DEVELOPMENT OF HETEROGENEOUS CATALYSTS FROM BIOMASS FOR BIODIESEL PRODUCTION

(A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY)

BY

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MARCH 2013

Abstract

The world has relied heavily on non renewable crude oil for more than a century. In recent years the rapid growth in industrialization and world population has increased the demand for energy. To date the fossil fuels accounts for 80 % of the world energy needs; out of which nearly 57% is utilized in transportation sector. At present, there is a big gap between world energy requirement and energy demand. Therefore, the world is facing twin problem of depleting fossil fuel reserves and increasing environmental degradation because of fossil fuel utilization. This depletion in oil reserves has resulted into decrease in world oil supply and increase in petroleum prices. The unstable increasing petroleum prices, limited fossil fuel reserves and increasing concerns about environment have escalated the search for alternative energy sources especially in the transportation sector. Because of these problems, in recent years, liquid biofuels such as biodiesel have become very attractive because of their environmental benefits.

Chemically biodiesel is defined as the mixture of methyl esters with long chain fatty acids and is typically made from nontoxic, biological resources such as vegetable oils, animal fats and waste cooking oils. Compared to conventional diesel fuel, biodiesel is technically and economically more competitive because of its renewability, liquid nature-portability, biodegradability, low emission profiles, high flashpoint and lower sulfur and aromatic content. Biodiesel has properties very similar to diesel fuels. The biodiesel blends up to B20 could be used in all the diesel equipments without any engine modifications. Biodiesel is produced by transesterification of triglycerides with alcohol in the presence of a catalyst. At present the most popular catalysts used on industrial basis for commercial biodiesel production are homogeneous base catalysts such as KOH or NaOH. The advantage of with alkali catalyst is that very high conversion is obtained under mild conditions and reaction in just 1 h. Moreover the reaction is 4000 times faster than the same amount of homogeneous acidic catalysts. However, transesterification in the presence of base catalysts has many disadvantages. The primary problem is the separation of catalyst from final reaction product, which is very difficult. In order to remove the catalyst from the product, large amount of waste water is generated. Moreover even a little amount of moisture can initiate oil hydrolysis to form free fatty acids and glycerol. The FFA then reacts with base catalyst to form soap, which is again an unwanted side-reaction. These limiting factors of homogeneous catalysts can be overcome by using solid catalysts instead of homogeneous catalysts.

Utilization of heterogeneous catalysts offers several process advantages which includes easy catalyst separation from final product, reusability and regenerability of the catalyst. In addition unlike homogeneous catalysts, these catalysts are less sensitive to water which makes them even more attractive for biodiesel production from a variety of feedstocks. Large number of heterogeneous catalysts such as metal oxides, alkaline earth metal oxides, transition metal oxides, mixed metal oxides, ion exchange resins, sulfated oxides, carbon based heterogeneous catalysts, enzyme supported heterogeneous catalyst have been reported in literatures for biodiesel production.

Among the reported heterogeneous catalysts vast study has been done in the field of different metal oxides for biodiesel production. Among the different metal oxides reported, the most popular metal oxide was found to be calcium oxide which was due to its easy availability, cheapness, low toxicity and high catalytic activity. Recently researchers have introduced a novel method of preparing CaO from waste mollusk and egg shells and used it for biodiesel production. However, the properties of CaO prepared from these shells were not reported to be altered for better catalytic activity in transesterification of vegetable oil.

Based on these findings we have undertaken the study for the preparation of solid catalyst from the waste shells of *Turbonilla striatula*. In our investigation we observed that the waste shells of *Turbonilla striatula* acted as an excellent raw material for the preparation of CaO because it was mainly composed of calcium carbonate. The CaO was prepared by calcining the raw material at temperature above 800 °C for 4 h. Therefore the catalyst preparation route was only one step method and less time consuming. In this study the shells calcined at 900 °C was considered to be the best catalyst as it exhibited maximum activity.

The catalyst calcined at 900 °C was employed for transesterification of mustard oil. It was observed that maximum yield of 93.3% was obtained with 9:1 methanol to oil ratio, 3.0wt% catalyst amount at 65±5 °C. The same catalyst was then used in the transesterification of waste cooking oil (WCO). It was observed that maximum conversion of 98% was achieved in 8 h with 12:1 methanol to oil ratio and 5 wt% catalyst amounts.

In order to increase the catalytic activity of the parent catalyst, it was doped with Li from (0.5-1.5) wt%. The results indicated that the basicity of the catalyst increased with increasing amount of Li loading and which in turn influenced the catalytic activity. It was observed that very high conversion of 98% was obtained with 1 wt% Li doped waste shell derived CaO in 4 h with 9:1

methanol to oil ratio and 2.0 wt% catalyst amounts. Similar to this investigation, the parent catalyst was also doped with Ba, which has a very high basicity. Doping with Ba resulted in significant enhancement of the catalyst basicity. It was observed that the Ba doped waste shell derived CaO were highly basic in nature. Complete conversions were obtained with 1% Ba doped CaO catalyst in only 3 h with 6:1 methanol to oil ratio and 1.0 wt% catalyst amount. This excellent conversion is also comparable with the conversions obtained with conventional catalysts such as NaOH and KOH.

Declaration

I do hereby declare that this thesis entitled "***DEVELOPMENT OF HETEROGENEOUS CATALYSTS FROM BIOMASS FOR BIODIESEL PRODUCTION***" being submitted to the Department of Energy, Tezpur University, Assam, India, is a record of original research work carried out by me. I also declare that neither this work as a whole or a part of it has been submitted to any other University or Institute for any other degree, diploma or award.

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CERTIFICATE BY SUPERVISORS

This is to certify that the matter embodied in the thesis entitled "***Development of heterogeneous catalysts from biomass for biodiesel production***" submitted by Jutika Boro, for the award of degree of Doctor of Philosophy of Tezpur University, is a record of bonafide research work carried out by her under our supervision and guidance. The results embodied in the thesis have not been submitted to any other University or Institute for the award of any degree or diploma.

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Certificate

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The committee recommends for the award of the Degree of Doctor of Philosophy.

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Acknowledgement

"All for one and one for all", may sound like a word of mouth; but for me these words have worked like inspiration during my research work as a research scholar. My life for the past four years in Biomass Conversion Laboratory has been the most constructive years and I had the opportunity to rediscover myself. This entire research was a team work and I must add that with perfect combination of inputs from my lab mates filled up my workplace with energy, fun and positive environment. My supervisors, lab mates, friends, and family members have acted like catalyst for the completion of this work. Therefore I want to take this opportunity to especially thank all of them in this section.

At the very outset I want to express my gratitude to my supervisor, Prof. D. Deka for his guidance, understanding and constant support throughout my Ph.D work. Without his suggestions and effort, it would have been hard for me to complete my work in time. In short, he is the catalyst of this research work.

I am also indebted to my co-supervisor Dr. A.J Thakur who has acted like a catalyst support and co-solvent in past four years. Despite his busy schedule, he was always attentive to my queries and concern about my work. He solved my problems and provided me with proper guidance whenever needed.

I also want to express my gratitude to University Grant Commission, Govt. of India, for supporting me financially by providing me with Rajiv Gandhi National fellowship.

I also take this opportunity to thank my doctoral committee for proper guidance and positive inputs for better outputs.

My heartiest thanks also go to the faculty members of Department of Energy, Tezpur University, especially to Sadhan Mahapatra sir, who did some of my characterization in IISC, Bangalore.

I am also thankful to Vice Chancellor, Mihir Kanti Chaudhuri, for inspiring towards research and his timely intervention supported me financially.

I also wish to thank Babul Talukdar & Mrinal Dutta along with all the finance official members who helped me with my fellowship for its continuation.

My special thanks also goes to my lab mates, Pitambar, Lakhya, Subrata and Plaban for their support, advice and making my workplace a worth place for work. Working every single day with my lab mates here was a joyful experience and they encouraged me for betterment of my work.

I am thankful to Prof. B Viswanathan, IIT Guwahati, IIT Mumbai, Ruhit Jyoti Konwar, Manash Gogoi, Ratan Baruah, Prakash Kurmi, Mayur Phukan, Dr. Harekrishna Deka, Vijay Kumar Das, Jeena Jyoti Baruah, Dr.Siva Prasad Das, Tapan Bora, Shankur Phukan and Technical staff of Tezpur University who helped me out with my characterization and research related problems.

I also want to thank Rupali, Shyam, Pinak, Shantibala, Chikun, Rashmi, Renuka, Doljeet, for their support during my PhD tenure.

I wish to give my sincere thanks to Dr. Maumita Chakraborty, Manoshi Goswami, Pallavi Dutta, Lipika Aidew, Rahul Singh Chutia, Bandana Singha, Samrat Paul, Moon moon Hilloidhari and Sampriti Kakoti.

I am thankful to School of Engineering canteen for providing waste cooking oil.

I am highly grateful to my husband Mriganka Deka for mental support, love and affection I needed very badly in time. He inspired me for my Ph.D and gave me strength to move on.

I also want to acknowledge the tremendous support and faith my parents and elder brothers had placed on me. Without their confidence and belief, Ph.D would have remained a dream and I would have never aspired for higher education in a lifetime.

I take this opportunity to thank my mother who made things happens for me and who encouraged me for higher education. She is the root of this work and strength of my heart. Mother, thank you for everything. I love you.

I thank my Mother-in-law who is not here to see this day. Mother I missed you, I love you.

Lastly, I want to thank my In-laws for the support and understanding they provided to me.

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Dedication

This thesis is dedicated to my parents and elder brothers who supported me constantly to complete this work successfully.

Jutika Boro

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List of Abbreviations

ASTM	American Society for Testing and Materials
BET	Brunauer–Emmett– Teller
DSC	Differential Scanning Calorimetry
EDX	Energy-dispersive X-ray spectroscopy
FAAE	Fatty Acid Alkyl Esters
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acids
FT-IR	Fourier Transform Infrared Spectrometer
GHG	Green House Gas
H_{-}	Hammett strength
IEA	International Energy Agency
IEO	International Energy Outlook
JCPDS	Joint Committee on Powder Diffraction Standards
NMR	Nuclear Magnetic Resonance Spectroscopy
SEM	Scanning Electron Microscope
TAG	Triacylglycerols
T-CaO	Waste shell catalyst calcined at 900 °C
TGA	Thermogravimetric Analysis
TMS	Tetramethylsilane
WCO	Waste Cooking Oil
XRD	X-ray Diffraction

CHAPTER 1

INTRODUCTION

Chapter 1

1. Introduction

The beginning of human civilization is marked by the use of energy. Throughout the centuries, the human society has evolved by increasingly using energy to the point where the consumption of energy is necessary for the functioning of the contemporary society, the prosperity of the nations and the survival of our civilization. The contemporary human society depends to a large extent on the use of energy in the form of electricity, natural gas, oil etc. The importance of energy in the human society is accentuated by cases when the supply of sufficient energy has been interrupted: the coal miners' strike in Britain in the winter of 1973–1974 resulted in the disruption of the transportation system, the reduction of the working week to a three-day week, economic recession and several deaths, which were due to lack of heating, electricity and lack of transportation. In addition, the economic impact of the energy supply and the energy trade in the world today cannot be ruled out. This is evident from the fact that the geopolitical activities of different nations are influenced by the need for sustainable and secure energy supply. Many pacts and treaties were signed internationally with energy resources as the primary issue of interest. The wars which have been fought after 1950s were basically fought to gain control and security of energy supplies [1-3].

At present, the major vectors which are providing most of the energy consumed on the global scale are from fossil, fissile and renewable energy sources. The first two forms of energy are essentially minerals which were formed several millions of years ago and are not renewable. The term fossil refers to an earlier geological age and it includes petroleum, coal, bitumens, natural gas, oil shales etc. On the other hand, the term fissile is related to materials which are fissionable and are capable of sustaining a chain reaction of nuclear fission. At present, the major fissile energy sources are uranium and thorium. As mentioned before, fossil fuels in the form of petroleum, coal and natural gas are the prime energy sources in the world today [4,5].

Today, energy demand has been growing worldwide tremendously. In a report prepared by U.S. Energy Information Administration (International Energy Outlook 2011, IEO

2011) it was projected that the world energy consumption will increase by 53 %, from 505 quadrillion Btu in 2008 to 770 quadrillion Btu in 2035. According to the report, the role of coal is expected to remain important but natural gas, petroleum and other liquid fuels will play a major role as largest global energy source with an increase of 26.9 million barrel per day and energy consumption together in China and India will account for half of the projected increase as presented in Figure 1.1. (IEO, 2011) [6].

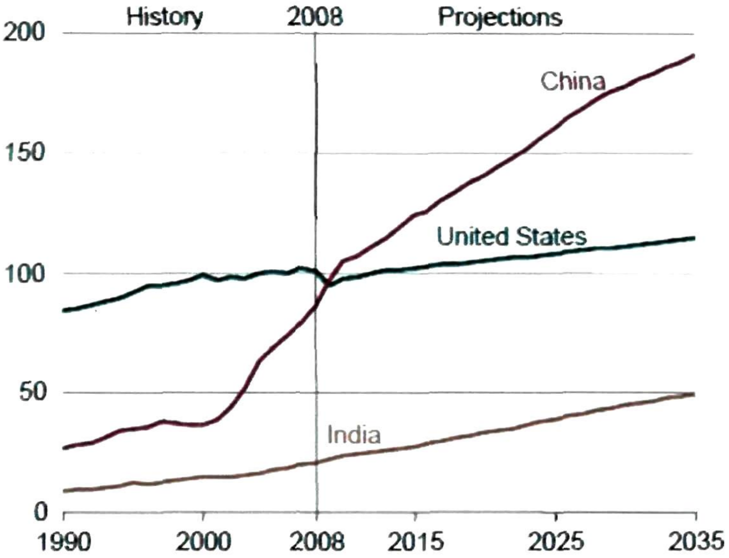


Fig.1.1. Energy consumption in the United States, China, and India, 1990-2035 (quadrillion Btu)

The exponential increase in fossil fuel consumption worldwide has resulted in increase amount of green house gas (GHG) emission which has led to global environmental degradation effects such as greenhouse effect, acid rain, ozone depletion, climate change, etc. and emerges as a major challenge for mitigation. Environmental concerns have increased significantly in the world over the past decades, particularly after the Earth Summit '92 [5, 7, 8]. These environmental implications are being felt in day-to-day life in the form of changing weather patterns, more severe winters and summer globally, foggy conditions in several parts of the world for a prolonged period during winter months. The combustion of fossil fuel also has an adverse affect on human health due to the increase of air pollution, acid rains, buildup of carbon dioxide, changing heat balance of the earth, etc. Hence the world is presently confronted with the twin crisis of fossil fuel depletion and environmental degradation. Progressive depletion of conventional fossil fuels with increasing energy consumption and GHG emissions have led to a move towards alternative, renewable, sustainable, efficient and cost-effective energy sources with lesser emissions [9-12].

Renewable energy sources such as solar energy, wind energy, hydro energy, and energy from biomass and waste have been successfully developed and used by different nations to limit the use of fossil fuels [13]. Renewable energy source is unending source of energy that quickly replenishes itself and does not cause pollution or releases toxic substances into the atmosphere (with an exception for hydroelectric dams which cause damage to flora and land area ; Wind turbines can be hazardous to flying birds). Most of the renewable forms of energy, other than geothermal and tidal power, are ultimately derived from solar energy. For example, energy from biomass is derived from plant material and is produced by photosynthesis using the power of the sun. Wind energy derives from winds, which are also generated by the sun's uneven heating of the atmosphere. Hydropower depends on rain, which again depends on the sunlight's power to evaporate water. Even fossil fuels are derived from solar energy since fossil fuels are originated from plant material [14-15].

Most of the current renewable energy options (e.g., wind, solar, and tidal energy, hydro, and geo-energy) are suitable for the production of electrical energy while more than a half of the current energy consumptions are based on liquid fuels [16-17]. However, there is an expanding market in the use of biomass for supplying both transport fuels and electricity/heat. In the former case, the interest is in producing derived liquid biofuel for transportation purpose via first or second generation processing technologies i.e. produced by physical, biological (fermentation), chemical or thermal processing [18].

1.2.Biomass as Potential Energy Source

Biomass ranks fourth as an energy source and provides, approximately 14% of the world's energy needs. Today biomass is seen as the most promising energy source to mitigate the greenhouse gas emissions and is important for implementing the Kyoto agreement to reduce CO_2 emissions by reducing the usage of fossil fuels [19]. In addition, the recent rising petroleum prices and decline of production–as well as concerns for the environment, rural prosperity, and national security– have heightened interest in biomass (renewable organic matter) as a source of fuel and energy related products. According to the International Energy Agency (IEA, 2007), bio-energy offers the possibility to meet 50% of our world energy needs in the 21st century. Hence, it is predicted that renewable energy from biomass will enter the energy market intensively in the near future to diversify the global energy sources [20].

The term biomass (Greek, bio, life + maza or mass) refers to all organic plant matters as well as organic waste derived from plants, humans, animals, and aquatic or marine life [5]. There are three general classes of feedstocks derived from biomass that are appropriate for the production of renewable fuels: starchy feedstocks (including sugars), triglyceride feedstocks, and lignocellulosic feedstocks. Among all the three feedstocks, the most abundant is the lignocellulosic feedstock which is mainly comprised of energy crops and waste biomass such as switch grass, agricultural residues, municipal wastes and waste generated from wood processing [21]. Starchy feedstocks are mainly composed of glucose polysaccharides which could be easily hydrolyzed into the sugar monomers for the preparation of first generation biofuel such as bioethanol. Examples of such feedstocks are sugarcane, sweet corn etc. The triglyceride feedstocks are the most investigated feedstock among all the biomass sources. Triglycerides, or animal fats and vegetable oils, are found in the plant and animal kingdom and consist of water insoluble, hydrophobic molecules that are made up of one glycerol unit and three fatty acids. More than 350 oil-bearing crops are known, and those with the greatest potential for fuel production, according to Peterson, are sunflower, safflower, soybean, cottonseed, rapeseed, canola, corn, and peanut. Currently, vegetable oils are being used for the production of biodiesel by transesterification [22, 23]. Despite their wide range of possible sources, biomass feedstocks are remarkably uniform in many of their fuel properties, compared with competing feedstocks such as coal or petroleum. Thus biomass can serve as an excellent alternative source to meet the present and future energy demands [24].

The research on biomass is very important in the transportation sector which is, at present, strongly depended on petroleum The liquid biofuels derived from biomass sources are unique in their similarity to the currently preferred fuel sources. As such, their implementation does not require extensive changes to the transportation infrastructure and the internal combustion engine [21]. The two most common and successful biofuels are biodiesel and bioethanol which are aimed at replacing mainly the conventional liquid fuels like diesel and petrol [25]. Again, among the liquid biomass fuels, biodiesel (vegetable oil ester) is noteworthy and research on its production as fuel for compression ignition engines is a rapidly growing technology. In addition the biodiesel is environmentally benign in nature and has the potential to reduce the level of pollutants as well as that of potential or probable carcinogens [5, 26]. Thus the substitution of diesel oil by biodiesel produced within the country could not only solve increasing ecological problems but also improve the economy.

1.1.1. Biodiesel

Background

Producing biodiesel from vegetable oils is not a new process. In fact, the idea of using vegetable oil as a fuel is as old as the diesel engine itself. The very first usage of vegetable oil was demonstrated by Sir Rudolf Diesel who used peanut oil to run one of his engines in Paris Exposition of 1900. After the successful demonstration, he declared that "the diesel engine can be fed with vegetable oils and will help considerably in the development of the agriculture of the countries which use it". Rudolf Diesel did extensive research on vegetable oil and pioneered the concept of using it as fuel but the availability of petroleum at cheaper price during those days did not widespread such a novel concept and after his death the use of vegetable oil as alternative fuel was also forgotten [2,3].

The use of vegetable oil surfaced again in World War II during which it was used as an emergency fuel. But, the importance of what Rudolf Diesel pioneered was understood from the time of the oil crisis of 1970s and extensive research was initiated on vegetable oil to replace diesel fuel. Although the oil crisis prompted the use of vegetable oils as alternative fuel but it was yet hard to use directly in the diesel engine due to the higher viscosity of vegetable oil than petrodiesel [5]. In order to solve this problem, a way was needed to lower the viscosity of the vegetable oil to such a point where it could be burnt properly in the diesel engine. Four major techniques have been proposed to reduce the viscosity of vegetable oil namely, dilution, micro-emulsification, pyrolysis and transesterification. Among all these methods, transesterification is the most preferred method where a new transesterified liquid fuel called biodiesel is produced in the process. Researchers have also introduced new methods for biodiesel production such as biox co-solvent [27, 28], supercritical alcohol process [29-31] and in situ biodiesel process [32, 33]. Overviews of these methods are given in Table 1.1.

The term "biodiesel" was coined by the National Soy Diesel Development Board (presently National Biodiesel Board), U.S. in 1992. The board was the pioneer in the commercialization of biodiesel in the U.S [37]. Chemically biodiesel is defined as a fuel composed of monoalkyl esters of long-chain fatty acids derived from vegetable oils or animal fats and its fuel properties are found similar to petro-diesel as reported elsewhere (Table 1.2) [38-40]. Moreover, the use of biodiesel in a conventional diesel engine substantially reduces emissions of unburned hydrocarbons, carbon monoxide, sulfates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons, and particulate matter [5].

1.2. Feedstocks for Biodiesel production

In view of the potential properties of the vegetable oils, a large number of investigations have been carried out worldwide to establish the suitability of different feedstocks available for biodiesel production. The availability of feedstock for producing biodiesel depends on the regional climate, geographical locations, local soil conditions and agricultural practices of any country. Globally there are many oil-bearing crops which have been identified for biodiesel production and are classified as edible, non–edible feedstocks. Apart from these crops, waste cooking oil and animal fats are also proposed as feedstocks for biodiesel synthesis. Figure 1.2 shows that feedstock alone represents about 75% of the overall biodiesel production cost [41, 42].

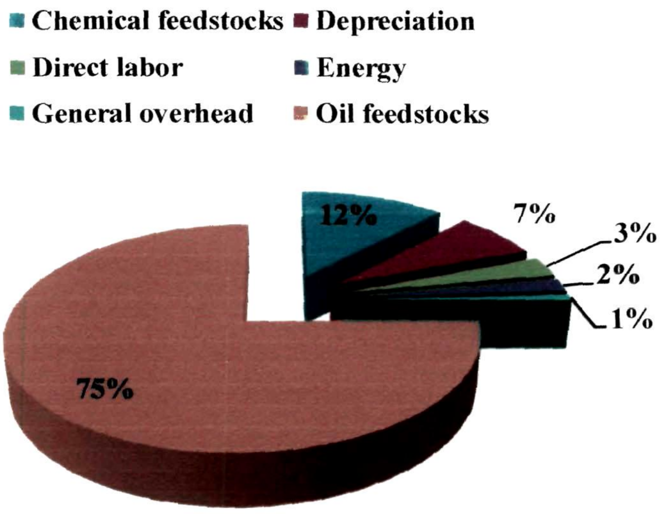


Fig.1.2. Biodiesel production cost factors

The utilization of edible vegetable oil for biodiesel production interferes with the food security of a country like India where there is a big gap between the demand and supply of edible oils and the prices of edible vegetable oils are also higher than that of diesel fuel. The rapidly growing population and rising consumption of biofuels are increasing demand for both food and biofuels. Thus, food and fuel shortages may together be exaggerated [43].

Generally it is expected that the feedstock for biodiesel should fulfill two main requirements which are – low production costs and large production scale. Therefore, the food-for-fuel controversy plaguing the biodiesel industry has shifted the interest of stakeholders and scientists alike to non-edible, waste oils and animal fats [43, 44]. Some of the non edible oil feedstocks investigated exclusively for biodiesel production are *Terminalia belerica* Robx. [45], *Jatropha curcus* [46], *Pongamia pinnata* [47], *Mesua ferrea* [48], *Camellia oleifera* Abel oil [49].

Other reasons for the increasing worldwide attention of non edible oil resources are their easy availability, elimination of competition for food security, could be found even in wastelands, reduction in deforestration, environment friendly and they are economical compared to edible oil feedstocks. Waste cooking oil has also been tried by researchers to prepare biodiesel. In fact, generation of waste cooking oil in any country of the world is in large amount and may result to environmental contamination if no proper disposal method is implemented. They have been found to be unsuitable for feeding animals and hence ensure economically viable feedstock for biodiesel production. However, the main problems in using these types of feedstocks are the presence of high moisture content and high free fatty acids (FFAs). Moisture and FFA lead to saponification and subsequent reduction in the methyl esters produced [50-52].

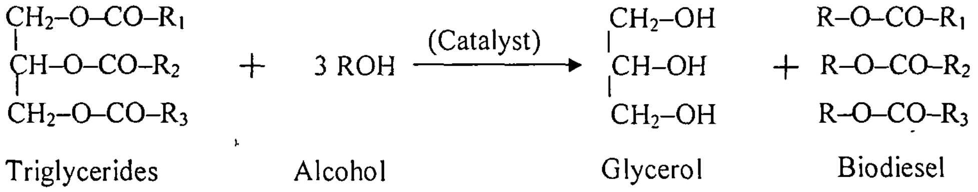
Recently, microalgae have been introduced as third generation feedstock for biodiesel production. Because of its high photosynthetic efficiency to produce biomass and high oil content compared to edible/non edible oil feedstocks, it is considered as promising feedstock for biodiesel production. They are easier to cultivate than many other plants and it could be grown in farm or bioreactors. However, the main problem in the commercialization of microalgae is the high production cost arising due to various factors needed during cultivation. The emergence of closed photobioreactors which can control the various factors such as light requirement, CO_2, water, inorganic salts adds to the overall production cost, making it an expensive process [5, 53, 54].

1.3. Biodiesel production methods

Although vegetable oils could only replace a very small fraction of transport fuel, considerable efforts have been made to develop vegetable-oil derivatives that approximate the properties and performance of hydrocarbon-based diesel fuels. Among all these methods transesterification process has been widely used to reduce the high viscosity of triglycerides and produce biodiesel with higher cetane number [43, 52].

1.3.1. Biodiesel synthesis via transesterification

At present, transesterification is regarded as the most suitable method among other approaches for biodiesel production due to its low cost and simplicity. Transesterification can be defined as the process in which the vegetable oil/animal fat is subjected to chemical reaction with alcohol in presence of a catalyst to form glycerol and ester [55, 56]. The chief product of this process is biodiesel and glycerol is another important by-product produced during the reaction which can be burnt for heat or be used as feedstock in the cosmetic industry. In foods and beverages, glycerol serves as a humectant, solvent, and sweetener, and may help preserve foods. It is also used as filler in commercially prepared low-fat foods (e.g., cookies), and as a thickening agent in liqueurs [57]. The simplified form of this chemical reaction is presented as:



$$\begin{array}{lcccll} \mathrm{CH_2{-}O{-}CO{-}R_1} & & & & \mathrm{CH_2{-}OH} & \mathrm{R{-}O{-}CO{-}R_1} \\ | & & & & | & \\ \mathrm{CH{-}O{-}CO{-}R_2} & + & \mathrm{3\,ROH} & \xrightarrow{\text{(Catalyst)}} & \mathrm{CH{-}OH} & + \ \mathrm{R{-}O{-}CO{-}R_2} \\ | & & & & | & \\ \mathrm{CH_2{-}O{-}CO{-}R_3} & & & & \mathrm{CH_2{-}OH} & \mathrm{R{-}O{-}CO{-}R_3} \\ \text{Triglycerides} & & \text{Alcohol} & & \text{Glycerol} & \text{Biodiesel} \end{array}$$

Where, R_1, R_2, R_3 are the fatty acid chains. The fatty acid alkyl esters produced from this process is called biodiesel.

Scheme 1. Generalized reaction scheme for biodiesel production

Transesterification is mainly affected by the methanol and oil molar ratio – which is used to drive the reaction towards forward direction, catalyst – which depends on the amount of free fatty acid present in the vegetable oil/animal fat, reaction temperature and reaction time. Different types of alcohols are also used which includes methanol, ethanol, butanol etc. and based on the type of alcohol employed for biodiesel production the product is named. For example, when methanol is used, biodiesel is called as fatty acid methyl ester while it is called as fatty acid ethyl ester when ethanol is used. In order to obtain the maximum conversion yield, these variables must be optimized. Generally, the biodiesel production via transesterification can be catalyzed in four basic routes viz. base- catalyzed, direct acid catalyzed, enzyme catalyzed and non catalytic transesterification using methanol or methanol with a co-solvent [58-60].

Table 1.1. Biodiesel production methods

Method	Definition	Advantage	Disadvantage	Ref
Biox co-solvent process	In this process, triglycerides are converted to esters through the selection of inert co-solvents that generate a one phase oil- rich system.	1. It uses inert, reclaimable cosolvents in a single-phase reaction that takes only seconds at ambient temperature and pressure. 2. No catalyst residues appear in either the biodiesel phase or the glycerol phase. 3. This process can handle both- grain based feedstocks but also waste cooking oils and animal fats.	1. The co-solvents, must be completely removed from the glycerol phase as well as from the biodiesel phase and the final products should be water free. 2. The recovery of excess alcohol is difficult	27-28
Supercritical alcohol process	This method of biodiesel production does not involve any co-solvent or catalyst. The reaction is carried out under Supercritical conditions such that the triglycerides dissolve well in the methanol.	1. Catalyst is not needed to accelerate the reaction. 2 Short reaction time and purification is easier	Requires a high temperature and pressure, hence requiring a high amount of energy.	29-31
In situ biodiesel process	In this method, to achieve transesterification of its acyglycerols, the oilseeds are directly treated at ambient temperature and pressure with a methanol solution in which the catalyst has been previously dissolved.	1. This method eliminates the need for the isolation of, and possibly for the refining of, the oilseed lipid. 2. The process could reduce biodiesel production costs, reduce the long size of the production system associated with the pre-extraction, degumming, and maximize the yield of the biodiesel production.	This process cannot handle waste cooking oils and animal fats, which can increase the cost of biodiesel production.	32-33
Pyrolysis Or Thermal Cracking	Method of conversion of one substance into another by application of heat with the aid of the catalyst in the absence of air or oxygen	1. Lower processing costs, compatibility with infrastructure, engines and fuel standards, and feed stock flexibility. 2. The final products are similar to diesel fuel in composition	Energy Intensive	34
Micro-emulsions	A microemulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1- 150 nm range formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles.	1. Fuel viscosity is lowered. 2. They can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles	Lower cetane number and energy content	35
Direct use and blending	Either use vegetable oil directly or is blended with diesel.	1. Liquid Nature and portability. 2. Heat content (~80% of diesel fuel). 3. Readily available ; renewability.	1. Higher viscosity. 2. Lower volatility. 3. The reactivity of unsaturated hydrocarbon chains.	36
Transesterification	Transesterifcation (also called alcoholysis) is the reaction of a fat or oil with an alcohol to form esters and glycerol.	1. Renewability; 2. Higher cetane number. 3. Lower emissions. 4. Higher combustion efficiency	Glycerol disposal and waste water problem	5

Table 1.2. Physical properties of biodiesel

Fuel properties	**Unit**	**ASTM method**	**ASTM D6751 (Biodiesel)**	**ASTM D975 (Petro-diesel)**
Density	g/cm^3	D 5002	0.86-0.90	0.834
Specific gravity	g/cm^3	D 287	0.88	0.851
Kinematic viscosity	mm^2/s	D445	1.9-6.0	1.9-4.1
Pour point	°C	C D97	-15to 16	-35 to -15
Cloud point	°C	D2500	-3.0 to 12	-15 to 5
Flash point	°C	D93	1 to 170	60-80
Sulfur contents	(%)	D4294	0.05	0.05
Acid number	mgKOH/g	D664	0.5	0.5

1.3.2. Transesterification mechanism

The transesterification reaction proceeds well in the presence of some homogeneous catalysts such as potassium hydroxide (KOH) and sodium hydroxide (NaOH) or heterogeneous catalysts such as metal oxides or carbonates. A catalyst is usually used to improve the reaction rate and biodiesel yield while excess alcohol is used to shift the equilibrium towards the product. The transesterification process consists of a sequence of three consecutive reversible reactions, which include conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides. Finally, the monoglycerides are converted into glycerol and yield one ester molecule in each step [61]. This is represented in three steps in Figure 1.3.

$$\text{Triglycerides} + \text{ROH} \xrightarrow{\text{(Catalyst)}} \text{Diglycerides} + \text{R}'\text{COOR} \longrightarrow \text{(Step I)}$$

$$\text{Diglycerides} + \text{ROH} \xrightarrow{\text{(Catalyst)}} \text{Monoglycerides} + \text{R}''\text{COOR} \longrightarrow \text{(Step II)}$$

$$\text{Monoglycerides} + \text{ROH} \xrightarrow{\text{(Catalyst)}} \text{Glycerol} + \text{R}'''\text{COOR} \longrightarrow \text{(Step III)}$$

Fig.1.3. Conversion of triglycerides into biodiesel

The mechanism of the most widely used alkali catalyzed transesterification was formulated in three steps by Eckey [62]. These steps can be summarized as follow:

Pre-step:

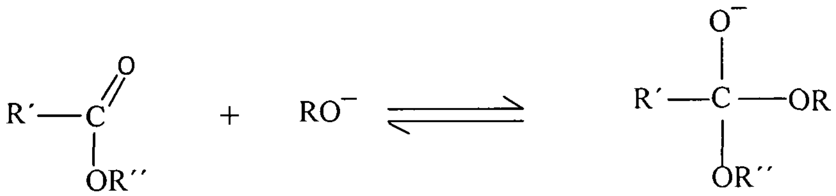
$$OH^- + ROH \rightleftharpoons RO^- + H_2O$$

Or,

$$NaOR \rightleftharpoons RO^- + Na^+$$

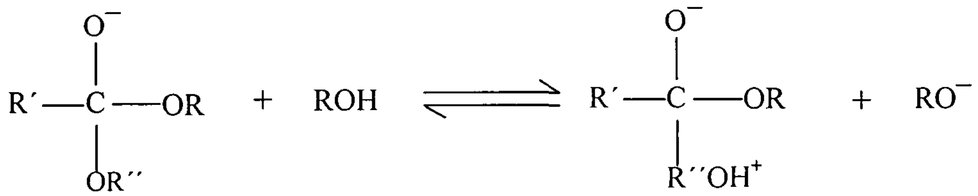
Step I

Carbonyl carbon atom of the triglyceride molecule is attacked by the anion of the alcohol to form tetrahedral intermediate.



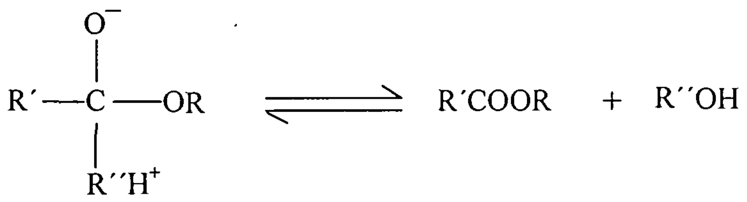
Step II

The tetrahedral intermediate reacts with an alcohol to regenerate the anion of alcohol



Step III

Tetrahedral intermediate rearrange itself to form fatty acid methyl ester and a diglyceride.



Accordingly, base catalysts such as NaOH or KOH react with alcohol to form alkoxide group which takes part in the reaction leading to the formation of fatty acid esters. It was also reported by different researchers that the alkali catalyzed transesterification proceeds 4000 times faster than acid catalyzed transesterification and hence is commercially popular [63].

The key step in acid catalysis is the protonation of the carbonyl oxygen which in turn increases the electrophilicity of the adjoining carbon atom, making it more susceptible to nucleophilic attack. Hence in the case of acid catalysis formation of electrophilic species is ultimately responsible for the observed activity. A simplified block flow diagram (BFD) of a typical acid-catalyzed process is shown in Figure 1.4. [61, 64].

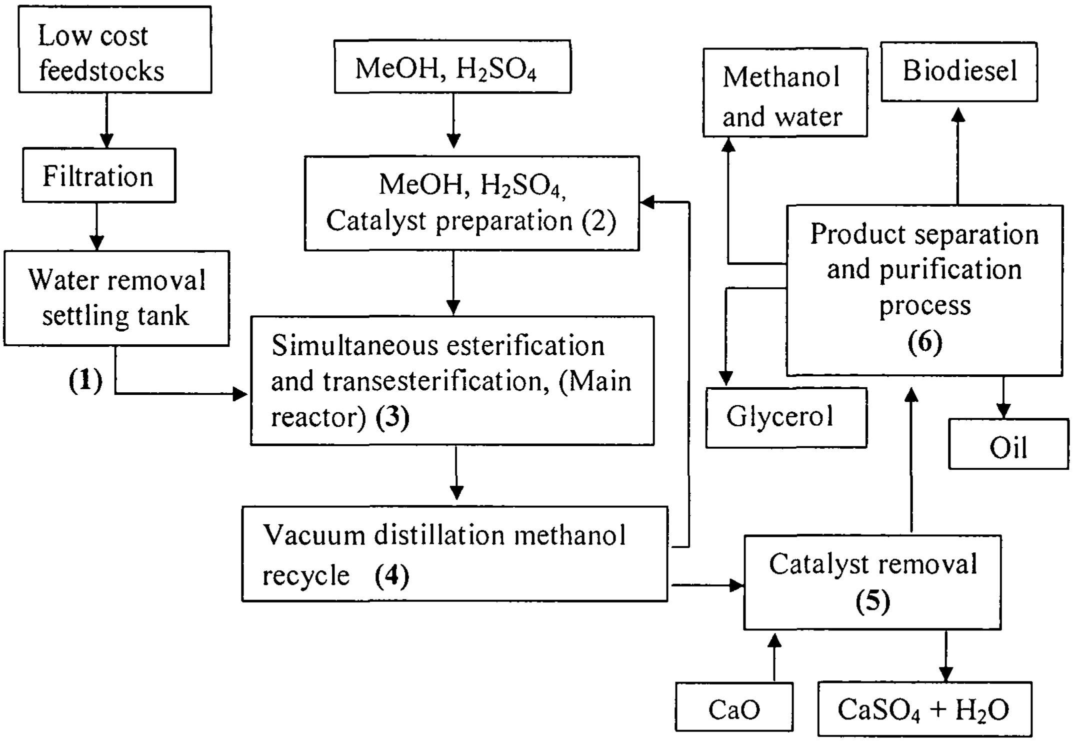


Fig 1.4. Simplified BFD of the acid-catalyzed process. The diagram includes the following: feedstock pretreatment (1), catalyst preparation (2), transesterification and esterification (3), alcohol recycle (4), acid catalyst removal (5), and biodiesel separation and purification process (6).

Lipase transesterification of triglycerides with an alcohol (alcoholysis) involves a two-step mechanism when looking at a single ester bond. The first step is hydrolysis of the ester bond and release of the alcohol moiety (equation 1) followed by an esterification with the second substrate (equation 2) [65-68].

$$E + Es_S \rightleftharpoons E\cdot Es_S \rightleftharpoons F\cdot B_P \rightleftharpoons F + B_P \longrightarrow \quad (1)$$

$$F + A_S \rightleftharpoons F\cdot A_S \rightleftharpoons E\cdot Es_P \rightleftharpoons E + Es_P \longrightarrow \quad (2)$$

Where, S is substrate, P is product. For biodiesel, A_S is alcohol substrate (i.e., methanol or ethanol), B_P is product with alcohol moiety (di- or monoglyceride or glycerol), E is free enzyme, Es_S is ester substrate (tri-, di- or monoglyceride), Es_P is fatty acid alkyl esters (FAAE), F is fatty acid.

As mentioned previously, transesterification can be performed with different types of catalyst and classifies into different types according to the type of catalysts used such as (a) base catalyzed transesterification, (b) acid-catalyzed transesterification, (c) enzyme-catalyzed transesterification etc. Besides, supercritical alcohol transesterification and some new techniques of transesterification namely, microwave-assisted transesterification [69], ultrasound-assisted transesterification [70], mixed methanol– ethanol system [71] are also employed for biodiesel production.

1.3.3. Factors influencing transesterification

(A) Influence of alcohol to oil ratio

The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid ester and one mole of glycerol. Since transesterification is an equilibrium reaction, excess of alcohol is required to drive the reaction towards forward direction [44] and to convert oil or fat completely to esters in a shorter time. But, an optimal amount of alcohol is to be added to the reaction so that excess amount of unreacted alcohol will not create difficulties during purification of biodiesel as well as recovery of glycerol as reaction products [72, 73]. Alcohol/oil ratio is also associated with the type of catalyst used for transesterification. For example, the alkali catalyst is found to exhibit the best catalytic activity with 6:1 alcohol/oil molar ratio while higher alcohol/oil molar ratios have been reported on using different types of heterogeneous catalysts for biodiesel production [74-76].

(B) Reaction Time

The ester conversion rate is also dependent on the reaction time. The initial reaction is found to be slower due to the incomplete mixing and dispersion of alcohol into the oil; after a while, the reaction proceeds very fast. Generally, the conversion rate of fatty acid esters increases with the increasing reaction time because with longer reaction time the reactants have a longer contact time. But, longer reaction time may result into loss of esters and leads to soap formation arising from the backward reaction of transesterification reaction [76-78].

Reaction time may also depend on different types of feedstocks used for biodiesel production. Wang et al. [75] studied the esterification of *Euphorbia lathyris* L.(ELO), *Sapium sebiferum* L.(DSSKO) and *Jatropha curcas* L.(JCO) in different reaction times. They reported that the optimal reaction times for ELO, DSSKO and JCO were 45, 30 and 30 min, respectively. In another study, conducted by Sanli et al. [80] on cottonseed and corn oil having high densities and viscosities, the reaction time of 1 h was not enough for complete ester conversion and the reactions were carried out for 8 h.

Reaction time is also related to the types of catalysts employed in the reaction. Complete conversion of same feedstock with different types of catalysts was reported for different reaction times by many researchers. For homogeneous base catalyst, the reaction was observed to be completed within 3 h while more than 10 h reaction time was reported for homogeneous acid catalyst. In the case of heterogeneous catalyst, catalyst composition is very important as it directly affects the reaction time. For example, a biodiesel yield of more than 90% was obtained in just 10 minute of reaction time with KF/Ca-Mg-Al hydrotalcite catalyst in the transesterification of palm oil [81] while 89.23% biodiesel yield was reported in a reaction time of 9.72 h with the same feedstock using KF/ZnO as catalyst [82].

(C) Reaction temperature

Transesterification is also influenced by reaction temperature. It is reported that at higher reaction temperature the viscosity of the feedstocks and the mass transfer limitations are reduced. It also provides an increased reaction rate and shortens the reaction time. However, the reaction temperature is expected to be less than the boiling point of the alcohol used in order to ensure that the alcohol will not escape to the vapor phase. The standard reaction temperature for biodiesel production is considered to be around 60 °C (73, 76, 83). However, depending upon the type of catalyst used and reaction procedures followed, the reaction temperature may vary. For example, Shu et al. synthesized biodiesel from cottonseed oil using a carbon-based solid acid catalyst at a reaction temperature of 270 °C while in a similar study biodiesel yield of 98.03% was obtained from palm oil with potassium hydroxide catalyst supported on palm shell activated carbon catalyst [84, 85]. Again, beyond optimal level, the biodiesel yield may also decrease due to saponification of the triglycerides [73].

(D) Influence of Catalyst

Catalyst plays vital role in transesterification and it is necessary to increase the reaction rate and final yield. Both acid and base catalysts are used in transesterification and their selections are dependent on the characteristics of feedstock. The catalysts can be classified as homogeneous or heterogeneous catalysts. Homogeneous catalysts act in the same liquid phase as the reaction mixture, whereas heterogeneous catalysts act in a different phase from the reaction mixture, usually as a solid [86]. At present, base catalysts such as NaOH or KOH are the most preferred catalysts for transesterification owing to their capabilities of completion of reactions at higher speeds, requirement of lower reaction temperatures and higher conversion efficiencies. However, the base catalysts cause the saponification when they react with FFAs present in the vegetable oils or triglycerides, particularly when the acid values of feedstocks are higher [87]. An alternative way to process these vegetable oils is to use an acid catalyst. However, homogeneous acids, such as hydrochloric acid and sulfuric acid require a long reaction time, significantly more than that of the alkaline catalysts, and this becomes a serious problem. To overcome the problems of homogeneous catalysts, research is focused towards the development of heterogeneous catalysts which are associated with easy product separation, regeneration & reuse of the catalyst and elimination of water washing step. In addition, usage of solid catalysts could also catalyze transesterification and esterification reaction simultaneously and are useful for those feedstocks with high FFAs [44, 88].

(E) Influence of Free Fatty acids (FFAs)

The major components of vegetable oils and animal fats are triacylglycerols (TAG; often also called triglycerides). Chemically, TAG are esters of fatty acids (FA) with glycerol. The TAG of vegetable oils and animal fats typically contain several different FA. Thus, different FA can be attached to one glycerol backbone. The different FA that are contained in the TAG comprise the FA profile (or FA composition) of the vegetable oil or animal fat. Because different FA has different physical and chemical properties, the FA profile is probably the most important parameter influencing the corresponding properties of a vegetable oil or animal fat [2]. The fatty acid compositions of different feedstocks are summarized in Table 1.3. The presence of free fatty acids in oils causes significant processing problems in standard biodiesel manufacturing, since the free fatty acid is readily saponified by the homogeneous alkali catalyst, leading to a loss of catalyst as well as increased purification costs [95,96].

Table 1.3. Percentage of fatty acid type for different vegetable oils

Oil	Palmitic (C16:0)	Palmitoleic acid (C16:1)	Stearic acid (C18:0)	Oleic acid (C18:1)	Linoleic acid (C18:3)	Linolenic (C18:3)	Other acids	Ref
Corn	6.0	-	2.0	44.0	48.0	-	-	89
Cottonsed	28.3	-	0.9	13.3	57.5	-	-	90
Olive	14.6	-	75.4	10.0	-	-	-	89
Palm	42.6	0.3	4.4	40.5	10.1	0.2	1.1	5
Peanut	11.4	-	2.4	48.3	32.0	0.9	9.1	90
Rapeseed	3.5	0.1	0.9	54.1	22.3	-	0.2	89
Safflower	7.3	0.1	1.9	13.5	77.0	-	-	89
Soybean	11.9	0.3	4.1	23.2	54.2	6.3	-	5
Sunflower	6.4	0.1	2.9	17.7	72.9	-	-	89
Tallow	29.0	-	24.5	44.5	-	-	-	89
J.curcus	14.2	0.7	7.0	44.7	32.8	0.2	-	91-92
P.pinnata	10.2	-	7.0	51.8	17.7	3.6	-	93
M.Indica	24.5	-	22.7	37.0	14.3	-	-	94

The fatty acids vary in their carbon chain length and in the number of unsaturated bonds they contain. The FFA content present in a feedstock determines the type of catalyst required for the production of biodiesel. If the feedstock contains FFA > 3 wt.%, homogeneous base catalysts such as NaOH or KOH will not be effective [88]. In such cases FFA reacts with the base catalysts for the production of water upon reaction (reaction [1], Figure 1.5.) which in turn participate in hydrolysis with biodiesel to produce additional FFA and methanol (reaction [2], Figure 1.5.) [76]. Therefore despite a high production cost, the integrated two-step transesterification is applied to prepare biodiesel from low cost/ non edible oil feedstock with high FFA content. Other potential strategies for the production of biodiesel from feedstocks with high FFA content include feedstock purification such as refining, bleaching, and deodorization to remove FFA content and other undesirable materials, if present [97]. Alternatively the employment of catalysts that are not destroyed by FFA in the production of biodiesel is another way of reducing the high FFA content in a feedstock.

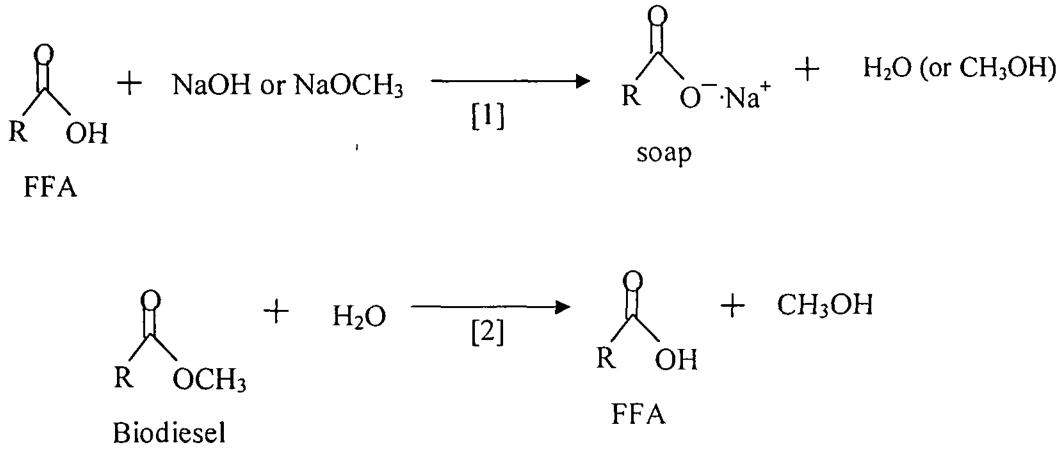


Fig.1.5. Formation of soap from reaction of free fatty acids (FFA) with catalyst (reaction [1]) and hydrolysis of biodiesel (reaction [2] to yield FFA and methanol

1.4. Catalysis in transesterification of vegetable oil

Generally, transesterification reaction can proceed in the presence or absence of catalysts and can be categorized as catalytic and non-catalytic transesterification system. The non catalytic transesterification occur at supercritical conditions and the biodiesel produced by this method could be purified easily as it does not require the separation of catalyst or saponified products unlike conventional processes. However, in non catalytic transesterification system, the reaction generally occurs at high reaction temperature, high methanol to oil ratio and high pressure which are backdrops of the system. On the other hand, in catalytic system, transesterification is performed at low temperature and low methanol to oil ratio. In general, there are three categories of catalysts used for biodiesel production namely alkalis, acids and enzymes. Although enzyme catalysts are gaining importance recently owing to simple purification processes and no soap formation during reaction, they are less often used commercially because of the longer reaction times and higher cost [98-100]. Compared to enzyme catalysts, the most common catalysts employed for biodiesel production are alkali and acid catalysts. The alkali and acid catalysts may be homogeneous or heterogeneous in nature which may be broadly classified as homogenous catalyst (acid or base) or heterogeneous catalysts (acid or base).

1.4.1. Homogeneous vs. heterogeneous catalysts

At present homogeneous alkali catalysts such as NaOH or KOH is widely used in industrial biodiesel production owing to their fast reaction rate and the fact that they are relatively cheap. However, one of the major disadvantages of homogeneous catalysts is that they cannot be reused or regenerated, because the catalyst is consumed in the reaction and separation of catalyst from products is difficult and requires more equipment which could result in higher production costs. Besides, the process is not environment friendly because a large amount of waste water is produced in the separation step [94]. In addition the homogeneous alkali catalysts are highly sensitive to water which directly limits the feedstocks to be used for biodiesel production. It means, it cannot be used for raw materials having high FFAs and is applicable only to feedstock having low FFAs such as refined soybean oil or sunflower oil. In such cases acid catalyzed transesterification is preferred over alkali catalyst. The advantage with acid catalysts is that it can catalyze esterification and transesterification simultaneously and being one-step process, is more economical than the base-catalyzed process which requires an extra step to convert FFA to reduce the FFA content [101,102]. However, these catalysts require severe reaction conditions such as high methanol to oil ratio, longer reaction time and high reaction temperature, which is a drawback of the catalyst. In order to solve these problems, the use of heterogeneous catalysts has been explored. The key benefit of using heterogeneous catalysts is that no polluting by-products are formed, the catalysts do not mix with biodiesel, it could be recovered and reused allowing the operation in continuous reactors instead batch reactors used with homogeneous catalysis. In addition to lower separation costs, less maintenance is needed as these catalysts are not corrosive. Moreover, there are some heterogeneous catalysts which could simultaneously catalyze the transesterification as well as esterification reaction. By the utilization of such catalysts one can avoid the pre-esterification step, thus these catalysts can also be employed for feedstocks with high free fatty acid content [103-106]. Recently, the solid catalyst derived from biomasses for biodiesel production has been reported by different researchers. Biodiesel production in the presence of such catalyst provides an alternative for a “green” process as the catalyst comes from a renewable biomass source. Therefore, the catalyst has gained popularity owing to its environmental friendly nature and its state of origin [107-109].

Keeping in mind the growing environmental constraints and various problems in the usage of homogeneous as well as heterogeneous catalysts, raw materials in the form natural sources or biomass can be targeted for the preparation of solid catalysts. Utilization of such materials for catalyst preparation could give an opportunity for an environmentally benign biodiesel production and at the same time does not pollute the natural environment. In addition catalyst prepared from such renewable biomass could be degraded easily and has the distinct characteristics of a "green" catalyst.

1.5. Objectives of the research

The present investigation has been undertaken with the following objectives:

1. To prepare solid heterogeneous base catalyst from waste biomass.
2. To improve catalytic properties of the prepared catalyst by doping with alkali and alkaline earth metals.
3. To characterize the prepared catalysts and examine their catalytic activities.
4. To analyze and characterize biodiesel produced by employing the above prepared catalysts
5. To compare the catalytic activity of the prepared catalysts.

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CHAPTER 2

LITERATURE SURVEY

Chapter 2

2. Review of Literature

The increasing concerns about depleting energy resources and environmental hazards have intensified the efforts for sustainable energy sources. In this respect, biodiesel plays a major role because it is nontoxic, biodegradable and is made from renewable sources such as vegetable oils and animal fats. It is produced by transesterification in which oil or fat is reacted with a monohydric alcohol in the presence of a catalyst. At present, biodiesel is produced commercially using homogenous basic catalysts such as sodium (or potassium) hydroxide or methoxide because the transesterification reaction is generally faster, less expensive, and more complete with basic catalysts than with acid catalysts [1]. The catalyst employed has a direct impact on the purity of the feedstock required, the kinetics of the reaction, and the extent of post-reaction processing required. In general, there are three categories of catalysts used for biodiesel production: alkalis, acids, and enzymes [2-4]. Studies on producing biodiesel by employing homogeneous catalysts such as NaOH, KOH have been reported elsewhere [5-10].

Darnoko et al. [11] conducted a two step transesterification reaction of waste cooking oil with KOH as base catalyst and observed that the exact amount of KOH was needed in the end to neutralize acidity. Nonionic base catalysts were also studied for the purpose of biodiesel production. For example, 90% methyl esters were produced by using only 1 mol% of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as homogeneous base catalyst and the biodiesel yield with TBD was very close compared with that of NaOH [12]. Based on this study several alkylguanidines namely, 1,3-dicyclohexyl-2-*n*-octylguanidine (DCOG), 1,1,2,3,3-pentamethylguanidine (PMG), 7-methyl-1,5,7- triazabicyclo [4.4.0]dec-5-ene (MTBD), and 1,2,3-tricyclohexylguanidine (TCG) were investigated under the similar reaction conditions. The catalytic activity were in the order of TBD > TCG > DCOG > MTBD > PMG, in line with their relative base strengths [13]. In a recent study, liquid amine based catalysts such as diethylamine (DEA), dimethylethanol amine (DMAE), tetramethyldiaminoethane (TEMED), and tertramethylammonium hydroxide (TMAH) were also successfully employed for transesterification of refined vegetable and frying oil. Highest conversion of 98% was achieved in 90 minutes at 65 °C with TMAH as catalyst. However, in these cases, catalysts requirement for transesterification were larger amount (13 wt.%). But, the advantage with these types of catalysts was that they also acted as solvents for both the reactants and products and helped to shift the reaction equilibriums towards the products [14]. The homogenous base-catalyzed transesterification reaction is about 4,000 times faster than the corresponding acid-catalyzed process [15,16] and it can be performed at low temperatures (around 60 °C), pressures, reaction times and are less corrosive to industrial equipment than acid catalyzed methods [17, 18]. However, the homogeneous acid-catalyzed reaction holds an important advantage over the base-catalyzed method in that the performance of acid catalyst is not adversely influenced by the presence of FFA. Moreover, acid catalyst can catalyze both esterification and transesterification simultaneously and being a one-step process, is more economical than the base-catalyzed process which requires an extra step to convert FFA to reduce the FFA content [19, 20]. Some of the acid catalysts employed for transesterification are sulfuric, sulfonic, phosphoric and hydrochloric acids [21-22]. Wang et al. [23] observed that the transesterification of waste cooking oil with H_2SO_4 as catalyst resulted in biodiesel yield of 90% at a reaction time of 10 h with a high methanol to oil ratio of 20:1 while Freedman et al. [24] reported 99% oil conversion by using 1 mol% of H_2SO_4 with a methanol to oil ratio of 30:1 in a 69 h reaction time. Apart from the traditional acid catalysts, researchers have also reported the use of new acid catalysts. For example, Miao et al. [25] studied the use of trifluoroacetic acid as catalyst for transesterification and reported high methyl ester conversion of 98.4% by one-step transesterification method. But, the reaction was operated at very high temperature of 120 °C. Lewis acids like $AlCl_3$ or $ZnCl_2$ were also used to catalyze the transesterification of canola oil with methanol in presence of tetrahydrofuran (THF) as co-solvent. In this study, $AlCl_3$ was found to be more effective than $ZnCl_2$ and could catalyze the esterification of stearic acid in a long reaction time of 18 h [26]. Indeed, the homogeneous acid-catalyzed process can deal with high-FFA feedstocks, carrying out simultaneously both esterification and transesterification, provided that water is removed during processing. However, the fact that acid-catalyzed transesterification process requires more severe reaction conditions (such as longer reaction time), higher methanol to oil ratio are the drawbacks of the acid catalyzed transesterification [27].

Therefore recent research has focused on the application of heterogeneous catalysts to produce biodiesel, because of their environmental and economic advantages. In addition, biodiesel synthesis using solid catalysts instead of homogeneous catalyst, could potentially lead to economical production costs because of reuse of the catalyst [28] and the possibility of carrying out both transesterification and esterification simultaneously [29]. Additional benefit with solid based catalyst is the lesser consumption of catalyst [30].

2.1. An overview of heterogeneous catalysts used in biodiesel production

The heterogeneous catalysts are associated with many advantages compared to homogeneous catalysts. The catalysts are not consumed or dissolved during the reaction and can be easily separated from the products. In addition these catalysts could be regenerated as well as reused and they are more environmentally benign because there is no need for acid or water treatment in the separation step. A variety of solid catalysts has been examined for the transesterification reaction and new materials/catalysts continue to be reported in the literature. These solid catalysts are classified either as acid or base catalysts as shown in Table 2.1. [31].

Table 2.1. Typical solid acid and base catalysts employed for transesterification

Solid acid catalysts	**Solid base catalysts**
Sulphonic ion exchanged resin	Hydrotalcites (Mg-Al)
Amberlyst -15, Nafion	Cs-exchanged sepiolite
Sulphated zirconia, Sulphated tin oxide	Oxides like MgO, CaO, La_2O_3, ZnO
Sulphated zirconia/alumina	Guanidine anchored cellulose/ polymer
Zeolites (H-Y) H-Beta, H-ZSM-5, ETS- 4,10	Metal salts of amino acids
MCM family	$CaCO_3$, $Ba(OH)_2$
Heteropoly acids	Cs exchanged faujasites
Zinc acetate on silica	Li-promoted CaO
Organosulphonic acid on mesoporous silica	Zinc aluminates
Mesoporous unstated zirconium phosphate	

Metal oxides are the mostly used heterogeneous catalysts for transesterification. Although some of them show low activity, the research is still undergoing on this field. The structure of metal oxides is made up of positive metal ions (cations) which possess Lewis acid and negative oxygen ions (anions) which possess Lewis base. In methanolysis of oils, metal oxides provide sufficient adsorptive sites for methanol, in which the O–H bonds readily break into methoxide anions and hydrogen cations (Figure 2.1.). Thus methoxide anions then react with triglyceride molecule to form corresponding fatty acid methyl esters [32,33].

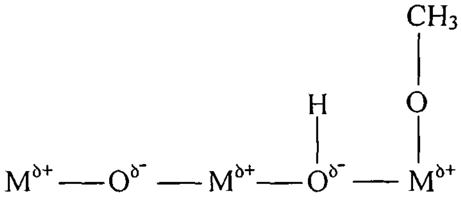

Fig.2.1. Surface structure of metal oxides

Among different metal oxides which are found to be useful in biodiesel production, calcium oxide is the most popular alkali earth metal oxides. It relatively possesses high basic strength and less environmental impacts due to its low solubility in methanol and can be synthesized from cheap sources like limestone and calcium hydroxide. Granados *et al.* [34] obtained a biodiesel yield of 94 wt.% with thermally activated CaO at a reaction temperature of 60 °C and 13:1 methanol: oil ratio. The study also indicated that CaO exposed to air for more than 20 days were found to be hydrated and carbonated which means that the active surface sites of CaO were poisoned with CO_2 and covered with H_2O. This problem was overcome when the authors thermally treated CaO at 700 °C. Although leaching of active sites was observed in the reaction media, the catalyst could be reused for eight times with a minimum yield of 73 wt.%. In a similar work, CaO calcined at 900 °C could yield 93% of soybean methyl ester in just 1 h while 98% of methyl ester was obtained with waste cooking oil in a 2 h reaction time. However, formation of calcium soap was found to deactivate the catalyst resulting into low biodiesel yield [36,37]. It was also reported that the uncalcined CaO could exhibit better activity than the CaO calcined at 500 °C in a reaction time of 10 h. This was attributed to the presence of surface hydroxide sites in uncalcined CaO which enhanced the rate of transesterification [38]. According to Liu et al. [39], the catalytic activity of CaO could be improved by the presence of small amount of water. They suggested that the presence of water, surface O^{2-} extracts H^+ from H_2O to form surface OH^- which is easily extracted by reactants in chemical reactions. Then, the OH^-extracts H+ from methanol to generate methoxide anion and H_2O. Methoxide anion is strongly basic and has high catalytic activity in transesterification. Apart from CaO, metal oxides such as MgO [40], SrO [41], Zirconium oxide [42, 43] and titanium oxide [44] were reported to be employed as catalysts for biodiesel production. Further, supported metal oxides such as potassium supported by zinc oxide [45], K_2CO_3 supported on MgO [46], KF/ZnO [47] and various mixed metal oxides, for examples, $CaMnO_3$, $Ca_2Fe_2O_5$, $CaCeO_3$, $CaZrO_3$ etc. were also reported as catalysts for biodiesel production[48].

Studies showed that hydrotalcite could be used either as catalytic materials or as catalytic supports. Hydrotalcites are an important group of catalyst as their acid and basic properties can be controlled by varying their composition. It is defined as anionic and basic clay found in nature which consists of brucite-like [$Mg(OH)_2$] network wherein an isomorphous substitution of Mg^{2+} ion by a trivalent cation M^{3+} occurs and the excess positive charge is compensated by gallery anions which are located in the interlayer along with water molecules [49,50]. Ilgen et al. [51] performed transesterification of canola oil using Mg-Al hydrotalcites as solid base catalysts. The catalyst was prepared by co-precipitation of magnesium and aluminum hydroxides from their nitrate solutions using an aqueous solution of sodium carbonate as the precipitating agent. A yield of 71.9% was achieved by using 3 wt % catalysts after 9 h of reaction at 60 °C with a 6:1 molar ratio of methanol to oil. The authors assumed that higher conversion could be achieved if the basicity of the hydrotalcites could be increased. To increase the basicity, Zeng et al. [52] prepared Na, K loaded MgAl hydrotalcite catalyst at different pH's using alkali and alkali-free methods and used it in the methanolysis of refined oil. The yield obtained was compared with glyceryl tributyrate which was taken as standard oil compound. The results indicated that catalyst prepared with alkali method have higher basicity and higher metal leaching than those of the alkali-free method. It was observed that the K-loaded hydrotalcite exhibited higher basicity than those with Na loaded. Direct use of the recovered catalyst indicated a loss in the catalytic activity which was caused by metal leaching and the blocking of the active sites by the product. This problem was overcome by calcining the recovered catalyst and reloading the respective metal. In another study catalyst activity was found to be enhanced when KF was loaded on HT. This was attributed to the formation of new crystal phase of $KMgF_3$ and $KAlF_4$ act as the active component of the KF/HT catalyst [53].

Research on the direct transesterification of lipid feedstocks into biodiesel using solid acid catalysts such as zeolites, heteropoly acids, and sulfated sulphated zirconia have also been reported [54,55]. Among the different types of inorganic solids that have been employed as catalysts for the production of biodiesel, the most popular ones are the zeolites. Since zeolites can be synthesized with extensive variation of acidic and textural properties, it is possible to tailor-make systems for optimum biodiesel production, overcoming the diffusional limitations [31]. Zeolites can be synthesized with different crystal structures, pore sizes, framework Si/Al ratios, and proton-exchange levels. In addition, zeolites provide the possibility to choose among different pore structures and surface hydrophobicities, according to the substrate‘s size and polarity. For example, the concentrations of Al_2O_3 and Na_2O in zeolite Y were varied and applied in the transesterification of waste cooking oil. The catalyst exhibited poor catalytic activity and the highest yield was only 26.6% when the reaction was carried out at a high reaction temperature of 460 °C. Similar results on low activity were also reported by different researchers [56-59]. Heteropoly acids are also used for carrying out esterification and transesterification simultaneously owing to its strong acidity, easier separation and reusability, higher proton mobility, and higher selectivity [31]. In addition these catalysts are water tolerant in nature. Transesterification of yellow horn oil in the presence of pure HPAs, $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$ exhibited good catalytic activities. Among which the best catalytic activity was observed with $H_3PMo_{12}O_{40}$. Catalysts were found to be soluble in the reaction medium which is a drawback of the catalyst as it creates separation problem after the completion of the reaction. To overcome this problem salts of alkaline cations such as Cs^+, NH^+_4, Ag^+, Na^+ were introduced in $H_3PW_{12}O_{40}$ and different reaction parameters were optimized by microwave assisted transesterification (MAT). Though high catalytic activity was observed for the newly incorporated catalysts but it was observed that apart from Na^+ impregnated HPA rest of the impregnated HPA catalyst were insoluble in water and alcohol. This insolubility of large monovalent ions was attributed to their ability in having micro and mesopores with high surface area and variation in the number of available active acid sites. On the other hand this feature is absent for small monovalent ions like Na^+. Owing to better activity and easy separation, more studies were conducted for Cs incorporated HPA. A high yield of 96% was obtained under the optimum reaction condition of reaction temperature: 60 °C, methanol/oil ratio: 12:1, catalyst amount: 1wt%, reaction time: 10 min. The catalyst was highly stable and it could be used upto nine consecutive cycles without any change in catalytic activity. However, the color of the catalyst changed and less catalyst could be recovered with the repeated cycles. Observation of the different reaction parameters during the MAT process and comparing the obtained results with H_2SO_4 catalyzed transesterification; the authors claimed that their catalyst has an advantage in terms of energy consumption as it took only 10 min for complete reaction [60]. Several studies are conducted on ZrO_2 as a heterogeneous acid catalyst for transesterification of different feedstock and excellent catalytic activity has been reported. The good catalytic performance of the sulfated silica-zirconia materials is attributed to a higher dispersion of zirconia to give higher acid site density and also to better tolerance of water. It was reported by Jitputti et al. [61] that SO_4^{2-}/ZrO_2 could produce promising results in transesterification of palm kernel oil and crude coconut oil with methyl ester yield reaching as high as 90.3% and 86.3%, respectively. However, when unsulfated ZrO_2 was used as catalyst instead of SO_4^{2-}/ZrO_2, only 64.5% (palm kernel oil) and 49.3% (crude coconut oil) of methyl ester yield were reported, respectively.

Zirconia-supported heteropoly and isopoly tungsten acids were also applied in biodiesel synthesis from sunflower oil and the result indicated that isopoly tungsten was more active than heteropoly tungsten since it possesses more Bronsted acid sites [62]. Oil conversion of 97% was reached after 5 h of reaction time under reaction conditions of temperature of 200 °C with catalyst content of 15 wt% and alcohol/oil molar ratio 15:1. Furuta et al. [63] evaluated the performance of tungstated zirconia–alumina (WZA) and sulfated zirconia–alumina (SZA) in the transesterification of soybean oil with methanol at 200–300 °C using a fixed bed reactor under atmospheric pressure. WZA was found to have a higher activity in transesterification as compared to SZA.

Mesostructure materials such as silica are also applied as heterogeneous acid catalyst in biodiesel production. These mesoporous materials (silica) consist of large mesopores which can significantly minimize the diffusion problem for reactants to access into the active sites of the catalyst. Apart from that, the physical and chemical properties of these mesoporous materials can be manipulated by incorporating suitable organic or inorganic functional groups into the mesoporous silica matrix [64]. Excellent catalytic activity was observed for propylsulfonic acid-functionalized mesoporous silica (SBA-15-SO_3H) in the esterification of beef tallow and a conversion of 95% was obtained at relatively short reaction time of 30 min at a reaction temperature 120 °C with 20:1 methanol to oil ratio. Despite adding propyltrimethoxysilane as hydrophobic agents to overcome the problem of leaching the catalytic activity reduced for consequent cycles. This decrease in activity was attributed to the accumulation of organic or carbonaceous matter on the catalyst surface that blocks the acidic sites [65].

Use of supported catalyst which can provide more specific surface area and pores for active species, where they can anchor and react with large triglyceride molecules is another solution for encountering the poor mass transfer problem faced by solid catalysts [66]. Research in the field of supported catalysts have also gain momentum recently and used in transesterification of different vegetable oils. Chemically for a heterogeneous catalyst system the majority of the reactions take place at the surface of the catalyst. Thus the exposed surface area of active phase and the stability have bigger role to play in a catalyzed reaction. Reasonable surface areas are generally obtained for particle sizes (1–10 nm) for the purpose. Since it is impossible to apply such small particles in reactors, support bodies are applied. Catalyst supports are in general porous materials, so as to allow a high loading of highly dispersed metal particles, while the particles of the active phase usually need to be synthesized in such a way that they are as small as possible [67]. KF loaded MgO [68], Alumina/silica supported K_2CO_3 [69], Na/SiO_2 [70] etc, are some of the recently reported supported catalysts for biodiesel production via transesterification.

A brief list of some of the heterogeneous catalysts used for transesterification along with their preparation conditions is presented in Table 2.2.

Table.2.2. Preparation and reaction conditions of different heterogeneous catalyst in the transesterification of different oil feedstock

Catalyst	**Feedstock**	**Preparation conditions**		**Reaction conditions**			**Conversion (C) Yield (Y) (%)**	**Ref**
		Method	**Calcination temperature(°C)**	**Methanol: oil ratio**	**Reaction temperature(°C)**	**Reaction time (h)**		
TiO_2– MgO	WCO	Sol–Gel	500– 700	30:1	150	6	92.3 (Y)	112
CaMgO, CaZnO	JCO	Coprecipit-ation method	800 & 900	15:1	65	6	80%< (C)	113
KF/Eu_2O_3	Rapeseed oil	Precipitation method	600	12:1	Methanol reflux temperature	1	92.5% (C)	114
$Ca(OCH_2CH_3)_2$	Soybean oil	—	Dried in oven at 105	12:1	65	1.5	95.0 (Y)	115
$Eu(NO_3)_3/Al_2O_3$	Soybean oil	Impregnation	300—900	6:1	70	6	63 (C)	116
Lithium-Doped ZnO	Soybean oil	Impregnation	500	12:1	65	3	96.3(C)	117
KF/ZnO	Soybean oil	Impregnation	500	10:1	65	9	87(C)	118
Na doped SiO_2	Jatropha oil	Sol–Gel	600	15:1	65	45	99 (C)	119

2.2. Waste shells in biodiesel production

The synthesis process of the most of heterogeneous catalysts is reported to be complex and thus their preparation conditions are found to be lengthy and their preparation routes also require special skills. Therefore, it is a great challenge to explore an ideal solid basic catalyst that is highly effective, low-cost, and ecologically friendly for biodiesel production [71-72]. To address these issues in recent years, the utilization of natural calcium sources from waste shells as an economic catalyst has been a new trend for biodiesel production. The growing research interest in this field has stimulated the research towards the preparation of an environmentally benign catalyst by using waste mollusk shells and eggs shells as the raw material for catalyst synthesis [72]. Besides, these catalysts could also be reused like the chemically synthesized solid catalysts and at the same time add value to the recycled waste.

2.2.1. Mollusk shell

Research on mollusk shell is not new rather it dated back to 17th century with the initial studies based on molluscs anatomy [73]. The investigation of mollusk shell microstructures, built of complex calcite and/or aragonite layer intergrowths, is of interest in many fields of science [74]. It is known that many invertebrates produce hard skeletons made of crystallized biogenic materials to protect and support their soft bodies [75]. The molluscan shell biomineralization involves the uptake of the mineral ions from the environment and their assembly into a functional organic matrix secreted by specialized cells of the outer mantle epithelium [76]. Mollusk shells are a natural ceramic composite with excellent fracture strength and fracture toughness, which are attributed to their unique microstructures. The shell material is composed of 95-99% crystalline calcite or aragonite (form of calcium carbonate, $CaCO_3$) and protein film which are used as the binder in varying amount from 0.1% to 5% by weight [77]. A molluscan shell can be divided into three primary sections: the outer layer is called as periostracum and mainly composed of conchiolins, the middle layer is known as prismatic layer consisting of oriented calcitic crystals and finally the nacreous layer which contains aragonite crystals. In 1930, Bøggild laid the foundation for all subsequent studies of molluscan shell structure in a classic paper in which he defined different types of structure and surveyed their distribution, and that of aragonite and calcite minerologies, among the mollusk [78]. The presence of shell organics was reported by French researcher Fremy who named it conchiolin. Crenshaw discovered soluble shell organic matrices and postulated the presence of sulphated polysaccharides as a nucleation factor [79-80]. The importance of sulphated sugars and acidic proteins was demonstrated in an experiment of acidic analysis on soluble shell organics. The result obtained indicated that acidic macromolecules were the key player in the nucleation of calcium carbonate. The acidic macromolecules recognized were acidic proteins and sulphated sugars [80,81]. Early studies carried out on conchiferan shell proteins were mainly focused on Asx and Glx. This research generally overestimated the acidity of those proteins and such analysis could not reveal the actual percentage of aspartic acid and glutamic acid in the shell [82]. Studies carried out with 2 D gel electrophoresis on the calcitic prismatic layer of *Pinctada margaritifera* and *Pinna nobillis* [83], the entire aragonitic shells of *Nautilus marcomphalus*, *Spirula spirula*, and *Sepia sp.* [84], and the nacre layer of *Unio pictorum* [85] showed the presence of acidic protein as one of their constituents. Weiner et al. [80] studied the insoluble shell organic matrices by using X-ray/electron diffraction in which it was revealed that chitin was present in the shell matrix. At the same time it was stated that the amount of chitin might differ with different mollusk shell or it may not be present in some mollusk shell. Chitin is a linear homopolymer consisting of β-(1-4)-linked N-acetyl-D-glucosamine subunits and according to some researchers it is one of those biopolymers identified in the organic parts of the mollusk shells which play an important role in the crystal orientation of mollusk shells. Levi-Kalisman et al. [86] proposed that the interlameller sheets in the shells were mainly composed of highly ordered and aligned β-chitin fibrils with little or no evidence for silk-like proteins. Weiss et al. [87] characterized chitin during the larval shell development by using Confocal laser scanning microscopy. In their investigation they reported that biominerilisation of mollusk shells was highly influenced by chitin on various levels of hierarchy.

Oyster is one of the dominant products of shell fish farms in some countries like Korea and Japan but the oyster shells are the unwanted waste product from mariculture and present a major disposal problem. This waste generated has not only affected the environment but also the ecosystem resources. It produces nasty smell as a consequence of the decay of flesh remnant attached to oyster or the microbial decomposition of salts into gases such as NH_3, H_2S and Amine [88]. Therefore conversion of the waste oyster shells to a beneficial and economically viable product can solve the problem partially, if not fully. Kwon et al. [89] used the waste oyster shells as an effective reagent for phosphorous removal from waste waters. The found that the shells contained mainly calcium carbonate but when it was heated at higher temperatures of 750 to 800 °C, it was converted to calcium Oxide. CaO formation was confirmed by XRD patterns obtained from the study. In another experiment, Chae et al. [90] recycled the oyster waste shells by treating it with plasma pyrolysis technique. These experiments showed that the oyster shells were mainly composed of $CaCO_3$ but when heated to certain temperatures lead to the formation of single metal oxide-CaO. This conclusion helped Nakatani et al. [91] to employ combusted oyster shell for transesterification. They combusted the waste oyster shells at different temperatures of 100, 500, 700, 800, 900 and 1000°C for 3 h and found that the XRD patterns obtained for the combusted oyster shells at and above 700°C were identical to those of CaO. They applied factorial design and response surface methodology to optimize the reaction conditions. It was observed that the most important factor affecting the biodiesel purity was the reaction time and catalyst concentration. From the second order model, the optimum reaction conditions of catalyst concentration and reaction time was found to be 25% wt. and 5 h, respectively. They claimed that the oyster shell combusted at higher temperatures could be reused as catalyst for biodiesel production and the yield obtained was comparable to that of CaO. Studies were also conducted on the waste mollusk shells of golden apple snail shell and meretrix venus shell by Viriya-empikul et al. [92] in the transesterification of palm olein oil. They calcined the shell at 800°C for 4 h and reported the formation of CaO at a temperature above 800°C. Though both the catalysts acts as a heterogeneous basic catalyst it was observed that better yield of 95% was obtained with golden apple snail shell. Apart from surface area and amount of Ca content present in the catalyst the catalytic activity was also influenced by the catalyst calcination temperature and methanol to oil molar ratio. However, reusability studies of the catalysts were not investigated which is an important aspect of a heterogeneous catalyst. Another popular seafood is Mud crab (*Scylla serrata*) which is farmed on a commercial scale in tropical countries but again in this case also the shell of mud crab is treated as waste. Boey et al. [93] investigated the use of waste shells of mud crab as catalyst for transesterification and compared its performance with laboratory grade CaO. For better understanding of the various variables affecting the reaction, they also conducted statistical analysis using a Central Composite Design. According to the statistical analysis the best fit model was observed to be the quadratic model which identified catalyst concentration as the most important parameter for biodiesel purity followed by reaction temperature and methanol to oil ratio. All the factors affecting transesterification were depended on each other and it was impossible to obtain minimum purity at the lowest level of any one factor. However, minimum biodiesel purity of 95.6% could be achieved at higher (+1) or centre levels (0) of different factors with the proposed catalyst. A big advantage of the calcined catalyst was reported in terms of its reusability as it could be reused for 11 times without much drop in its activity. Similar studies were also conducted in the optimization of reaction variables in the transesterification of chicken fats with the combined waste shells of crab and cockle. They reported that under the optimal condition of 4.9 wt% catalyst amount and 0.55:1 methanol to oil mass ratio, above 98% methyl esters conversion was achieved. The authors also concluded from their study that different waste containing CaO could be combined to produce methyl esters. Yang *et al.* [94] prepared shrimp shell catalyst through a tristep route in which initially the shrimp shells were incompletely carbonized, loaded with KF followed by calcination. The major constituent of the shrimp shells is chitin which occupies 69% of the dry weight of the shrimp shell. During incomplete carbonization small molecules present in the shell were evaporated and water was eliminated from the chitin molecules leading to the formation of a stereo polymer composed of six-member heterocyclic compounds with increased surface area (Fig. 2) called as quasiaromatic compounds. The incompletely carbonized shells were loaded with KF which act as a modifier and during activation active sites were formed by the reaction of the shells with KF. The authors reported that the catalytic activity of the catalyst proposed was highly influenced by the carbonization temperature, KF loading and activation temperature. Detailed study revealed the optimum preparation condition as– carbonization temperature at 450 °C, 25 wt% KF loading and activation temperature at 250

°C. Under these optimum preparation conditions, the conversion reached to 89.1% when the reaction was carried out at 65 °C with a catalyst amount 2.5 wt %, a methanol/rapeseed oil molar ratio 9:1 for a reaction time of 3 h. Reusability studies for the same catalyst showed a drop in catalytic activity which was attributed to the loss of active sites due to covering by the resultant. The catalyst has an advantage that it could be regenerated by treating it in soxhlet's apparatus with petroleum ether as solvent for 3 h. In a similar experiment carried out by Xie *et al.* [95] biont shell catalyst were prepared by incomplete carbonization followed by impregnation with KF. The high activity of the catalyst was attributed to the formation of active sites during the reaction between incompletely carbonized chitin and KF. In addition the weak polar nature of the biont shell was found to prevent reverse glycerolysis reaction which ultimately contributes to the high catalytic activity. Hu et al. [96] used freshwater mussel shells as catalyst in the transesterification of Chinese tallow oil. They reported that biodiesel yield above 90% was achieved when the optimal calcinations temperature was 900 °C, reaction temperature 70 °C, methanol/oil molar ratio of 12:1, a catalyst concentration of 5% and a reaction time of 1.5 h. The catalyst could be reused for seven consecutive cycles.

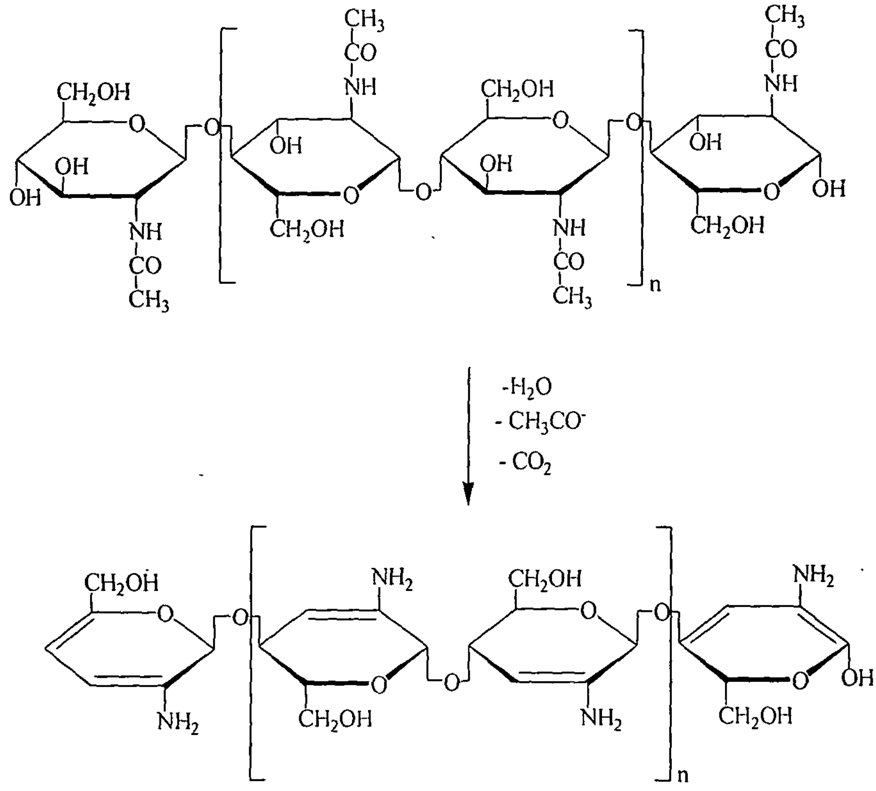

Fig.2.2. The transformation of Chitin Molecules during the incompletely carbonization

2.2.2. Eggshell

Eggshell is a bioceramic composite which consists of a mineral part containing 95% calcite aggregates pervaded with an organic matrix resulting in a structure which has excellent mechanical properties [97]. The chicken eggshell comprises calcified shell and shell membranes including inner and outer membranes. These membranes retain albumen and prevent penetration of bacteria. Shell membranes are also essential for the formation of eggshell which not only protect the contents of the egg from mechanical impacts but also form microbacterial invasions like Salmonella. They also control the exchange of water and gases through the pores during the extrauterine development of the chick embryo [98]. It also acts as a source of nutrient, primarily calcium, to the developing embryo. During the initial research on the composition of the chicken egg shells, Burley [99] reported that the organic matter of egg shell and the shell membrane mainly contained protein along with carbohydrate and lipids in small amounts. It was also reported by Bronsch et al. [100] that the egg shells also contained uronic acid which affected the breaking strength of the shell. Further investigations on chicken egg shell have revealed that the chicken egg shells are mainly composed of calcium carbonate along with some traces of magnesium carbonate, phosphate, sodium, potassium, carbon, zinc, manganese, iron and copper. In the elemental composition of eggshell, it has been reported that the major element is calcium and its amount is about 98.2% in the shell. The other elemental compositions are 0.9% magnesium and 0.9% phosphorus (present in shell as phosphate) [101].

Development of value-added by-products from egg-shell waste is of great interest as eggs are part of daily meal in most of the countries. Investigations related to the utilization of the egg shell as a renewable catalyst was taken up by many scientists in different work. Montilla et al. [102] used egg shells as catalyst to produce lactulose from milk ultrafiltrate as source of lactose. Some other researchers have used egg shells for preparing dielectric material and zeolite type A [103,104], as a support for immobilizing a variety of enzymes and in CH_4 reforming [105,106]. Detailed studies related to the effect of temperature on the X-ray diffraction (XRD), infrared (IR) and ESR spectra of chicken egg shell in the temperature range 298–1173 K were conducted by Engin et al. [107]. They confirmed that the egg shells were mainly composed of calcites and upon heating at higher temperature it got converted into CaO. This confirmation was a matter of interest for researchers who used these shells as catalyst in the transesterification reaction.

Wei et al. [108] introduced egg shells as catalyst in the methanolysis of soybean oil. The shells were initially washed and dried followed by calcination at a temperature range of (200 °C—1000 °C) for 2 h. They observed that upon calcination the morphology of the shell remained the same till calcination at 600°C and the changes in the shell structure started to appear at 700 °C. Calcination above 800 °C reduced the particle size and the particle shape became more irregular. This was attributed to the changes in the composition of the shell upon calcination. XRD patterns obtained for shells calcined at different temperature revealed that the shells calcined below 700 °C contained $CaCO_3$ as a major constituent and peaks of CaO started to appear at higher calcination temperature. Furthermore the biodiesel yield was also found to be in accordance with the calcination temperature. The yield was found to be maximum for shell calcined above 800 °C. They also studied the effect of methanol/oil ratio, catalyst amount and reaction time on biodiesel production. Under the optimum condition of 9:1 molar ratio of methanol to oil, 3 wt % egg shells calcined at 1000 °C, reaction temperature of 65 °C biodiesel yield of 95% was obtained when the reaction was carried out for 3 h. Viriya-empikul et al. [92] also observed the same XRD patterns for the calcined egg shells as Wei et al. In the reaction carried out with palm olein oil as raw material they observed that the biodiesel yield was 95% after a reaction time of 2h. They reported that the yield increased with an increasing methanol to oil ratio and the optimum methanol to oil ratio in their study was 12:1. Egg shell catalyst exhibited a high surface area with small particle size which was concluded to be the reason behind the high yield obtained during the study. Sharma et al. [109] used chicken egg shells for the transesterification of Karanja oil. They reported that the initial weight loss for the calcined catalyst occurred at around 400°C – 480 °C which was attributed to the decomposition of $Ca(OH)_2$. The next weight loss observed at 700 °C was due to the decomposition of calcium carbonate along with the loss of some inorganic impurities. Upon calculation of the particle size it was found that the particle size of the uncalcined catalyst was larger than the calcined catalyst. This decreased in particle size during calcination resulted in decreasing crystallinity of the catalyst. It was attributed to the presence of water in CaO. However, the XRD patterns of the calcined shells confirmed the formation of calcium oxide at higher calcination temperature. They found that optimum catalyst used for the best yield was 2.5% whereas it was 3.0% in the case of Wei et al. [108]. They found that a reaction time of 2.5 h was found to be best suited for the biodiesel yield of 95% and reaction beyond that time did not increased the yield of biodiesel. Cho et al. studied the transesterification reaction with quail and chicken eggshell. It was observed that after acid treatment with HCl for 2 h, the quail egg shells had large amount of strong basic sites and it showed high catalytic activity compared to chicken egg shells. The acid-treated, quail eggshell catalyst steadily maintained high conversions of over 98% during repeated fivefold usage at 65 °C with a reactant composed of methanol/ oil (as mol) = 12/1 and oil/catalyst (as g) = 2/0.03 [110].

Apart from the studies on egg shells and mollusk shells, fish scale of L. rohita were also calcined and used for the purpose of transesterification. A very high FAME yield of around 97.73% was obtained with methanol/oil molar ratio, 6.27:1, calcination temperature, 997.42 °C and catalyst concentration of 1.01 wt.% of oil. The catalyst was reusable for six consecutive cycles [111].

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CHAPTER 3

MATERIALS & METHODS

Chapter 3

3. Materials and Methods

The flow diagram for the methodology is presented in Figure 3.1.

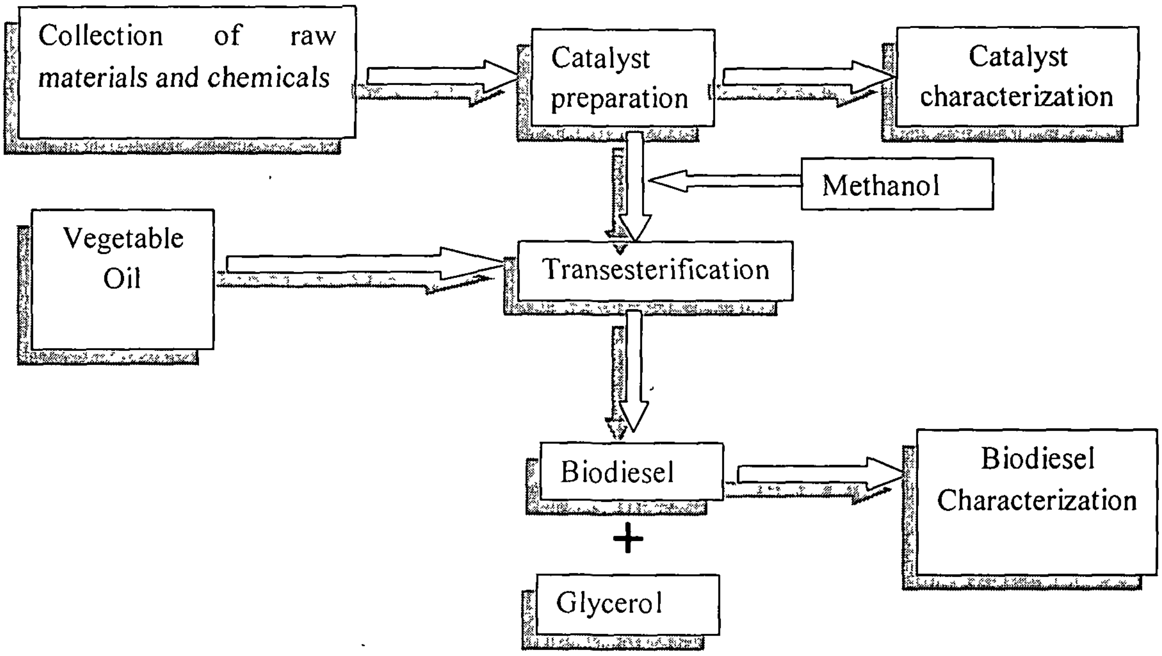

Fig.3.1. Flow diagram of methodology adopted for the study

3.1. Materials

In this investigation, parent catalyst was prepared from the waste shells of *Turbonilla striatula* [Figure 3.2.]. Waste shells of *Turbonilla striatula* were obtained from a local household of Chirang district of Assam, India. *Turbonilla striatula* is a genus of ectoparasitic sea snails, marine gastropod mollusks of the family, pyramidellidae. It is easily available in Chirang district of Assam, India [1] and widely distributed in swamp areas, rivers and agricultural fields of this area. The meat of the mollusks remaining inside the shell is used as one of the food items and after taking out the meat, the shells have no practical use and are thrown out as waste materials. These shells were collected and used as raw material for the preparation of the parent catalyst. Further, the prepared parent catalyst was doped with lithium and barium separately via wet impregnation method.

Fig.3.2. Waste shells of *Turbonilla striatula*

In this investigation, the above catalyst was tested for transesterification by using vegetable oil as feedstock. For this purpose, commercial edible-grade mustard oil was purchased from the market and used without further purification. Waste cooking oil was collected from the canteen of the School of Engineering (SOE), located inside the Tezpur University campus, Assam, India. Synthesis-grade methanol ($\geq$99% assay and $\leq$0.2% water content), anhydrous sodium sulfite, sodium chloride, KOH, barium chloride and lithium carbonate were purchased from Merck Limited, Mumbai, India and were used as received.

3.2. Catalyst preparation

3.2.1. Solid oxide derived from waste shells of *Turbonilla striatula*

The collected waste shells of *Turbonilla striatula* were washed with distilled water several times to remove any impurity attached to it and then allowed to dry in an oven at a temperature of 120 °C for 24 h. After drying, the shell was crushed using a pestle and mortar followed by grinding in a grinder machine till it became powder. It was then allowed to pass through a 0.8 mm sieve mesh. The powdered shell was then calcined at different temperatures ranging from 100 to 900 °C for 4 h and then stored in a desiccator for future use.

3.2.2. Li doped waste shell derived CaO

For preparing Li doped CaO, the parent CaO was taken from the waste shells of *Turbonilla striatula* calcined at 900 ^{0}C, named as T-CaO. Different ratios of Li doped T-CaO varied in the range from 1-1.5% was prepared by wet impregnation method. 10g of the T-CaO was suspended in double distilled water for 2 h followed by addition of appropriate amount of lithium carbonate. The whole mixture was then allowed to stir continuously for 10 h with the mechanical stirrer. The final slurry was then filtered and dried in an oven at 120 °C for 6 h. After drying, catalyst was calcined at 900 °C for 3 h to activate it and the prepared catalyst was kept in a desiccator for future use. The catalysts were named as Li 0.5 T-CaO, Li 1.0 T-CaO and Li 1.5 T-CaO based on the amount of Li doped in T-CaO.

3.2.3. Ba doped waste shell derived CaO

The parent CaO for preparing Ba doped CaO was also taken from the waste shells of *Turbonilla striatula* as reported in section 3.2.2 and designated as T-CaO. 10 g of the T-CaO was suspended in double distilled water for 2 h. Another solution was prepared by dissolving 0.5–1.5% of barium chloride in distilled water. Both the solutions were mixed together and allowed to stir continuously for 10 h followed by filtration under vacuum pressure. The filtrate was then dried in an oven at 120 °C followed by calcinations at 900 °C. The catalyst after calcination was kept in a desiccator for future use. The catalysts were named as Ba0.5T-CaO (5% Ba doping), Ba01T-CaO (1% Ba doping), and Ba1.5T-CaO (1.5% Ba doping) respectively.

3.3. Instrumental analysis

The thermal stability of the parent catalyst was evaluated in a thermogravimetric analysis (TGA) instrument (Perkin Elmer STA 6000) from room-temperature to 890 °C at a ramping rate of 10 °C min^{-1} under a flow of nitrogen. The structures of all the prepared catalysts were examined by means of X-ray diffraction (XRD), scanning electron microscope (SEM), Energy-dispersive X-ray spectroscopy (EDX) and Fourier transform infrared (FT-IR) spectroscopy. The powder X-ray diffractograms were recorded on a Rigaku miniflex diffractometer (Cu-Kα radiation, λ=1.5406 Å) in 2θ range 10–70° at a scanning rate of 2 °C min^{-1}. The Brunauer–Emmett–Teller (BET) surface areas and pore sizes were measured by the multipoint N_2 adsorption–desorption method with ASAP® 2020 Accelerated Surface Area and Porosimetry Analyzer, USA at liquid nitrogen temperature (-196 °C). SEM and EDX were performed on a Jeol, JSM-6290LV instrument. IR spectra were recorded in KBr pallets on a Nicolet (Impact 410) FT-IR spectrophotometer. The chemical composition of the catalyst was estimated by EDX. The basic strength (H_) and basicity were determined according to the methods based on the colour change of Hammet indicators. The H_ indicators used in this study (their H_ values are given in parentheses) were: indigo carmine (12.2), 2,4-dinitroaniline (15.0) and 4-nitroaniline (18.4). Oil conversion to Fatty Acid Methyl ester (FAME) was determined with the help of using ^{1}H NMR. Sample aliquots were withdrawn periodically from the reactor undergoing transesterification and analyzed by ^{1}H NMR on a Jeol JNM-ECS400 NMR spectrometer at 25.5 °C with $CDCl_3$ and TMS as solvent and internal standard respectively. Determination of biodiesel components was performed in GC-MS (Perkin Elmer Claurus 600) equipped with TCD detector and elite wax column. The column temperature was programmed from 60 °C–220 °C and the rate of increase was 3 °C/min. The carrier gas used for the purpose was helium and the flow rate was maintained at 1 ml/min.

3.4. Biodiesel production

Transesterification was carried out in a laboratory scale 250 ml round bottom two neck flask equipped with a water cooled condenser and a constant temperature magnetic stirrer with hot plate [Figure 3.3.]. Catalyst was activated by dispersing the catalyst with methanol at 40 °C under magnetic stirring. After 1 h of the catalyst activation mustard oil was added to the mixture and then the mixture was vigorously stirred and refluxed at 65 °C under stirring at 900 rpm. After the reaction, the catalyst was separated from the biodiesel product by centrifugation and the excessive amount of methanol was evaporated under reduced pressure in a rotary evaporator. Oil conversions were determined by ^{1}H NMR spectroscopy using $CDCl_3$ as solvent and TMS as the internal standard [2]. The conversion was calculated using the following formula:

$$\text{Conversion, C (\%)} = \frac{2\,A_{Me}}{3\,A_{CH2}} \times 100\,\%$$

Where,

C = percentage conversion of triglycerides to corresponding methyl esters

A_{Me} = integration value of the methoxy protons of the methyl esters and

A_{CH2}= integration value of α-methylene protons

The yield of the biodiesel was calculated by using the equation according to literature [2-4]:

$$\%\ \text{Yield} = \frac{\text{Weight of biodiesel produced}}{\text{Weight of oil used}} \text{X}100\ \%$$

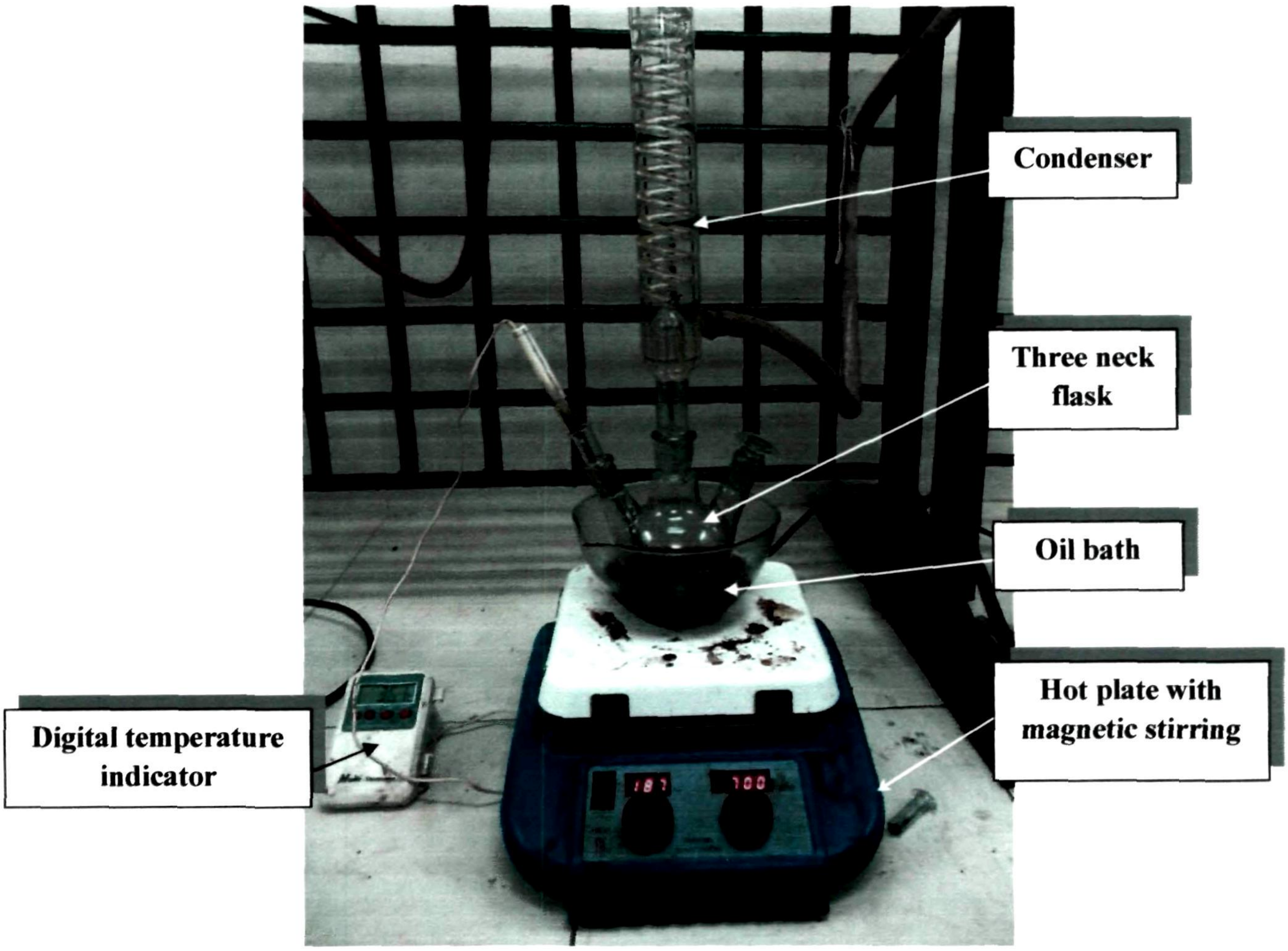

Fig.3.3. Transesterification set up

3.5. Feedstock analysis

3.5.1. Acid value

The acid number is a measure of the amount of carboxylic acid groups in a chemical compound such as a fatty acid. Acid values of the various vegetable oils were determined as per ASTM D 664. 0.2 – 0.5g of oil was mixed with ethanol and then heated on a water bath to dissolve the sample. This solution was titrated against 0.1M KOH using phenolphthalein as indicator. The acid value was determined as follows:

$$\text{Acid value} = \frac{\text{A x M x 56.1}}{\text{W}}$$

Where,

A = ml of 0.1M KOH consumed by sample

M = Molarity of KOH

W = weight in grams of the sample

3.5.2. Density

Density of the oil samples were measured according to ASTM D287-92. This test method is based on the principle that the gravity of a liquid varies directly with the depth of immersion of a body floating in it. The floating body, which is graduated by API gravity units in this method, is called an API hydrometer. The API gravity is read by observing the freely floating API hydrometer and noting the graduation nearest to the apparent intersection of the horizontal plane surface of the liquid with the vertical scale of the hydrometer, after temperature equilibrium has been reached. The temperature of the sample is read from a separate accurate ASTM thermometer in the sample or from the thermometer which is an integral part of the hydrometer (thermo hydrometer).

3.5.3. Water content

Water content in oil was determined by volumetric Karl Fischer (KF) titration using HYDRANAL ® reagents. In a typical process, HYDRANAL® Composite 2 was used as a titration agent. Ethanol-based, HYDRANAL® CompoSolver E (30 mL) was placed in the titration vessel and titrated to dryness with HYDRANAL® Composite 2. The biodiesel sample (5 mL), precisely measured using differential weighing, is injected into the titration vessel and titrated similarly.

3.5.4. Saponification value

The saponification value of the vegetable oil was determined according to the method of ASTM method D 5558-95. 2-5g of the oil was mixed with 25ml of 0.5M ethanolic KOH and the resulting mixture was refluxed for 60 minutes. The resulting solution was subsequently titrated against 0.5 M HCl with phenolphthalein as indicator. The resulting end point was obtained when the pink colour changed into colourless. The same procedure was used for the blank. The Saponification value (SV) was then calculated using the expression;

$$\text{Saponification value (S.V.)} = \frac{\text{(A - B) x N x 56.1}}{\text{W}}$$

Where,

A = HCl, for blank, mL

B= HCl, for sample, mL

W =Weight of sample (dry basis), g

N = Normality HCl solution

56.1 = equivalent weight of potassium hydroxide

3.5.5. Iodine value

Iodine value of the oil samples was determined according to EN ISO 3961. 0.5g of oils was weighed into conical flask and 20ml of carbon tetrachloride was added to dissolve the oil. 25ml of Wij's reagent was added to the flask using a measuring cylinder in a fume chamber. Stopper was then inserted and the content of the flask was vigorously swirled. The flask was then placed in the dark for 35minutes. At the end of this period, 20ml of 10% aqueous potassium iodide and 100ml of water were added using a measuring cylinder. The content was titrated with 0.1M sodium thiosulphate solution. Few drops of 1% starch indicator were added and the titration continued by adding the sodium thiosulphate drop wise until coloration disappeared after vigorously shaking [4]. The same procedure was used for the blank test. The Iodine Value (I.V) is given by the expression:

$$\text{Iodine Value (I.V)} = \frac{12.69C\,(V_1 - V_2)}{M}$$

Where,

C = concentration of sodium thiosulphate,

V_1 = volume of sodium thiosulphate used for blank,

V_2 = volume of sodium thiosulphate used for determination

M = mass of sample

12.69 = Constant.

3.5.6. Carbon residue

Carbon residue of oil samples was determined according to ASTM D 189-01. A weighed quantity of sample is placed in a crucible and subjected to destructive distillation. The residue undergoes cracking and coking reactions during a fixed period of severe heating. At the end of the specified heating period, the test crucible containing the carbonaceous residue is cooled in a desiccator and weighed. The residue remaining is calculated as a percentage of the original sample, and reported as Conradson carbon residue.

3.6. Biodiesel analysis

3.6.1. HAAKE Falling Ball Viscometer Type C

Viscosity of the sample was determined by falling-ball viscometer (Haake, Type C). It meets the requirements of the German DIN 53015 as well as ISO 12058 standards. The sample to be measured is pulled into the syringe without bubbles and placed into the temperature controlled holder of the HAAKE MicroVisco 2 unit. The sample reached the test temperature after approx. 5 min, and the measuring ball was pulled in the upper start position by means of a magnet. The ball then rolls down the wall of the syringe, which is inclined (15°C) to avoid bouncing. The fall of the ball is delayed by the resistance of test fluids. The falling ball time is proportional to its viscosity. The test result is the falling time for a defined distance which is measured electronically and converted into viscosity units by the stored calibration factors [5]. The dynamic viscosity η (in mPa.s) is calculated using the following equation:

$$\eta = K\,(\rho_1 - \rho_2)\,.t$$

where,

K = ball constant in mPa.s.cm^3/g.s

ρ_1 = density of the ball in g/cm^3

ρ_2 = density of the liquid to be measured at the measuring temperature in g/cm^3

t = falling time of the ball in seconds

The dynamic viscosity η can be converted to the kinematic viscosity v by the following equation:

$$v = \frac{\eta}{\rho}$$

v = kinematic viscosity (mm^2/s) (1 mm^2/s = 1 cSt); η = dynamic viscosity (mPa.s);
ρ = density of the liquid sample (g/cm^3)

3.6.2. Flash point

Flash point of biodiesel was determined according to ASTM D93-12 which corresponds to the standard test methods for flash point by pensky-martens closed cup tester. 70 ml of a sample are heated in a closed cup with a predetermined temperature rate. A test flame is lowered into the vapor space at regular intervals to observe a flash, the so called 'Closed Cup Flash Point'.

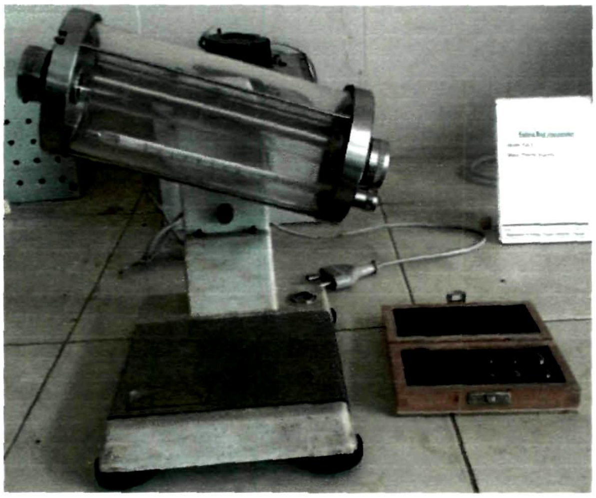

Fig.3.4. HAAKE Falling Ball Viscometer Type C

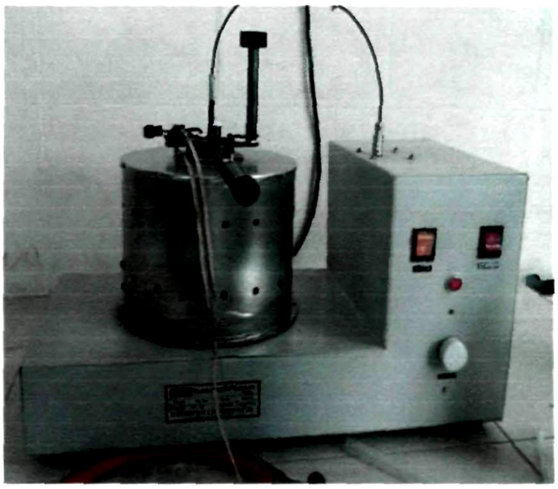

Fig.3.5. Pensky-martens closed cup tester

3.6.3. Calorific value (CV)

The CV of the vegetable oils and their methyl esters were measured in a bomb calorimeter according to ASTM D2015 standard method. An oxygen – bomb was pressurized to 3 Mpa with an oxygen container. The bomb was fired automatically after the jacket and a bucket temperature equilibrates to within acceptable accuracy of each other [6].

3.6.4. Cloud point

The cloud point and pour point of biodiesel were determined according to ASTM D 2500. To determine the cloud point, the oil sample is cooled and examined visually until first cloud appears.

3.6.5. Carbon residue

The carbon residue of biodiesel was determined similar to the procedure reported in subsection 3.5.6.

3.6.6. Density

The density of biodiesel was determined similar to the procedure reported in subsection 3.5.2.

Fig.3.6. Cloud point & pour point bath

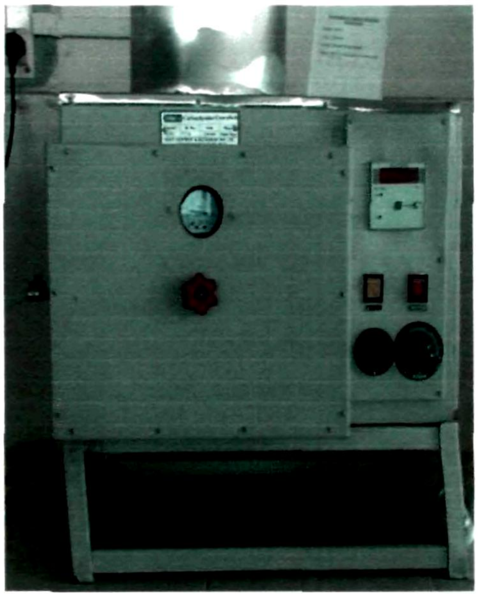

Fig.3.7. Conradson carbon residue apparatus

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CHAPTER 4

RESULTS & DISCUSSION

This chapter is divided into four sub-chapters which are as follows:

- **Chapter 4A: Solid oxide derived from waste shells of *Turbonilla striatula***

In this chapter, we have presented the characterization of the shells calcined at different temperatures and influence of parameters on their catalytic activity during transesterification of mustard oil. This study was also extended to a comparative study between the calcined shell exhibiting excellent catalytic activity and conventional catalysts such as NaOH, manufactured CaO in the transesterification of waste cooking oil. Properties of biodiesel are also included in this chapter.

- **Chapter 4 B: Li doped waste shell derived CaO**

This chapter includes characterization of the prepared catalysts and discussion on the influence of different parameters influencing the catalytic activity of the catalyst during transesterification of waste cooking oil. Properties of the biodiesel prepared in the presence of the doped shell catalyst exhibiting maximum conversion are also presented.

- **Chapter 4 C: Ba doped waste shell derived CaO**

This chapter includes characterization of the prepared catalysts and influence of different parameters influencing the catalytic activity of the catalyst during transesterification of waste cooking oil. Properties of the biodiesel prepared in the presence of the doped shell catalyst exhibiting maximum conversion are also presented.

- **Chapter 4 D: Biodiesel analysis by NMR spectroscopy**

The NMR spectra for biodiesel prepared with the different catalyst synthesized in this investigation are alike. So we have presented the analysis of biodiesel by using ^{1}H NMR and ^{13}C NMR spectroscopy in details, in this chapter.

CHAPTER 4A

Solid oxide derived from waste shells of *Turbonilla striatula*

Chapter 4A

Solid oxide derived from waste shells of *Turbonilla striatula*

4.1. Feedstock analysis

For this experiment, commercial grade mustard oil was used as feedstock. The fatty acid compositions according to the manufacturer [1] are given in Table 4.1 and characteristics of mustard oil used are shown in Table 4.2 respectively. The acid value was determined according to ASTM D 664 and the water content was determined according to ASTM D 6304-07. It was observed that the acid value and water content of the feedstock was low enough for effective base catalyzed transesterification (water content < 299 ppm and acid value < 1).

Table 4.1. Fatty Acid Composition (%) of Mustard Oil

Fatty acid	Structure	Range
Palmitic	C16:0	1-3%
Stearic	C18:0	0.4-3.5%
Arachidic	C20:0	0.5-2.4%
Behenic	C22:0	0.6-2.1%
Lignoceric	C24:0	0.5-1.1%
Oleic	C18:1	12-24%
Eicosenoic	C20:1	3.5-11.6%
Erucic	C22:1	40-55%
Linoleic	C18:2	12-16%
Linolenic	C18:3	7-10%

Table 4.2. Some physical properties of mustard oil

Properties	ASTM Method	Mustard oil
Acid value (mg KOH g^{-1})	D 664	0.85
Water content (ppm)	Karl Fisher method	299
Saponification Value	D 5558-95	172
Iodine Value	EN ISO 3961	104
Viscosity	ISO 12058	44

4.2. Catalyst Characterization

4.2.1. X-Ray Diffraction (XRD) analysis

Figure 4.1 depicts the XRD patterns for the shell calcined in the range of 600 – 900 °C. The spectra were obtained with Cu Kα radiation (λ = 0.15406 nm) at 30 kV, 15 mA in a scan range of 10-70. The peaks obtained were compared with the joint committee on powder diffraction standards (JCPDS) file. We considered only four calcination temperatures starting from 600 °C as shell calcined from 100 – 600 °C showed similar XRD patterns. For shell calcined at 600 °C, the main peak were observed at 2θ = 29.47°, 36.37°, 39.48°, 43.55°, 47.87°, 49.05° and 57.89°. These peaks were the characteristic peaks of calcium carbonate corresponding to the JCPDS file no 85-1108. Peaks of calcium oxide along with some peaks of calcium hydroxide appeared when the shell was calcined at 700 °C. The peaks for calcined shell at 800 and 900 °C appeared at 2θ = 32.14, 37.22, 53.57, 64.24 and 67.49, which were the characteristic peaks for calcium oxide (JCPDS file no. 48-1467). This confirmed the formation of calcium oxide at a calcination temperature of 800 °C [2] and [3].

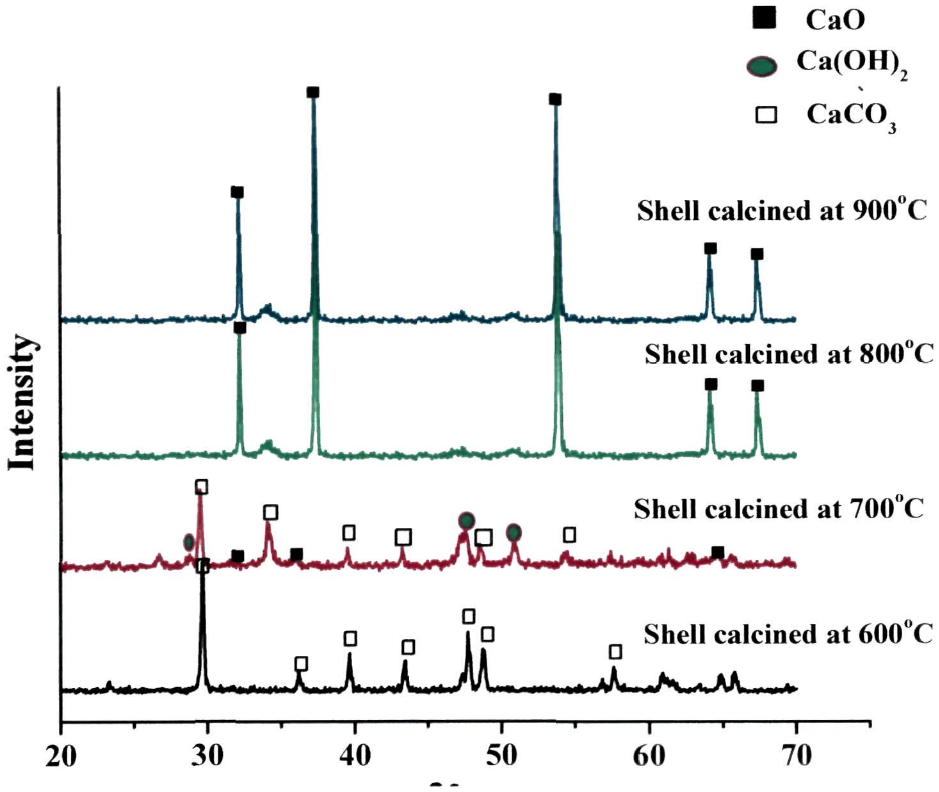
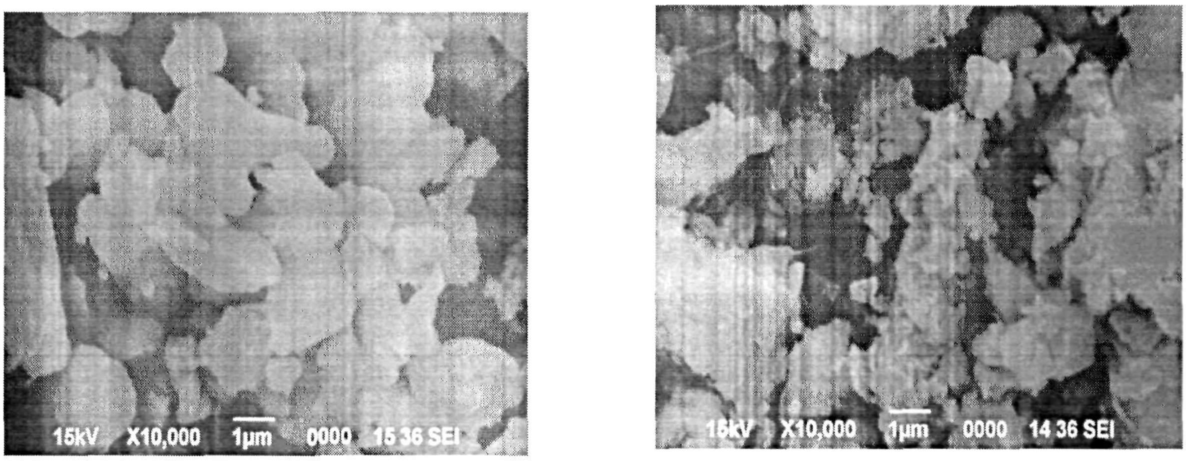


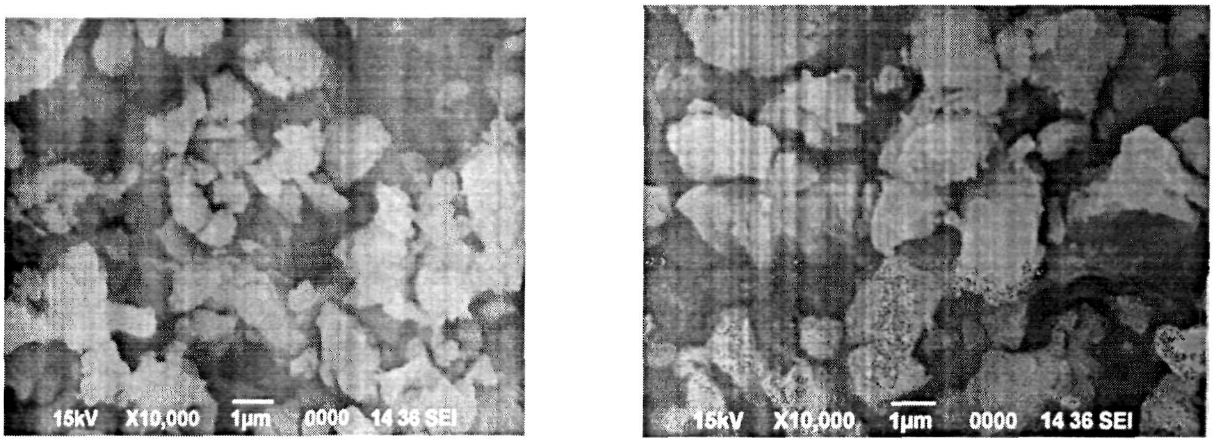
Fig.4.1. XRD pattern for shells calcined at different temperature

4.2.2. Scanning electron microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDX) analysis

The morphology of the catalyst calcined at different temperatures was observed by SEM [Figure 4.2 (a-d)]. It was seen from the image that the catalyst calcined at 600 °C was not uniform and aggregated rather a cluster kind of arrangement was observed at the catalysts surface. With higher calcination temperatures it was found that the clustered surface was slowly vanishing and instead the particles of various size and shape were becoming visible.



(a)Sample calcined at 600 °C (b)Sample calcined at 700 °C



(c)Sample calcined at 800 °C (d)Sample calcined at 900 °C

Fig.4.2. SEM images of waste shells calcined at different temperatures

In order to investigate the influence of calcination temperature on the catalyst surface, EDX was also carried out. The EDX analysis revealed that the chemical composition of the catalyst surface was highly influenced at higher calcination temperatures. The elemental compositions of the shells calcined at different temperatures obtained from EDX analysis are presented in the Table 4.3. It is seen from the Table 4.3 that the content of Ca, Na, Mg, Si and Sc are 21.22, 0.37, 1.02, 1.78 and 3.07 % (w/w) respectively at 600 °C calcination temperature. The catalyst prepared at 700 °C contains calcium as the main component of the shell along with some traces of scandium, silicon and bromine. Bromine is not detected at 600 °C calcination temperature. It is also seen from Table 4.3 that calcium and oxygen are the only elements present at 800 – 900 °C calcination temperature.

Table 4.3. EDX analysis of waste shell calcined at different temperatures

Shell calcination temperature (°C)	Element	Weight (%)	Atomic (%)
600	O	58.77	66.32
	Ca	21.22	9.56
	Sc	3.07	1.23
	Si	1.78	1.15
	Mg	1.02	0.76
	Na	0.37	0.29
700	O	44.84	44.59
	Ca	15.32	6.08
	Sc	2.19	0.78
	Si	0.52	0.30
	Br	0.82	0.16
800	O	66.57	83.30
	Ca	33.43	16.70
900	O	63.66	81.44
	Ca	36.34	18.56

4.2.3. Fourier transform infrared spectroscopy (FTIR) analysis

Figure 4.3 depicts the FTIR spectra of all the shell calcined at different temperature along with pure CaO (commercial) together. It is found that the shell calcined at (a) 600 °C has major absorption band at 1424.29 cm^{-1} which is attributed to the asymmetric stretch for CO_3^{2-} group present in the shell. The other bands for the same sample occur at 873.95 cm^{-1}

and 711.26 cm^{-1} which represent the out-of-plane band and in-plane band vibration modes respectively of the CO_3^{2-} group. Sharma et al. [4] had also observed the similar band ranges for calcium carbonate found in their study for egg shell. Calcination at higher temperature shifts the bands to higher energy. This is due to the decrease in the reduced mass of the functional group attached to carbonate ion and consecutively the shell starts to lose carbonate. It is observed from the Fig. 4.3 that upon calcining at 700 °C, a sharp OH^- stretching band also starts to appear at 3644.95 cm^{-1}. Calcination at 800 °C temperature indicates that the bands are shifted to higher energy levels. The presence of moisture content was also reported by Lengyel et al. [5] who observed the band for water around 3600 cm^{-1}. Moreover, the peaks of shells calcined at 900 °C and the FT-IR pattern of manufacture CaO were observed to be similar.

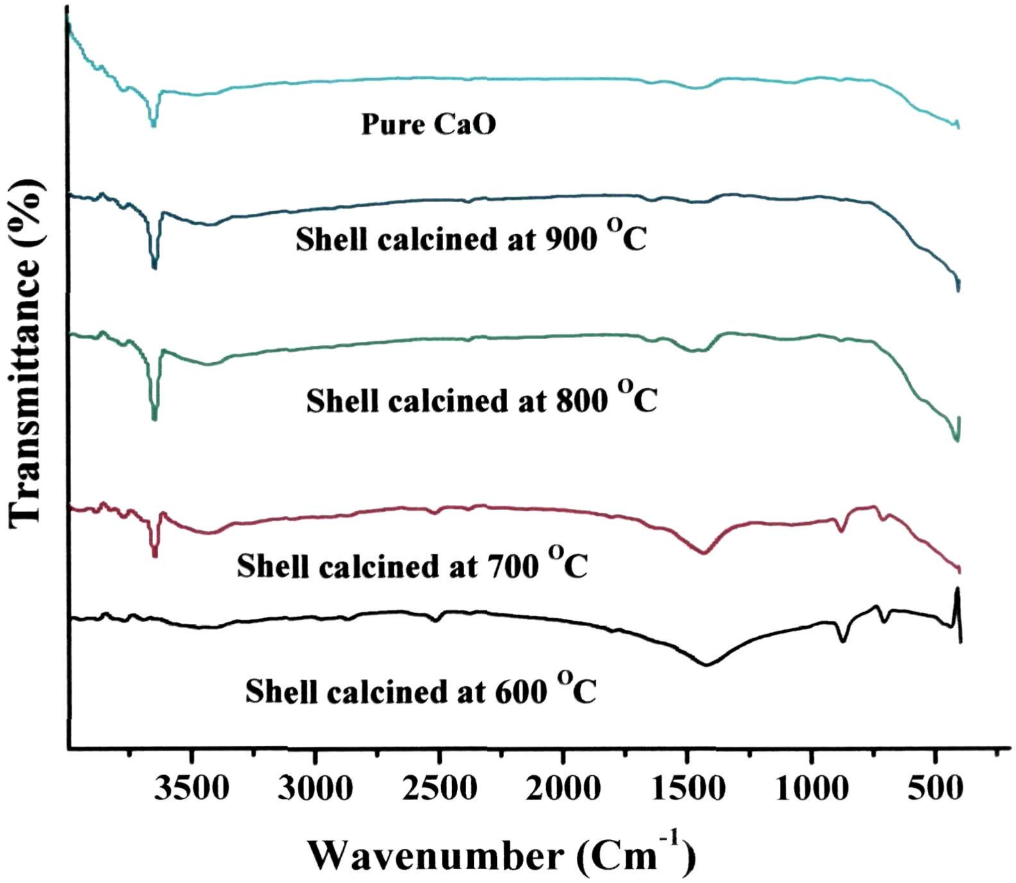


Fig. 4.3. FT-IR pattern for calcined shells and CaO

4.2.4. Thermogravimetric—Differential scanning calorimeter (TGA-DSC) analysis

Comparisons of the TGA and DSC measurements for the samples heated at the intermediate rate of 10 °C min^{-1} in nitrogen are presented in Figure 4.4 and Figure 4.5 respectively. The shell calcined at 600 °C exhibits a single thermal decomposition mass loss beginning at 587.33 °C with a total weight loss of 42.5%. Shell calcined at 700 °C shows two mass losses. The first mass loss in the range of 371.07- 434.60 °C is due to the removal of $Ca(OH)_2$ and the second loss in the temperature range of 577.78 – 812.35 °C is attributed to the decomposition of $CaCO_3$ to CaO and CO_2 along with some loss of inorganic impurities. This finding in our study has shown similarities with the finding of Lim et al. [6] who reported the evolution of CO_2 at a temperature of around 600 °C to around 830 °C. The decomposition of $Ca(OH)_2$ at 500 °C was also reported by Granados et al. [7]. The presence of $Ca(OH)_2$ and formation of CaO in the catalyst at 700 °C is also confirmed by the XRD pattern obtained in our study. The curve obtained also reveals that although the decomposition of $CaCO_3$ starts at around 700 °C, the decomposition is found to be completed at 800 °C. Calcination temperature above 700 °C indicates the formation of one single compound. The decomposition of $CaCO_3$ into CaO and CO_2 at higher temperature was also reported by some researchers [8] and [9].

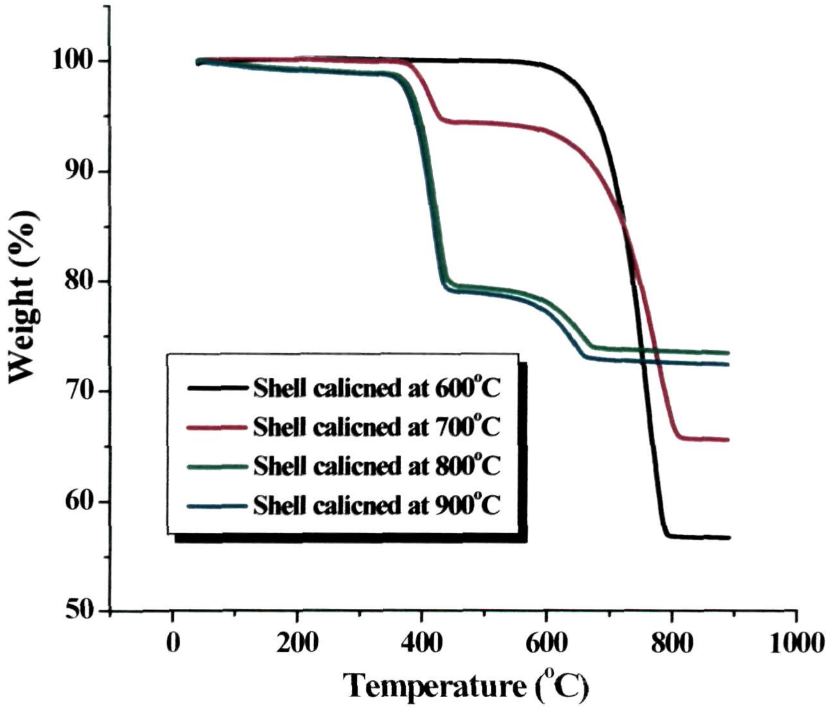


Fig. 4.4. TGA curve of calcined waste shells

The finding in TGA is also supported by the DSC curve obtained. The DSC curve for shell calcined at 700 °C exhibits an exothermic peak at 424.25 °C which can be attributed to evaporation of water and more probable decomposition of organic components or due to possible rearrangement in the structural arrangement within the compound itself. It may also indicate the crystallization of the compound. A broad endothermic peak located in the range of 643.26 – 788.98 °C shows the decomposition of $CaCO_3$ according to the following dissociation equation [10-11]:

$$CaCO_3 (s) \rightarrow CaO (s) + CO_2 (g)$$

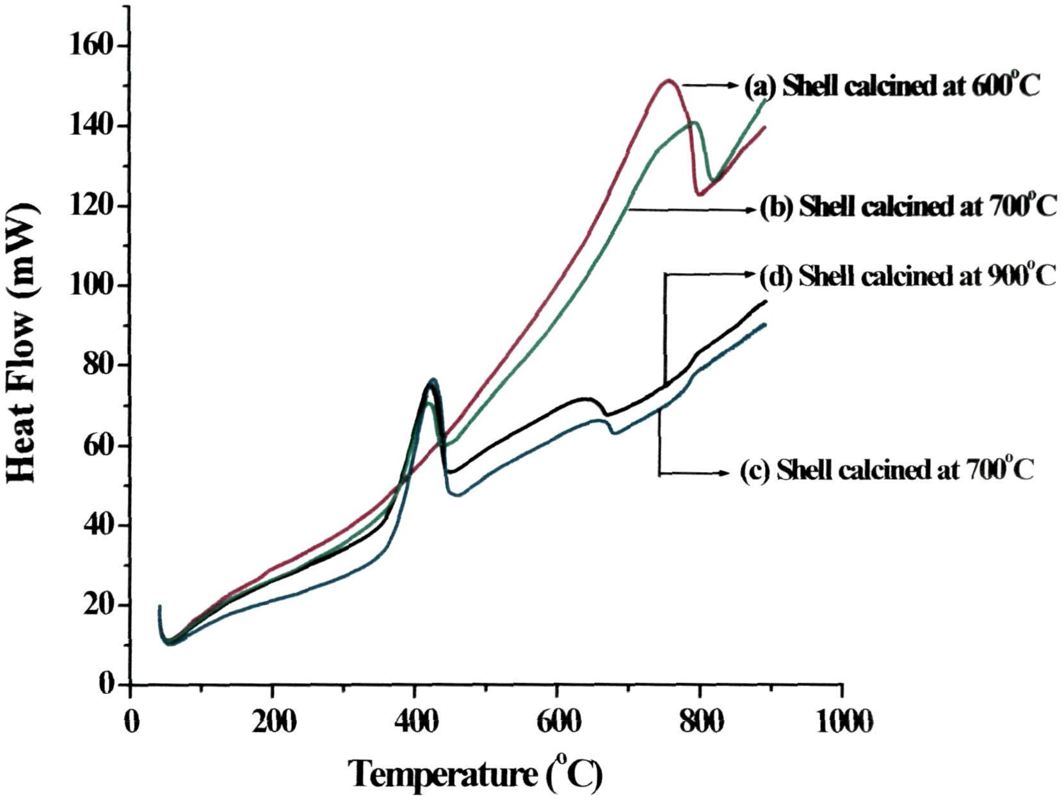


Fig. 4.5. DSC curve of calcined waste shells

4.2.5. Surface and pore volume analysis

The Brunauer–Emmett–Teller (BET) surface area and the total pore volume of the calcined catalysts are presented in Table 4.4. It was observed that the shells calcined at 600 °C had total pore volume of 0.0128/cm^3 g^{-1} and did not show any noticeable BET surface area. For shells calcined in the temperature range of 700 °C - 900 °C, the BET surface areas were in between 2.092 – 8.359 m^2/g. The increase in BET surface area correlated with the weight loss steps in the TGA curves. For the catalyst calcined at 700 °C, the surface area increased probably due to a modification of the sample composition during calcination. Further increase in BET surface area for shells calcined above 800 °C, might be due to the crystal growth of calcium oxide. Calcination of shells at higher temperature also induces an increase of pore volume value which can be attributed to the development of porosity in the calcined shells. The formation of pores in the catalyst prepared was caused by the evolution of gaseous carbonization products (CO_2 in the present investigation) and partly due to the formation of CaO.

Table 4.4. BET surface area and total pore volume of calcined waste shells

	Surface area/m^2 g^{-1}	Total pore volume/cm^3 g^{-1}
Catalyst calcined at 600 °C	-	0.0128
Catalyst calcined at 700 °C	2.092	0.0153
Catalyst calcined at 800 °C	4.680	0.0507
Catalyst calcined at 900 °C	8.359	0.0571

4.3. GC analysis of the Biodiesel components

The ester compositions of the biodiesel are given in Table 4.5 and the GC-MS chromatogram is shown in Figure 4.6. Five major peaks were observed in the chromatogram and peaks were identified by comparison with reported data and the profiles from the NIST and Wiley GC-MS libraries. These five peaks were identified as Octadecanoic acid (2.3%), Octadecenoic acid (27.61%), 9,12-Octadecadienoic acid (14%), 9,12,15-Octadecatrienoic acid (6.9%), 9-Hexadecenoic acid (46.6%).

Table. 4. 5. Fatty acid methyl esters composition of biodiesel synthesized from mustard oil

Peak no.	Retention Time (min)	Fatty acid methyl esters	Corresponding Acid
1	33.24	Octadecanoic acid	Stearic acid
2	39.34	Octadecenoic acid	Oleic acid
3	40.55	9,12-Octadecadienoic acid	Linoleic acid
4	42.24	9,12,15-Octadecatrienoic acid	Linolenic acid
5	49.53	9-Hexadecenoic acid	Palmitoleic acid

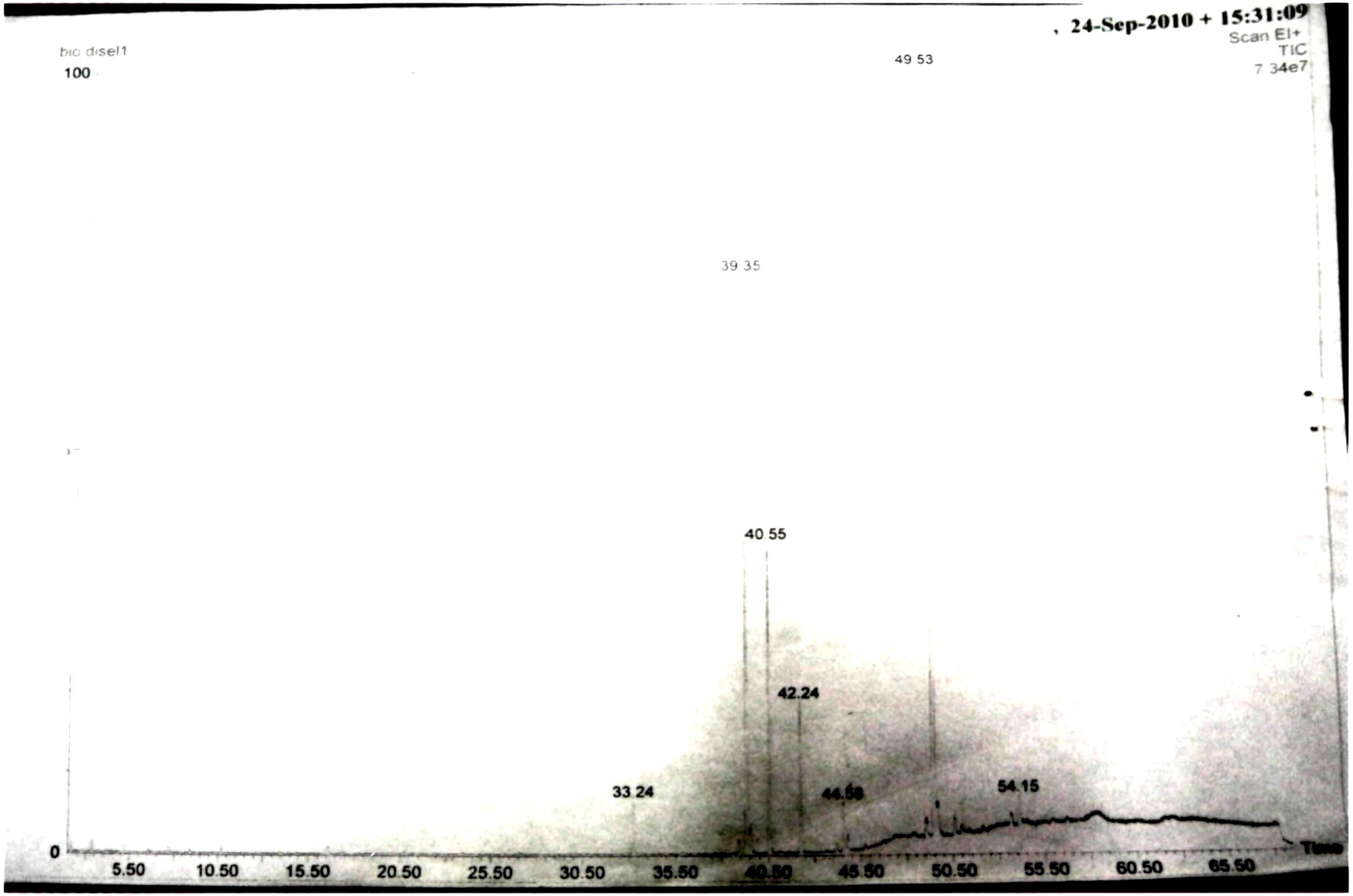


Fig.4.6. GC-MS chromatogram for biodiesel produced with waste shell calcined at 900 °C

4.4. Influence of different parameters on transesterification

4.4.1. Influence of reaction time

Figure 4.7 depicts the reaction time dependence on the yield of FAME during transesterification by employing the waste shells derived catalysts calcined at different temperatures. Biodiesel yield was calculated at a regular interval of 1 h. FAME yields of 93.3% and 90.6% were obtained for a reaction time of 6 h with catalysts calcined at 900 °C and 800 °C respectively. This high yield is attributed to the formation of CaO at the calcination temperatures of 800 °C and 900 °C. The biodiesel yield with the shell calcined at 600 °C after the same interval was found to be very low and a moderate yield was obtained with the shell calcined at 700 °C which may be due to the formation of CaO and presence of $Ca(OH)_2$. This explanation may also be supported by the XRD patterns as discussed above in section 4.2.1.

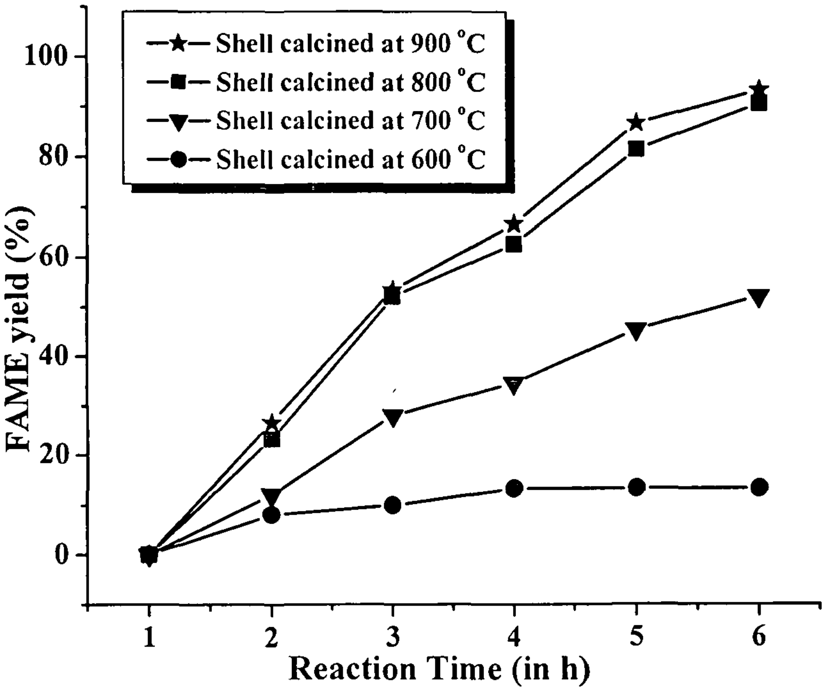


Fig. 4.7. FAME yield with reaction time

4.4.2. Influence of shell calcination temperature

To determine the influence of calcination temperature on the activity of the catalyst during transesterification, the shells were calcined at different temperatures from 100 to 700 °C and then tested for the transesterification of mustard oil. The results are presented in Table

4.6. It was observed that the shell calcined at temperature above 700 °C was more active than the shell calcined at 600 °C and 700 °C. The higher activity for shells calcined at 800 °C and 900 °C was attributed to the formation of CaO after calcinations at respective temperatures.

Table 4.6. FAME yield for shells calcined from 600–900 °C

S.No.	Catalyst calcinations temperature (°C)	FAME yield (%)
1.	600	15
2.	700	45
3.	800	90
4.	900	93

4.4.3. Influence of methanol to oil ratio

The influence of methanol to oil molar ratio on biodiesel yield was also investigated. Figure 4.8 depicts the percentage (%) yield of FAME with respect to the different methanol to oil molar ratio employed for transesterification. Transesterifications were carried out with 3:1, 6:1, 9:1 and 12:1 methanol to oil molar ratio and it was found that the yield increased with increasing methanol to oil ratio. The highest FAME yield of 93% was obtained in 9: 1 ratio. This may also be seen from the Figure 4.8. It is due to the formation of methoxy species on the catalyst surface which helps in shifting the reaction towards forward direction.

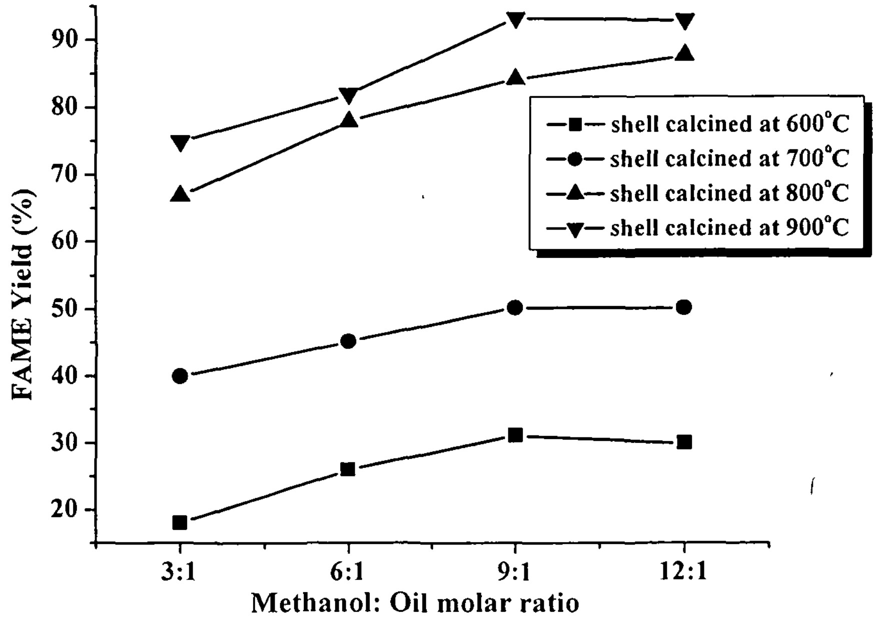


Fig. 4.8. Influence of methanol to oil ratio on methyl ester yield

4.4.4. Influence of reaction temperature

The influence of reaction temperature was also investigated and the results are presented in Figure 4.9. It was observed that an optimum yield of 90% was achieved when the reaction was carried out at 60 ± 5 °C and the reaction at higher temperature of 70±5 °C resulted in loss of FAME yield. This decrease in yield was probably due to the loss of methanol at higher temperature.

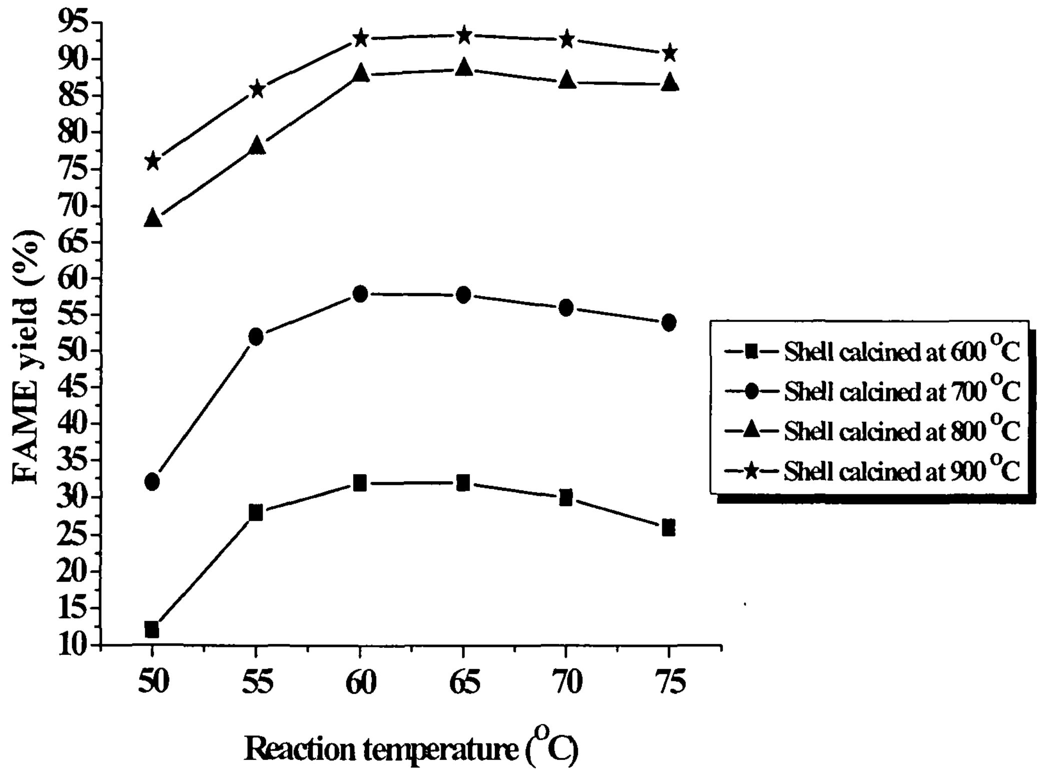


Fig.4.9. Influence of reaction temperature on methyl ester yield

4.4.5. Influence of catalyst amount

Influences of catalyst amount on FAME yield are depicted in Figure 4.10. It was observed that the yield increased with increasing amount of catalyst. Maximum yield of around 90% was obtained when the reaction was carried out with 3 wt% with 6:1 methanol to oil molar ratio at 60 °C reaction temperature. Beyond the catalyst amount of 3 wt%, the FAME yield was found to be decreased. The use of 1% and 2% of catalyst concentration rendered biodiesel yield of 66% and 81% respectively.

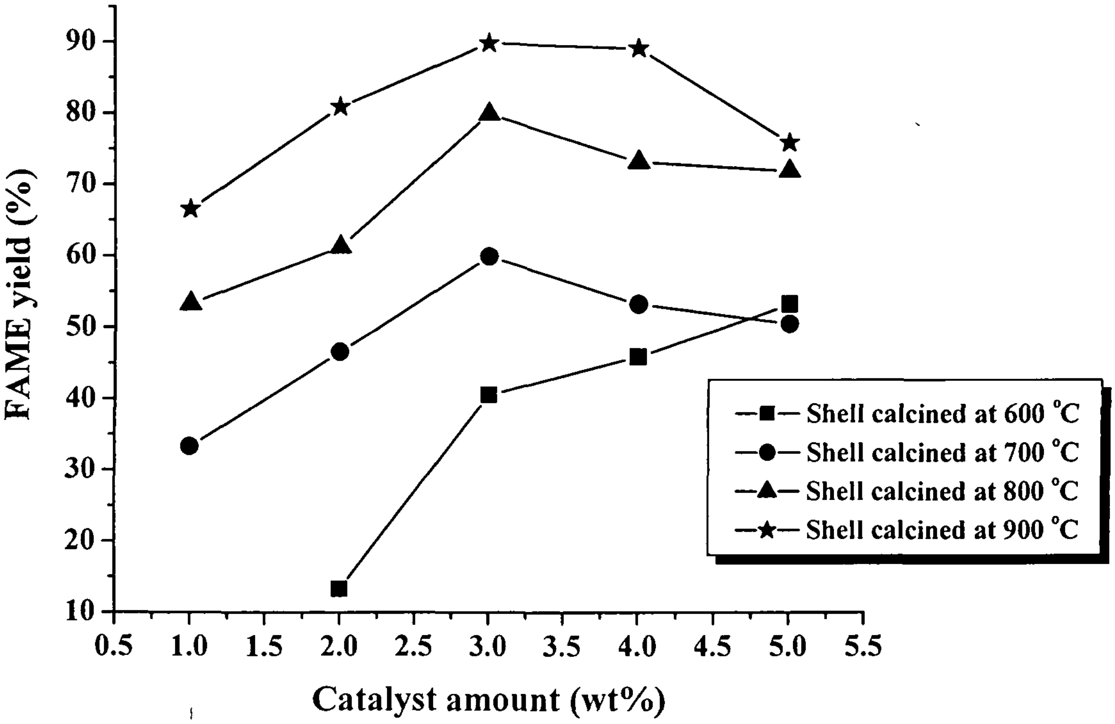


Fig.4.10. Influence of catalyst amount on methyl ester

4.4.6. Reusability of the catalyst

The reusability of the catalysts prepared at the optimum preparation conditions was investigated by carrying out subsequent reaction cycles. After 6 h of the reaction, the catalysts were separated from the reaction mixtures by filtration followed by washing with methanol to remove any adsorbed stains. Afterwards, the recovered catalysts were dried at 120 °C in an oven for 3 h and were used again for repeated reaction cycles under the same reaction conditions as before. The results are shown in Figure 4.11. The results indicated that the yield decreased with the repeated use of the waste shell derived catalysts and it exhibited poor catalytic activity after being used for more than three times. This deactivation was probably due to the structural changes leading to the failure to maintain the form of CaO or its transformation to other form such as $Ca(OH)_2$. This may also be due to the loss of some amounts of catalysts during the process of washing, filtration and calcination. However, the recovered catalyst regained its catalytic activity when it was calcined at 900 °C in air for 3 h.

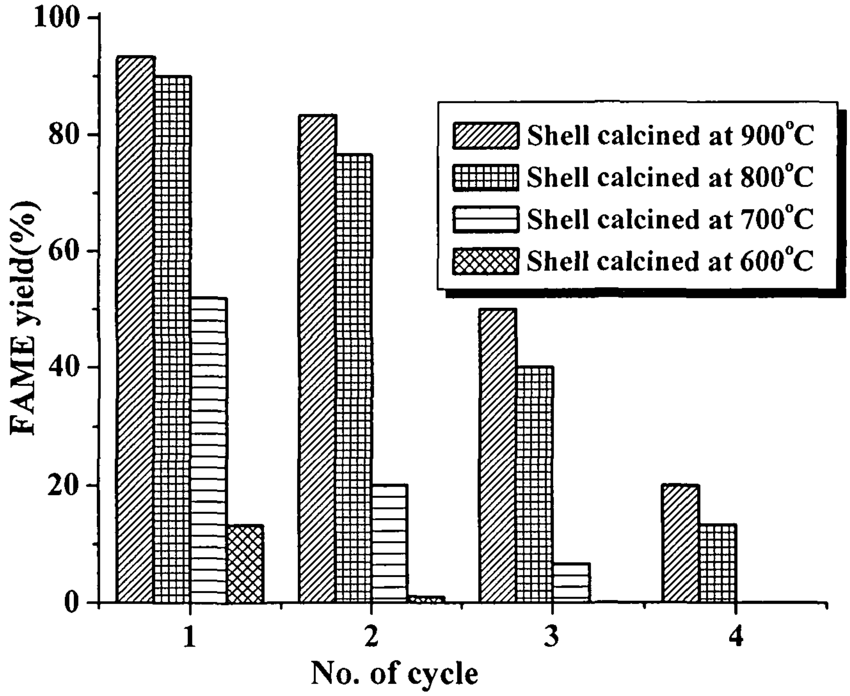


Fig.4.11. Reusability study of calcined waste shells

4.5. Conclusions

The heterogeneous catalyst derived from the waste shells of *Turbonilla striatula* for biodiesel production exhibited excellent catalytic activity under mild reaction conditions. The catalyst was prepared by calcining the waste shells and then employed for transesterification of mustard oil for biodiesel production. The shells calcined at 900 °C, under the optimum condition of 3.0 wt% catalyst, 9:1 methanol to oil ratio and a reaction temperature of 65±5 °C exhibited the best catalytic activity when the reaction was carried out for 6 h.

4.6. Comparative study of catalytic activity of prepared catalysts with conventional catalysts

After successful utilization of CaO as catalyst derived from waste shell of *Turbonilla striatula* for biodiesel production, a comparative study of the derived CaO with conventionally used catalysts such as NaOH and laboratory CaO for biodiesel production was also investigated using waste cooking oil as feedstock. In earlier investigation, mustard oil was chosen as feedstock for biodiesel production by employing the waste shell derived catalyst. In order to make the biodiesel process cost influenceive, we extended the applicability of the waste shell catalyst for transesterification of non-edible oil feedstock such as waste cooking oil. The physical properties of waste cooking oil were determined as per standard methods available and are presented in Table 4.7. It was observed that the acid value (acid value<1) and water content (water content<398 ppm) of the feedstock were low enough for effective base catalyzed transesterification.

Table 4.7. Some physical properties of waste cooking oil

Properties	Test method	Waste cooking oil
Acid value (mg KOH g^{-1})	ASTM D 664	0.99
Water content (ppm)	ASTM D 6304-07	398
Iodine value	EN ISO 3961	139
Saponification value	ASTM D 5558-95	182
Viscosity @40 °C mm^2/s	ISO 12058	34

For determining comparative catalytic activities, catalyst derived from waste shells calcined at 900 °C , renamed as T-CaO, was taken for the study as it exhibited excellent catalytic activity for transesterification.

4.6.1. Catalytic activity based on amount of the three catalysts

Transesterification was carried out with methanol/oil ratio of 6:1 with different catalyst amounts till the completion of the reaction. Concentration of NaOH was varied in the range of 0.5 to 2.0 wt% while T-CaO and Lab CaO were varied in the range of 1-5 wt%. Maximum conversions of 96.8%, 98% and 95% were obtained with NaOH, T-CaO and lab CaO catalysts for 1.5 wt%, 5 wt% and 3 wt% respectively (Figure 4.12.). It was seen that although higher amount of T-CaO catalyst was required for maximum conversion compared to Lab CaO and NaOH, T-CaO exhibited better activity than Lab CaO. This may indicate that catalyst derived from waste shell may also be used as one of the heterogeneous catalysts for biodiesel production.

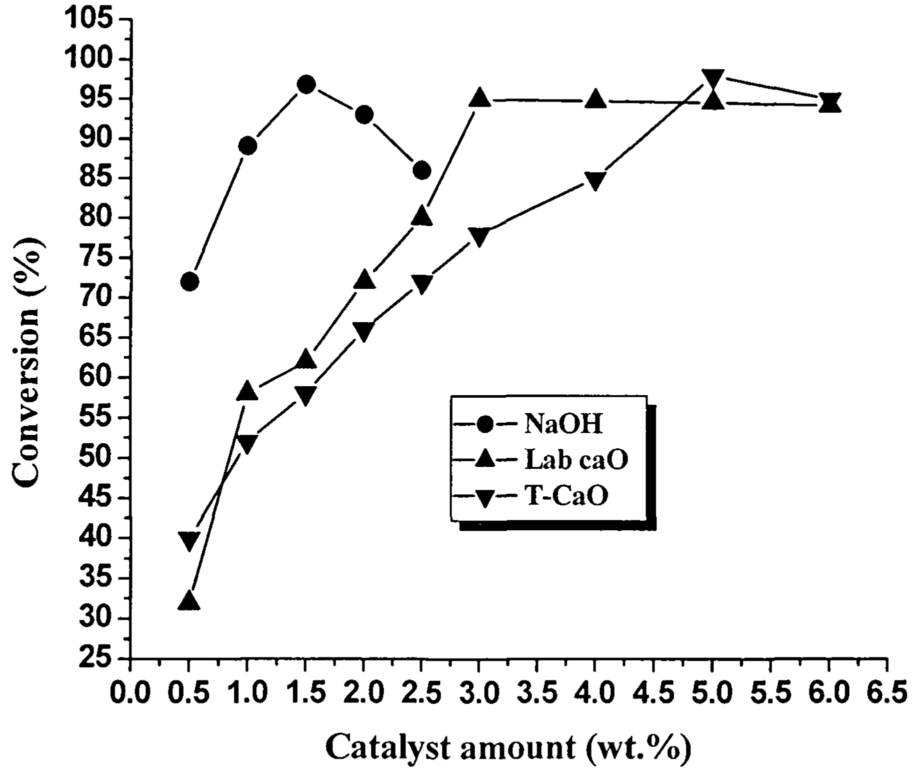


Fig.4.12. Influence of Catalyst amount on methyl ester yield

4.6.2. Influence of methanol to oil ratio on catalytic activity

The effect s of methanol/oil ratio on the catalytic activities of NaOH, Lab CaO and T-CaO were investigated for molar ratio of 3:1 to 15:1. The results are shown in Figure 4.13. It was observed that for all the catalyst the conversion increased with increasing methanol/oil ratio but the conversion either decreased or remained constant after certain methanol to oil ratio. The conversion with NaOH as catalyst increased to the ratio of 6:1 beyond which the catalytic activity was found to be constant. Lab CaO exhibited maximum conversion of 96% with 12:1 methanol/oil ratio while 9:1 methanol/oil ratio showed 98% conversion for T-CaO catalyst. Therefore, 9:1 and 12:1 were taken as optimum methanol/oil ratio for lab CaO and T-CaO respectively. It was further recorded that the catalytic activity was found to be decreased when the methanol/oil ratio was increased beyond the observed optimum value for T-CaO and Lab CaO catalysts. This may be due to the leaching of active species to the reaction medium during transesterification.

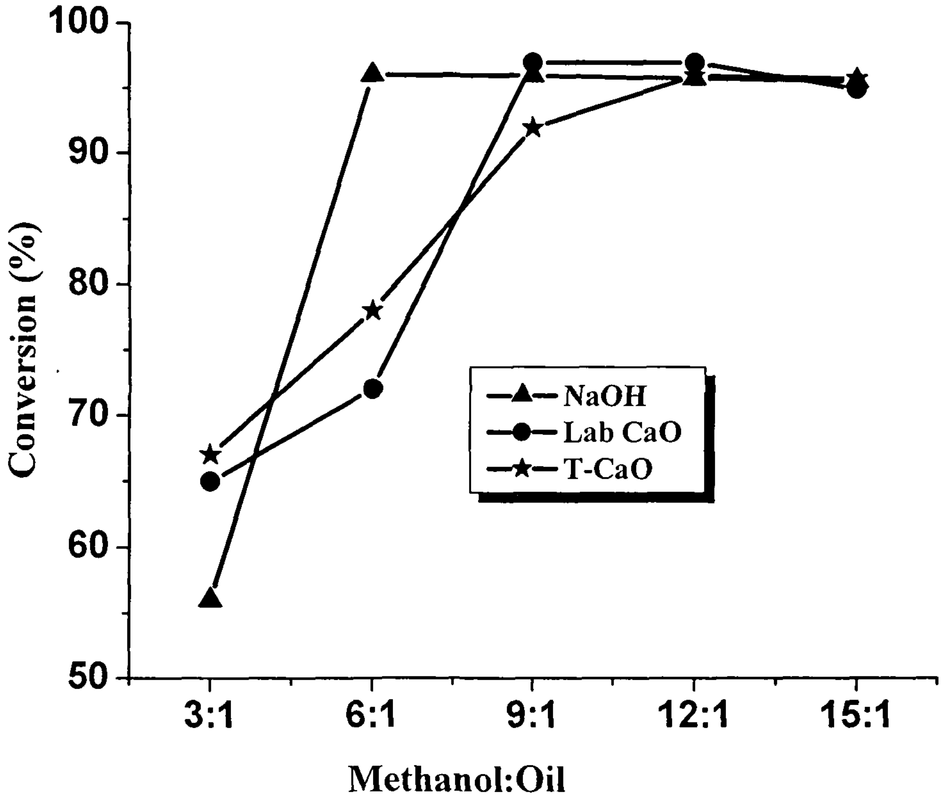


Fig.4.13. Influence of methanol to oil ratio on methyl ester yield

4.6.3. Influence of reaction time and reaction temperature on catalytic activity

Considering the above optimized parameters of the sections 4.5.1 and 4.5.2, the influence of reaction times on catalytic activities of the three catalysts viz. NaOH, T-CaO and Lab CaO were also investigated. Maximum FAME conversion of 97%, 98% and 95.8% were recorded after 2 h, 8 h and 7 h for NaOH, T-CaO and Lab CaO catalysts respectively. Investigation for an optimum reaction temperature, the maximum conversion with NaOH could be obtained at 60 ± 1 °C, T-CaO could be obtained at 70 °C and Lab CaO could be obtained at 65 °C.

4.6.4. Reusability of T-CaO and Lab CaO

Although reusability study for NaOH was not possible, we have studied the reusability of T-CaO and Lab CaO to evaluate its performance as a heterogeneous base catalyst in biodiesel production. The results are shown in Figure 4.13. It can be seen from the figure that the T-CaO catalyst can be reused up to 3 cycles with a slight loss in catalytic activity but Lab CaO shows almost same yield even after being used for more than four times. These results are in agreement with the study of Granados et al [7] who reported that CaO could be used for eight consecutive cycles without loss in activity.

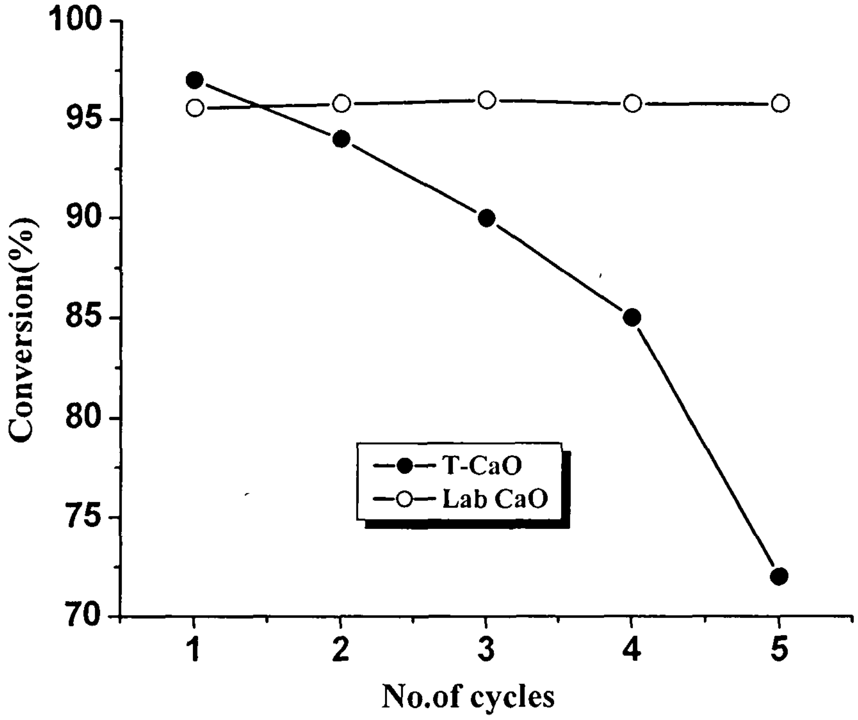


Fig.4.14. Reusability study of lab CaO and T-CaO

In order to improve the activity of T-CaO, we washed the recovered catalyst with methanol and calcined it again at 900 °C for 4 h. It was observed that after used of calcined recovered catalyst, the initial activity ≈97% could be obtained under the optimal reaction conditions. Hence, the waste shell catalyst after recovery may exhibit better reusability, if it is purified and calcined again.

In order to investigate the loss in catalytic activities, XRD patterns of freshly prepared T-CaO, recovered catalysts after 3rd run and recovered catalysts after 5th run were compared and is presented in Figure 4.14. The catalytic activity of the recovered T-CaO was decreasing on increasing the catalytic cycles. The loss in activity was perhaps caused by the blockage of active sites by glycerol formed during the reaction or leaching of active sites to the reaction medium.

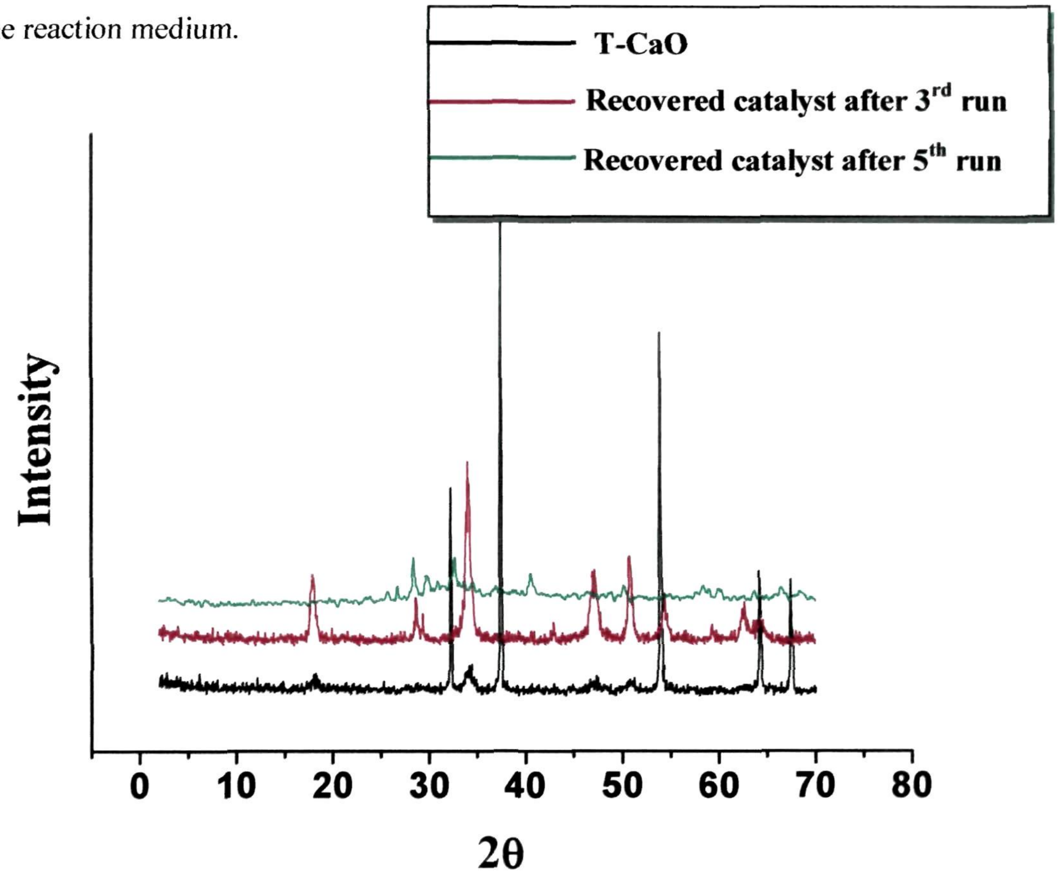


Fig.4.15. XRD pattern of fresh and reused catalysts

4.7. Fuel properties of biodiesel

The synthesized biodiesel prepared by the transesterification of WCO in the presence of T-CaO was characterized for its physical and fuel properties employing the methods of the American Society for Testing and Materials (ASTM) and the results are given in Table 4.8 along with the recommended values for biodiesel (ASTM-D6751) and petrodiesel (ASTM-D975). The determined density of biodiesel at 40 °C, was 0.88 gcm^{-3} which is within the ASTM D6751 limits for biodiesel. Viscosity is another important property of biodiesel which affects the operation of fuel injection equipment, particularly at low temperatures. The determined viscosity of biodiesel prepared from WCO was 3.00 mm^2/s which is within the ASTM D6751 value for biodiesel and within the ASTM values for petro-diesel. Flash point is another important parameter that affects the handling, storage and safety of fuels.

The observed flash point for biodiesel prepared from WCO was found to be greater than 135 °C and is within the limits of ASTM D6751. The high flash point indicates that biodiesel prepared via transesterification in the presence of WS-T is safer than the petrodiesel.

Table 4.8. Fuel properties of biodiesel (in the presence of T-CaO catalyst)

Fuel Properties	**Biodiesel ASTM D6751**	**Petrodiesel ASTM D975**	**Biodiesel (WCO)**
Acid Value (mg KOH $^{-1}$)	0.5	0.11	0.30
Calorific value (kJ/g)	33–40	43.8	38
Flash point (°C)	100–170	60–80	135<
Cloud point (°C)	- 3.0 to 12	-15 to 5	4.3
Viscosity @40 °C mm^2/s	1.6–3.5	1.3–4.1	3
Density g/cm^3	0.86–0.90	0.83	0.88
Carbon residue	0.30	1.5	0.22

4.8. Conclusions

The waste shells calcined at 900 °C was used as catalyst in the transesterification of waste cooking oil and its catalytic activity was compared with conventional catalysts. Maximum conversion of 98 % was achieved with T-CaO under the optimum reaction condition of 5 wt% catalyst amounts, 12:1 methanol to oil ratio and reaction temperature of 70 °C. However, compared to lab CaO the reusability of T-CaO was very poor but after proper purification and calcinations of the recovered catalyst, its initial catalytic activity could be achieved again.

CHAPTER 4B

Li doped waste shell derived CaO

Chapter 4B

Li doped waste shell derived CaO

The feedstock for conducting experiments with Li doped waste shell derived CaO to produce biodiesel was waste cooking oil (WCO). The physical properties of the WCO have already been presented in Table 4.7. The waste shells calcined at 900 °C, renamed as T-CaO was used as parent catalyst for preparing Li doped waste shell derived CaO.

4.9. Catalyst characterization

4.9.1. X-ray diffraction (XRD) analysis

In order to understand the structure of the prepared catalysts, XRD patterns were obtained and observed that the catalysts were highly crystalline in nature. The XRD patterns are presented in Figure 4.16. From the Figure 4.16, it is seen that peaks of lithium oxide start to appear and the peaks become more intense with higher Li loading. The peaks corresponding to 2θ= 32, 37, 54, 64, 57 corresponds to JCPDS card no. 01-078-0649 which belongs to that of calcium oxide. On the other hand the peaks which appear at 2θ = 19, 29, 30, 47, 51 belongs to lithium oxide (JCPDS file no. 01-073-1640). As the doping increases the peaks of lithium oxide are observed to dominate the XRD pattern and the peaks of CaO are reduced which indicates that the final Li doped catalyst might have overshadowed the peaks of parent catalyst due to overloading.

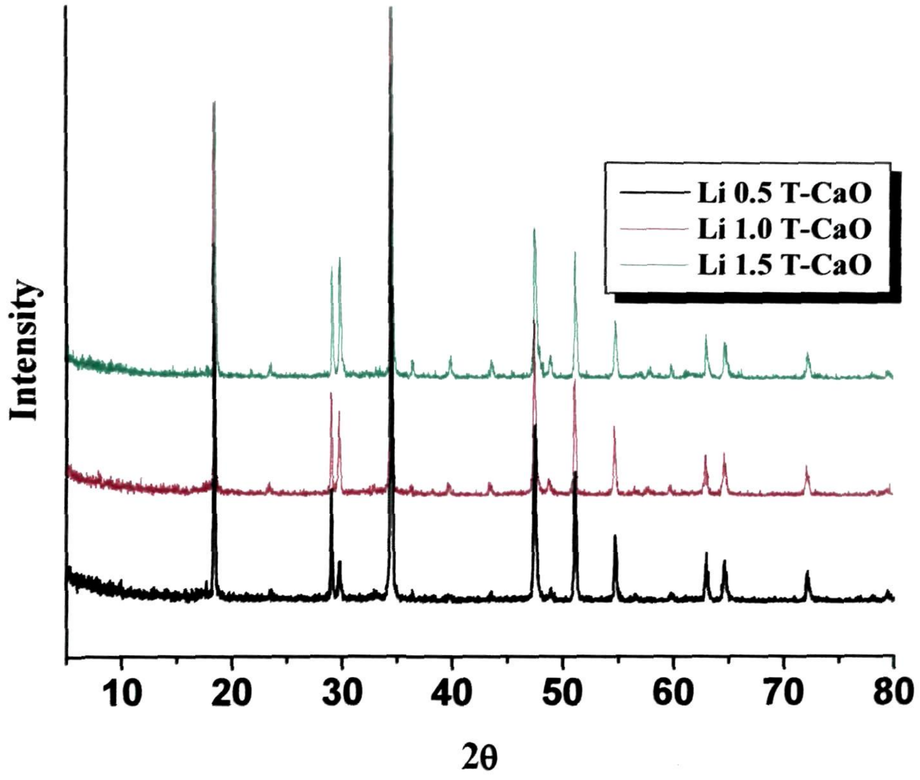


Fig.4.16. XRD pattern of Li doped T-CaO catalyst

4.9.2. Fourier transform infrared spectroscopy (FT-IR) analysis

The FT-IR spectra of the Li doped CaO and CaO derived from waste shells are shown in Figure 4.17. It is observed from the figure that new bands appear in the Li doped samples. In the spectra, the narrow band which appears around 3600 cm^{-1} is assigned to OH group. New bands which appear around 1400 cm^{-1}, 1000cm^{-1}, 850cm^{-1} correspond to Li=O stretching, Li-O broad band stretching and Li-O-Li group respectively [12-13].

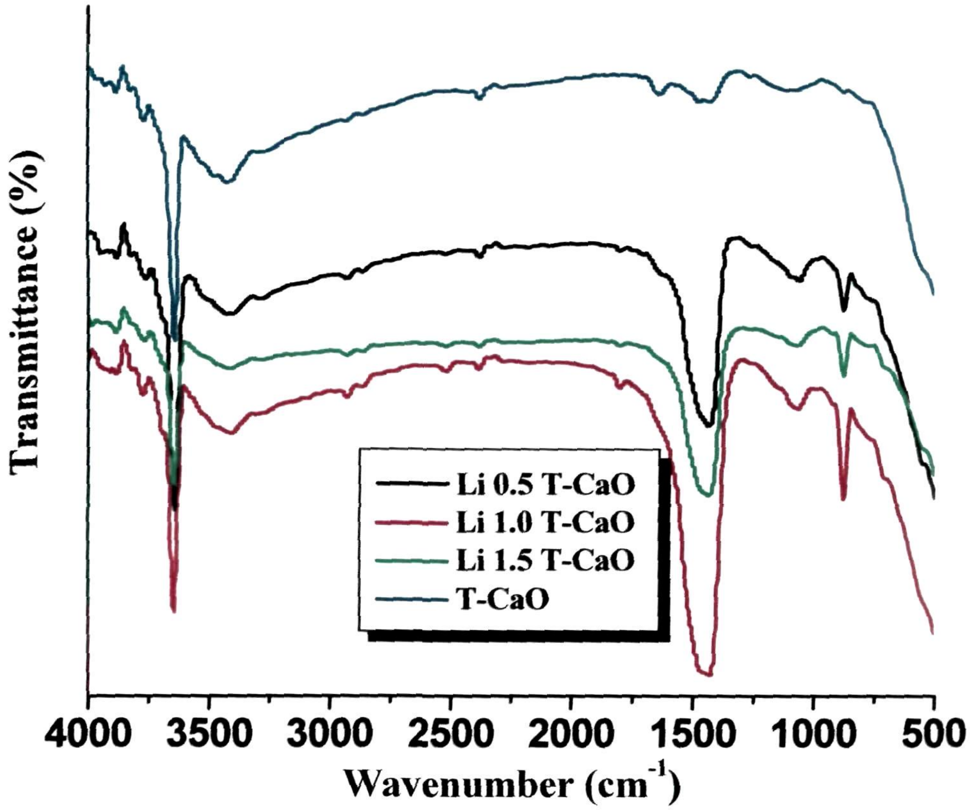


Fig.4.17. FT-IR pattern of Li doped T-CaO catalyst

4.9.3. BET analysis and basicity of the catalyst

The basicity as well as BET surface area of the Li doped T-CaO and T-CaO are presented in Table 4.9. It is seen from the Table that the basicity of the catalyst increases and surface area decreases with increasing Li loading. The drop in surface area is attributed to the dissolution of the framework during catalyst synthesis and filling of pore by Li loading. The lowest surface area as observed for Li1.5 T-CaO suggests that the support is overloaded with excess alkali metals ions.

Table 4.9. Basicity and BET analysis

Catalysts	Basicity (H_)	Surface area (m^2/g)
T-CaO	$9.8<H\_<10.1$	8.359
Li0.5T-CaO	$15<H\_<18.4$	5.88
Li1.0T-CaO	$15.0 < H\_ < 18.4$	5.02
Li1.5T-CaO	$15.0 < H\_ < 18.4$	1.35

4.9.4. Scanning electron microscope (SEM) analysis

The SEM images of Li are presented in Fig.4.18. It was observed that the surface of the parent catalyst (T-CaO) was full of distinct particles of different size and shapes. When T-CaO was doped with Li, new particles which could be easily identified on the surface of T-CaO started to appear. Most of these particles are oval in shape and form cluster kind of arrangement. This arrangement appears even more condensed at higher Li loading. For 1.5 wt% Li doped T-CaO, the surface morphology of T-CaO is totally changed and it appears to be covered with new particles which are attached to each other. The average particle size for 1.5 doped Li was found to be 5 μm.

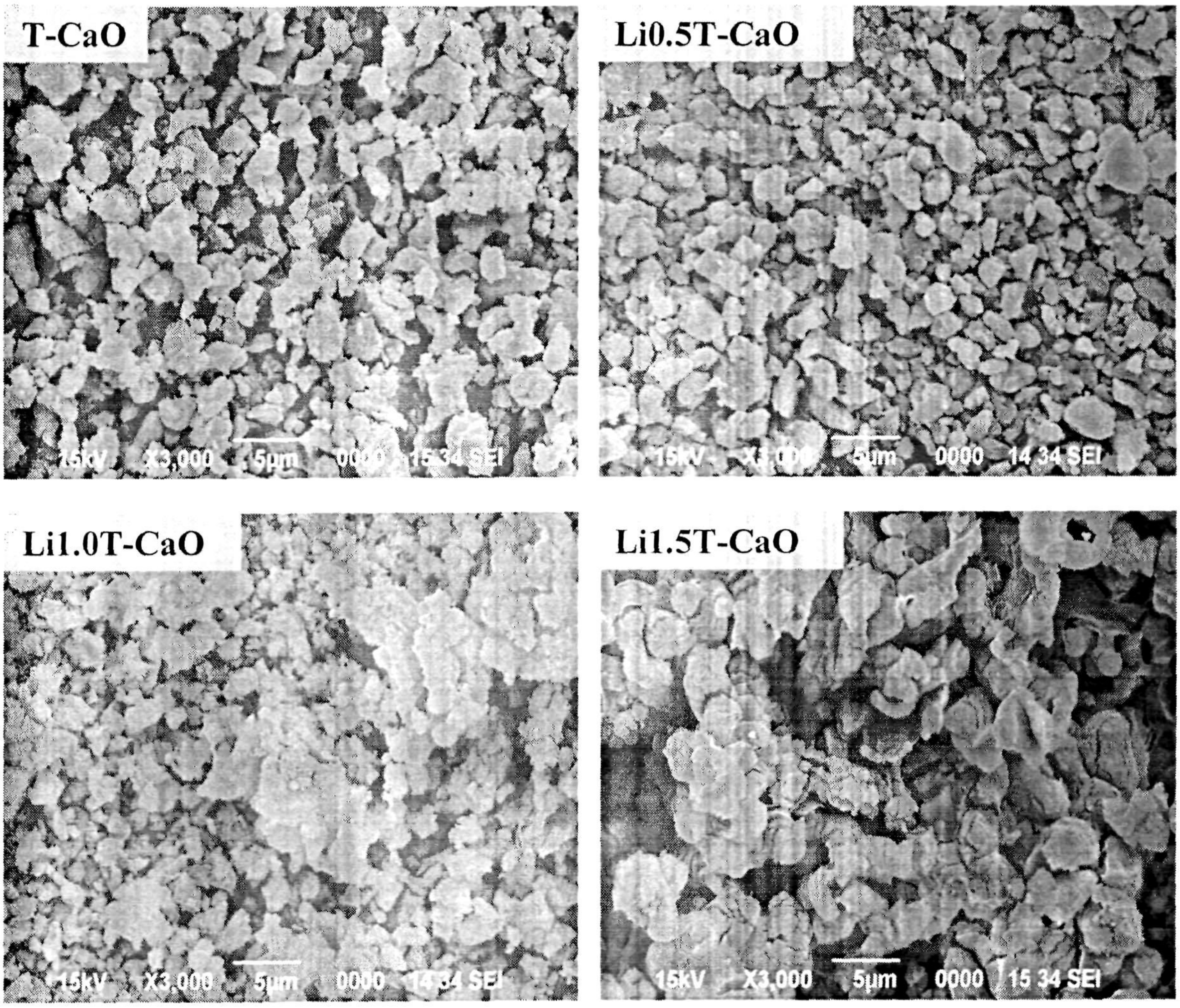


Fig.4.18. SEM images of Li doped T-CaO

4.10. Influence of different parameters on catalytic activity

4.10.1. Influence of Li doping

In order to determine the optimum amount of Li concentration to be doped for achieving maximum conversion, transesterification was carried out with 6:1 methanol to oil ratio at 60 °C for 8 h. Figure 4.19 presents the FAME conversion against Li loading (wt%). It can be seen from the Figure 4.18 that Li1.0T-CaO and Li1.5T-CaO show similar catalytic activities and 98.0% FAME conversion is achieved for both the catalysts. Therefore, lesser amount of 1wt. % Li-doped catalyst prepared from T-CaO is considered as optimum concentration for Li.

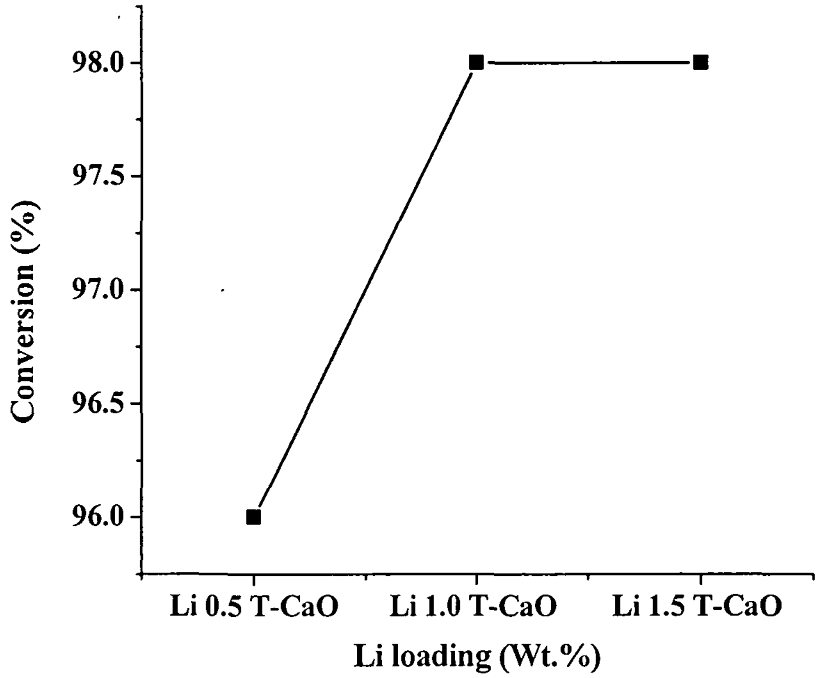


Fig.4.19. Influence of Li loading on methyl ester

4.10.2. Influence of catalyst amount

The effec of catalyst amount required for transesterification is another important factor affecting the transesterification processes. In order to obtain the optimal catalyst amount, reactions were performed with 6:1 methanol to oil molar ratio by varying the catalyst amount ranging from 1-3.5 wt% and the results are presented in Figure 4.19. It can be seen from the Figure 4.20 that the catalytic activities for the three Li doped T-CaO catalysts increase with increasing catalyst amount. The catalyst amount required for achieving maximum conversion with Li1.0T-CaO and Li1.5T-CaO is observed to be 2wt% while it is 2.5 wt% for Li0.5T-CaO. Therefore, the optimal catalyst amount required for transesterification is taken to be 2.0 wt% for this investigation.

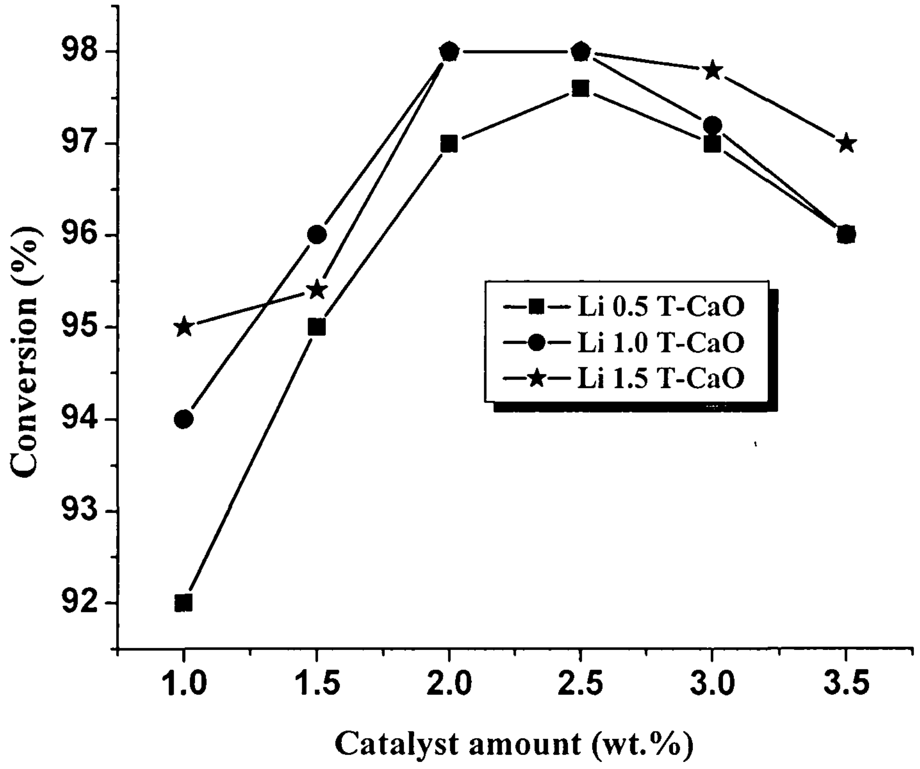


Fig.4.20. Influence of catalyst amount on methyl ester

4.10.3. Influence of methanol to oil ratio

Stoichiometrically, one mole of triglyceride requires three moles of methanol for the transesterification reaction in order to produce fatty acid methyl ester or biodiesel. During reaction, methanol is converted into methoxide on the catalyst surface which in turn reacts with the ester functional groups of the oil leading to methyl ester conversion. In order to study the influence of methanol to oil molar ratio, transesterification was performed by varying the methanol to oil molar ratio from 3:1 to 15:1 and the results are presented in Figure 4.21. It was observed that for the three prepared Li doped catalysts, FAME conversion of 98% was achieved with 9:1 methanol to oil ratio beyond which the conversion either remained the same or dropped slightly. It is already reported that higher methanol content generally accelerates transesterification towards forward direction, which is also observed in our investigation. During reaction, the active species may react with the reactants efficiently, and thus, the mass transfer difficulty as observed in the case of solid catalysts may be overcome. The drop in conversion at higher ratio of 15:1 may occur due to dissolution of oil, intermediates and final product which may result into reduction of reaction rate.

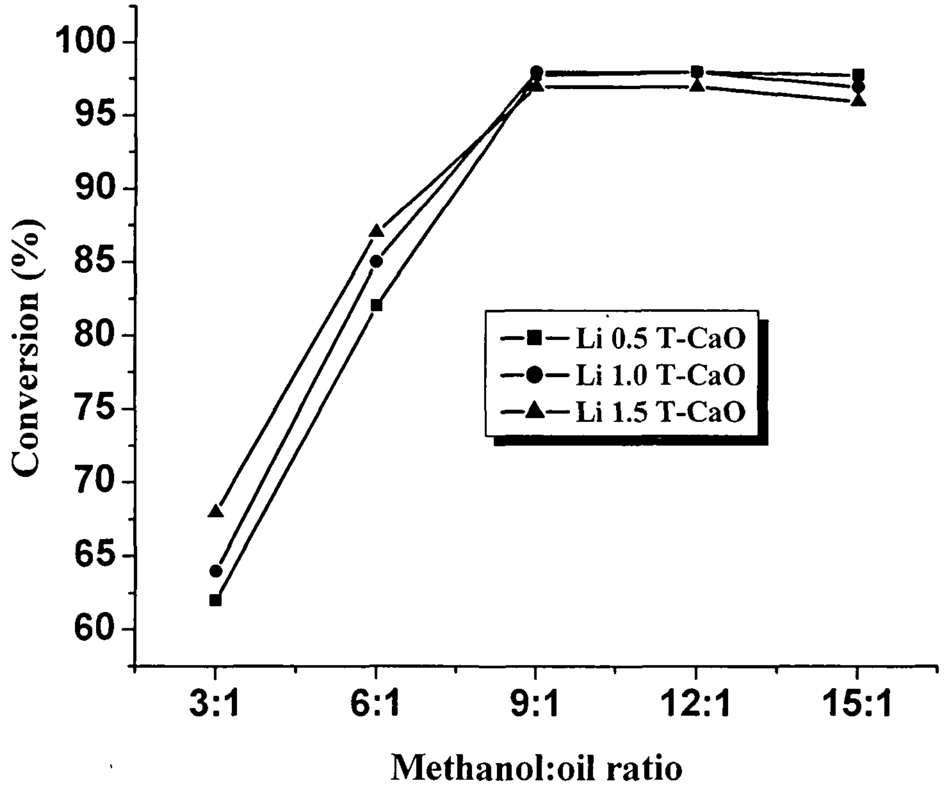


Fig.4.21. Influence of Methanol to oil ratio on methyl ester

4.10.4. Influence of reaction temperature

The study of the influence of reaction temperature plays an important role in a heterogeneously catalyzed reaction. Figure 4.22 shows the influence of reaction temperature on methyl ester conversion. It can be observed from the Figure 4.22 that the conversion is maximum at 65 °C reaction temperature beyond which the conversions for all the catalysts under study either decrease or remain the same. The low conversion at low temperature may be due to the fact that, at low temperature the catalyst does not gain enough energy to break down the bonds between the triglycerides for ester conversion. As the temperature increases, the mass transfer among the reactants also increases and the reaction is shifted towards ester formation. However, when the reaction is conducted at temperature higher than the boiling temperature of methanol, the methanol may evaporate leading to less interaction among the reactants which will ultimately reduce methyl ester conversion. Hence in this study the optimal reaction temperature is taken to be 65 °C.

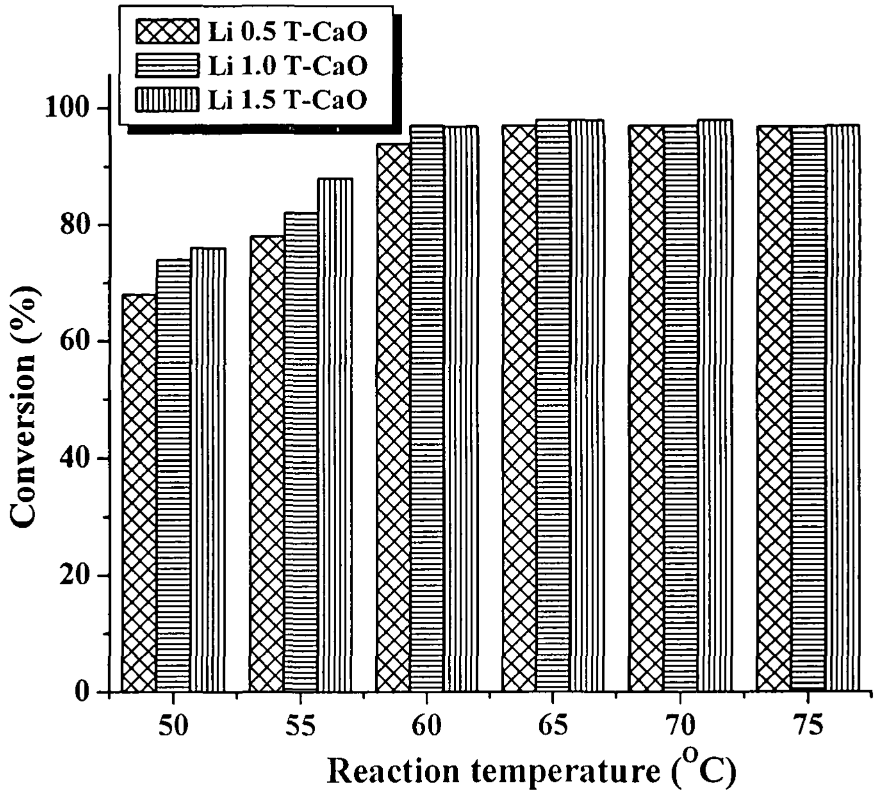


Fig.4.22. Influence of reaction temperature on methyl ester yield

4.10.5. Influence of reaction time

It is reported by many researchers that methyl ester conversion is also a function of reaction time. In this study we have also investigated the influence of reaction time by performing the reaction under optimal catalyst amount, methanol ratio and reaction temperature. The result of the influence of reaction time on FAME conversion is presented in Figure 4.23. It is observed from the Figure 4.22 that the FAME conversion of 98% is achieved after 4 h of reaction time with Li1.0T-CaO and Li1.5T-CaO catalyst. This high conversion may be due to the presence of calcium oxide and lithium oxide as active species presence of which is already shown in the XRD pattern of the catalyst. The conversion with Li1.5T-CaO is seen to be decreased after 6 h while conversion with Li1.0T-CaO decreases slightly only after 7 h of reactions. This may be due to the excessive loading of Li in Li1.5T-CaO and low surface area arising due to structural distortion of parent catalyst. Hence, in this study, 4 h is taken as optimal reaction time.

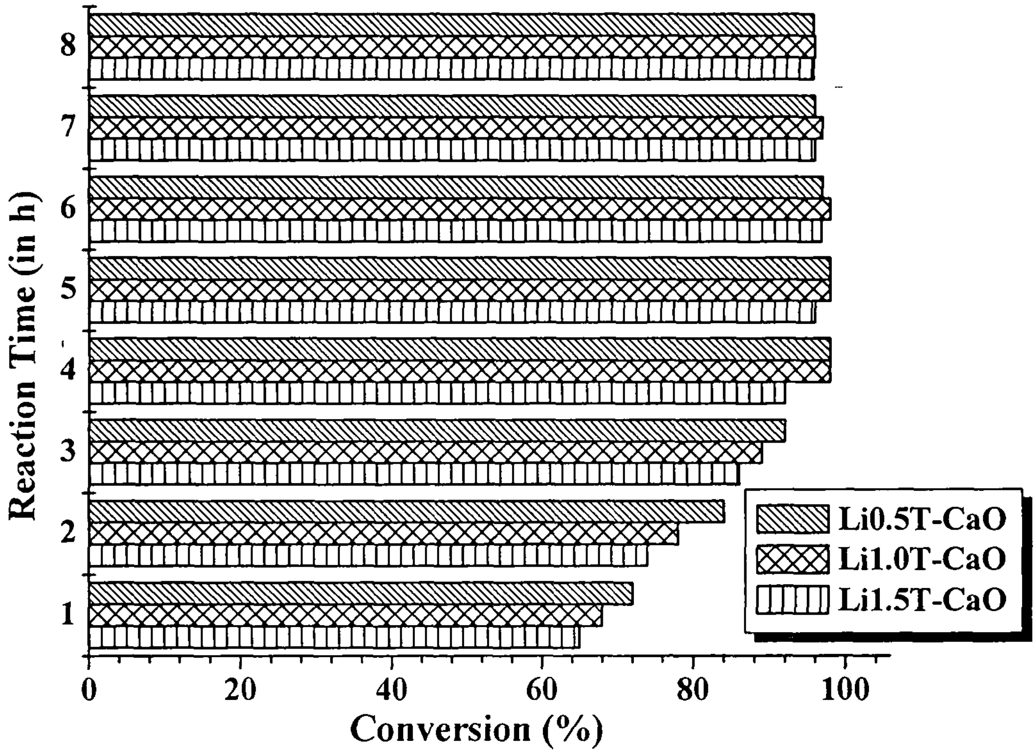


Fig.4.23. Influence of reaction time on methyl ester yield

4.10.6. Reusability study

Reusability studies were also carried out for the prepared catalysts and the results are displayed in Figure 4.24. The used catalyst was recovered by filtration and washed many times by methanol followed by drying in an oven at 100 °C for 30 min. After drying, the catalyst was used again for next cycle of transesterification. It was observed that the catalyst could maintain its activity for five consecutive cycles with a slight loss in activity.

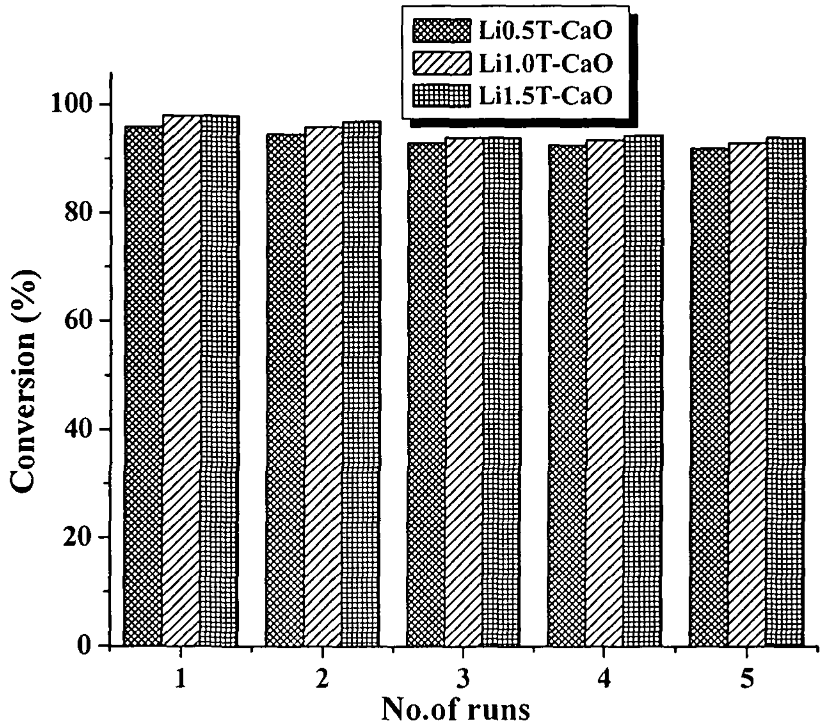


Fig.4.24. Influence of reusability of catalyst on methyl ester yield

4.11. Fuel properties of biodiesel

The fuel properties of biodiesel which was prepared by transesterification of waste cooking oil in the presence of Li1.0T-CaO are presented in Table 4.10 along with the recommended values for biodiesel (ASTM-D6751) and petrodiesel (ASTM-D975). The density and flash point are observed to be 0.89 g/cm3 and 140 °C respectively. The calorific value and acid value were found to be 39 kJ/g and 0.10 mg/ KOH.

Table 4.8. Fuel properties of biodiesel (in the presence of Li1.0T-CaO catalyst)

Fuel Properties	Biodiesel ASTM D6751	Petrodiesel ASTM D975	Biodiesel (WCO)
Acid Value (mg KOH^{-1})	0.5	0.11	0.10
Calorific value (kJ/g)	33–40	43.8	39
Flash point (°C)	100–170	60–80	140
Cloud point (°C)	- 3.0 to 12	-15 to 5	3.0
Viscosity @40 °Cmm^2/s	1.6–3.5	1.3–4.1	3.2
Density g/cm^3	0.86–0.90	0.83	0.89
Carbon residue	0.30	1.5	0.20

4.12. Conclusions

In this investigation, Li in the range 0.5-1.5 wt% are doped into the waste shell derived CaO catalyst and are used as heterogeneous catalysts for biodiesel production. Li1.0T-CaO and Li1.5T-CaO catalyst showed conversion higher than 98 % under the optimum reaction conditions of 9:1 methanol to oil ratio, 2.0 wt% catalyst amounts, 65 °C reaction temperature and 4 h reaction time. On the other hand, Li0.5T-CaO showed maximum activity with 12:1 methanol to oil ratio, 2.5 wt%, reaction temperature of 65 °C and reaction time 5 h. moreover all the catalyst could be reused for five times with negligible loss in catalytic activity.

CHAPTER 4C

Ba doped waste shell derived CaO

Chapter 4C

Ba doped waste shell derived CaO

The feedstock for conducting experiments with Ba doped waste shell derived CaO to produced biodiesel was also waste cooking oil (WCO). The physical properties of the WCO may be seen in Table 4.7. The parent catalyst for preparing Ba doped catalyst was also CaO derived from waste shells calcined at 900 °C (T-CaO).

4.13. Catalyst characterization

4.13.1. X-Ray Diffraction (XRD) analysis

Figure 4.25 represents the XRD patterns of Ba doped T-CaO and T-CaO. The formation of sharp peak indicates the formation of highly crystalline materials. The diffraction peaks are identified using a standard JCPDS file. For undoped T-CaO, the peaks that appeared at 2θ = 32.14, 37.22, 53.57, 64.24 and 67.49 are the characteristic peaks for calcium oxide (JCPDS file no. 48-1467). Doping with Ba does not bring any shifting or changes in the XRD pattern of the T-CaO. The non visibility of the peaks in the doped samples may arise due to the fact that the *d* value of diffraction peaks of tetragonal phase barium oxide (JCPDS file no. 00-001-0642) is very close to the cubic phase of CaO and may overlap each other. However, when the Ba loading increases from 0.5% to 1.5% there is a sharp decrease in the crystalline peaks of T-CaO and is more prominent for Ba1.5T-CaO. The decrease in peak intensity of T-CaO is observed because of the large ionic radius of barium (around 0.134 nm) which can overshadow the peaks of CaO resulting in shading off of the characteristic peaks of T-CaO. With higher barium loading the crystalline peaks of T-CaO are totally reduced to a large extent indicating that the original peaks of the CaO are totally covered by excess barium compounds.

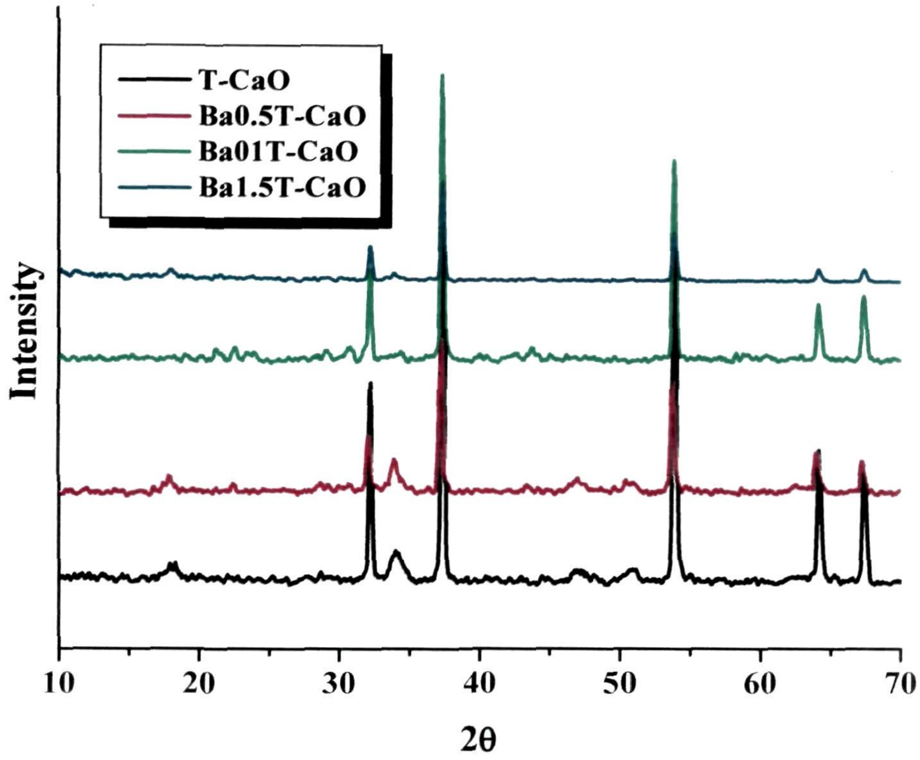


Fig.4.25. XRD pattern of Ba doped waste shells

4.13.2. Fourier transform infra red (FT-IR) analysis

The findings in XRD are also supported by FT-IR spectra for the catalysts with different barium loading which are presented in Figure 4.26. The most obvious band ascribed to BaO is the sharp one observed at around 847–885 $cm^{-1}$and the bands around the frequency region of 500 – 580 $cm^{-1}$are assigned to the stretching vibrations of Ba–O bond. The appearance of broad bands around 1370-1585 cm^{-1} might have arisen due to the asymmetric stretching vibrations of Ba–O bond. The intensity of band around 3400 cm^{-1}which corresponds to the OH group, becomes broad with progressive substitution of barium. The band at 3600 cm^{-1} becomes more intense with Ba addition and it corresponds to vibrations of OH groups bonded to metal ions [14]. The bands which appear around 1600 cm^{-1} in the Ba doped catalysts are not found to be prominent in the IR spectra of T-CaO. This indicates that it may belong to the combined band originating from BaO lattice vibrations.

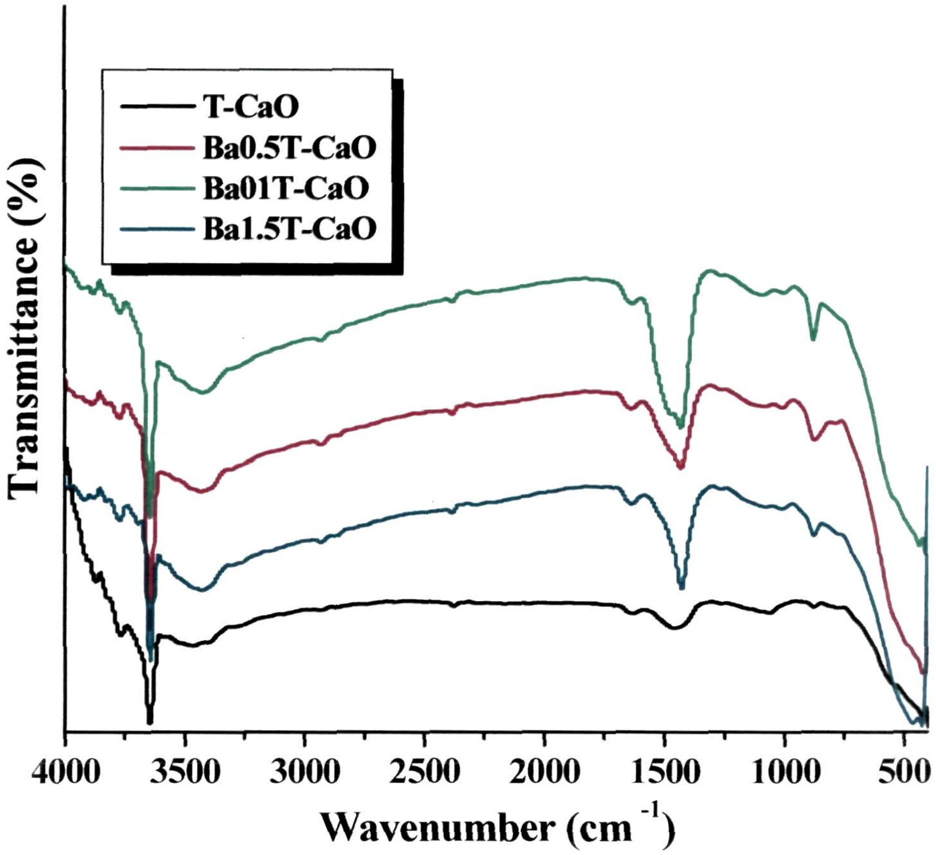


Fig.4.26. FT-IR pattern of Ba doped waste

4.13.3. Scanning electron microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDX) analysis

The surface morphology of the prepared catalysts was studied by SEM (Figure 4.27). It is observed from the Figure 4.27 that in the SEM image of the catalysts doped with 0.5 wt% barium (Ba0.5T-CaO), the catalysts surface contains particles spherical in structure along with non uniform size particles. The content of spherical size particles increases for 1.0wt% doped barium(Ba01T-CaO) and the SEM image of 1.5 wt% barium (Ba1.5T-CaO) reveals that the spherical shape particles covers the almost the entire surface of the catalyst. These spherical shape particles are perhaps active Ba species. The SEM image for Ba1.5T-CaO indicates that the catalyst surface is covered with Ba species.

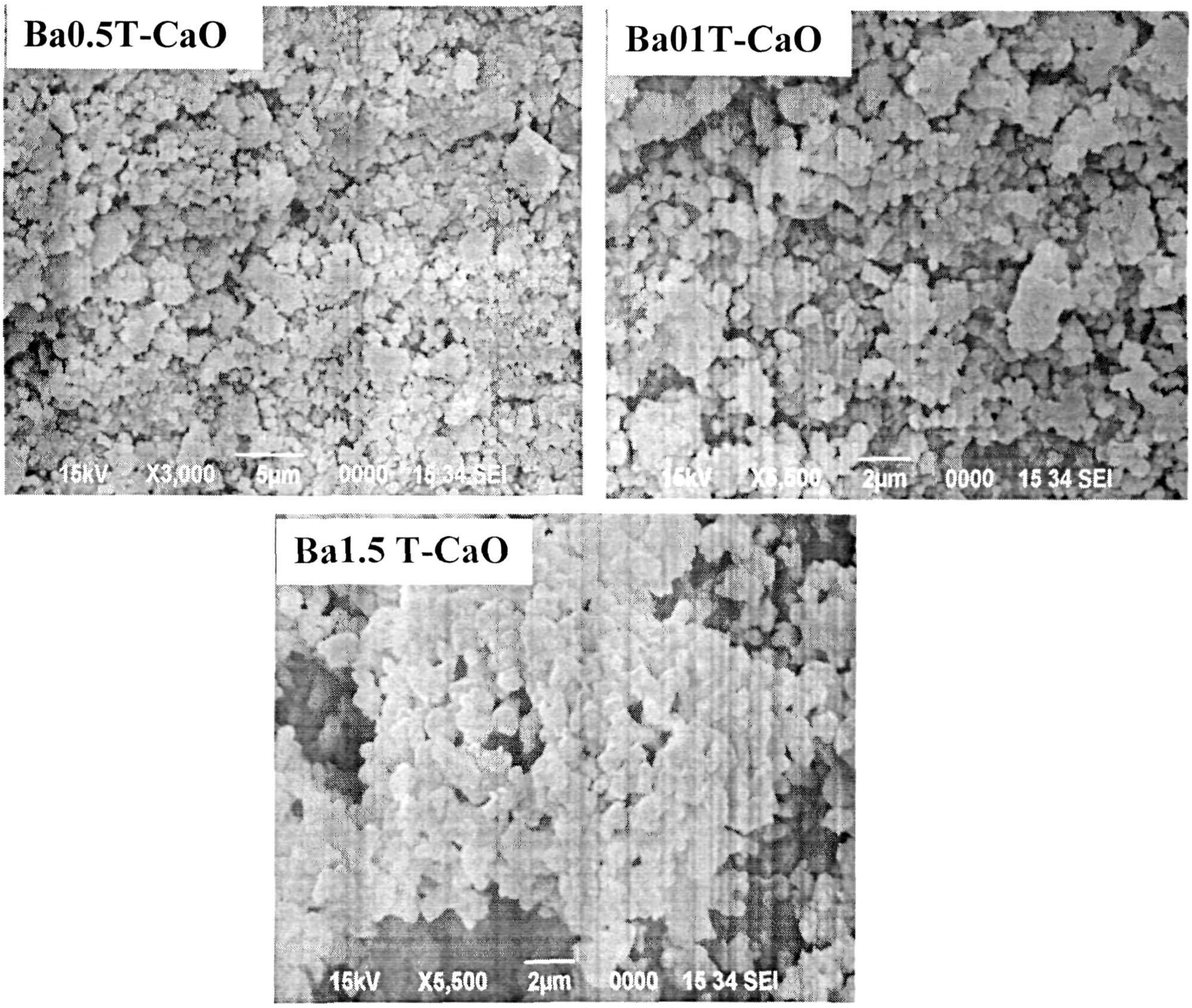


Fig.4.27. SEM images of Ba doped T-CaO

EDX analysis was also carried out to determine the elemental compositions of the catalyst and the results are presented in Table 4.11. It is seen from the Table 4.11 that for Ba0.5T-CaO, the contents of Ca and Ba are found to be 29.46% and 1.51% (w/w) respectively while the contents are found to be 40.85% and 1.73% (w/w) respectively for Ba1.0T-CaO. The contents for Ba1.5T-CaO are found to be 40.92 % (Ca) and 4.15% (Ba).

Table.4.11. EDS analysis of barium doped waste shell CaO

Catalyst	Element	Weight(%)	Atomic (%)
Ba0.5T-CaO	O	69.03	85.26
	Ca	29.46	14.53
	Ba	1.51	0.22
Ba1.0T-CaO	O	57.42	77.67
	Ca	40.85	22.06
	Ba	1.73	0.27
Ba1.5T-CaO	O	54.93	76.56
	Ca	40.92	22.77
	Ba	4.15	0.67

4.13.4. Basicity and surface area

The basicity of the doped catalysts was also investigated. The results for the different Ba loaded catalyst with their basicity values are depicted in Table 4.12. It is seen form the Table 4.12 that basicity is found to be increased till 1% of Ba loading beyond which it decreases for 1.5 % of Ba loading. The increasing basicity for Ba0.5T-CaO and Ba1.0T-CaO catalysts may be due to the presence of BaO and CaO active species. It has already been shown in XRD and FT-IR pattern of Ba1.5T-CaO that CaO species are reduced and the dominant species are associated only with Ba. Therefore, the catalysts prepared (Ba doped T-CaO) were highly basic in nature compared to the parent catalyst (T-Cao) as also evident from the Table 4.12.

The surface areas of the catalysts prepared can also be seen in Table 4.12. The surface area of 0.5% Ba loading catalyst is found to be higher than the T-CaO catalyst. But, surface area for Ba loading catalyst decreases with increasing loading of Ba. The decrease in surface area is attributed to the incorporation of barium to the CaO surface. The increase in surface area in Ba0.5T-CaO catalyst may occur due to incomplete dispersion of Ba on the support.

Table.4.12. Basic Strengths of Ba doped T-CaO

Catalyst	Hammett indicator ($H\_$)	Basic strength (mmol/g)	Surface area (m^2/g)
T-CaO	$7.2 < H\_ < 9.8$	0.10	8.359
Ba0.5 T-CaO	$15.0 < H\_ < 18.4$	0.16845	11.56
Ba1.0 T-CaO	$15.0 < H\_ < 18.4$	0.2375	4.86
Ba1.5 T-CaO	$15.0 < H\_ < 18.4$	0.1925	2.00
Recovered Ba1.0 T-CaO	$7.2 < H\_ < 9.8$	0.128	–

4.14. Influence of different parameters on methyl ester conversion

4.141. Influence of Ba loading

The influence of Ba loading on conversion was studied by conducting transesterification at 60 °C, 6:1 methanol ratio for 8 h of reaction time. We have selected 8 h because in our previous study (section 4.5.3) the best activity for the parent catalyst T-CaO was obtained for 8 h. Figure 4.28. presents the influence of Ba loading on the methyl ester conversion. it is observed from the Figure 4.28 that more than 98% FAME conversion is possible with 1.0 wt% Ba loading beyond which the conversion decreases slightly. The increase in conversion with Ba loading is attributed to the presence CaO and BaO which might have acted like active species during the reaction.

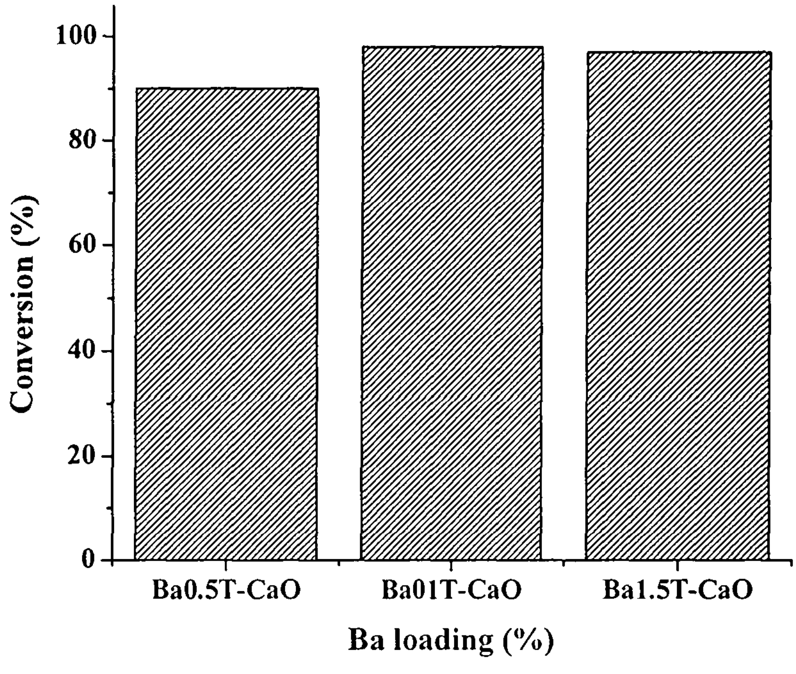


Fig.4.28. Influence of Ba loading on methyl ester

4.14.2. Influence of catalyst amount

To determine the optimum catalyst amount required for the reaction, transesterification with different amount of Ba doped T-CaO catalysts were carried out and the results are presented in Figure 4.29. The reaction was carried out at 60 °C for 8 h with a methanol/oil ratio of 6:1. It can be seen from the Figure 4.29 that the conversion increases with the increasing amount of Ba and complete conversion is obtained for 1.0 wt% catalyst amount. Based on this, we have taken 1.0 wt% as the optimum amount for the catalyst in our study. The introduction of catalyst in the reaction system provides active sites which interact with the reactants and facilitates the biodiesel formation. It is reported in another study that biodiesel formed during the reaction acts as a co-solvent in later stage of the reaction [14]. However, the drop in catalytic activity with 1.5% Ba loading may be due to the coverage of basic sites by the excess Ba loading which obstructs the interaction of reactants. This is also supported from the XRD pattern (Figure 4.25) where the crystalline peaks of T- CaO is reduced completely indicating the coverage of surface basic sites by excess Ba compounds in Ba1.5 catalyst.

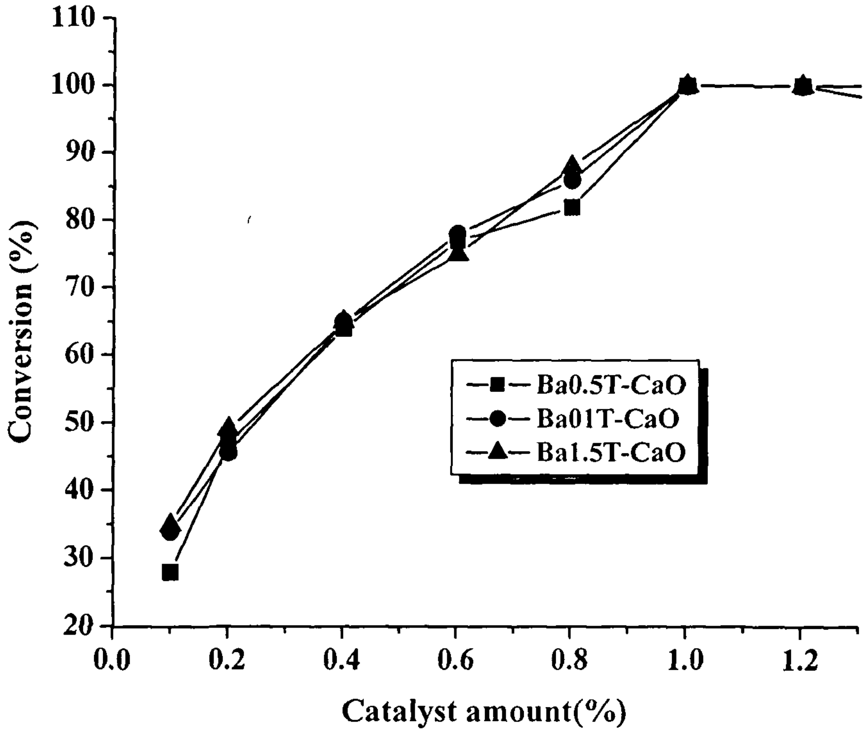


Fig. 4.29. Influence of catalyst amount on methyl ester

4.14.3. Influence of Reaction time

The influence of reaction time on FAME conversion is presented in Figure 4.30. It is seen from Figure 4.30 that complete conversion of FAME with Ba01T-caO and Ba1.5T-CaO was achieved in only 3 h beyond which the conversion remains the same. Maximum activity with Ba0.5T-CaO could be achieved at 4 h beyond which the conversion remains the same. Therefore, in this investigation the optimum reaction time taken was 3 h.

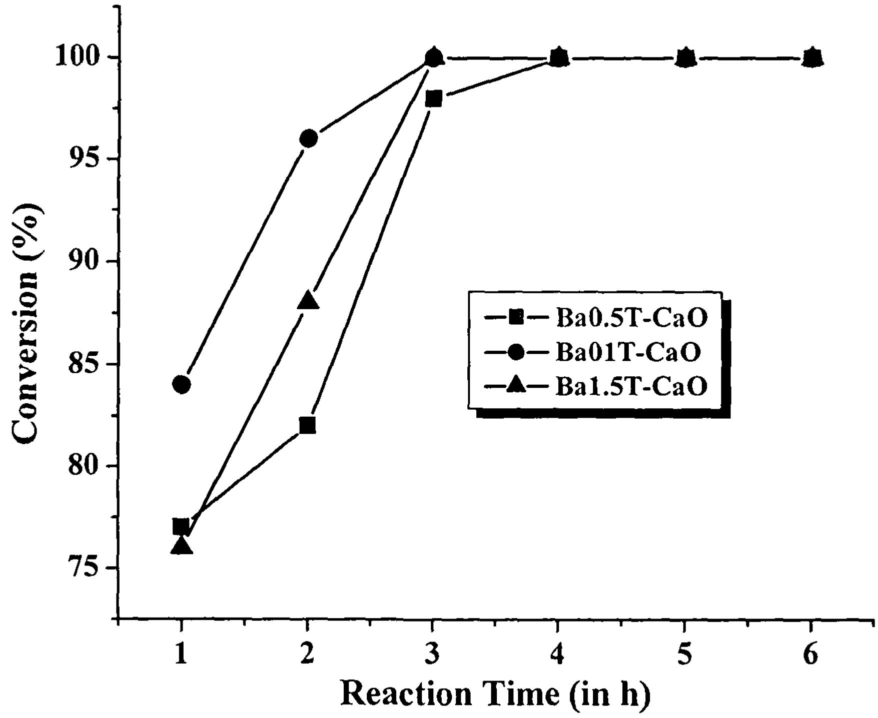


Fig.4.30. Influence of reaction time (in h)

4.14.4. Influence of methanol/oil ratio

In this investigation, the influence of methanol to oil molar ratio was studied by varying the amount of methanol to oil ratio with an optimum catalyst amount of 1% for 3 h and the results are presented in Figure 4.31. It can be observed from the Figure 4.31 that Ba01T-CaO and Ba1.5T-CaO show complete conversion with 6:1 methanol/oil molar ratio whereas Ba0.5T-CaO shows complete conversion with 9:1 molar ratio. The excess methanol used in the reaction can be collected with a rotary evaporator and can be reused for the next reaction.

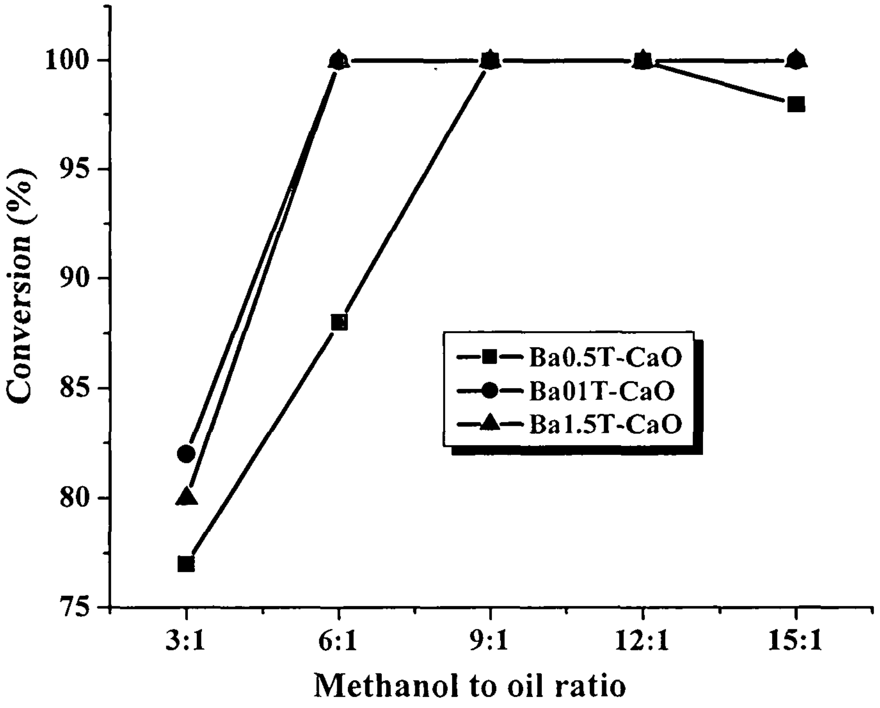


Fig.4.31. Influence of Methanol to oil

4.14.5. Influence of reaction temperature

In order to determine the optimum reaction temperature, transesterification was carried out by varying the reaction temperature from 50 to 75 °C in a step increment of 5 °C. When the reaction was carried out at reaction temperature of 50–55 °C, conversion of 62%, 65% and 64% were obtained with Ba0.5T-CaO, Ba01T-CaO and Ba1.5T-CaO respectively. When the reaction was carried out at reaction temperature above 55 °C, the conversion increased with increasing reaction temperature and almost complete conversion was obtained at 65 °C and above. These results are presented in Figure 4.32. It is seen form the Figure 4.32 that negligible loss in catalytic activity is found above 65 °C reaction temperature. This is probably due to the fact that methanol has a boiling point near 65 °C and reaction above this temperature may cause the loss of methanol.

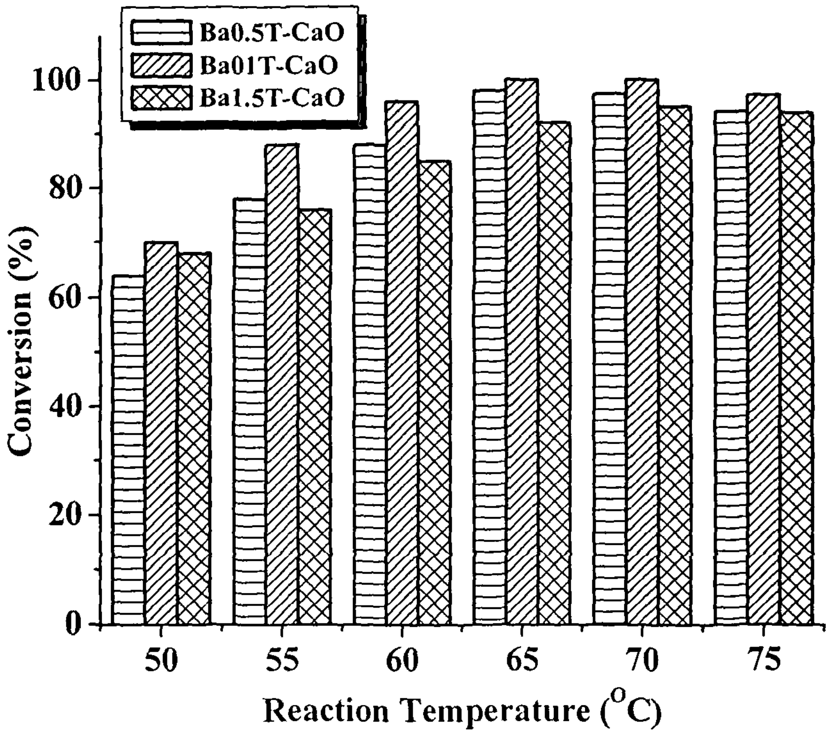


Fig.4.32. Influence of reaction temperature (°C)

4.14.6. Reusability study

Ba01T-CaO catalyst was taken for this investigation as it showed better catalytic activity during FAME conversions. The reusability study was conducted for 4 consecutive cycles under the optimum conditions ascertained earlier in our studies. After the completion of the reaction the catalyst was recovered by filtration under vacuum pressure followed by washing with methanol. After methanol washing, the catalyst was dried in oven at 120 °C and reused for next cycle. The results are presented in Figure 4.33. A gradual drop in catalytic activity in consecutive cycles is observed as in Figure 4.33.

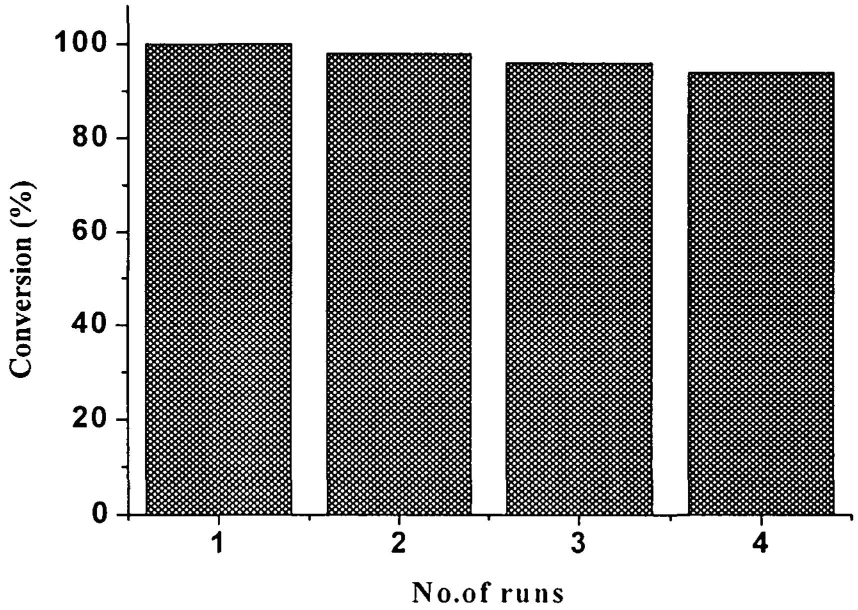


Fig.4.33. Reusability study for Ba01T-CaO

XRD analysis of the fresh catalyst and recovered catalyst after 4th run were conducted to study the loss in catalytic activity and the results are presented in Figure 4.34. It is seen from the Figure 4.34 that the fresh catalyst losses its crystalline nature in recovered catalyst. Hence, recovered catalyst may lose its catalytic activity. This is attributed to the probable deposition of reaction products on the catalyst active sites leading to catalyst poisoning. Moreover, the basicity of the recovered catalyst was observed to be reduced in comparison to the freshly prepared catalyst (Table 4.12). This may be another reason for the loss in catalytic activity.

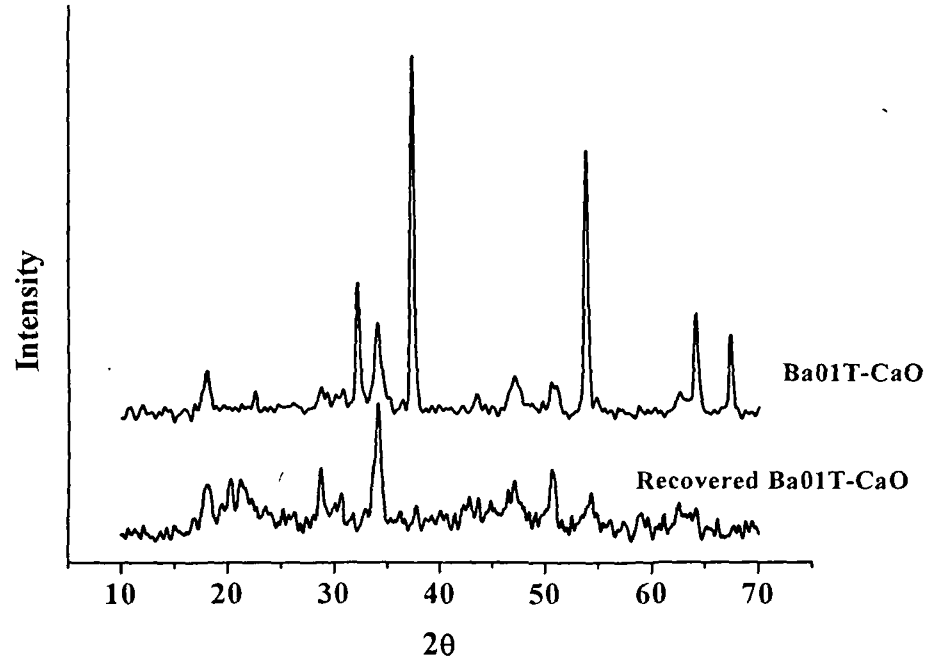


Fig. 4.34. XRD patterns of freshly prepared Ba01T-CaO and recovered Ba01T-CaO

4.15. Fuel properties of biodiesel

Similar to discussed in section 4.7, the fuel properties of biodiesel prepared by transesterification of WCO in the presence of Ba01T-CaO were also determined and are presented in Table 4.13. the determined values for different properties of biodiesel are compared with ASTM D 6751 and ASTM D975. It was observed that the viscosity, density and flash point determined were 3.2 m^2/s, 0.87 g/cm^3 and 138 °C respectively and all of these properties were within the limits of ASTM D6751 and are comparable with ASTM D 975 for petrodiesel. It can also be seen from the Table 4.13 that other properties such as acid value, calorific value were also within the ASTM limits which indicates that the biodiesel prepared in the presence of Ba doped waste shell is also compatible with petrodiesel.

Table 4.13. Fuel properties of biodiesel (in the presence of Ba01T-CaO catalyst)

Fuel Properties	Biodiesel ASTM D6751	Petrodiesel ASTM D975	Biodiesel (WCO)
Acid Value (mg KOH^{-1})	0.5	0.11	0.10
Calorific value (kJ/g)	33–40	43.8	39
Flash point (°C)	100–170	60–80	138
Cloud point (°C)	- 3.0 to 12	-15 to 5	2.0
Viscosity @40 °Cmm^2/s	1.6–3.5	1.3–4.1	3.2
Density g/cm^3	0.86–0.90	0.83	0.87
Carbon residue	0.30	1.5	0.20

4.16. Conclusions

In this study the Ba doped T-CaO catalyst was prepared and investigated as heterogeneous catalysts for biodiesel production. Under optimal condition of 6:1 methanol: oil ratio, reaction temperature 65 °C we found that complete conversion was achieved with Ba01T-CaO and Ba1.5T-CaO catalyst in 3 h. The reusability studies of Ba01T-CaO catalyst showed continuous drop in catalytic activity which was attributed to the loss of active sites and deposition of product on the catalyst itself.

CHAPTER 4D

BIODIESEL ANALYSIS BY NMR

Chapter 4D

Biodiesel studies by Nuclear magnetic resonance (NMR) spectroscopy

4.17. ^{1}H NMR analysis

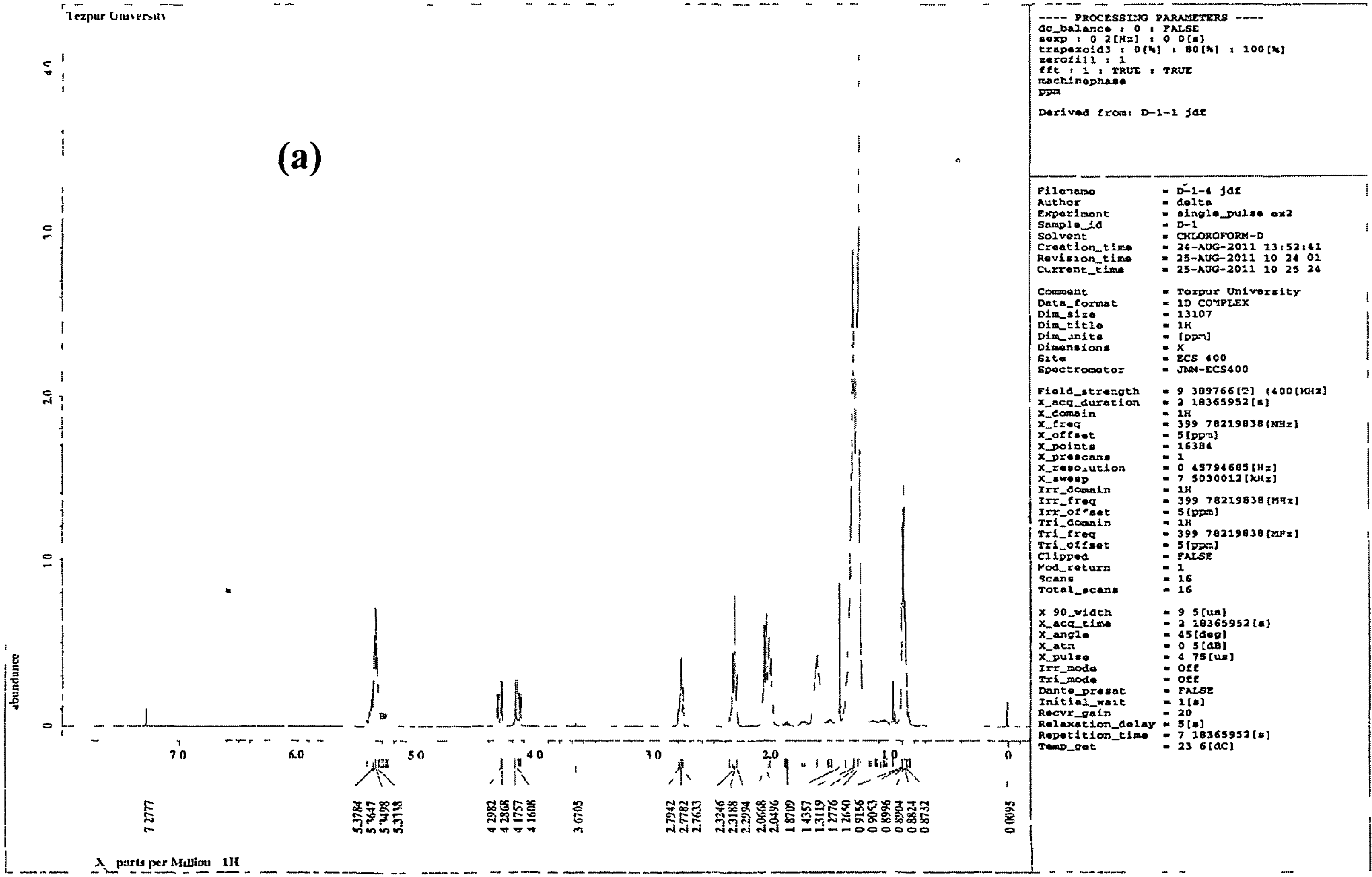
Biodiesel produced in the transesterification of different feedstocks is characterized by ^{1}H NMR spectroscopy [Figure 4.35. (a & b)]. The frequency range between $\delta = 3$ and 5 ppm (where d is chemical shift) represents the resonances of the molecules containing oxygenates or the methoxy groups of FAME. As shown in Figure 4.35 (a), the ^{1}H NMR spectrum of the feedstock (WCO) shows a multiplet at 4.1-4.2 and 5.3 ppm which is due to the presence of glyceridic protons along with other hydrocarbon proton peaks at their normal positions [16,17].

The major difference between the ^{1}H NMR spectra of the feedstock and resulting methyl ester formation is the disappearance of these glyceride protons and appearance of methyl ester protons around 3.6 ppm. As can be seen from the Figure 4.35 (b) a single peak appears at 3.6 ppm and a multiplet peaks at 2.2-2.3ppm appears which is attributed to the methoxy group. These peaks confirm the presence of fatty acid methyl ester (FAME) in biodiesel. A triplet near 0.8 ppm in the spectrum appears for the terminal methyl protons, a strong signal at 1.2-1.3 ppm is related to the methylene protons of carbon chain, multiplet around 1.6 is due to the β –carbonyl methylene protons and the peaks around 5.3 ppm are assigned to the olefinic hydrogens respectively [18-22].

4.18. ^{13}C NMR analysis

Figure 4.36 (c & d) represents the spectrum of ^{13}C NMR of biodiesel and feedstock respectively. The peaks around 62 and 68 ppm in the ^{13}C NMR spectrum of the feedstock (Figure 4.36 c) are attributed to the –O–CH– and –O–CH$_2$– functional groups of TAG. These two peaks disappear when methyl esters are formed and a new peak at around 51.27 ppm appears which is associated with –OCH$_3$carbon [Figure 4.36 (d)]. Characteristic peak of ester carbonyl (– COO–) appears at 174 ppm while the peaks around 130, 127 and 129 ppm indicate the presence of unsaturated fatty acids in the ^{13}C NMR spectrum of biodiesel. In the spectral region from (35–11 ppm), the peak from 28.88–29.40 ppm are related to O–CH$_2$–CH$_2$– group of FAME. Signal around 14 ppm is ascribed to the CH$_3$ group of the methyl ester formed [17, 18-22].

(a)



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Tri_domain         = 1H
Tri_freq           = 399 78219838[MHz]
Tri_offset         = 5[ppm]
Clipped            = FALSE
Mod_return         = 1
Scans              = 16
Total_scans        = 16

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X_acq_time         = 2 18365952[s]
X_angle            = 45[deg]
X_atn              = 0 5[dB]
X_pulse            = 4 75[us]
Irr_mode           = Off
Tri_mode           = Off
Dante_presat       = FALSE
Initial_wait       = 1[s]
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Relaxation_delay   = 5[s]
Repetition_time    = 7 18365952[s]
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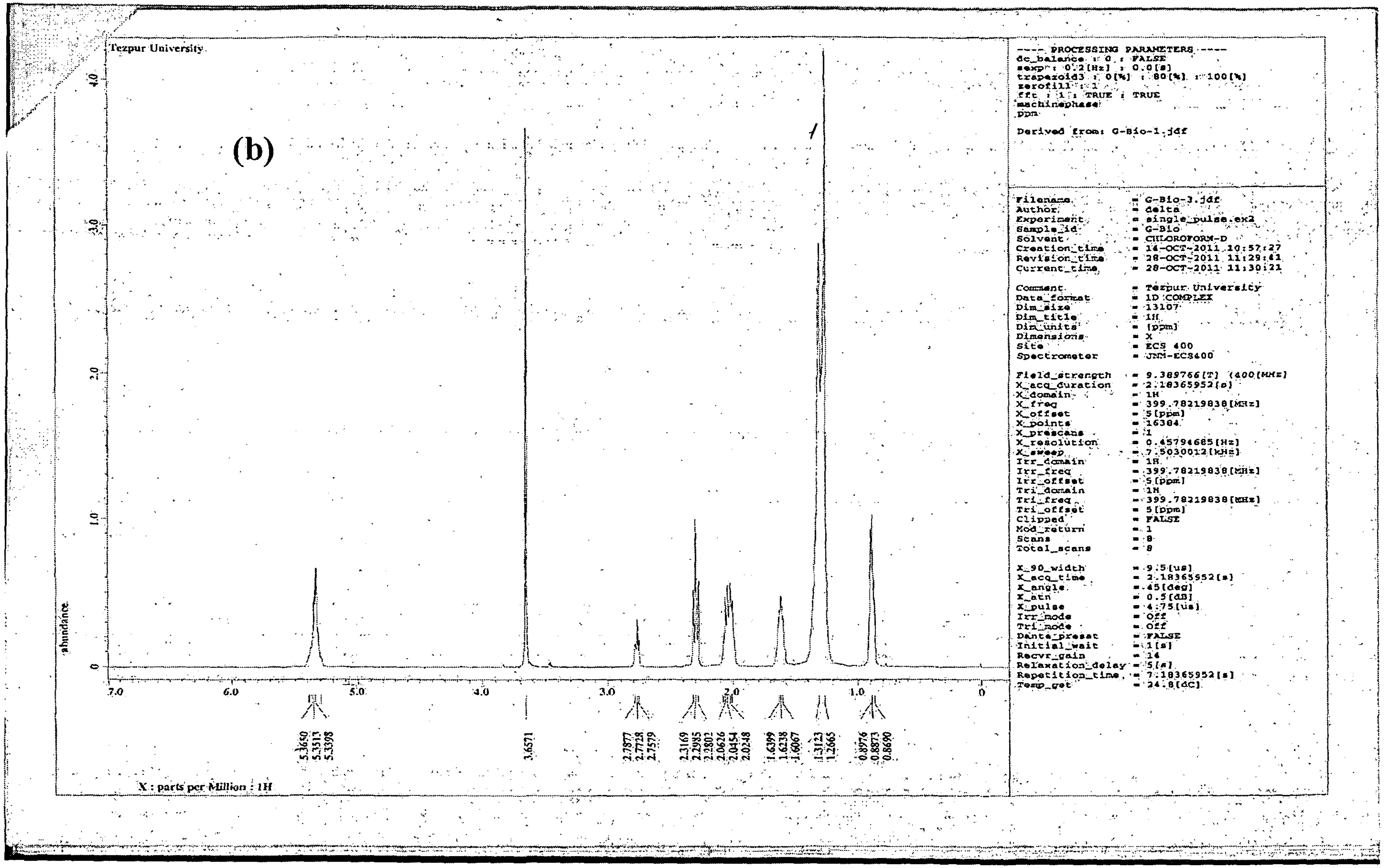

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machinephase
ppm

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Current_time        = 28-OCT-2011 11:30:21

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Dim_title           = 1H
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Dimensions          = X
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Spectrometer        = JNM-ECS400

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Tri_mode            = Off
Dante_presat        = FALSE
Initial_wait        = 1[s]
Recvr_gain          = 14
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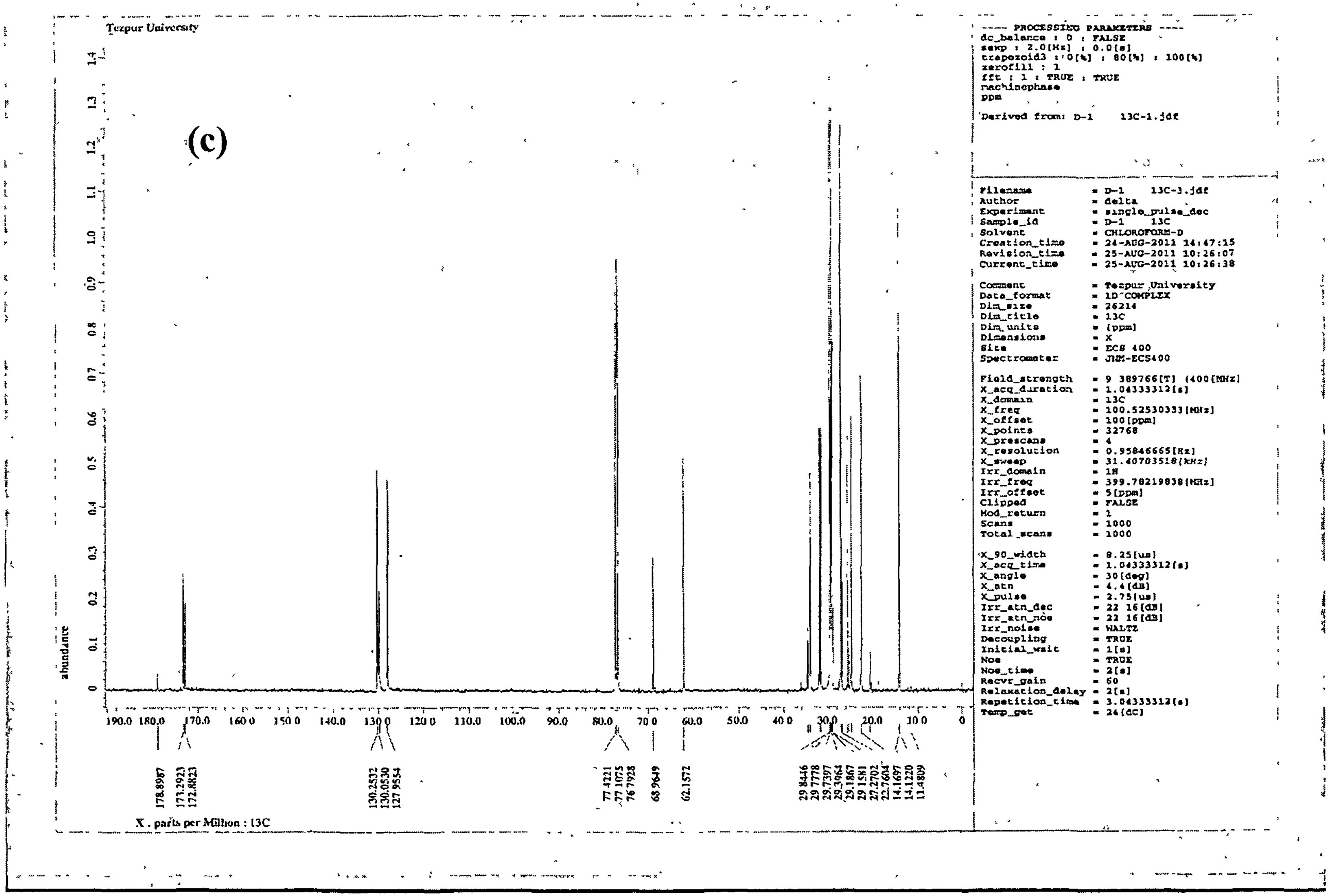
Fig.4.35. ^{1}H NMR spectra of (a) feedstock (b) biodiesel



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ppm

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Spectrometer       = JNM-ECS400

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X_offset           = 100[ppm]
X_points           = 32768
X_prescans         = 4
X_resolution       = 0.95846665[Hz]
X_sweep            = 31.40703518[kHz]
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Irr_freq           = 399.78219838[MHz]
Irr_offset         = 5[ppm]
Clipped            = FALSE
Mod_return         = 1
Scans              = 1000
Total_scans        = 1000

X_90_width         = 8.25[us]
X_acq_time         = 1.04333312[s]
X_angle            = 30[deg]
X_atn              = 4.4[dB]
X_pulse            = 2.75[us]
Irr_atn_dec        = 22 16[dB]
Irr_atn_noe        = 22 16[dB]
Irr_noise          = WALTZ
Decoupling         = TRUE
Initial_wait       = 1[s]
Noe                = TRUE
Noe_time           = 2[s]
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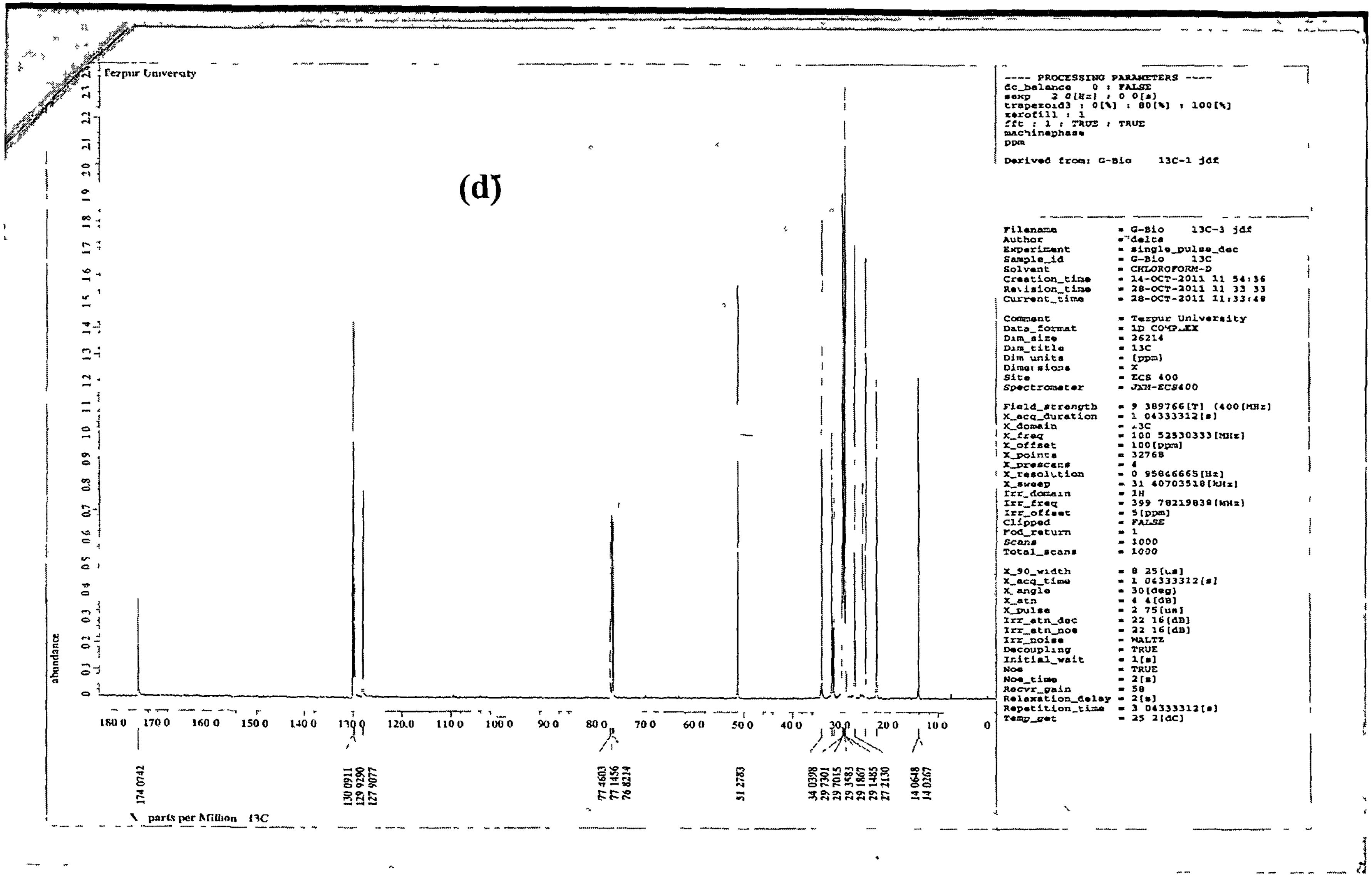
Relaxation_delay   = 2[s]
Repetition_time    = 3.04333312[s]
Temp_get           = 24[dC]
```



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zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

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Dim units           = [ppm]
Dimensions          = X
Site                = ECS 400
Spectrometer        = JNM-ECS400

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X_acq_duration      = 1 04333312[s]
X_domain            = 13C
X_freq              = 100 52530333[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_resolution        = 0 95846665[Hz]
X_sweep             = 31 40703518[kHz]
Irr_domain          = 1H
Irr_freq            = 399 78219838[MHz]
Irr_offset          = 5[ppm]
Clipped             = FALSE
Mod_return          = 1
Scans               = 1000
Total_scans         = 1000

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X_acq_time          = 1 04333312[s]
X_angle             = 30[deg]
X_atn               = 4 4[dB]
X_pulse             = 2 75[us]
Irr_atn_dec         = 22 16[dB]
Irr_atn_noe         = 22 16[dB]
Irr_noise           = WALTZ
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Initial_wait        = 1[s]
Noe                 = TRUE
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Recvr_gain          = 58
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Repetition_time     = 3 04333312[s]
Temp_get            = 25 2[dC]
```

Fig.4.36. ^{13}C NMR spectra of (c) feedstock (d) biodiesel

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CHAPTER 5

SUMMARY & CONCLUSIONS

Chapter 5

Summary & Conclusions

The waste shell of *Turbonilla striatula* was successfully employed for biodiesel production via transesterification of mustard oil. The catalysts were prepared by calcining the waste shells of *Turbonilla striatula* from 600 to 900 °C. It was observed that the catalytic activities of the calcined shell catalysts were dependent on the calcination temperature and the shell calcined at 900 °C exhibited maximum activity. The catalytic activities of the catalyst were also influenced by the methanol to oil molar ratio, reaction temperature and catalyst amount. The optimum reaction condition for achieving maximum catalytic activity was found to be 3.0 wt% catalyst amounts, 9:1 methanol to oil ratio, a reaction temperature of 65± 5 °C and the shell calcinations temperature of 900 °C.

The waste shell calcined at 900 °C was also utilized for transesterification of waste cooking oil. The catalytic activity of the waste shell derived catalyst was also compared to the catalytic activity of the conventional catalysts namely NaOH and manufacture CaO. The catalyst proposed exhibited excellent catalytic activity compared to NaOH and laboratory CaO. The waste shell derived catalysts could be reused for next consecutive 4 cycles but the catalytic activity decreased continuously. However, after proper purification and calcinations of the recovered catalyst, its initial catalytic activity could be achieved again. Moreover T-CaO catalyst may be considered as an environmental friendly catalyst as it has been prepared from waste biomass source. Therefore, the catalyst also possesses the characteristics of a “green catalyst”.

In order to increase the activity of the waste shell derived catalyst calcined at 900 °C, it was further doped with Li which in turn increases the basicity of the parent catalyst. It was observed that the parent catalyst doped with 1wt% Li could achieve maximum conversion of 98% in 4 h with 9:1 methanol to oil ratio at reaction temperature of 65 °C. Although parent catalyst doped with 2 wt% showed similar conversion under the similar reaction conditions but we have consider 1% Li doped T-CaO as the better catalyst because of its low Li loading and high conversion. The reusability study of Li01T-CaO showed that the catalyst was reusable for five times with negligible loss in catalytic activity. After study on Li doped waste shell derived CaO, we conducted our study on Ba doped waste shell derived CaO. Since basicity has a big role to play in the catalytic activity of a catalyst, it was expected that the parent catalyst in our study may show very high conversion if its basicity is increased. In order to achieve the goal we doped the parent catalyst with Ba and studied the different parameters affecting the catalytic activity of the Ba doped T-CaO. It was observed that complete conversion was obtained for Ba01T-CaO and Ba1.5T-CaO under the optimal reaction conditions of 6:1 methanol: oil ratio, reaction temperature 65 °C and reaction time of 3 h. The catalyst was reusable for four times with slight drop in its catalytic activity.

Comparing the catalytic activities among the prepared catalysts, it was observed that the waste shell derived CaO could exhibit maximum conversion of 97.6% for a methanol to oil ratio of 9:1, catalyst amount 5 wt% and reaction time of 8 h. For Li impregnated waste shell derived CaO catalysts, the maximum conversion of 98% was achieved with optimum amount of 1% of Li impregnation concentration, catalyst amount of 2 wt.%, reaction time of 4 h with 9:1 methanol to oil ratio. The best activity of 98% was recorded for 1 % of Ba loading on the CaO prepared from the waste shells in 3 h reaction time, 6:1 methanol to oil ratio and 1wt% of catalyst amount.

Future study

The catalyst prepared in the current investigation can further be investigated by doping it with different transition metal elements. Magnetization of the parent catalyst would be another thoughtful experiment which may ease the separation of catalyst from the final product. Different raw materials which can be potential source of calcium oxide and are abundant in supply may also be explored in future for further investigation.

List of Publications

1. **Boro, J.**, Thakur, A. & Deka, D. Solid oxide derived from waste shells of *Turbonilla striatula* as a renewable catalyst for biodiesel production, *Fuel Process Technol* **92,** 2061–2067, 2011.
2. **Boro, J.** & Deka D. A Review on Biodiesel, *J Bio Mat Bio* **6**, 1–17, 2012.
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4. **Boro, J.**, Konwar, L.J., Das, S. & Deka, D. Comparative study of CaO derived from waste shells of turbonilla striatula and commercial CaO for biodiesel synthesis, *JASS* **53(1)**, 2012.
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10. Bora, P., **Boro, J.**, & Deka, D. A study on the development of *Mesua ferrea* L. seed oil based microemulsified fuel system, *IJETAE* 3(3), 47-51, 2013.

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1. **Boro, J.** & Deka, D. 2008. Hydrogen production by photocatalytic degradtion of water: an alternative source of energy. *In the proceedings of the National Conference on Emerging trends and recent advances in electrical engineering and renewable energy* held at Sikkim Manipal Institute of Technology, Sikkim during 22-24 December, 2008.
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3. **Boro, J.**, Thakur, A. & Deka, D. 2011. Transesterification of mustard oil using Mollusca shells as catalyst. In the proceedings of the International Conference on Renewable Energy (ICRE-2011) held at Jaipur, India from 17-21 January,2011 organized by Centre for Non-conventional Energy Resources, University of Rajasthan, Jaipur-302055.
4. **Boro, J.**, Konwar, L.J., Thakur, A. & Deka, D. 2011. Review on carbon based catalysts for biodiesel production via transesterification. In the proceedings of *International Congress on Renewable Energy (ICORE-2011)* held at Tezpur University, India from 2-4 November, 2011 organized by Solar Energy Society of India, New Delhi.
5. **Boro, J.**, Konwar, L.J., Das, S. & Deka, D. 2011. Comparative study of CaO derived from waste shells of turbonilla striatula and commercial CaO for biodiesel synthesis. In the proceedings of UGC sponsored National Seminar on "*Frontier Areas of Research in Chemistry*" organised by Cotton College, Guwahati from October 24-25, 2011.

List of Conferences and Workshops attended

1. One Day workshop on Renewable Energy Resource Assessment of Assam - present Status and Future Strategies held on 25/08/08 at Department of Energy, Tezpur University.
2. Participated and delivered invited lecture on "Transesterification of vegetable oils for biodiesel production using heterogeneous catalysts-a review" in the *National Seminar on New and innovative renewable energy and energy efficiency"* Organized by Environmental Watch and Management Institute sponsored by Ministry of New and Renewable Energy, Government of India held at Regional Science Centre, Khanapara, Guwahati-781022 from 10-11 July, 2010.
3. Participated and Contributed to Oral presentation at International Conference on Renewable Energy (ICRE-2011) held at Jaipur, India from 17-21 January, 2011 organized by Centre for Non-conventional Energy Resources, University of Rajasthan, Jaipur-302055.
4. UGC sponsored National Seminar on *"Frontier Areas of Research in Chemistry"* organised by Cotton College, Guwahati from October 24-25, 2011.
5. Participated and Contributed to Oral presentation at International Congress on Renewable Energy (ICORE-2011) held at Tezpur University, India from 2-4 November, 2011 organized by Solar Energy Society of India, New Delhi and Tezpur University, Assam.
6. International Seminar and Workshop on Energy, Sustainability and Development (Special focus on Nanoscience and Nanotechnology) held at Sibsagar from 12-14 October, 2012 organized by Sibsagar College, Assam.
7. Indian-Finnish-Swedish 'IFS seminarium' on Heterogeneous Catalysis and its Applications, organized by Åbo Akademi University, Turku Finland from 19.3-23.3.2012.