possibly due to initial decomposition at temperature 100 to 200 °C involving loss of water. In temperature range of 600-800 °C the weight loss (<0.5%) is due to transformation of unreacted $CaCO_3$ present in the calcium titanate with loss of carbon dioxide.

TGA depicts three stage weight losses for nanosized $CaTiO_3$ (Fig. 5.6). Up to temperature of 200 ^oC, weight loss may be due to loss of water and methanol (2%). At temperature of 200-400 ^oC, the weight loss is due to decomposition of calcium methoxide, which is present on the surface of the nanosized calcium titanate as a protecting layer. At 600-800 ^oC, the weight loss indicate thermal decomposition of unreacted $CaCO_3$ present in the original sample to form CaO with loss of CO_2.

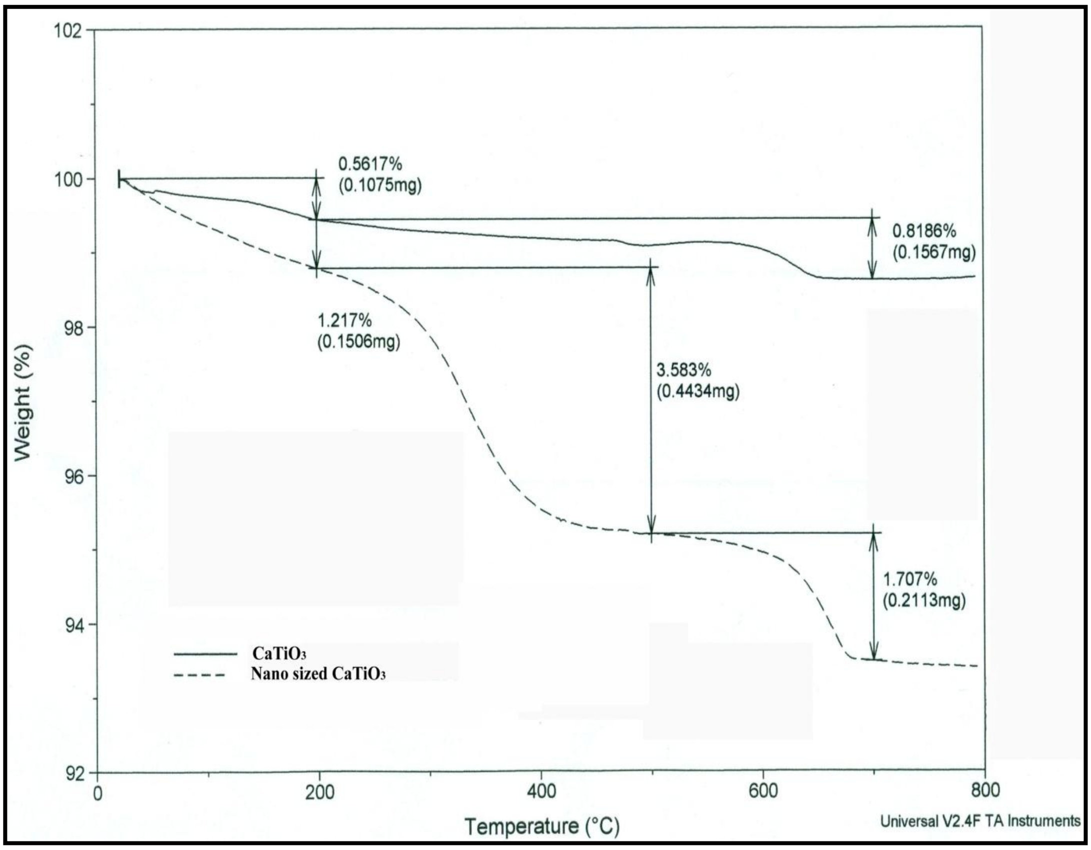


Fig. 5.6: TGA of micron and nanosized Ca-Ti catalyst

Particle size Analysis

The average particle size reduced to 740 nm after processing with 1.6 mm beads from initial particle size of more than 10µ and further reduced to 280 nm after processing with 0.5 m beads. The particle size distribution is shown in Fig. 5.7. The nano sized calcium titanate powder prepared is slightly polydisperse having FWHM of 35 nm.

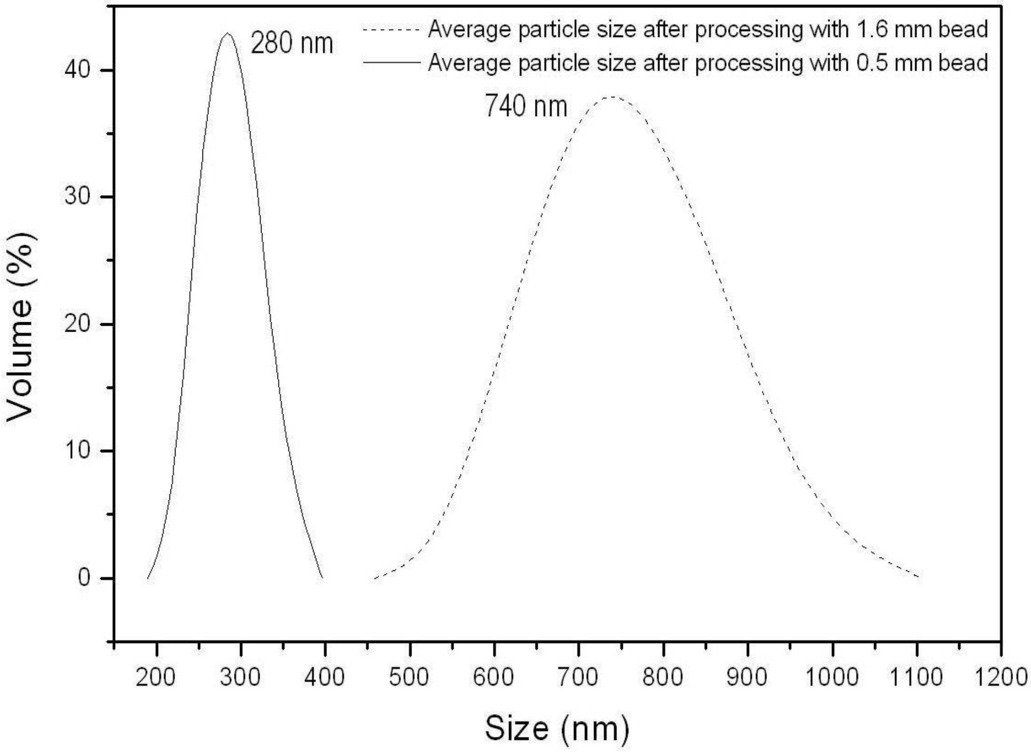


Fig. 5.7: Particle Size of nanosized Ca-Ti catalyst

Surface Studies

The BET surface area was increased from 7.59 m^2/g to 32 m^2/g after conversion of $CaTiO_3$ to nanosized $CaTiO_3$. The average particle size and surface area values are in tandem with each other. Average pore size of $CaTiO_3$ and nanosized $CaTiO_3$ were 70 and 91 Å respectively. While, total pore volume of $CaTiO_3$ and nanosized $CaTiO_3$ were 0.01 and 0.04 cm^3/g respectively.

Scanning Electron Microscope Studies

The Scanning electron micrograph of $CaTiO_3$ and nanosized $CaTiO_3$ catalysts are depicted in Fig. 5.8 A and 5.8 B. The micrograph displays more regular shape particles of nanosized $CaTiO_3$. The average particle size of $CaTiO_3$ is found to be around 218-266 µm. However, the average particle size of nanosized $CaTiO_3$ is coming around 94-122 nm. The agglomerates are spherical in shape and having uniform distribution.

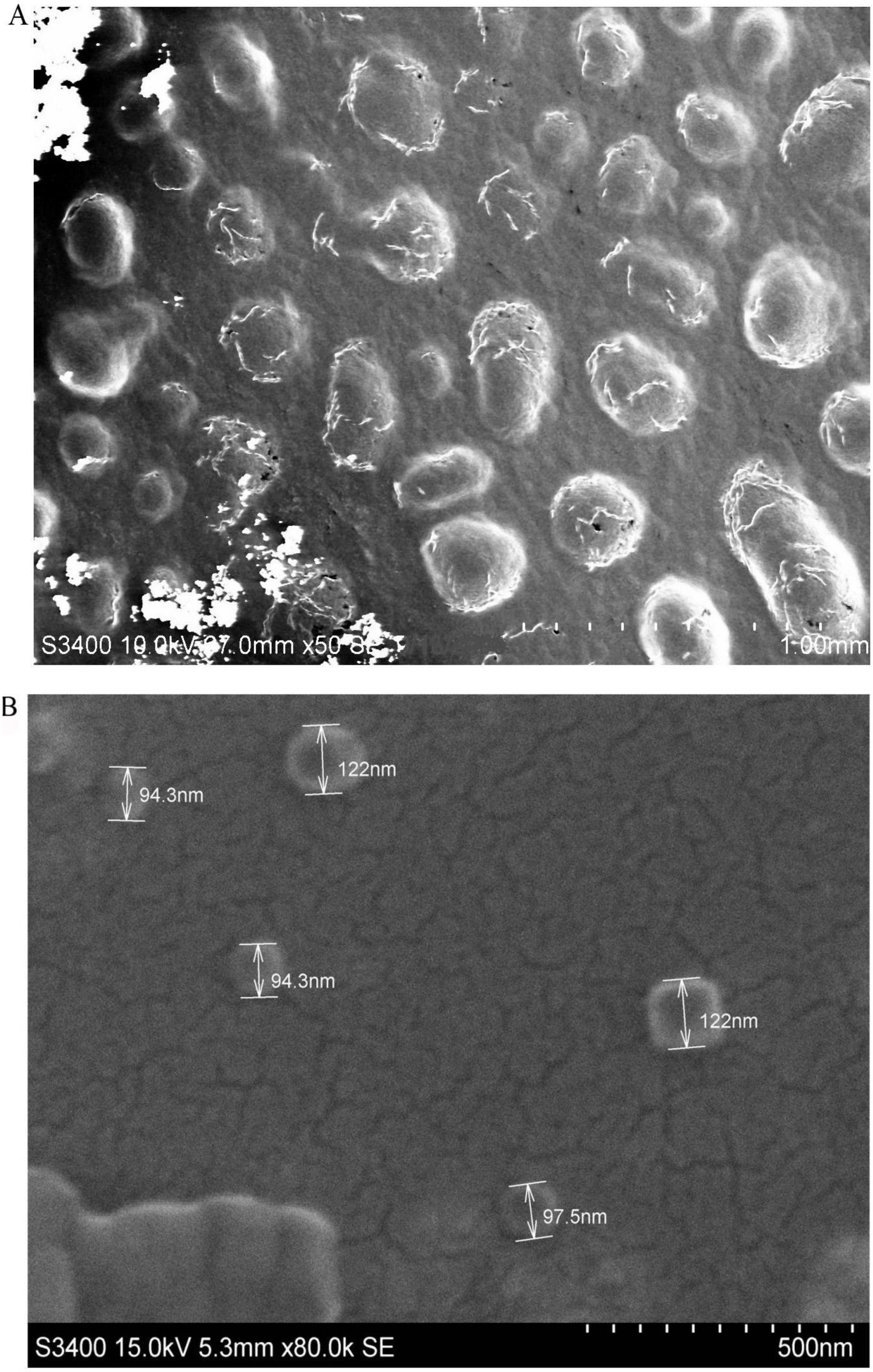


Fig. 5.8: SEM of micron and nano sized Ca-Ti catalyst. A: SEM of micron sized Ca-Ti catalyst; B: SEM of nanosized Ca-Ti catalyst

Basic Strength Studies

The catalyst changed the colour of bromothymol blue (H_=7.2) from green to blue but failed to change the colour of phenolphalein (H_=9.3). Thus basic strength of the nanosized $CaTiO_3$ was found to be 7.2 < H_ <9.3. Table 5.2 summarizes the surface area, pore size, pore volume and basic strength of synthesized nano sized and micron sized Ca-Ti catalysts.

Table 5.2: Characteristics of Ca-Ti based catalyst

Catalyst Characterization	$CaTiO_3$ (micronsized)	$CaTiO_3$ (nanosized)
BET Surface Area (m^2/g)	7.59	32
Pore Size (Å)	70	91
Pore Volume (cm^3/g)	0.01	0.04
Basic Strength	7.2<H_<9.3	7.2<H_<9.3

5.4.2. Reaction Kinetic Study of Ca-Ti based Catalyst for Biodiesel Synthesis

Effect of Catalyst Concentration on Biodiesel Yield

The biodiesel yield vs catalyst concentration plot is as illustrated in Fig. 5.9. The experiments were carried out with catalyst concentrations of 3, 5, 7, 10 and 12 wt% of oil with 1:20 molar ratio of oil and methanol at 170 ^oC temperature and 80 bar pressure. It was observed that at low catalyst concentration of 3 wt%, reaction rates were insufficient having low yield of biodiesel (>65%). However with nano sized catalyst there is an enhancement in biodiesel yield by more than 20%. It was also observed that the reaction time decreased with the increase in catalyst concentration for both nano and micron sized catalyst. At all the catalyst concentrations, there was a significant reduction in time for the transesterification reaction with nanosized catalyst.

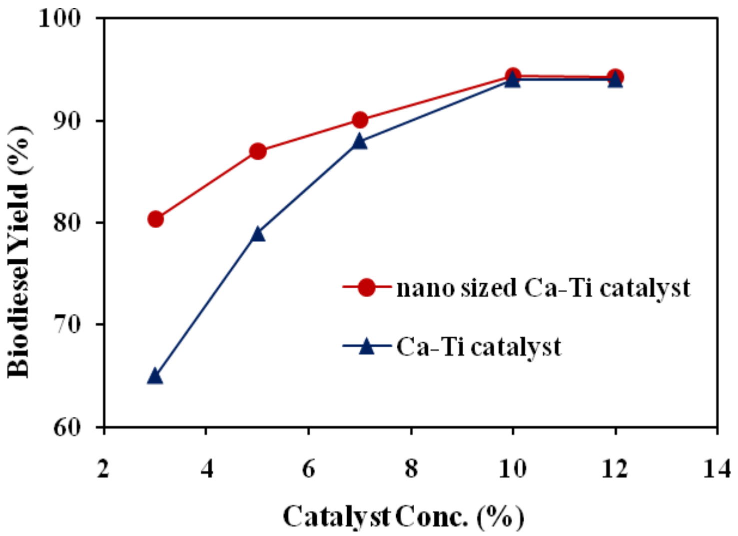


Fig. 5.9: Effect of catalyst concentration on biodiesel yield

Effect of Catalyst Concentration on Reaction Time

The result of effect of variation of the catalyst concentration on the reaction time is illustrated in Fig. 5.10. The maximum biodiesel yield (95%) was obtained at catalyst concentration of 10 wt% at a reaction time of 3 h for $CaTiO_3$ catalyst whereas it was obtained in 2 h using nanosized $CaTiO_3$ catalyst. At higher catalyst concentration of > 10 wt% not much improvement in biodiesel conversion was observed. It can be also observed that the optimum catalysts concentration (for both catalysts) for transesterification of jatropha oil to biodiesel is considered to be around 10%.

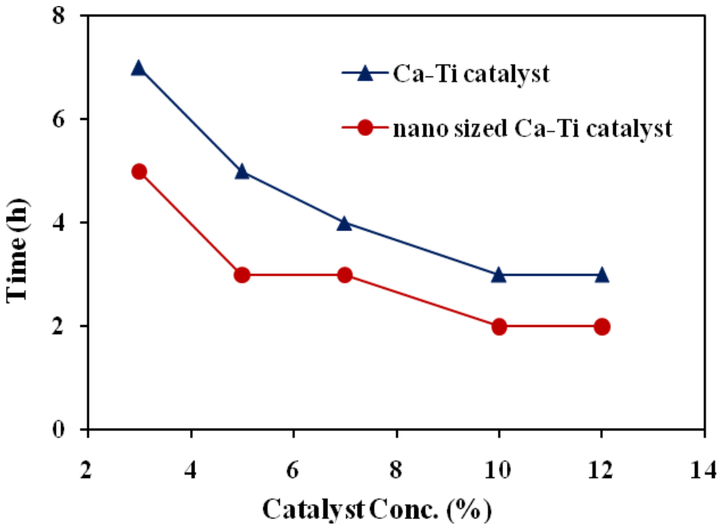


Fig. 5.10: Effect of catalyst concentration on reaction time

Effect of Methanol to Oil Ratio on Biodiesel Yield

The effect of variation of ratio of vegetable oil to methanol (wt/wt) ratio was studied under 170 °C temperature and 80 bar pressure with 10 wt% catalyst concentration. Experiments were carried out with molar ratio of 1:5, 1:10, 1:15, 1:20, 1:25, and 1:30 of oil to methanol. At a molar ratio of MeOH to oil at 5, the nanosized catalyst showed 20% more conversion than the normal $CaTiO_3$ catalyst. The results show that at 1:20 molar ratio, the maximum biodiesel conversions wcere obtained and after that the reaction progress remains constant. The result for the effect of oil to methanol ratio on biodiesel yield is shown in Fig. 5.11.

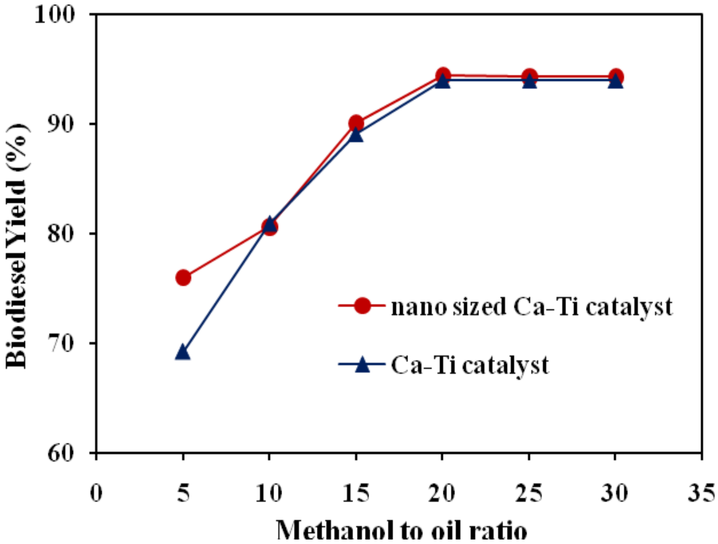


Fig. 5.11: Effect of oil to methanol ratio on biodiesel yield

Effect of Variation of Methanol to Oil Ratio on Reaction Time

Fig. 5.12 shows the effect of different molar ratio of oil to methanol on reaction time. In this study, higher biodiesel yield was obtained by employing an excess methanol in shorter periods for both the catalysts. However at all methanol concentrations, the nano sized catalyst could complete the reaction much faster than that of normal sized $CaTiO_3$.

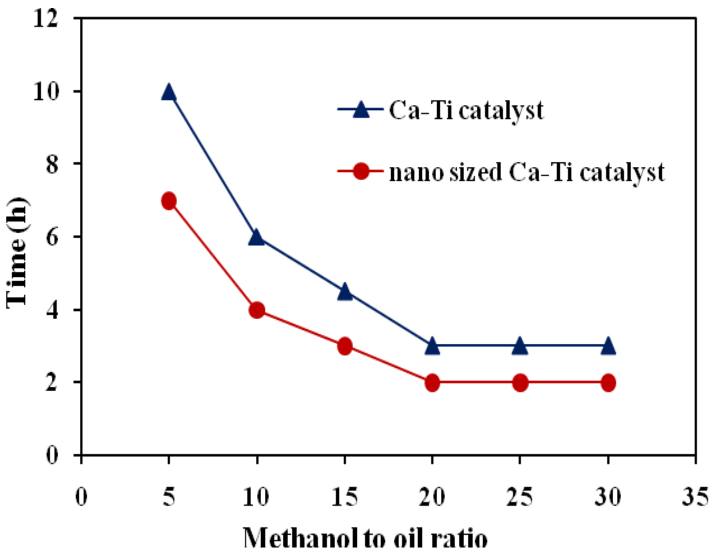


Fig. 5.12: Effect of oil to methanol ratio on reaction time

Catalyst Stability and Reusability

Nanosized catalyst durability was studied by repeating the transesterification reaction of jatropha oil for 4 times using recovered catalyst under optimized conditions of T=170 ^{o}C, P=80 bar, oil: methanol molar ratio of 1:20, catalyst concentration of 10 wt% and reaction time of 3 h. After every use, catalysts were filtered, washed with methanol and dried at 100 ^{o}C for 1 h. There is no significant weight loss of the catalyst in the reaction and XRD patterns show no change after repeated use establishing the durability of nano $CaTiO_3$ catalyst (Fig. 5.13).

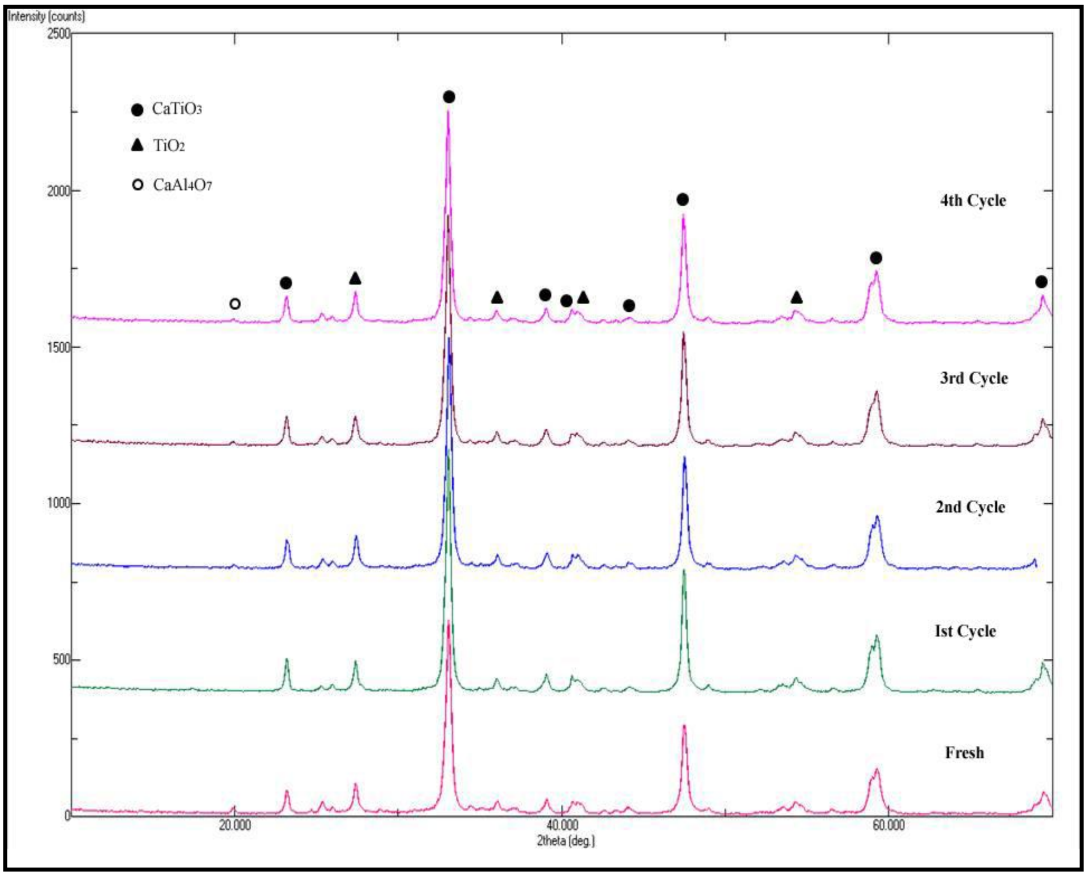


Fig. 5.13: Effect of recyclability on XRD of nanosized catalyst

5.4.3. Evaluation of Synthesized Biodiesel

The biodiesel prepared by transesterification of jatropha oil using nano sized $CaTiO_3$ meets both ASTM 6751 and IS 15607 standards.

5.5. CONCLUSIONS

A convenient method has been reported for preparation of nano sized $CaTiO_3$. Nano based calcium titanate catalyst has been prepared through top down approach and characterized for spectral, thermal and surface properties. The synthesis of fatty acid methyl ester (FAME) from jatropha oil has been investigated using nano $CaTiO_3$ as catalyst in compared to normal and conventional $CaTiO_3$. Nano $CaTiO_3$ was found to be effective in terms of higher yields and shorter reaction times due to its large surface to volume ratio. The prepared nano based $CaTiO_3$ catalyst was also found to be stable and reusable. Easy preparation method of nanosized $CaTiO_3$ can lead to new industrial procedure for large scale preparation of biodiesel.

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BULK PREPARATION, CHARACTERIZATION AND TESTING OF $CaTiO_3$, $Ca_2Fe_2O_5$ IN PILOT UNIT

6.1. INTRODUCTION

Several heterogeneous catalysts, specially of mixed metal oxide type, have shown good promise for the transesterification of vegetable oils. Their cumbersome preparation methods and cost of the catalyst have been areas of main concern. This is preciously the reason that heterogeneous catalyzed transesterification is yet to see large scale commercial application. Efforts by various research groups [1-4] concentrated on developing heterogeneous catalyst which are easier to prepare, relatively inexpensive, made from easily available raw material and moreover are stable and have long catalyst life.

A quick scan of the published literature indicated that mixed metal oxide of calcium and titanium and that of calcium and iron are one of the best heterogeneous catalyst which give high yields of biodiesel by transesterification of the vegetable oils. However, their methods of preparation were still cumbersome and raw materials were rather expensive. In earlier chapters, the synthesis of calcium titanate and calcium ferrite has been successfully achieved in batches at the laboratories scale. The calcium part has been derived from eggshells and seashells which are abundantly available and are waste natural raw material. Complete method of synthesis of $CaTiO_3$ and $Ca_2Fe_2O_5$ has been described. The catalysts have been characterized by XRD, FT-IR and TGA. To get extra confidence for integrity of prepared catalyst, these were compared with calcium titanate or calcium ferrite which was prepared from normal calcium carbonate.

Large number of systematic experiments was performed in a pressure autoclave and the effect of variation of reaction temperature, catalyst concentration, methanol to oil ratio and reaction time was studied. The optimum conditions for maximum conversion of jatropha oil in to the corresponding biodiesel were arrived that. The catalyst life i.e. recyclability of the catalyst was also studied.

In order to evaluate the performance of these catalysts and to see the suitability for commercial scale operation, the data obtain from the pressurized autoclave experiment may not be useful directly. The major problems in an autoclave conditions are the effective mass transfer of catalyst in to reaction media. Though the experiments was done to good stirring conditions, still vast differences in the density of catalyst and reaction media made it very difficult to obtain complete contact of catalyst with the reactants. This contact can be increased by increasing the catalyst amount but this again is limiting. The autoclave conditions of reaction temperature and pressure are not accurate in the sense that considerable amount of time is taken to bring the autoclave to desired temperature and hence the reactants take longer time to reach to the steady state conditions. Similarly, autoclave takes a longer time for cooling down to the room temperature after the reaction has been stopped. Therefore, it is almost impossible to estimate accurately, the time for which reactant have been kept at a particular temperature. These limitations of experiments in autoclave necessitates that the developed catalyst must be evaluated in a continuous reactor system in which there is a better control of a reaction time and amount of catalyst.

Therefore, the autoclave conditions, although being simpler, generally are used for screening and premilary evaluation of developed catalyst but for systematic evaluation of catalyst in a proper continuous flow pilot study is unavoidable. Keeping this in view, the earlier develop catalysts, $CaTiO_3$ and $Ca_2Fe_2O_5$ from the egg shell and seashell material were systematically evaluated in continuous pilot plant specifically designed for evaluation of heterogeneous catalyst. The fixed bed biodiesel pilot plant used in this study allows continuous circulation of vegetable oil and methanol over a fixed bed of catalyst and variation in temperatures and pressures can be made is an accurate manner. This fixed bed operation has main advantage that catalyst to feed ratio in reactor is very high as compare one in pressurized autoclave. This large availability of catalyst allows the reaction to proceed very fast and reactions are generally completed in a residence time of few minutes and the reactants are continuously converted to biodiesel in the fixed bed reactor system. Therefore, for commercial operations, fixed bed reactor systems are preferred.

6.2. AIM OF THE PRESENT WORK

The present research work was directed to develop solid extruded $CaTiO_3$ based heterogeneous catalyst for biodiesel production in a continuous fixed bed reactor system. The catalyst were prepared from abundant waste material i.e. egg shells/sea shells transition ABO metal oxide and evaluated their performance for biodiesel production from non-edible jatropha oil in fixed bed pilot plant. Process optimization was carried at various reaction conditions to obtain high biodiesel yielding conditions. Biodiesel obtained was tested as per IS 15607:2005 specifications. The outline of work methodology is as follows:

- Preparation of novel, economical, recyclable extruded catalyst which has major ingredient of waste eggshell.
- Characterization of the synthesized catalyst using techniques such as TGA, XRD, IR, surface area, pore size, pore volume, SEM and basic strength.
- Study of synthesis and kinetic properties (temperature, pressure, molar ratio of methanol to oil and liquid hourly space velocity (LHSV)) of biodiesel synthesis using $CaTiO_3$ and $Ca_2Fe_2O_5$ extruded heterogeneous catalysts in fixed bed continuous pilot plant.
- Study of comparative catalytic activity of extruded $CaTiO_3$ and extruded $Ca_2Fe_2O_5$ catalysts.
- The catalyst activity was evaluated over repeated cycles to validate catalyst recyclability and catalyst life.
- Detailed physico-chemical characteristics of synthesized biodiesel as per IS/ASTM standards.

6.3. EXPERIMENTAL

6.3.1. Reagents and Materials

Commercial non-edible-grade jatropha oil having typical acid value of 8.2 mg-KOH/g and viscosity at 40 ^{o}C (37.18 cSt) was procured from the Surendra Nagar, Gujarat, India (jatropha plantation carried out by Indian Oil Corporation, R&D Centre) and used without further purification. Titanium oxide (72%) (Rankem, India), and ferric Oxide, pseudoboehmite, nitric acid (85%) (CDH, India), methanol, hexane were of laboratory grade.

Eggshells were collected from local market. The eggshells were cleaned to remove protein and other organic substances by washing several times with warm water. Washed shells were dried overnight in oven at 110 ^{o}C to remove traces of water and then calcined at 550 ^{o}C in a furnace for 3 h. The sea shells were also treated in the same manner.

6.3.2. Bulk Preparation of $CaTiO_3$ Catalyst

For preparation of $CaTiO_3$ catalyst, calcined eggshells ($CaCO_3$) and TiO_2 in molar ratio of 1:1.2 (25 g $CaCO_3$ and 24 g TiO_2) were milled in mortar for 15- 20 min. The mixture was calcined at 550 ^{o}C for 3 h and then at 1050 ^{o}C for 3.5 h to obtain $CaTiO_3$ as white solid powder (77%) which was stored in dry container and kept in a desiccator.

The formed catalyst was extruded by mixing with pseudoboehmite or γ-aluminium oxyhydroxide (AlO.OH) (as a binder) in ratio of 3:1 by weight and using 2.5% (v/v) solution of nitric acid as peptizing reagent. The final mixture was extruded in an extruder (Collin E 30 P) (Fig. 3.1) to obtain cylindrical shaped 1/10 inch diameter catalyst and again calcined at 550 ^{o}C and then 1050 ^{o}C. The extruded catalyst is abbreviated as $CaTiO_3$ (E) and its physical appearance is as shown in Fig. 6.1.

6.3.3. Bulk Preparation of $Ca_2Fe_2O_5$ Catalyst

Preparation of powder $Ca_2Fe_2O_5$ catalyst was carried out with calcined eggshells ($CaCO_3$) and ferric oxide (Fe_2O_3) milled in molar ratio of 2:1 (25 g $CaCO_3$ and 20 g Fe_2O_3) in mortar for 15 min (solid-state reaction). The mixture was calcined at 900 °C for 3 h and then at 1050 °C for 3.5 h to obtain $Ca_2Fe_2O_5$ as red brown solid powder (74.66%), which was stored in a dry container and kept in a desiccator.

The prepared catalyst was extruded by mixing with pseudoboehmite or γ-aluminium oxyhydroxide (AlO.OH) (act as a binder) and palygorskite or magnesium aluminium phyllosilicate $[(Mg,Al)_2Si_4O_{10}(OH).4(H_2O)]$ (one of the types of fuller's earth) in ratio of 4:1.5:1 by weight and using 6% (wt/v) solution of nitric acid as peptizing reagent. The final mixture was extruded in an extruder (Collin E 30 P) to obtain cylindrical shaped 1/10 inch diameter catalyst. The extruded catalyst is abbreviated as $Ca_2Fe_2O_5$ (E) and is depicted in Fig. 6.1.

While in the extrusion process, $CaTiO_3$ was easily extruded in to cylindrical shaped when mixed with pseudoboehmite (a binder), but in the case of $Ca_2Fe_2O_5$ it is very difficult to extrude when mixed with pseudoboehmite because of brittle nature of iron. So it was also mixed with palygorskite clay because clay is malleable, ductile and can be easily molded to any shape.

Fig. 6.1: $CaTiO_3$ and $Ca_2Fe_2O_5$ extruded catalysts

6.3.4. Physico-Chemical Properties of Prepared Catalysis

The catalysts were characterized with the help of analytical techniques as described in chapter III.

6.3.5. Catalysts Evaluation using Fixed Bed Reactor Pilot Unit

The fixed bed reactor is a continuous unit for preparation of biodiesel designed by IOC, R&D and constructed by M/S Texol Engineering of Pune. This consists of two identical tube reactors in which 80-100 g catalyst can be charged (Fig. 6.2). The reactor is fed with vegetable oil and methanol through a calibrated pump. Since methanol and vegetable oils has limited miscibility, these are first pumped into a pre heater having a static mixture before charging it to a reactor. Both the reactors have independently temperature controlled furnaces and can be pressurized by nitrogen so as to keep methanol in the liquid form. The vapour-liquid equilibrium curve (Antoine equation) for methanol is used to calculate the pressure required at any given temperature so as to keep methanol in liquid phase.

In a fixed bed pilot reactor, the catalyst can not be loaded in a powder form as it leads to blockage and excessive back pressure. Therefore, the catalyst is generally used in extruded form in which some inert binder is used so as to obtain catalyst as extrudes in order to have lower back pressure. These methods are explained in experimental section. The continuous plant used for transesterification reaction conditions can be operated temperature range of 170-200 ^{o}C and can be pressurized up to 80 bars. Under these conditions methanol exist predominantly in liquid state which results in better interaction between methanol, vegetable oil and catalyst.

Fig. 6.2: Front view of biodiesel pilot plant

Catalyst Loading

Catalyst loading is very important parameter in these experiments. For catalyst loading, first a layer of glass wool is placed at one end of reactor tube, so that aluminium ball remains fixed in their position as represented in Fig 6.3. Above that aluminum balls are loaded up to the desired height and then, once again a layer of glass wool is loaded. Thereafter the catalyst is loaded to the desired amount followed by a plug of the glass wool. After loading the catalyst, a band of aluminium balls are loaded on top and plugged again with glass wool. This procedure gives a tight band of catalyst held in place by the aluminium balls and glass wool plugs. A general outlook of catalyst loading is shown as below:

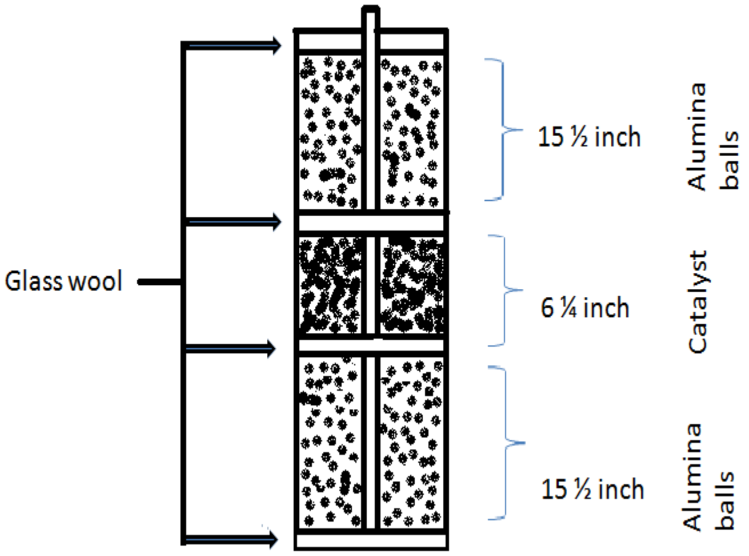

Fig. 6.3: Diagram of Catalyst Loading in Fixed bed Reactor in Pilot Plant

The plant has maximum biodiesel production capacity of 540 ml/h. In a fixed-bed reactor the catalyst pellets are held in a reactor tube and do not move with respect to a fixed reference frame. The fixed bed pilot plant consists of five sections i.e.

- Feed Section
- Reactor Section
- Distillation Section
- Separation Section
- Drying Section

The block diagram of transesterification reaction procedure in fixed bed pilot plant unit is shown in Fig. 6.4.

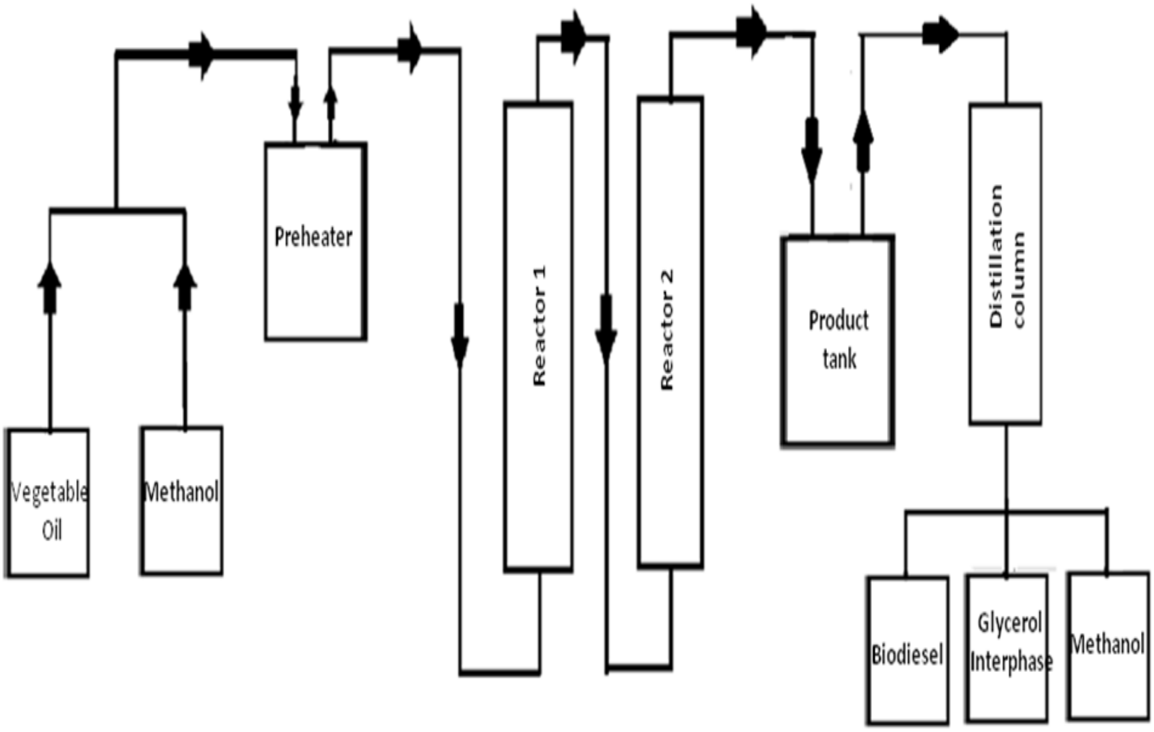

Fig. 6.4: Block Diagram of Biodiesel Pilot Plant unit

6.3.6. Determination of Product Selectivity and Conversion Data

The catalyst is charged into the reactor column and placed with alumina balls/ glass wool combination. The raw materials, jatropha oil and methanol are loaded in feed tanks. The reactors are pressured with desired N_2 pressure using HP N_2 line and N_2 pressure tank are balanced with mild N_2 pressure of 1-2 bar.

After the reactors have been brought the desired temperature, vegetable oil and methanol are pumped by pump at a desired flow rate (LHSV) through a static mixer and pre heater into reactor from bottom to top direction. The temperatures of reactor are controlled through thermo couples.

The contact time of reaction mixture with catalyst is regulated for completion of reaction. The performance of reaction is monitored by TLC and GPC analysis. The reaction mixture from reactor-2 outlet gets collected into product tank. The lower glycerol layer is removed from product tank. The product is then transferred to distillation unit. The product is distilled under vacuum at various temperatures to obtain cuts of methanol, biodiesel and glycerol. After distillation, methanol is recovered into the methanol tank after it has passed through the drying column in which molecular sieves are filled. Biodiesel produced was evaluated for various physico-chemical characteristics as per IS/ASTM standards.

Explanation of being liquid hourly space velocity (LHSV) and method of calculation is explained in annex-I. Antoine equation is helpful to determine the relationship between temperatures and vapour pressure of a component.

The significance of Antoine equation in context of determination of phase of methanol at various pressure and temperature is explained in annex-A.

6.3.7. Evaluation of $CaTiO_3$ (E)

The transesterification of jatropha oil with methanol in presence of catalyst was conducted in fixed bed reactor shown in Fig. 6.2. The 80 g of the catalyst of cylindrical pellets of size approx. 1/10 inch was charged into the middle three zone of each of the reactor. The preheating and post heating zones were filled with alumina ball of 3 to 4 mm size. Initially the reactors were pressurized with nitrogen gas up to 50 bar pressure. The reactors were heated in ramp of 60 ^{o}C per hour to achieve the final temperature of 170 ^{o}C. The vegetable oil and alcohol were fed into first stage reactor through a static mixture. After stabilizing the feed to the reactor, the internal reactor temperatures were maintained at isothermal temperature by adjusting the reactor furnace temperatures. The details of various operating parameters are reported in Table 6.1.

Table 6.1: Reaction conditions

Operating Parameters	Details
Oil Feed	Jatropha Curcas oil
Alcohol	Methanol
Water content in jatropha oil (ppm)	1020
Water content in methanol (ppm)	600
Catalyst in each reactor (g)	80
Temperature (^oC)	170-200
Pressure (bar)	50-80
LHSV in R-1 (h^{-1})	0.23-0.36
LHSV in R-2 (h^{-1})	0.23-0.36
Methanol to oil molar ratio	12:1 to 107:1
Biodiesel conversion by GPC (%)	54 to 88.6

6.3.8. Evaluation of $Ca_2Fe_2O_5$ (E)

The reactor system shown in Fig. 6.2 was used to conduct the transesterification of jatropha curcas oil with methanol in presence of the extruded $Ca_2Fe_2O_5$ as catalyst. The 72.5 g of the catalyst of cylindrical pellets of size approx. 1/10 inch was charged into the middle three zone of each of the reactor. The preheating and post heating zones were filled with alumina ball/ glass wool combination of 3 to 4 mm size. Initially the reactors were pressurized with nitrogen gas up to 50 bar pressure. The reactors were heated in ramp of 60 ^oC per hour to achieve the final temperature of 170 ^oC. The vegetable oil and alcohol were fed into first stage reactor through a static mixture. After stabilizing the feed to the reactor, the internal reactor temperatures were maintained at isothermal temperature by adjusting the reactor furnace temperatures. The details of various operating parameters are reported in Table 6.2.

Table 6.2: Reaction conditions

Operating Parameters	Details
Oil Feed	Jatropha Curcas oil
Alcohol	Methanol
Water content in jatropha oil (ppm)	1020
Water content in methanol (ppm)	600
Catalyst in each reactor (g)	72.5
Temperature (^{o}C)	170-190
Pressure (bar)	50-80
LHSV in R-1 (h^{-1})	0.23-0.36
LHSV in R-2 (h^{-1})	0.23-0.36
Methanol to oil molar ratio	12:1 to 21:1
Biodiesel conversion by GPC (%)	84 to 96

6.4. RESULTS AND DISCUSSIONS

6.4.1. Physico-Chemical Properties of Prepared Catalyst

X-ray Diffraction (XRD)

Fig. 6.3 depicts the XRD patterns of $CaTiO_3$ (extruded) calcined at 1050 ^{o}C. XRD of the catalyst sample showed characteristic peak of $CaTiO_3$ and minor peak of TiO_2 (rutile) indicating conversion of calcium carbonate to calcium oxide and its subsequent reaction with TiO_2 to form desired $CaTiO_3$ complex. However some traces of calcium dialuminate; Grossite ($CaAl_4O_7$) was also observed by XRD (Fig. 6.5).

The intense peaks at 2θ~ 33.1, 47.4, 32.9, 33.3, 59.4 and 69.5 to the d value of 2.71, 1.91, 2.70, 2.69, 1.56 and 1.35 respectively of calcium titanate. The titanium oxide peaks were observed at 2θ~ 27.4, 54.3 and 36.1 to the d value of 3.25, 1.68 and 2.48 respectively (Fig. 6.5).

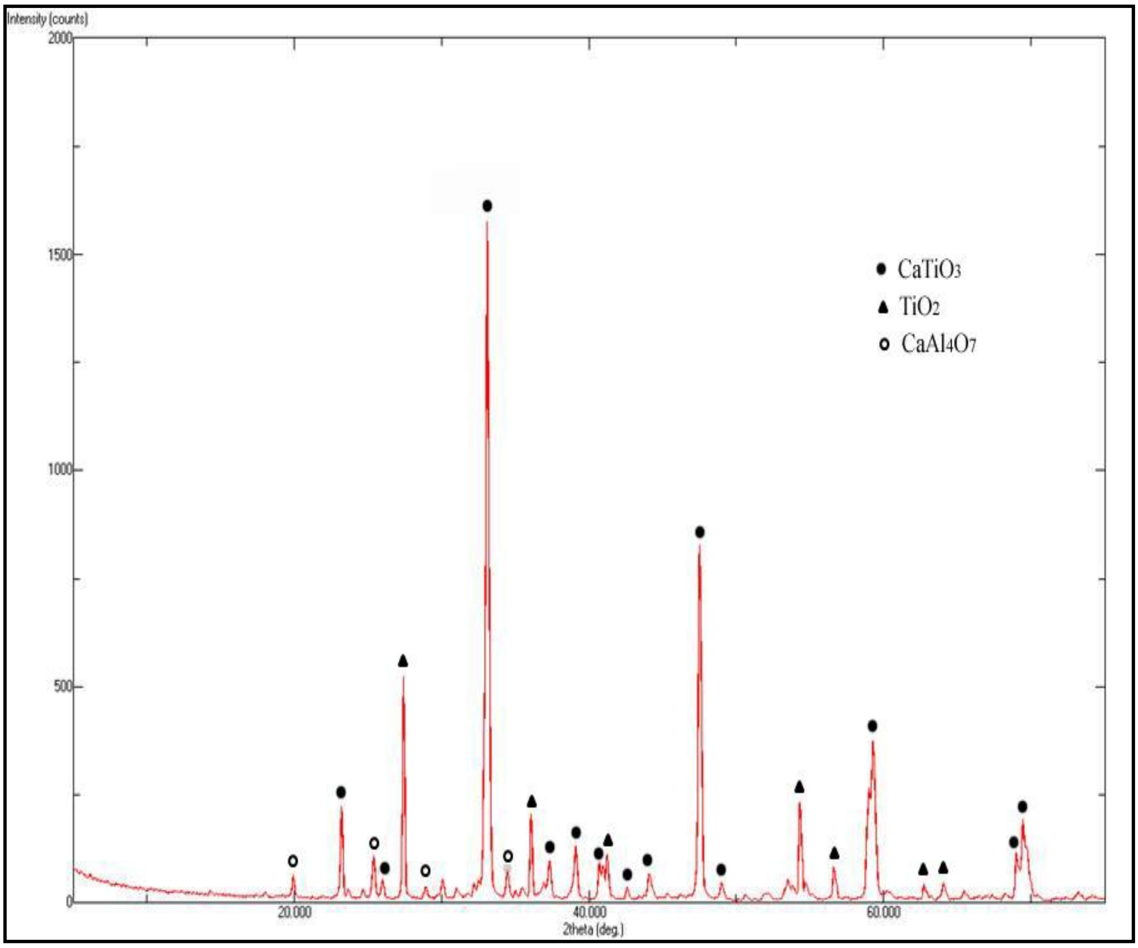

Fig. 6.5: XRD patterns of Ca-Ti (extruded) based catalyst

XRD patterns of $Ca_2Fe_2O_5$ (extruded) is depicts in Fig. 6.6. XRD of catalyst sample showed characteristic peak of $Ca_2Fe_2O_5$ (Srebrodolskite phase) and minor peak of pseudoboehmite (γ-AlO(OH)) and SiO_2 (Quartz). However some traces of calcium iron oxide ($CaFe_2O_4$) were also observed by XRD.

The intense peaks at 2θ~ 22.8, 24.1, 31.9, 33.0, 33.4, 43.5, 46.6, 49.3 and 49.6 to the d value of 3.88, 3.69, 2.79, 2.71, 2.67, 2.07, 1.94, 1.84 and 1.83 respectively of calcium ferrite ($Ca_2Fe_2O_5$). The pseudoboehmite (γ-AlO(OH)) peaks were observed at 2θ~ 14.4, 28.4, 38.2, 49.3 and 70.2 to the d value of 6.11, 3.13, 2.35, 1.84 and 1.33 respectively. The quartz (SiO_2) and calcium iron oxide ($CaFe_2O_4$) peaks were observed at 2θ~ 26.6 and 35.5 to the d value of 3.34 and 2.52 respectively (Fig. 6.6).

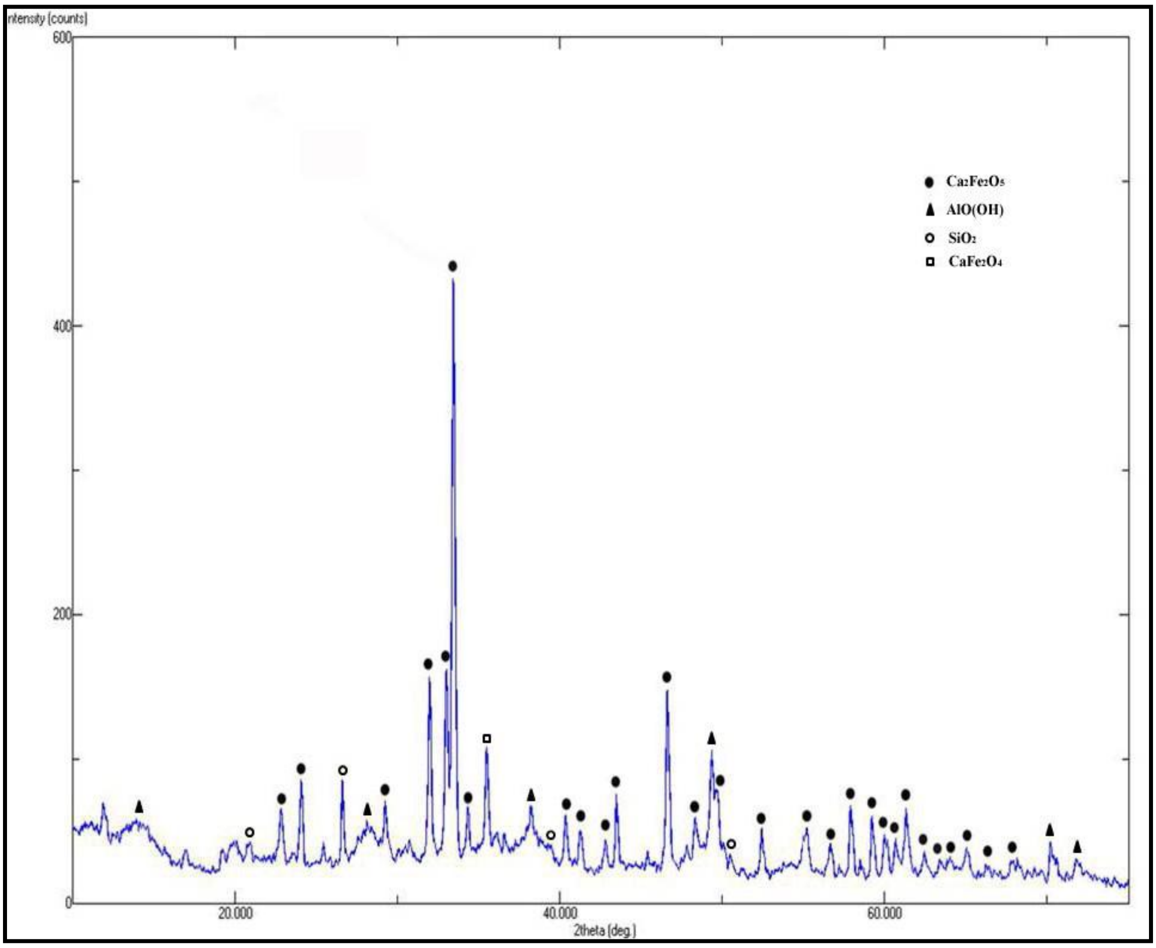

Fig. 6.6: XRD patterns of Ca-Fe (extruded) based catalyst

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of $CaTiO_3$ (Fig. 6.7) calcined at 1050 ^{o}C temperature revealed the formation of $CaTiO_3$ phase in the region 400- 600 cm^{-1}. The two peaks at ~ 576 and ~ 447 cm^{-1} are the representative peaks of $CaTiO_3$, where the former peak is due to Ti-O stretch and the later to Ti-O_3 torsion, respectively [5].

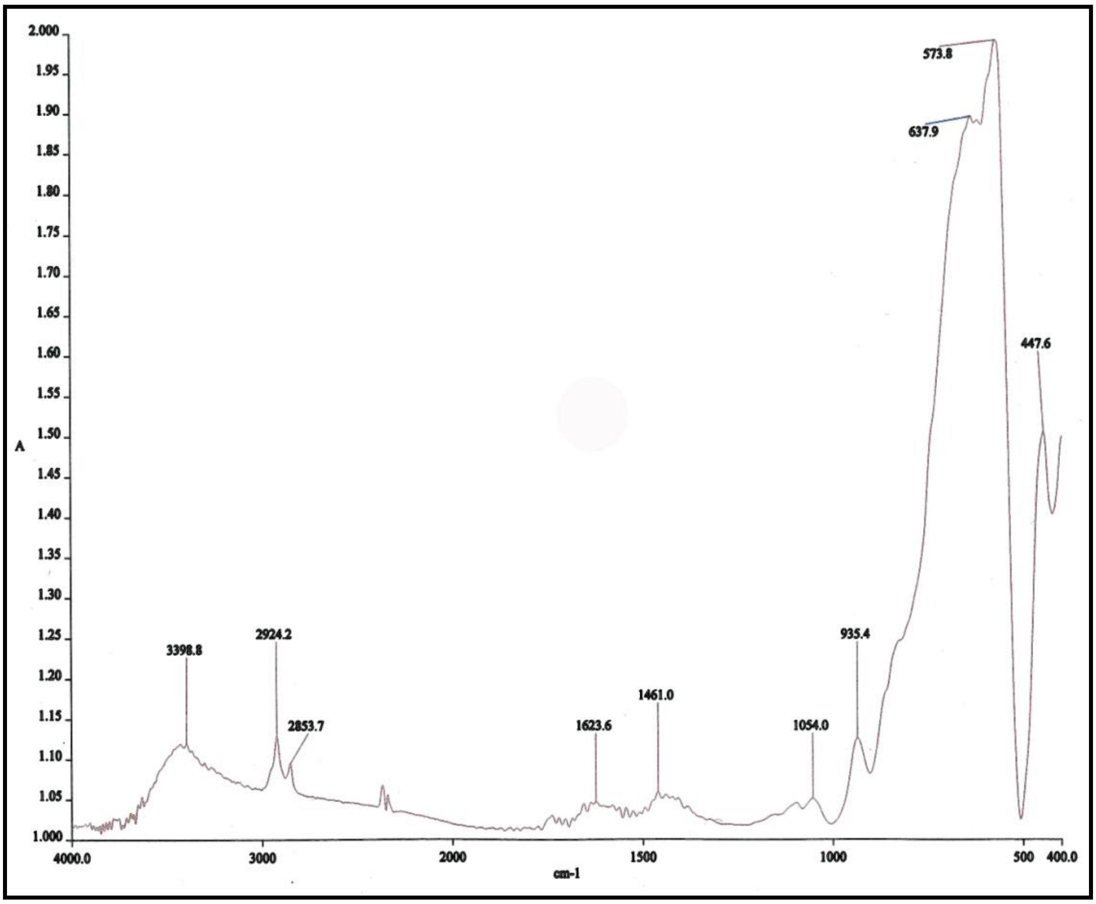

Fig. 6.7: IR spectra of Ca-Ti based catalyst

FTIR spectra of $Ca_2Fe_2O_5$ (Fig. 6.8) calcined at 1050 ^{o}C temperature revealed the formation of $Ca_2Fe_2O_5$ phase in the region 500- 600 cm^{-1}. The strong absorption band around ~567 cm^{-1} was ascribed to the Fe-O bond stretch [6]. The IR spectrum show characteristic peaks of hydroxyl groups of pseudoboehmite (AlO.OH) vibrate between 2800-3700 cm^{-1} for stretching vibrations and 900-1100 cm^{-1} for bending vibrations. The absorption band between 700 and 400 cm^{-1} indicates Al-O vibrations. In addition, absorption band around 1634 cm^{-1} was attributed due to the presence of molecular water. The poorly defined peak at ~875 cm^{-1} is due to the presence of carbonate ion [7]. The characteristic SiO_2 peak like the Si-O-Si stretching (~1034 cm^{-1}) frequencies was also recognized [8].

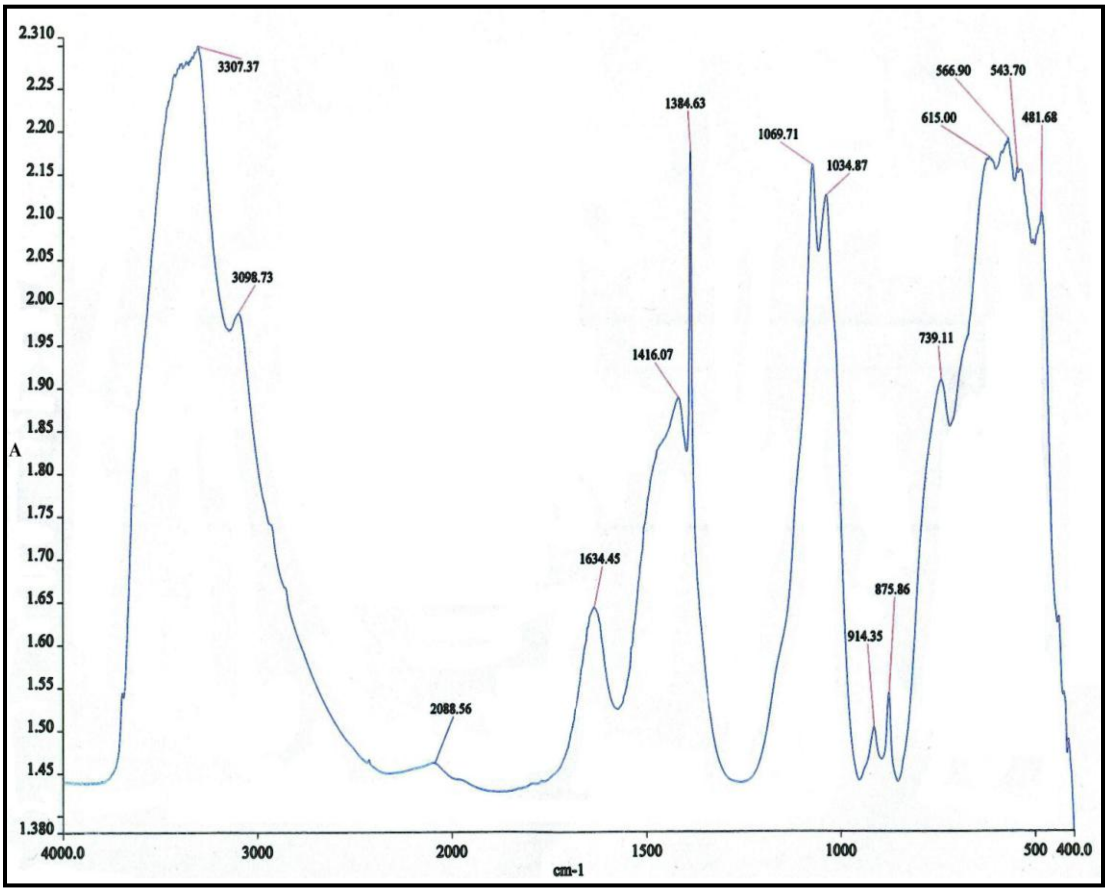

Fig. 6.8: IR spectra of Ca-Fe based catalyst

Thermogravimetric Analysis (TGA)

Thermo gravimetric analysis (Fig. 6.9) of synthesized $CaTiO_3$ depicted two stages of weight loss. First stage of weight loss (0.5578 %) was possibly due to initial decomposition at temperature 100 to 200 ^oC involving loss of water. At about 650-800 ^oC the plot shows a plateau. The weight loss (1.377 %) was indicating thermal decomposition of $CaCO_3$ to form CaO with loss of carbon dioxide. The CaO phase can react with the other active ingredient TiO_2 to form $CaTiO_3$.

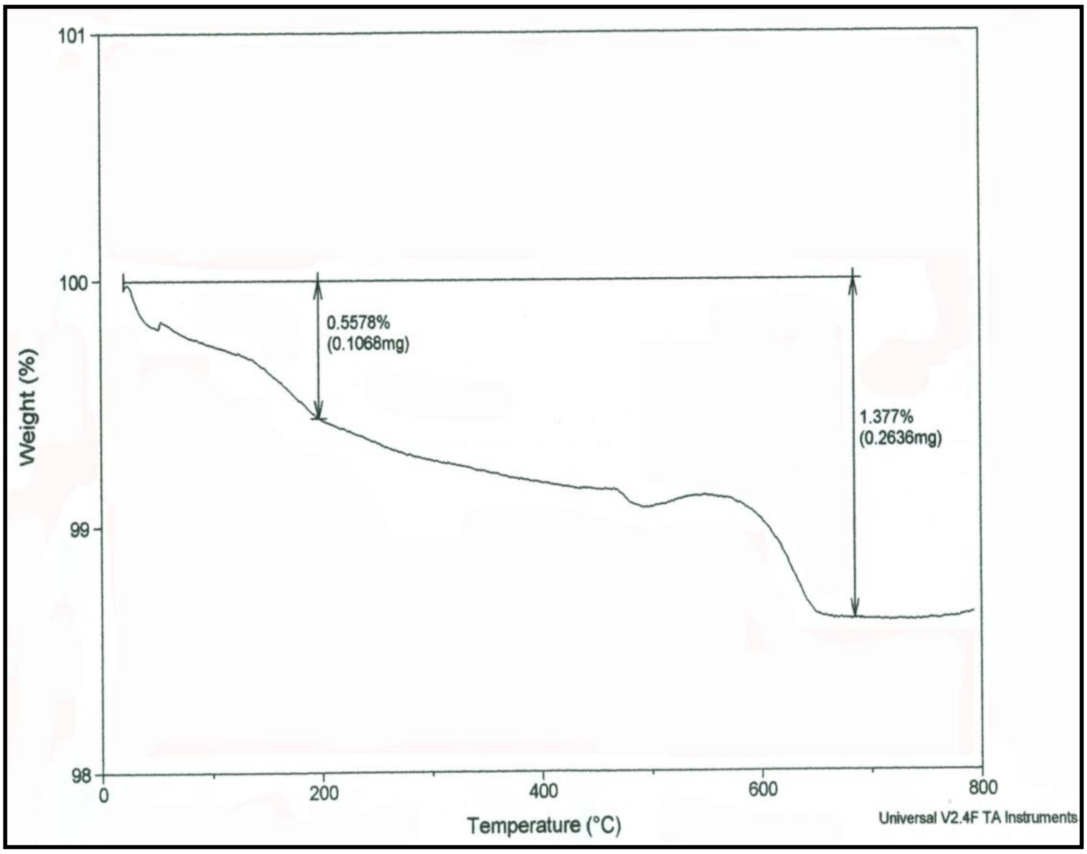

Fig. 6.9: TGA of Ca-Ti (extruded) Catalyst

However, Thermogravimetric analysis of synthesized $Ca_2Fe_2O_5$ (E) depicted gradually weight loss (total weight loss is 17.179 %) due to multi-component system (Fig. 6.10). The mass loss around 110 ^{o}C may be attributed to the loss of surface water. At 130 °C to 350 °C, the weight loss is assigned to the loss of hydration water from the Na^+ ion. Then, at temperature of 350-500 ºC weight loss can be attributed to the decomposition of $Ca(OH)_2$. The weight loss around 500-600 ^{o}C is due to the loss of structural water (OH groups attached to Al and Si) [9] and also transformation of boehmite into γ-alumina. Further when temperature is increased to about 600-800ºC, the weight loss (0.8331%) due to thermal decomposition of $CaCO_3$ to form CaO with loss of carbon dioxide. The CaO phase reacts with the other active ingredient Fe_2O_3 to form $Ca_2Fe_2O_5$.

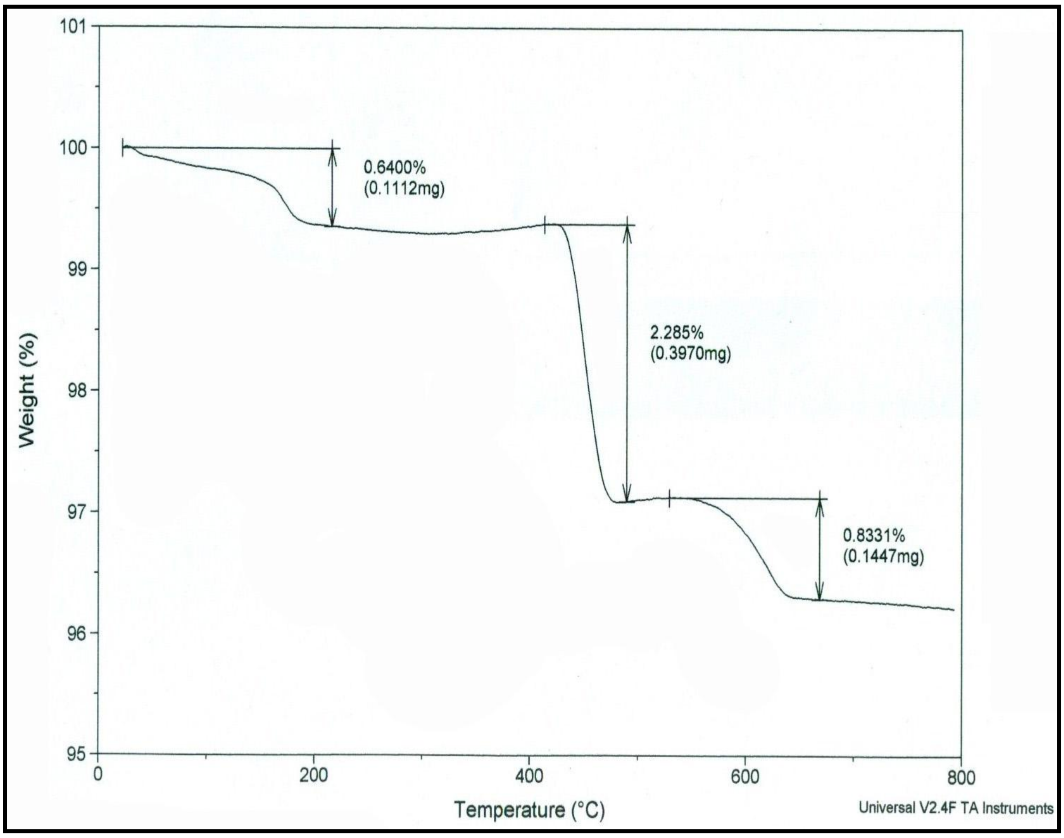

Fig. 6.10: TGA of Ca-Fe (extruded) Catalyst

BET Surface Area, Average Pore Size and Total Pore Volume

BET surface area of $CaTiO_3$ (extruded) was found to be 7.59 m^2/g, average pore size 70 Å and 0.01 cm^3/g of total pore volume. Whereas, Surface area, average pore size and total pore volume of $Ca_2Fe_2O_5$ (extruded) were 50.07 m^2/g, 71 Å and 0.07 cm^3/g respectively.

The reason of large surface area of $Ca_2Fe_2O_5$ extruded catalyst is that comparatively more amount of pseudoboehmite was used as $CaTiO_3$ (E) in extrusion process. Other reason is being calcination temperature i.e. after extrusion $CaTiO_3$ is calcined at 550 °C and after that at 1050 °C. Surface area and total pore volume of $CaTiO_3$ (E) are small due to its high calcination temperature, whereas, after extrusion, $Ca_2Fe_2O_5$ is not calcined, thus the surface area and total pore volume are large. This is because, as after calcination at 1050 °C, the catalyst structure ($Ca_2Fe_2O_5$) was converted in to $Ca_2Al_2SiO_7$ (Gehlenite, syn) and Fe_2O_3. Further, transesterification reaction was slow and completed in 7 h by using this catalyst (extruded $Ca_2Fe_2O_5$ with calcined at 1050 ^{o}C) in high pressure reactor. While, if same is compared with extruded without calcined, the reaction was completed within 3 h.

However, before calcined extruded $CaTiO_3$ was in major intense peak of TiO_2 (rutile) and $Ca(OH)_2$ and minor peak of $CaTiO_3$. While when it was calcined at 1050 ^{o}C, the major crystalline peak was of $CaTiO_3$ and minor peak was of TiO_2 along with some traces of $CaAl_4O_4$. Whereas, $Ca(OH)_2$ peak disappeared after calcined at 1050 ^{o}C.

Scanning Electron Microscopy (SEM)

The Scanning electron micrograph of $CaTiO_3$ is depicted in Fig. 6.11. The agglomerates are spherical in shape and having uniform distribution. The average particle size of $CaTiO_3$ is found to be around 218-266 μm.

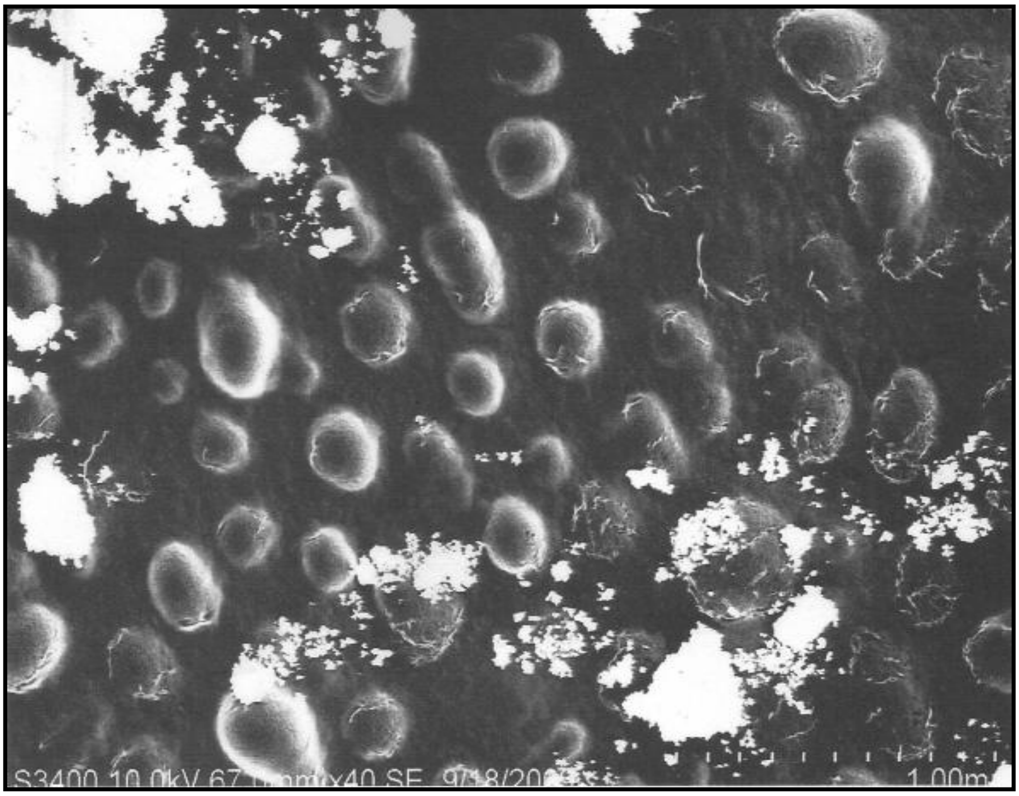

Fig. 6.11: SEM of Ca-Ti (E) Catalyst

The Scanning electron micrograph of $Ca_2Fe_2O_5$ (extruded) is depicted in Fig. 6.12. The SEM image shows that the particles are agglomerated having spherical in shape. The average particle size of $Ca_2Fe_2O_5$ is found to be around 633 nm-1.48 μm.

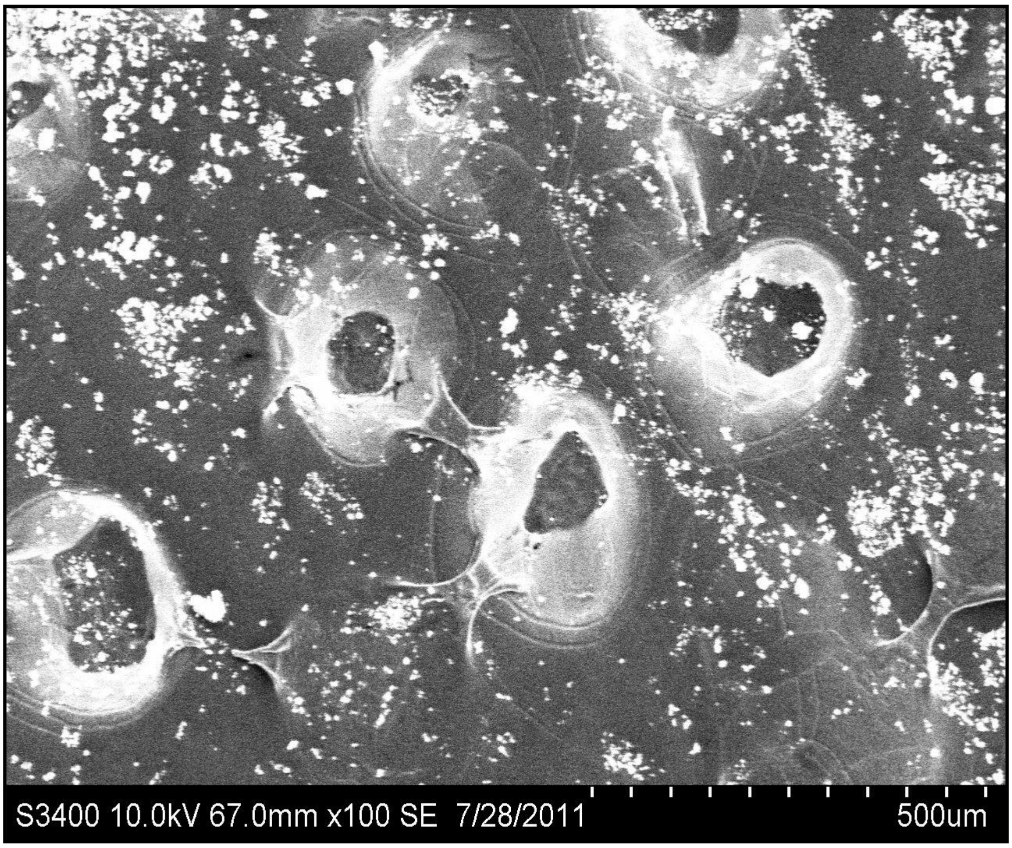

Fig. 6.12: SEM of Ca-Fe (E) Catalyst

Basic Strength

Basic strength was determined as per procedure described earlier. The results are given in Table 6.3.

Table 6.3: Characteristics of extruded Ca-Ti and Ca-Fe based catalysts

Catalyst Characterization	$CaTiO_3$ (extruded)	$Ca_2Fe_2O_5$ (extruded)
BET Surface Area (m^2/g)	7.59	50.07
Average Pore Size (Å)	70	71
Pore Volume (cm^3/g)	0.01	0.07
Basic Strength	$7.2<H\_<9.3$	$15.0<H\_<18.4$

6.4.2. Optimization of Variables to Maximize Product Selectivity and Conversion

Calcium Titanate ($CaTiO_3$) Extruded

Effect of variables like reactor temperature, pressure, liquid hourly space velocity (LHSV) and ratio of vegetable oil to methanol were studied in systematically designed experiments. For each experiment, steady state conditions were developed and the samples of product were withdrawn for analysis in small lots at a time difference of 2-3 h from the steady state. The results obtained are summarized in Table 6.4.

Table 6.4: Effect of reaction parameters studies on biodiesel conversion

Exp. No	Temperature (^oC)	Pressure (bar)	Molar ratio of methanol to oil	LHSV (h^{-1})	Biodiesel conversion by GPC (%)
1	170	40	12:1	0.23	54.0
2	170	80	12:1	0.23	58.6
3	170	80	38:1	0.26	73.3
4	170	80	85:1	0.3	75.0
5	170	80	38:1	0.36	61.6
6	180	80	85:1	0.3	77.3
7	190	80	85:1	0.3	85.4
8	190	80	107:1	0.36	83.1
9	190	80	107:1	0.3	88.6

At a temperature of 170 ^oC, methanol to oil ratio of 12:1 and at LHSV of 0.23 h^{-1}, pressure in the system was kept at 40 bars. The biodiesel conversion efficiency under these conditions was 54%. Keeping all other variables same, the reactor pressure was enhanced to 80 bars and conversion rate increased to 58.6%. This indicated that at lower pressure of 40 bar and the reactor temperature of 170 ^oC methanol may not be fully in the liquid form throughout the reactor and by increasing pressure to 80 bar, it was ensured that all the methanol present in both reactors was in liquid form. Therefore, in order to ensure that all the experiments were conducted in which methanol was in complete liquid phase, reactor pressure was increased to 80 bars in subsequent experiments.

The effect of change of methanol to oil ratio was studied while keeping the reactor temperature, LHSV and pressure constant. By increasing the oil to methanol ratio from 12:1 to 38:1 (experiment 2 and 3), a significant increase in the biodiesel conversion efficiency was observed from 58.6% to 73.3%. This observation is in line with the results obtained in autoclave experiments and also observed in base catalyzed homogeneous catalyzed reactions. Excess of methanol does helps to obtain more conversion. In experiment 4, the oil/methanol ratio was increased from 38:1 to 85:1 while keeping all other variables constant. The increase in conversion efficiency was not significant (73.3% to 75%) indicating that about 30 to 40 molar excess of methanol is good enough to get higher conversions.

The effect of variation of LHSV on the biodiesel conversion efficiency was studied next. At 170 ^{o}C, 80 bars and methanol: oil ratio of 38:1 (experiment 4), flow at LHSV of 0.23 h^{-1} showed 73.3% biodiesel conversion efficiency. However at same conditions when LHSV was increased to 0.36 h^{-1} (experiment 5) very significant fall in biodiesel conversion efficiency i.e. from 73.3 to 69.6% was observed. This indicates that any increase in LHSV over the optimum flow will result in lower conversion efficiency and this looks fairly simple to explain. Though the catalyst is fairly active, but it needs enough contact time with the reactants. At 190 ^{o}C, 80 bar pressure, methanol to oil ratio of 107:1 and LHSV of 0.36 h^{-1}, biodiesel conversion efficiency was 83.1% (experiment 8) and when the LHSV was lowered to 0.30, the conversion efficiency increased to 88.6% (experiment 9).

Effect of reaction temperature was studied next. In experiment 6 at 180 ^{o}C, 80 bars, methanol: oil ratio of 107:1 and LHSV of 0.3 h^{-1}, biodiesel conversion efficiency of 83.1 % was obtained. However, under similar conditions was temperature was raised to 190 ^{o}C (experiment 9), conversion efficiency showed improvement (88.6%).

Above discussion and experiments indicate that $CaTiO_3$ (E) showed better activity for biodiesel conversion at elevated temperature, pressure, higher oil: methanol ratio and lower LHSV. However, increase in each variable has limits and the costs attached to it. High reactor temperature means more input energy, hence cost. Higher oil: methanol ratio though gives higher conversion efficiency but more energy will be required at later stage to recover methanol. Lower LHSV is good for biodiesel conversion efficiency, but the overall production rate will suffer.

A close look at all the experiments conducted indicates that optimum conditions for cost effective biodiesel conversion by using $CaTiO_3$ are as follows:

Reactor temperature: 180 ^{o}C
Methanol: oil: 35:1
Pressure: 80 bar
LHSV: 0.3 h^{-1}

Calcium Ferrite ($Ca_2Fe_2O_5$) Extruded

As in the case with $CaTiO_3$, described earlier, increase of pressure, temperature and methanol: oil ratio resulted in better biodiesel conversion efficiency. The optimum condition for quantitative biodiesel conversion was the following.

Reactor temperature: 170 ^{o}C
Reactor pressure: 80 bar
Methanol: oil: 12:1
LHSV: 0.49

Experiments were also conducted to monitor the health of catalyst over long duration. In experiment 1 after 10 h the yield was 94.6% and under similar condition the yield at the end of day 2 and day 5 (experiment 2 and 3) was about the same, which indicated that the catalyst was robust and had maintained its activity over long usage.

However, when LHSV was increased from 0.38 (experiment 3) to 0.49 (experiment 4), keeping all other conditions constant; a fall in biodiesel conversion efficiency from 96.5 to 87.2% was observed. The LHSV was increased further from 0.49 (experiment 5) to 0.7 h^{-1} (experiment 6) and a steep fall in conversion efficiency from 95.3% to 90.8% was observed. The results obtained are summarized in Table 6.5.

Table 6.5: Effect of reaction parameters studies on biodiesel conversion

Exp. No	Temperature (^{0}C)	Pressure (bar)	Molar ratio of methanol to oil	LHSV (h^{-1})	Biodiesel conversion by GPC (%)
1	170	80	12:1	0.38	94.6
2	170	80	12:1	0.38	96.5
3	170	80	12:1	0.38	96.0
4	170	80	12:1	0.49	87.2
5	170	80	21:1	0.49	95.3
6	170	80	21:1	0.70	90.8

It was observed that $Ca_2Fe_2O_5$ (E) catalyst was much more effective than $CaTiO_3$ and afforded almost compete conversion of jatropha oil to biodiesel.

This catalyst has a longer life, retains activity and hence is a good case for commercial application.

6.4.3. Investigation of Reaction Products

The synthesized products were investigated as described earlier with the help of GPC, GC and NMR.

6.4.4. Property Determination of Synthesized Product (Standards Test Methods)

The synthesized products were tested for their physico-chemical properties using various standards to find its suitability as diesel fuel and the product was found meeting ASTM D6751 and IS 15607 specification. Glycerin obtained was tested for purity by NMR and was found to > 97%.

6.5. CONCLUSIONS

Calcium based metal oxide catalysts $CaTiO_3$ and $Ca_2Fe_2O_5$ were evaluated in fixed bed pilot plant for continues production of biodiesel from nonedible jatropha oil. The catalysts were prepared from low value abundant natural raw material viz. egg/sea shell and extruded in cylindrical shape using a binder for prevention of catalyst leaching and having lower operating back pressure. The catalysts efficiency was tested by varying parameters such as temperature, pressure, molar ratio of methanol to oil, flow rate of feed and LHSV. The synthesized biodiesel was tested for its physico-chemical properties as per ASTM D 6751 and IS 15607 test specifications. The following conclusion can be drawn:

- The conversion of biodiesel from jatropha oil using $Ca_2Fe_2O_5$ extruded catalyst was 97% whereas, it was lower for $CaTiO_3$ (89%) due to large surface area and basic strength of $Ca_2Fe_2O_5$ vis a vis $CaTiO_3$.
- The maximum biodiesel conversion of 88.6% was obtained by using $CaTiO_3$ (E) at optimized reaction condition of 190 ^oC temperature, 80 bar pressure, 107:1 molar ratio of methanol to oil and 0.3 h^{-1} LHSV.
- While for $Ca_2Fe_2O_5$ (E), the maximum biodiesel conversion of 96.5% was obtained at 170 ^oC temperature and 80 bar pressure, 12:1 molar ratio of methanol to oil and 0.38 h^{-1} LHSV.
- Both the catalysts were robust and had long productive life.
- $CaTiO_3$ and $Ca_2Fe_2O_5$ extruded catalysts have potential for use in industrial preparation of biodiesel with later being slightly better in performance than former catalyst.
- The glycerin obtained in this process was more than 97% pure.

6.6. REFERENCES

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