

**Synthesis of mussel shell based CaO nano-catalysts doped
with praseodymium to optimize biodiesel production from
castor oil**



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DEDICATION

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Abstract

Excessive use of fossil fuels due to increased energy demand globally has caused a massive decrease in their quantity as well as environmental destruction and global warming. Production of greener, emission free biofuels play significant role in energy production through biochemical or thermochemical processes using castor oil for biodiesel production. This study reports the synthesis of Pr doped mussel shell-based Pr-CaO catalyst for transesterification reaction. The characterization of catalysts was carried out through X-ray diffraction (XRD), SEM, and TGA. Sharp characterization peaks were observed through XRD results while the crystal size was 23.56 nm for CaO and 15.78 nm for 7% Pr-CaO. The SEM characterization of the catalyst depicts flower structure of 7% Pr doped catalyst with an average crystallite size of < 16 nm and thermal stability below 900 °C. Catalyst testing has been done according to ASTM standards for castor oil biodiesel production and found to be within specifications. The obtained catalyst exhibited high catalytic activity for biodiesel production through transesterification of castor oil and methanol. Flashpoint of CaO was and Pr doped CaO was with a FAME yield of 80% and 87.42% respectively through 7% Pr-CaO mixed oxide catalyst at optimum reaction conditions (i.e., 2.5 wt.% catalyst, methanol to oil ratio of 8:1 and 65 °C) while the yield of FAME obtained through undoped, calcined CaO was about 80%.

Keywords: nano-catalyst, biofuel, transesterification, castor oil, biodiesel

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List of Abbreviations

BD	Biodiesel
FAME	Fatty Acid Methyl Ester
GCMS	Gas Chromatography Mass Spectrometry
BET	Brunauer Emmett Teller
Ca	Calcium
Pr	Praseodymium
MeOH	Methanol
SEM	Scanning Electron Microscopy
EDS	Energy Dispersive Spectroscopy
TGA	Thermal Gravimetric Analysis
FTIR	Fourier Transform Infrared Spectroscopy
XRD	X-Ray Diffraction
TEM	Transmission Electron Microscopy

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Chapter 1: Introduction

1. Introduction

1.1. Background

Being the key energy source globally, fossil fuels are a potential source of increasing pollution, environmental hazards, global warming, ozone layer degradation, and greenhouse gas emissions [1]. Not only their active participation in climate destruction is one of the major universal issues but their scarcity and rapid depletion due to overexploitation, high prices, fluctuating and unpredictable political circumstances in the Middle East is also alarming [2]. The consumption of Petro-fuels by 2030 will reach up to 136.8 million barrels per day as per an estimation. These factors divert the attention of the world towards greener, eco friendlier, adequately available, and economically viable non-depleting renewable resources. Among these non-conventional resources of energy, biomass is a promising source to produce various biofuels and useful byproducts by its conversion through thermochemical, biochemical and extraction methods. Being the 4th substantial source of global primary energy source, biomass makes it almost 12% of the total energy utilization. It is because of its easy and everywhere availability in the world in enormous quantity [3]. Other than just being renewable resource of energy, Biodiesel has various advantages over conventional fuels as it is environmentally benign, less toxic, contains high content of oxygen and is biodegradable [4,5]. Due to no requirement of engine modification, biodiesel can be conveniently used in standard diesel engines because of its miscibility with Petro-diesel and compatibility with infrastructure of fuel delivery. Over low sulfur Petro-diesels, biodiesel offers improved lubricating efficiency and helps in the reduction of wearing of engine components [6]. To obtain liquid fuels and energy from this biomass resource, there are various thermochemical and biochemical routes to be adopted depending on the operating conditions and the substrate availability due to their effective use in waste to energy production plants, production of hydrogen rich gaseous fuels and liquid fuels while least effecting the environment and declining GHG production. Biomass derived biofuels are predicted to be a key alternative energy source to mitigate CO₂ as according to the 2 °C scenario (2DS), CO₂ emissions should be reduced by 70% relative to 2014 in 2060 [7].

There are three different generations for the substrates to obtain biodiesel that are first generation mainly including edible sources such as sugarcane, soybeans and corns, second generation comprising of non-edible sources such as waste oils, castor oil, jatropha and third generation consists of microalgae [8]. Among these sources, castor oil, a non-volatile and viscous oil, being non-edible feedstock, is an important potential substrate for biodiesel production. It is not only inexpensive but also environmentally friendly [9]. It is basically obtained by extracting the seeds of a plant *Ricinus Communis* from the *Eurphorbiaceae* family. The world's largest producer of castor oil is India while other significant producers include China, Brazil, Russia, Philippines [9,10]. It is quite beneficial due to its non-competent behavior with food chain and multi uses such as in pharmaceuticals, inks, dyes, coatings, waxes, and lubricants. More than 30 countries of the world cultivate this crop in 1.525 million hectares producing 1.58 million tons of the seed to extract castor oil [11]. Being recognized as an agricultural country and 70% of its population belonging to agricultural sector, Pakistan still lacks in the cultivation of castor crop though millions of hectares are lying vacant and uncultivated. In Pakistan, castor is cultivated on a very small area in Punjab and Baluchistan, but large area of Sindh is still uncultivated. Since 1979, castor oil cultivation is continuously declining in the country. During 1980-85, the average area ranged between 20,000 to 30,000 hectares, during 1985-90, further decline up to 14,000 hectares occurred. In 1991-92, castor was planted only on 3050 hectares. From year 2000 onward, there was a fluctuation in the castor cultivation area from 2,100 hectares to 5,000 hectares. Subsequently, during 2007-08, this crop was cultivated on 3,567 hectares, out of which 2,247 hectares were in Sindh province. Castor oil constitutes 90% triglycerides of ricinoleic acid while the other fatty acids include 4.4% linoleic acid, 2.8% oleic acid, 0.9% stearic acid, 0.7% palmitic acid and 0.2% linolenic acid. It exhibits unique properties among other vegetable oils due to the presence of *cis*-12-hydroxyoctadeca- 9-enoic acid and its high viscosity, specific gravity and solubility in alcohols due to high hydroxyl value makes it one of the strong contenders among other oils for biodiesel production [12].

Among various biomass derived products, biodiesel was well received globally due to its biodegradability, inexhaustible and environmentally benign nature, high flash point, reduction in pollution due to CO₂ mitigation and non-transferable carcinogens [13]. The synthesis of biodiesel methyl ester of fatty acids is carried out by the reaction of transesterification of an oil and alcohol by using a catalyst. During transesterification, a monoglyceride molecule is

ultimately obtained by the conversion of a triglyceride into a diglyceride. The conversion of monoglyceride then produces methyl esters and glycerol [14]. The production of biodiesel may have some limitations because of the catalysts being used during the process to enhance the yield. For example, the production of biofuels through transesterification in the presence of base catalysts causes corrosion of the reactor and engine manifolds. Also, these catalysts cannot be regained once the process is completed as it demands massive amount of energy. Other metal heterogenous catalyst, like alumina and silica face the problems of deactivation and structural inconsistency on exposure to high operating conditions e.g., temperature and pressure. This results in catalyst leaching and contamination of the product which makes the overall process quite costly. This demands for the development of more efficient, economic, greener and environment friendly nano-catalysts to deal with these problems and to maximize the overall yield. Nano-catalysts are gaining increasing momentum in the processes to produce biofuels due to their enhanced effects on metabolism of bioprocesses [15,16]. The applications of nano-catalysts either homogenous or heterogenous for biofuel production through various thermochemical and biological processes is becoming the center of attention for researchers. These increasingly interest gaining particles in biofuel production are still a fancy approach to maximize the yield [17].

Though the reaction taken place with homogenous catalyst is rapid and complete mixing of catalyst with reactants is done but the catalyst recovery from the mixture and the purification of the obtained product becomes quite complicated. On the other hand, heterogenous catalysts are reusable and easy to be separated once the reaction is completed, which lowers the biodiesel production cost [5]. Among other heterogenous catalyst, CaO is quite effective towards biodiesel production due to its higher basicity, easy handling, environmentally benign nature and economic advantages [18]. The evaluation of different waste egg-shells, seashells, oyster shells [19], mussel shells [20], snail shells [21], scallop shells [22], chicken bones [23] and duck shells [24] have been done in the past to achieve CaO after its calcination before transesterification to synthesize biodiesel with a high yield.. However, this high activity of CaO caused the leaching of Ca ions into polar phase and these dissolved Ca ions act as homogenous catalysts resulting in the extra cost for the post treatment and a reduced catalyst lifetime [25]. To improve the lifetime and the activity of the catalyst, various rare earth metals such as lanthanum [26] and cerium [27]

have been previously used to modify CaO for biodiesel production. A dramatic increase was observed in the catalytic activity, stability, and its lifetime by doping with these elements.

1.2. Problem statement

Due to the lack of a well-developed, efficient, and affordable system for the biodiesel production process, it is still considered as an expensive alternative in comparison to petro diesel. This all happens due to the improper selection of raw material and catalyst for the process accompanied with other technological deficiencies and factors effecting the yield of biodiesel and its purity [28]. The transesterification reaction taken place with homogenous catalyst is rapid and complete mixing of catalyst with reactants is done but the catalyst extraction from the mixture and the purification of the obtained product becomes quite complicated which makes the biodiesel production quite expensive in comparison with petro diesel. On the other hand, heterogenous catalysts are reusable and easy to be separated once the reaction is completed, which lowers the biodiesel production cost. Among other heterogenous catalysts, CaO is quite effective towards biodiesel production due to its higher basicity, easy handling, environmentally benign nature, and economic advantages. However, this high activity of CaO caused the dissolution of Ca ions into polar phase acting as homogenous catalysts resulting in the extra lowered catalyst lifetime and post-treatment expenditure. To improve the lifespan and the activity of the catalyst, various rare earth metals such as lanthanum [26] and cerium [27] have been previously used to modify CaO for biodiesel production. A dramatic increase was observed in the catalytic activity, stability, and its lifetime by doping with these elements.

Praseodymium oxide is a basic catalyst. Due to the formation of a homologous series of many stoichiometrically defined oxides, praseodymium oxides hold a special position within the series of rare earth oxides. Among the lanthanide series, these oxides have the highest oxygen ion mobility due to which the fast variations in the oxygen state of praseodymium are possible due to the variety of stable phases. This feature makes this oxide system particularly appealing for catalytic applications. Praseodymium oxides are widely used in a variety of processes in both the industrial and environmental sectors as catalysts or as ingredients in catalyst formulations (as promoters or stabilizers). For instance, 1,3-butanediol and 2-butanol's dehydration and dehydrogenation were catalyzed by Pr_6O_{11} oxide [29]. The sintering of CeO_2 due to its poor thermal stability at high temperature causes the ability of ceria to store oxygen and its catalytic

activity to quickly diminish. Studies showed that praseodymium cations can greatly improve the OSC of ceria due to the defective structure created by the different sizes of ions compared with Ce cations and $\text{Pr}^{+4}/\text{Pr}^{+3}$ redox couple. It was concluded that adding praseodymium oxide to ceria makes it more active during the combustion of methane and carbon monoxide. [27,30]. Pr-CaO mixed oxide catalysts were synthesized in this study to enhance the physio-chemical properties, catalytic activity, and reusability of the bulk CaO in transesterification of castor oil. The purpose of this research work was to investigate the role of rare earth metal oxides as catalyst for the conversion of methanol and castor oil into biodiesel through transesterification by using waste mussel shells as raw material for the preparation of CaO. In order to optimize the various factors impacting the transesterification process and to investigate its reusability, this Pr doped CaO was further utilized as a heterogeneous catalyst in the transesterification of castor oil.

1.3. Hypothesis

To improve catalytic activity for biodiesel production, synthesis of rare earth doped nano-catalysts can prove to be quite effective and efficient materials as they provide a large surface area for the transesterification reaction to carry on by increasing the reaction rate which results in the increased yield of biodiesel. These materials being heterogeneous reduce the shortcomings that occur during biodiesel synthesis i.e., saponification, catalyst degradation and difficulties in separation [31].

1.4. Research objectives

1. To Synthesize and characterize mussel shell based rare earth doped catalyst for biodiesel production through transesterification.
2. To investigate the catalytic activity of calcium oxide and Pr doped calcium oxide catalysts for transesterification
3. To increase the biodiesel yield by using the prepared (Pr-CaO) nano-catalysts as a result of improved basicity and BET surface area and to analyze the quality of the produced biodiesel in accordance with the given standards

1.5. Organizational structure of the study

The organization structure of the study begins with the synthesis of CaO and pr doped CaO catalyst which were characterized through thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and X-ray diffraction (XRD) techniques. These doped and undoped catalysts were then used for the transesterification reaction. The synthesized biodiesel samples were analyzed by performing standard tests of pH, flashpoint, calorific value, Gas Chromatography Mass Spectroscopy (GCMS), Fourier Transform Infrared Spectroscopy (FTIR), iodine number, cetane number, saponification value, viscosity, density, specific gravity.

1.6. Scope

- The research work aimed to study the rare earth metal oxides as catalyst for castor oil and methanol transesterification into biodiesel by using waste mussel shells as raw material for the preparation of CaO.
- The synthesis and analysis of the prepared undoped and. doped catalysts and obtained biodiesel was carried out at laboratory scale.
- This Pr doped CaO was further used as a heterogeneous catalyst in the transesterification of castor oil, to optimize the different parameters affecting the transesterification reaction and to study its reusability.

1.7. Limitations

- The pilot scale synthesis of the desired catalyst and the product was not carried out due to limited resources and shortage of time.
- The transesterification reaction was conducted under specific factors that is specific temperature, atmospheric pressure to obtain the desired results. Fluctuations in these physical conditions may affect the yield.
- The synthesis of the catalysts was done through calcination and wet chemistry route under specific conditions and obtained the catalysts with specific pore volume, pore diameter, and surface area. Other synthesis routes for catalyst synthesis may be followed to observe changes in catalytic structure, morphology, surface area and shape which can affect the obtained yield.

Summary

This chapter briefly discusses about the energy crisis in the country along with environmental problems that are caused by the utilization of fossil fuel resources. Castor oil is a very potential and non-edible resource to produce biodiesel which is a benign and renewable energy resource. Moreover, the process of biodiesel production is briefly discussed along with the point of focus in this study which is the synthesis of undoped and doped CaO and Pr-CaO as prospective catalysts in the production process.

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Chapter 2: Literature Review

2. Literature Review

2.1. Biodiesel overview

Being the key energy source globally, fossil fuels are a potential source of increasing pollution, environmental hazards, global warming, ozone layer degradation, and greenhouse gas emissions [1]. Not only their active participation in climate destruction is one of the major universal issues but their scarcity and rapid depletion due to overexploitation, high prices, fluctuating and unpredictable political circumstances in the Middle East is also alarming [2]. The consumption of Petro-fuels by 2030 will reach up to 136.8 million barrels per day as per an estimation. These factors divert the attention of the world towards greener, eco friendlier, adequately available, and economically viable non-depleting renewable resources. Among these non-conventional resources of energy, biomass is a promising source to produce various biofuels and useful byproducts by its conversion through thermochemical, biochemical and extraction methods [3]. Among various biomass derived products, biodiesel was well received globally due to its biodegradability, inexhaustible and environmentally benign nature, high flash point, reduction in pollution due to CO₂ mitigation and non-transferable carcinogens [4]. The synthesis of biodiesel methyl ester of fatty acids is done by the reaction of transesterification of an oil and alcohol by using a catalyst. During transesterification, a monoglyceride molecule is ultimately obtained by the conversion of a triglyceride into a diglyceride. The conversion of monoglyceride then produces methyl esters and glycerol.

Almost 21 distillery units around the country sufficient to process around 2 million tons of the molasses producing 400,000 tons of bioethanol are the main source of alcohol production from sugar cane though it exceeds the country's needs plus export by 318,000 tons. Thus, we have sufficiently excess stock of alcohol for the process of transesterification for biodiesel production. Although methanol is more often used for this process because of its low price. Pakistan has the production capacity of 56 million tons of biodiesel after cultivating all the uncultured land around while the current requirement is nearly 8.5 million tons though a 10% increase of energy is expected per year. Hence biodiesel has an encouraging future in Pakistan because there are

enough raw materials available and certain energy generation programs. Being recognized as an agricultural country and 70% of its population belonging to agricultural sector, Pakistan still lacks in the cultivation of castor crop though millions of hectares are uncultivated and unoccupied. [5].

2.2. Biodiesel production

Biodiesel is a well-received alternative fuel globally due to its biodegradability, inexhaustible and environmentally benign nature, high flash point, reduction in pollution due to CO₂ mitigation and non-transferable carcinogens in comparison to diesel fuel [6]. The main production process used to obtain biodiesel is transesterification of various feedstocks such as animal fats, vegetable oils, other edible and non-edible feedstocks in the presence of an alcohol and acidic, alkaline, or enzymatic homogeneous or heterogeneous catalysts [7,8]. The production of biodiesel production is carried out by involving the transesterification of a triglyceride molecule with an alcohol molecule by using a catalyst either homogenous or heterogenous which ultimately produces a by-product that is a combination of glycerol and fatty acid methyl esters (FAME) [9]. Figure 2-1 represents the chemical reaction mechanism of the transesterification to produce FAME.



Figure 2-1: Chemical reaction mechanism of biodiesel production.

There are three different generations for the substrates to obtain biodiesel that are first generation mainly including edible sources such as sugarcane, soybeans and corns, second generation comprising of non-edible sources such as waste oils, castor oil, jatropha and third generation consists of microalgae [10]. The main production process used to obtain biodiesel is transesterification of various feedstocks such as animal fats, vegetable oils, other edible, and non-edible feedstocks in the presence of an alcohol and acidic, alkaline, or enzymatic homogenous or heterogenous catalysts. There are several parameters on which the process of transesterification hinge on to have an optimized conversion which includes the properties of the

substrate oil like moisture and FFA content or other physical and chemical properties, duration of reaction, rate of agitation or stirring, pressure, temperature, type of alcohol, alcohol to oil molar ratio, catalyst type and its quantity. The yield and purity of the product depend on all these parameters. The reaction temperature in this process plays an important role and usually set closer to that of the boiling point of the alcohol. According to several studies, the reaction temperature should be kept between 60 and 80 °C with a 6:1 alcohol to oil molar ratio. Although it keeps changing depending on the type of the catalyst and other conditions in the process, the molar ratio of alcohol to oil is also a useful parameter. [11]. Castor oil, a non-volatile and viscous oil, being non-edible feedstock, is an important potential substrate for biodiesel production. It is not only inexpensive but also environmentally friendly. It is basically obtained by extracting the seeds of a plant *Ricinus Communis* from the *Eurphorbiaceae* family. The world's largest producer of castor oil is India while other significant producers include China, Brazil, Russia, Philippines. It is quite beneficial due to its non-competent behavior with food chain and multi uses such as in pharmaceuticals, inks, dyes, coatings, waxes, and lubricants. More than 30 countries of the world cultivate this crop in 1.525 million hectares producing 1.58 million tons of the seed to extract castor oil [12].

2.3. Status of catalyst application for biodiesel production

Several studies have been conducted for the synthesis of catalytic material to accelerate the process efficiency of any reaction. A catalyst is an ingredient that expedites a chemical reaction without changing itself. It will offer the areas where the reactants can be ignited and interact with one another. Using either acidic or basic catalysts, the transesterification process can produce biodiesel. However, due to their drawbacks, such as equipment damage through corrosion and stagnant reaction rates, acidic catalysts are not widely used. The rate of reaction of basic catalysts is 4000 times better than acidic catalysts . Although being cheap and widely available, basic catalysts also have some limitations. The catalysts used in transesterification are mainly homogenous, heterogenous or enzymatic catalysts. It is challenging to segregate homogenous catalysts from the reaction mixture and can't be reused effectively. Also, they need excessive amount of water to be separated from the product. Heterogenous catalysts are easy to separate and reused after the process completion. This is due to the catalysts and reactants being diphasic. But the activity of the heterogenous catalysts is reduced due to their leaching in the reaction

system so the recovery of the active catalysts becomes challenging. That's why the current center of attention of researchers is the development of highly active and specific catalysts to synthesize biodiesel with a high yield. The advancement of nano-catalysts seems to be the solution to the drawbacks of different catalysts because of their large surface areas and catalytic activity. There are several reported examples of heterogeneous nano-catalysts as metal oxides, transition metal oxides, mixed metal oxides, and metal oxides that have been doped with alkali [13]. The following table 2-1 represented a comparison of catalytic performance for the reaction of transesterification of rare earth metal doped and undoped CaO catalyst from different feedstocks.

Table 2-1: Comparison of catalytic performance for the process of transesterification.

Feedstock	Catalyst	Calcination (°C)	Catalyst wt. %	Reaction Temperature (°C)	Yield %	Ref
Jatropha curcas L. oil	(CaLaO)	800	1	240	93	[14]
Palm oil	CaO–CeO ₂	600	5	65	95	[15]
Palm oil	CaO–CeO ₂	650	5	85	>90	[16]
Waste cottonseed oil	x-Ni/Zn/CaO,	550	5	65	98	[17]
Sunflower oil	CaO	600	-	65	70	[18]

Due to the short comings regarding source of raw material for the biodiesel production, non-edible domain is gaining focus. Homogenous catalyst causes the problem of intoxication and saponification during the conversion of Chinese tallow seed for example KOH, NaOH and CH₃ONa, due to higher acid value than that of rapeseed oil and soybean oil. Chinese tallow seed oil was converted by using acid-tolerant solid base catalyst to biodiesel. KF/CaO nano-catalyst synthesized through impregnation method showed 96.8% biodiesel yield potential for industry use. Several countries like France, USA, Germany, Italy, Japan and so on are utilizing large amount of biodiesel. The green approach of heterogeneous catalyst use is introduced for the preparation of biodiesel which is occasionally mass transfer resistant, inefficient and time consuming. The limited applications for industry intrigue more focused research in this domain Biodiesel can also be known as environmentally benign fuel. An easier transesterification process for palm tree oil was carried out with help of TiO₂–ZnO nano catalyst which is a stable and active heterogeneous mixed metal oxide [19]. Under optimized conditions of 8% catalyst concentration, 50 min under 50 °C and a methanol to oil ratio of 7:1, 97% yield of biodiesel was obtained using Mn-ZnO mixed oxide catalysts [20] . Thangaraj et al. reported the synthesis of heterogenous polyacid coated ZnO nano-catalysts by using co-precipitation and calcination method and a yield of 95% was obtained from the transesterification of madhuca oil with

methanol under 55 °C for 5h [21]. Transesterification of waste cooking oil (WCO) and neem oil was carried out to obtain 97% biodiesel yield using copper doped ZnO nanorods through co-precipitation method [5,22]. Facile impregnated nano-magnetic KF/CaO-Fe₃O₄ nano-catalysts were investigated and reported by Hu et al. in the transesterification of stillingia oil to obtain 95% biodiesel [23]. The transesterification of rapeseed oil and methanol produced 98.71% biodiesel depicting highest catalytic activity of magnetic nanoparticles of Ca prepared from Ca-aluminate reacting with iron (III) oxide [24]. Transesterification of simarouba oil using ZnO and Ag doped ZnO catalysts was reported by Nagaraju et al. the biodiesel yield obtained from ZnO was 80.1% and Ag-ZnO was 84.5% [25]. Castor oil biodiesel yield of 90% was obtained using Iron (II) doped ZnO as a nano-catalyst in the transesterification . The effect of the Copper ion coupled ZnO nano-ferrites (Ni_{0.5}Zn_{0.5}Fe₂O₄) was studied on transesterification of soybean oil by Dantas et al [26]. He reported that due to the inclusion of Cu ions the conversion improved up to 85% of biodiesel yield. Potassium carbonate impregnated CaO nano-catalysts were used in the transesterification of canola oil and a biodiesel yield of 97.67% was obtained. Ni doped Zn composites (Ni-ZnO) prepared by the co-precipitation were subjected to transesterification of castor oil and a yield of 95.2% was achieved under 55 C temperature for 60 min [27]. ZnO/BiFeO₃ magnetic nano-catalysts were prepared by co-precipitation and subjected to the transesterification of canola oil yielding 95.43% biodiesel [28]. Borah et al. reported the transesterification of Mesua ferrea oil using Co doped ZnO (Co-ZnO) with the reaction conditions of 1:9 ratio of methanol to oil for 3h under 60 C. a biodiesel yield of 98.03% was obtained [29] . The investigation of five different sources of Ca embedded with Au nanoparticles from eggshell, mussel shell, calcite, dolomite and commercial CaO were subjected to the transesterification of sunflower oil for biodiesel synthesis. A yield up to 97% was obtained under optimum conditions [30] .

The developmental phase of biofuel energy largely depends upon catalytic reactions. Moreover, the integration of nanotechnology in the catalytic activity of biofuel production speeds up the process enhancing the product quality and amount of yield. The common problems caused using heterogeneous catalysts e.g., mass transfer resistance, fast deactivation, time consumption and inefficiency; can be resolved by replacing them with nano regime catalysts. The most demanded type of biofuel as biodiesel could be produced by nano catalysts which use nonedible feed substrate. The research done yet directs towards the fact that application of nanosized catalysts

advances the production and efficiency rate of biofuel even at mild operation parameters with comparison to bulk catalysts [21]. Table 2-2 discusses different catalyst used for biodiesel production using a various substrate. Different studies are being carried out to produce biodiesel from variant substrates using NaOH, KOH and other metal composites as catalysts giving potential percentage yield.

Table 2-2: Comparison of mussel shell with reported heterogeneous catalysts to produce biodiesel.

Feedstock	Catalyst	Methanol: Oil	Catalyst loading (wt.%)	Temp. (°C)	Time (h)	Yield (%)	Ref.
Soybean oil	Mussel shell	24:1	12	60	8	94	[31]
Palm oil	Freshwater bivalve mussel shell	10:1	4	60	5	90	[32]
Waste frying oil	Snail shell	8.45:1	2	60	7	87.59	[33]
Sunflower oil	Crab shell	6:1	3	60	3	83.1	[34]
Sunflower oil	Oyster shell	9:1	2	60	4	89.2	[35]
Castor oil	Mussel shell	6:1	2	60	3	91.17	[36]
Palm oil	Mussel, Cockle and Scallop shells	9:1	10	65	3	95	[37]
Waste cooking oil	waste shells of Turbonilla striatula	6:1	1	65	3	>98	[38]
Soybean oil	Oyster shell	6:1	2.5	65	5	73.8	[39]
Dairy scum oil and Hydnocarps wightiana oil	Snail shell	12.7:1 and 12.4:1	0.866 and 0.892	58.56 and 61.6	2 and 2.41	96.929 and 98.93	[40]

2.4. Significance of operating conditions in biodiesel production

The catalytic performance for transesterification is significantly impacted by reaction factors such the catalyst loading rate, stirring rate, methanol to oil ratio, temperature, and time. In order to determine the ideal reaction conditions, the impact of these parameters on the catalyst's performance was investigated.

2.4.1. Effect of catalyst loading

During the reaction of transesterification of methanol and castor oil, the maximum yield of biodiesel (87.42%) was obtained at a catalyst loading rate of 2.5% while the other variables such as temperature, time, and the methanol to oil ratio were kept constant i.e., 8:1, 65 °C and 240 min respectively. With a 1% catalyst loading rate of , a high yield of biodiesel was not obtained and a very high catalyst loading rate resulted in the formation of a viscous mixture of reactants and catalyst leading to problem in mixing which required high power for mixing [41]. To overcome these problems, the catalyst loading rate was varied between the percentages i.e., 2

wt.%, 2.5 wt.%, 3 wt.%, 3.5 wt.% and 4 wt.% during the transesterification reaction of castor oil. The biodiesel yield increased with a catalyst loading rate from 2 to 2.5% but beyond this the yield decreased. Methanol was transformed into nucleophilic methoxide ions by the active sites of CaO, which attacked the electrophilic carbonyl carbon of the glyceride molecule to produce biodiesel. Because there was increased amount of catalyst present, there were more overall active sites for the reaction, which led to an increase in biodiesel production [42,43]. However, as the reaction mixture got more viscous due to an increase in the catalyst concentration over 2.5% lowering the yield of the transesterification, poor reactant diffusion in the reaction system resulted in the decreased FAME yield. [44].

2.4.2. Effect of methanol to oil molar ratio

Another vital factor that affects the FAME yield is the methanol to oil ratio. According to stoichiometry, 3 moles of methanol are necessary for every 1 mole of glycerol. But a little higher volume of methanol was added in order to keep the equilibrium moved to the right [45]. By varying the methanol to oil ratios (6:1, 8:1, 10:1, and 12:1) while maintaining a constant catalyst loading rate of 2.5% at a reaction temperature of 65 °C for 4 hours, this parameter was optimized. The best yield of biodiesel was achieved with a methanol to oil ratio of 8:1, which was the reaction's ideal ratio, and it was 87.42%. Beyond this range the biodiesel yield started getting deteriorated due to the excess methanol dissolving the glycerol and a backward reaction takes place causing hindrance to the reaction of methanol with the catalyst and oil.

2.4.3. Effect of reaction time and temperature

For the optimization of reaction time and temperature, transesterification was carried out at different temperatures (50 °C, 55 °C, 60 °C, 65 °C) with different time intervals (2h, 3h, 4h, 5h) under the optimum conditions of 2.5% catalyst loading rate and 8:1 methanol to oil ratio. The effect of reaction time was investigated, and the results of the experiments revealed that by increasing time the yield also increased and achieved the maximum yield of 87.42% after 4h. Because hydrolysis of the esters may begin to occur with a longer reaction time, resulting in more fatty acids triggering saponification, the yield began to decline after 4 hours [46]. In addition, a reverse reaction may occur once the equilibrium is achieved due to the reversibility of the reaction, resulting in decreased yield.

2.4.4. Effect of mixing speed

Mass transfer limitation can significantly affect the yield of transesterification because of immiscibility of oil and alcohol. The reaction of castor oil with methanol was carried out at different speeds ranging from 400 to 1200 rpm while other factors (i.e., 2.5 wt.% catalyst, 8:1 of methanol to oil ratio and 65 °C) were kept constant in order to determine the reaction's ideal mixing speed and to reduce the impact of mass transfer limitation. By increasing the speed from 400 to 800 rpm, the FAME yield increased up to 87.42%. The oil conversion and process yield were unaffected by the additional speed increase from 800 to 1200 rpm [47]. To make sure that mass transfer limitation was minimized or eliminated, the, the mixing speed was kept constant at 800 rpm.

Summary

This chapter initially reviews the potential of biodiesel as a renewable energy source in Pakistan then the status of biodiesel production around the world and in Pakistan in specific reference to castor oil. The second part of the review of literature covers the assessment of the status of catalyst synthesis for biodiesel production in world and the review of rare earth metal doped catalyst for biodiesel production. Due to the short comings regarding source of raw material for the biodiesel production, non-edible domain is gaining focus. For the commercial execution of transesterification process it is required to prepare cost effective heterogeneous catalysts as this is the limiting factor for their application in industrial use. The energy produced from biomass is renewable and eco-friendly, so it is highly suggested to be applied while there has been fast growth in the introduction of nanotechnology studies into biomass transformation. Rare earth metal doped catalysts have high specific surface and high activity of catalysis, which can solve the above problems. Recent study has focused on them. Moreover, the factors effecting the biodiesel production are also discussed along with their significance.

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Chapter 3: Materials and Methods

3. Materials and Methods

Calcium oxide (CaO) and praseodymium doped calcium oxide (Pr-CaO) catalysts are synthesized through calcination method and wet chemistry route respectively. The prepared doped catalyst is heterogenous solid catalyst. Transesterification of castor oil with methanol was carried out after the characterization of these catalyst, transesterification of castor oil with methanol was carried out.

3.1. Materials used for experimentation

The chemicals used in the carried-out transesterification reaction and their purities have been mentioned in table 3-1. The castor oil was purchased from Pakistan. Analytical grade methanol (ACS reagent 99.8%) and praseodymium nitrate hexahydrate $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9% Aldrich) were purchased from Sigma Aldrich. Mussel shells were provided by the sea food restaurants in Thailand. Following properties of the substrate were reported: density= 0.959 g/mL, flash point = 145 °C, viscosity= 889.3 cS which corresponded well with the values reported in literature [1].

Table 3-1: List of chemicals used in the synthesis of materials

Sr #	Name	Purity	Purpose
1	Methanol	99%	Material Synthesis and Purification
2	Distilled water	99%	Material Synthesis
3	Castor oil	99%	Material Synthesis
4	Mussel shells	99%	Material Synthesis
5	$\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	99%	Material Synthesis

3.2. Material Synthesis

3.2.1. Synthesis of CaO from raw mussel shells

The preparation of the catalyst was done using calcination method [2]. Waste mussel shells were collected, cleaned, washed with warm water several time and then dried completely at ambient temperature. Dried mussel shells were calcined for four hours at a temperature of 700–1,000 °C in air atmosphere and a heating rate of 10 °C/min for 4h by implying an electric furnace (Yamato Standard Electric Furnace FO 610) [3]. The resultant solid powder was then crushed and sieved

with 63 μm . The obtained product was white powder [2]. The calcined sample were kept in closed vessel to prevent the reaction with carbon dioxide (CO_2) and humidity. Following figure represents the preparation process of mussel shell-based catalyst through calcination.



Figure 3-1: Calcination of Raw Mussel Shells.

3.2.2. Synthesis of Pr doped CaO

To synthesize 3-11 wt.% compositions of Pr-CaO, incipient wet chemistry route was implied [4]. The praseodymium precursor used for all compositions was praseodymium nitrate hexahydrate $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9% Aldrich). 100 mL of distilled water was added to dissolve the necessary amount of CaO, and a complimentary 100 mL praseodymium nitrate was added to the solution. The mixture was gradually heated to evaporate some water while being continually agitated to produce a homogeneous solution. After that, it was further dried for overnight at 100 $^\circ\text{C}$ in the oven [5]. After drying, sample was calcined in a furnace at 700 $^\circ\text{C}$ with a heating rate of 10 $^\circ\text{C}/\text{min}$. The above-mentioned synthetic catalysts are identified by the symbols as xCa-Pr where x= 3, 5, 7, 9 and 11 wt.%. Figure 3-2 illustrates the synthesis of Pr doped CaO catalysts through wet chemistry route.

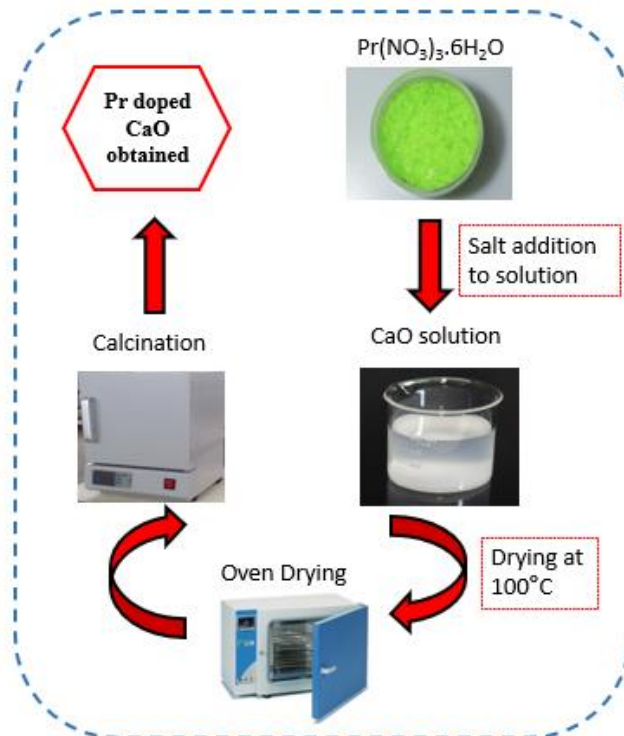


Figure 3-2: Wet chemical route synthesis of Pr-CaO.

3.3. Material characterization techniques

A high characteristic analysis is required for research based on material synthesis which is carried out by several characterization techniques. This analysis includes structural examination, elemental composition and other chemical and physical properties which help in the accurate assessment of the sample to be used for further application process. To determine the thermal behavior of the prepared material, Thermogravimetric Analysis/Differential Thermal Analysis (TGA/DTA) was performed using DTG-60H. To assess the percentage weight loss, the thermograms obtained were taken in a continuous N_2 flow of 50 mL/min from 20 °C to 950 °C at a heating rate of 10 °C/min. X-ray diffraction (XRD) analysis of the prepared catalyst was done using Bruker's X-ray Diffractometer (D8 Advance) (Germany). The scanning of samples was carried out using 2θ from 10° to 70°, scanning rate of 0.06°/min. The K-Alpha 1 and K-Alpha 2 wavelengths for the sample scanning were 1.5406 and 1.5443 nm respectively. JADE 6.0 was used to evaluate all XRD patterns and peaks were identified through a search and match option with built-in Joint Committee on Powder Diffraction Standards (JCPDS) or Powder Diffraction File (PDF) repository of software [6]. The diffraction follows Bragg's equation (Eq. (1)) where

n = integer, λ = wavelength of light, d = spacing between crystal planes in the material and θ = angle of incident light.

$$n\lambda = 2d\sin\theta \quad (1)$$

The crystal sizes of the nano-catalysts were estimated by employing Scherer's equation (Eq. (2)) [7]

$$D = 0.9 / \cos\theta \quad (2)$$

Scanning electron microscope and energy dispersive X-ray (SEM and EDX) were used to evaluate the morphology of the prepared catalysts performed in TESCAN VEGA 3. Fourier transform infrared spectroscopy (FTIR) was carried out using Cary 630 FTIR, Agilent Technologies, USA. The wavelength range for sample scanning was 4000-650 cm^{-1} . The ZnSe diffused reflectance accessory (DRA) was used for sample diffusion via reflectance method. The Raman analysis was done using BTC162E-532S-SYS Raman spectrometer to analyze the species present on the surface of the catalyst. Scanning electron microscope and energy dispersive X-ray (SEM and EDX) were used to evaluate the morphology of the prepared catalysts performed in TESCAN VEGA 3. To analyze the pore volume, specific size of the synthesized material and its specific surface area, the Brauner-Emmett Teller (BET) analysis was performed using Quanta chrome NOVA 2200e (USA) analyzer. Before performing the adsorption analysis, the samples were vacuum dried at 80 °C for 24 h and then degassed for 6 h. By using the BET adsorption curve, the surface area of the samples was determined.

3.4. Biodiesel production

3.4.1. Transesterification of Castor oil

In a three neck round bottom flask placed on a heating mantle with magnetic stirring and a reflux condenser for consistent agitation of the reaction mixture, the transesterification of castor oil was carried out with methanol. The optimum reaction conditions are briefly described as 2.5 wt.% of the catalyst was first combined with methanol (8:1 molar ratio of methanol to oil) and heated at 50 °C to activate the catalyst. The activated catalyst-methanol mixture was then added to the required amount of castor oil at a reaction temperature of 65 °C with continuous stirring speed of 800 rpm for approximately 4 hours. The catalyst was then separated by using syringe filter after the completion of the reaction while the excess methanol was separated by heating from the

product. The resultant mixture was poured in a separating funnel to separate biodiesel from glycerol (which is insoluble and denser than biodiesel). The lighter phase containing biodiesel was then separated as the process yield and subjected to further analysis.

3.4.2. Experimental Inventory

For all the biodiesel production, transesterification reaction along with the catalyst activation was followed. Some feasibility experiments were performed initially with undoped CaO and doped Pr-CaO catalysts. Later, a complete set of optimization reactions were performed with variant conditions to reach the maximum yield. The process flow diagram has been added as Fig 3-3.

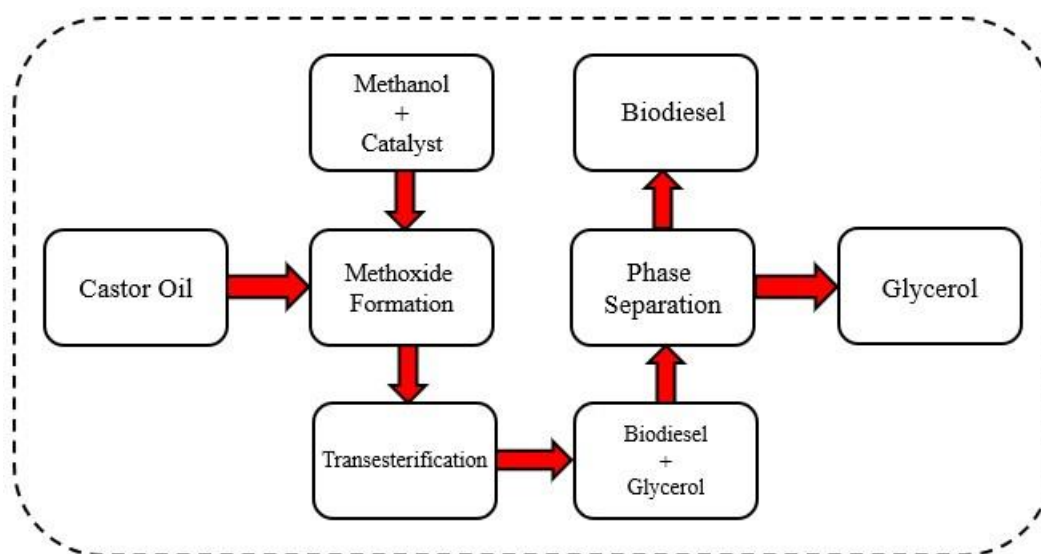


Figure 3-3: Schematic presentation of the process of transesterification.

3.5. Biodiesel characterization

Various techniques and parameters were used to characterize biodiesel and to compare it with ASTM (6751) standards such as viscosity, specific gravity, density, pH, calorific value, FTIR, flashpoint, cetane number, saponification value and iodine value. For transportation and storage of a fuel, its flashpoint is very critical [8]. The biodiesel sample was tested using Seta Flash Series 3 Active Cool Small-Scale Flash Point Tester (UK). The chamber was fed with the samples to be tested where flame was present. The specific temperature at which the biodiesel sample produces enough vapors to catch the flame is its flashpoint. To determine the pH value of biodiesel sample, HI9829 Multiparameter pH/ISE/EC/DO/Turbidity Waterproof Meter (USA)

was used. Referring to literature, to control the pH at approximately 7.5 is quite suitable for biodiesel production [9]. The calorific value of biodiesel expressed in joules per kilogram used to analyze the energy content of the sample was determined using 6200 Isoperibol Calorimeter (USA). At a starting temperature of 21 °C, 0.5g of sample was kept in the 1108 Oxygen Combustion Bomb, with a rise of 2 °C for further analysis obtaining the calorific value of the sample [10]. To analyze the absorption spectra of the biodiesel, same equipment was used as for the catalyst. But due to sample being liquid, the attenuated total reflectance (ATR) method using 5 bounce ZnSe attenuated total reflectance module was used. 3-5% material was mixed with KBr before being subjected to FTIR spectrometer. To calculate the density of the sample, a specific volume was taken and weighed on weighing balance to obtain the values of mass and volume. The specific gravity was calculated using following (Eq. (3))

$$SG = \rho_{sample} / \rho_{water} \quad (3)$$

The amount of KOH required to saponify biodiesel is known as its saponification value (SV). To obtain the saponification value of the sample, 0.5 g of biodiesel was mixed with 0.5 N KOH (20 mL). This mixture was then refluxed and heated up to 40 °C to get a clear solution which suggests a reaction towards saponification. Once the mixture was cooled down, phenolphthalein indicator was added in it to examine the color change. The mixture was further titrated against 0.5 N HCl till the disappearance of the pink color. The SV is calculated according to the given (Eq. (4)) [11]

$$SV = [(B - S) * N * (56.1/W)] \quad (4)$$

Where N= normality of HCl, W= weight of biodiesel, B= blank value, S= sample value. The iodine value of the sample was analyzed by mixing (0.1 g) of it was 20 mL CCl₄ in 25 mL Wijis reagent flask. After being well shaken, the flask was put in dark for 30 min. Afterwards, 20 mL KI (15%) and 100 mL distilled water was added into the flask one by one. The titration of the sample was done against 0.1 N Na₂S₂O₃.5H₂O. the indicator applied was starch and the endpoint was the disappearance of the yellow color. The IV was calculated according to the following (Eq. (5))

$$IV = [(B - S) * N * 12.69/W] \quad (5)$$

Where B= volume of 0.1 N Na₂S₂O₃.5H₂O for blank, S= volume of 0.1 N Na₂S₂O₃.5H₂O for sample, N= normality of Na₂S₂O₃.5H₂O, W= weight of biodiesel. To check the ignition quality of biodiesel, its cetane number was calculated as following (Eq. (6))

$$CN = [46.3 + (95458/SV) - (0.255 * IV)] \quad (6)$$

The assessment of components of FAME in biodiesel was done using Shimadzu GCMS-QP2020 NX (Japan). A 25 mg sample of biodiesel was dissolved in 0.5 mL n-hexane and the solution was then filled in the autosampler vial and injected in Gas Chromatography/Mass Spectrometry (GC-MS) to analyze the composition of FAME. The flow of He gas in the column (HP-5MS column (30 m*0.32 mm*0.25 μm)) was 1.5 mL/min. The injection was of 1.0 μL with a 10:1 split ratio and a 150 °C set temperature and initial retention time of 5min for the detection of FAME. The maximum temperature reached was 220 °C with a heating rate of 10 °C/min for a retention time of 15 min. The analysis of yield of biodiesel (Y_{BD}) was done using (Eq. (7)) [11] where the yield is calculated in percentage.

$$Y_{BD} (vol\%) = [BD \text{ Produced} / Oil \text{ Feed} * 100] \quad (7)$$

Summary

This chapter includes the experimental methodology for catalyst synthesis and biodiesel production. The first part of the study involves the synthesis of undoped CaO catalyst by using calcination method and synthesis of Pr doped CaO by wet chemistry route. The characterization of the prepared standard materials was done using techniques like TGA, XRD and SEM. The process of catalyst synthesis and working principle of characterization method is explained in this chapter. The second part of the chapter is biodiesel production involving transesterification reaction. Afterwards the biodiesel samples were analyzed using characteristic analysis techniques as pH, calorific value, cetane number, FTIR, flash point, density, GCMS, specific gravity, FTIR, saponification value and iodine value. The results were assessed with the standard physical characteristics of biodiesel to analyze the quality of the product.

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Chapter 4: Results and Discussion

4. Results and Discussion

4.1. Physical analysis of the prepared catalysts

4.1.1. Thermo-gravimetric analysis (TGA)

Thermal analysis of calcined CaO obtained from raw mussel shells was conducted in a TG analyzer to evaluate the thermal decomposition process. The peak of the temperature curve was obtained nearly at 613 °C. Islam et al., (2013) studied the formation of two distinct phases in calcium carbonate (CaCO_3) decomposition [1]. The elimination of the alkyl group and water caused a relatively little weight loss in the initial phase. The second phase started at 457 °C and ended at 781 °C. The increase in temperature change from 600-900 °C represented quick weight changes as the removal of volatile matter in the sample, and CaCO_3 contained in the mussel shells was transformed into CaO. The weight of the sample remained constant until 900 °C temperature. This showed process completion, and the sample was left as residue [2]. The TGA curve for the catalyst CaO is presented in the Fig. 5. For thermal analysis of the doped catalyst, 3.270 mg of calcined sample was introduced into the instrument and the TGA curve was developed because of the weight loss of the sample with a rise in temperature from room temperature to 900 °C. There were four stages of weight loss for the doped catalyst. The TGA curve of the sample catalyst showed the first mass loss of 7.8% with a fraction loss of 0.25506 mg in the temperature range of 50-300 °C due to CO_2 removal and water loss from the surface and the crystal lattice. Due to the removal of the water of crystal in $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ the second mass loss of 17.5% with a fraction loss of 0.57225 mg occurred in the temperature range of 350-500 °C. By further increasing the temperature, a third mass loss of 25.2% with a fraction loss of 0.82404 mg was generated by the decomposition of $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ from 450-600 °C. The last mass loss of 11.2% with a fraction loss of 0.36624 mg for the decomposition of carbonate was observed from 600-740 °C [3]. After this, the weight of the sample remained constant until 900 °C, which is thus selected for the catalyst activation. The thermal decomposition of 7% Pr doped CaO is shown in Figure 4-1.

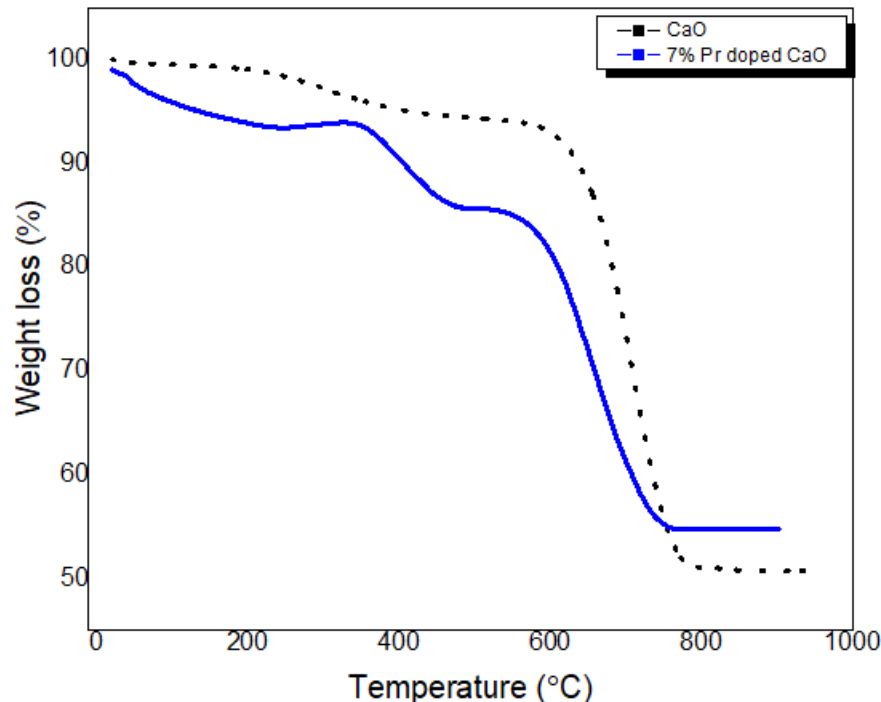


Figure 4-1: TGA analysis of Calcined CaO and 7% Pr doped CaO.

4.1.2. X-ray Diffraction (XRD) analysis

To study the phase identity of the synthesized catalyst, X-ray diffraction (XRD) analysis was performed. Figure 4-2 (a) showed the decomposition of the calcined catalyst at and above 900 °C where it was completely transformed from CaCO_3 to CaO with the evolution of CO_2 . No significant effect was observed on the XRD pattern of the catalyst by further increasing the calcination temperature above 950 °C which indicated the complete conversion of CaCO_3 compound found in mussel shells into CaO . The well crystallized structure of CaO were represented by narrow but high intense peaks. The orientations for sharp XRD reflections are (111), (200), (220), (311), and (222) which indicated well crystallization of the calcined catalyst. CaO was detected at (JCPDS# 77-2010) at 32.19 (111), 37.34 (200), 53.84 (220), 64.13 (311) and 67.35 (222) respectively and it revealed a high crystalline cubic structure. The average crystallite size of 23.56 nm was measured for CaO . Debye Scherrer's equation was implied to calculate the crystalline size of the catalysts [4]. The detected space group for CaO is Fm-3m (225). For the 7% doped catalyst, Pr_6O_{11} peaks were observed at $2\theta=$ 28.137 (111), 32.612 (200), 46.945 (220), 55.679 (311), 58.279 (222) and PrO_2 peaks at $2\theta=$ 28.641 (111), 33.190 (200), 47.645 (220), 56.540 (311), 59.298 (222) represented in figure 4-2 (a). The rare earth metal

doped catalyst also exhibited a highly crystalline cubic structure with an average crystallite size of 15.78 nm. The reduction in the crystalline sizes of mixed oxide catalyst may be caused due to homogeneous dispersion of CaO and Pr-O [5]. The detected space group for Pr_6O_{11} and PrO_2 is also Fm-3m(225) [6].

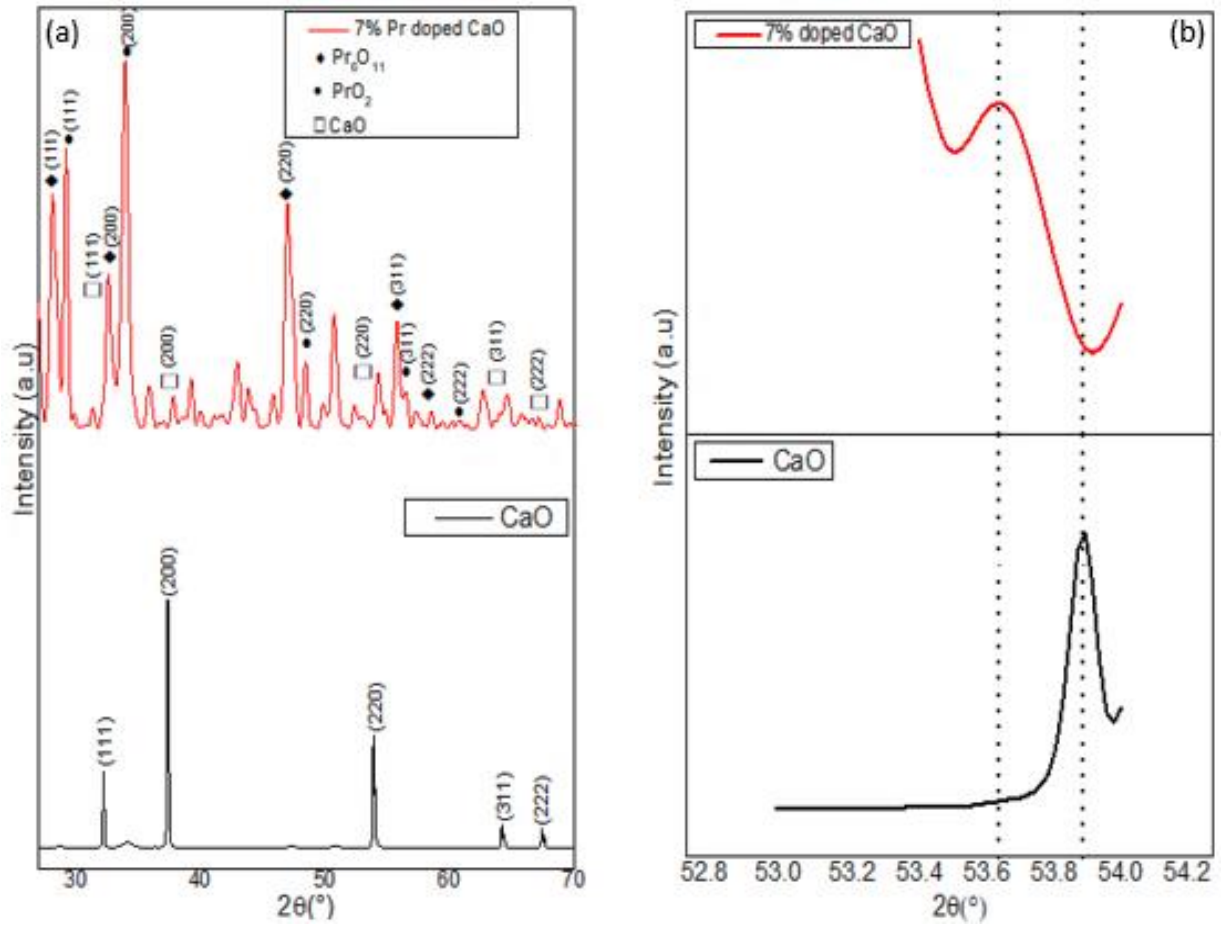


Figure 4-2: (a) XRD pattern of Calcined CaO and 7% Pr doped CaO

(b) Shifting in the position of peak for (220).

The phenomenon of doping of rare earth metal on to CaO took place along with some impurities through wet chemistry route as can be observed through XRD of doped and undoped catalyst in Figure 4-2 (b) because the difference in the peak intensities of CaO and Pr-CaO was observed as the addition of Pr reduced their degree of crystallinity. Also, the shifting of peaks to lower 2θ due to lattice expansion indicated the incorporation of Pr ions into CaO lattice. The similar phenomenon was observed by Ghazali et al., in the evaluation of cockle shell derived CaO doped with La [7]. A detailed XRD analysis of both undoped CaO and Pr doped catalysts have been mentioned in table 4-1 representing the crystallite sizes, space groups and hkl indices of each sample.

Table 4-1: XRD analysis of synthesized CaO and Pr doped CaO.

Samples	2θ	Space group	PDF #	hkl indices	d-spacing (nm)	Crystallite size (nm)
CaO	32.193	Fm-3m (225)	77-2010	(1 1 1)	0.27782	27.4706278
	37.344			(2 0 0)	0.24060	26.12846956
	53.842			(2 2 0)	0.17013	22.35412237
	64.134			(3 1 1)	0.14509	20.96428411
	67.355			(2 2 2)	0.13891	20.88114736
Pr₆O₁₁	28.249	Fm-3m (225)	42-1121	(1 1 1)	0.31565	12.54232444
	32.739			(2 0 0)	0.27331	17.55908071
	46.993			(2 2 0)	0.19320	12.84322395
	55.706			(3 1 1)	0.16487	20.82952555
	58.424			(2 2 2)	0.15783	14.10273913
	68.588			(4 0 0)	0.13671	13.45716766
	75.732			(3 3 1)	0.12549	12.39953666
	78.082			(4 2 0)	0.12229	19.03350671
87.265			(4 2 2)	0.11163	19.26754056	

4.1.3. Fourier transform infra-red spectroscopic analysis (FTIR)

The absorption bands for the FTIR of calcined calcium oxide (CaO) appearing at 1421, 1132 and 865 cm^{-1} as shown in Figure 4-3 represented the bending vibration modes of calcium oxide. Due to the absorption of small amount of water absorbed in the crystalline CaO, the appearance of a

strong absorption band was detected at 3628 cm^{-1} attributing to hydroxyl stretching vibrations. In this spectrum no other peaks for other groups (impurities) were observed [7,8] .

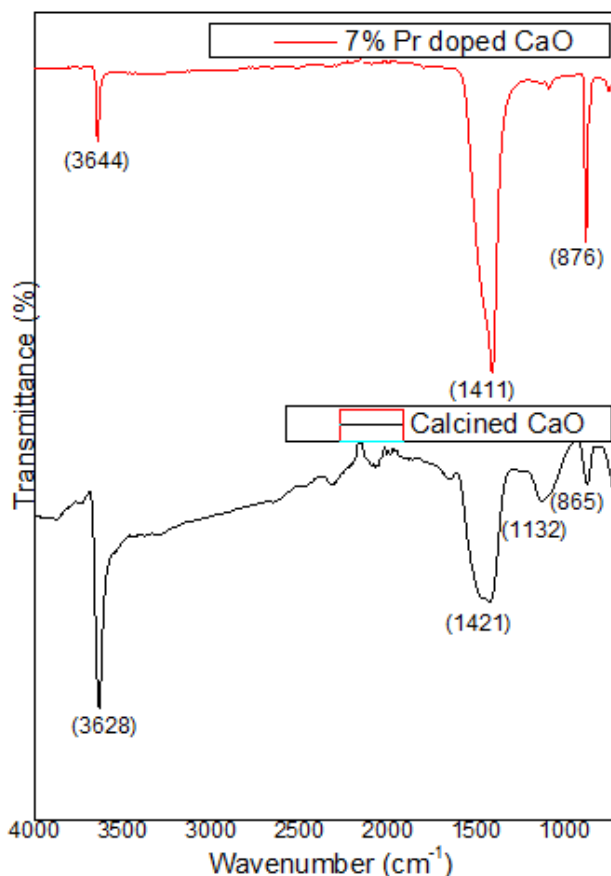


Figure 4-3: FTIR spectra of Calcined CaO and 7% Pr doped CaO.

In the FTIR spectra recorded for calcined mussel shell doped with praseodymium metal, a less intense band at 3644 cm^{-1} represented the O-H stretching vibration of CaO on the heterogeneous catalyst surface as depicted in Figure 4-3. The peak observed at 876 cm^{-1} is assigned to the bending vibrations of M-O where M represented Ca or Pr metal ion [9,10]. The absence of NO_3^{-2} ion on the surface of the doped catalyst confirmed the decomposition of $\text{Pr}(\text{NO}_3)_3$ to Pr_6O_{11} and PrO_2 .

4.1.4. Raman spectroscopic analysis

Figure 4-4. showed the Raman spectra of waste mussel shells calcined at 900 °C. The spectra obtained showed the vibrational bands of the CaO calcined at 900 °C at (573.15, 3110.14 cm⁻¹).

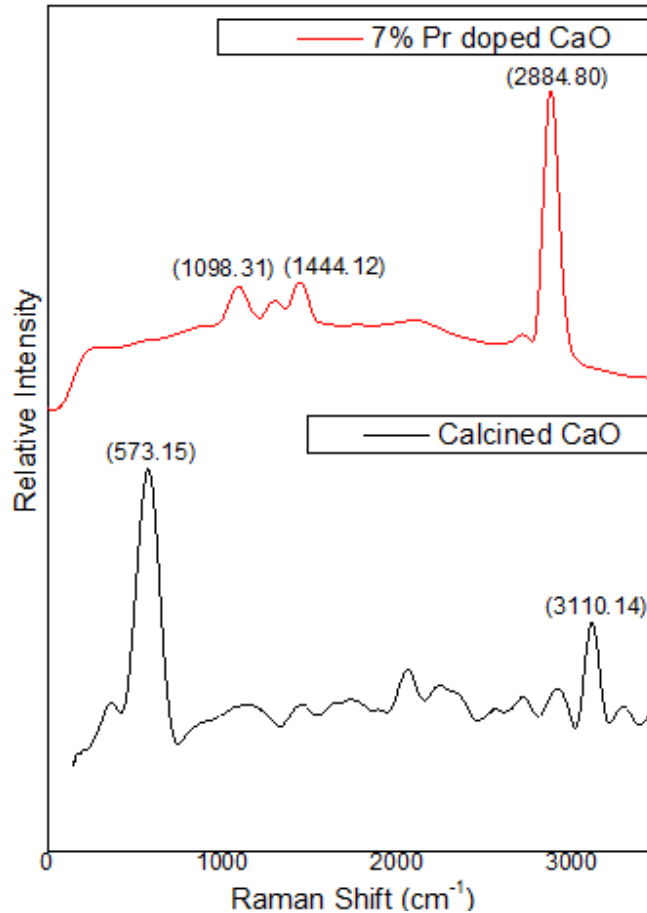


Figure 4-4: Raman spectra of Calcined CaO and 7% Pr doped CaO.

The Raman spectra of 7% Pr doped CaO obtained by Pr (NO₃)₃.6H₂O and CaO mixed oxides is represented in Figure 4-4. Two weak bands at 1098.31 and 1444.12 cm⁻¹ were found for pure CaO [11]. As contrary to this, the mixed oxide doped catalyst sample generated spectra with a significantly strong band at 2884.80 cm⁻¹ that was attributed to the Pr-O vibration unit [12]. The intensity of this band increased as the Pr/CaO molar ratio increased. These two bands originated from distortions in the Pr₆O₁₁ and PrO₂ crystal structure on the surface [13]. Because the Pr ion has a valence of 4 or 3, higher than that of 2 for the Ca ion, some vacancies were generated when Ca ions were substituted by Pr ions in the calcium oxide lattice to maintain charge neutrality in

the ionic crystal. These vacancies induced the lattice distortion and defects that were favorable for heterogeneous catalysis. The presence of those two bands (1098.31 and 1444.12 cm^{-1}) is strong evidence for the existence of an interaction between CaO and Pr [14].

4.1.5. Brauner-Emmett-Teller analysis (BET)

The specific surface area and pore size of both doped and undoped catalyst were calculated using BET. The BET results illustrated that the surface area of the catalyst lowered as the particle size of the catalyst increased with the calcination temperature [15]. The adsorption isotherms obtained for pure CaO and Pr doped CaO are shown in Figure 4-5. The isotherms in Figure 4-5 (a) were used to find out the specific surface area of the samples. The N_2 adsorption-desorption isotherms depicted a type IV having an H_2 hysteresis loop which indicates successful synthesis of mesoporous material [16]. It was concluded that the mesopores were of large size from the shifting of hysteresis loop to high P/P_0 values that is >0.8 . In the mixed oxide catalyst, the BET surface area of the catalyst increased with CaO. This increase in surface area is closely related to the crystalline sizes [17]. The BET surface area of the mixed oxide catalyst as presented in Figure 4-5 (b) (7% Pr doped CaO) was well agreed with its respective crystalline size, as the smaller crystalline size of the mixed oxide catalyst possessed high surface area [18].

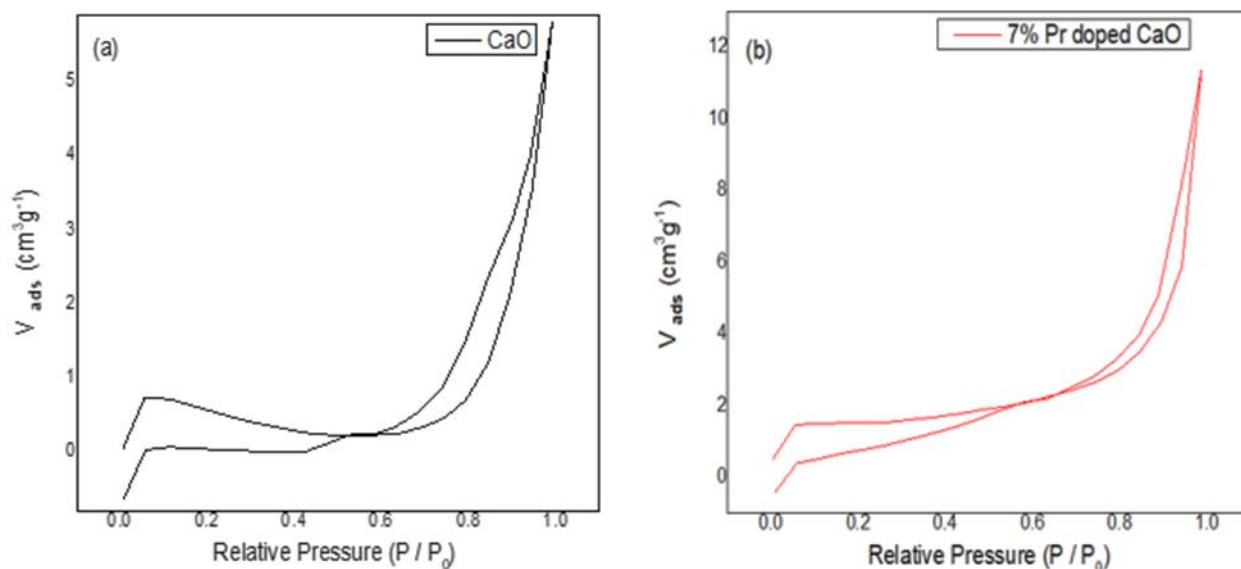


Figure 4-5: N_2 adsorption-desorption pattern of (a) Calcined CaO (b) 7% Pr doped CaO.

There was an increase in pore volume and surface area for mixed oxide catalyst with an increase in the amount of praseodymium added which suggested that the praseodymium was infused with the calcium oxide and well distributed on the sample surface. The increase in the volume and specific surface area could be caused by a decrease in the size of the particles and/or due to the addition of the dopant which changes the textural properties of the catalyst by the formation of a new phase [19]. The pore diameters of the samples as presented in table 4-2 were in the range of mesoporous category which is beneficial because mesoporous catalysts can be effectively used to reduce the internal mass transfer limitation in the transesterification of large reactants like triglycerides [20].

Table 4-2: Textural properties of synthesized CaO and 7% Pr doped CaO through BET analysis.

Catalyst sample	Specific surface area, (S _{ABET}) (m ² /g)	Pore volume (V _{Pore}), (cm ³ /g)	Pore diameter (D _{Pore}) (nm)
CaO	1.339	0.010	11.9426
Pr-CaO	4.842	0.016	3.6528

4.1.6. Scanning electron microscopic analysis (SEM)

To observe the changes on the surface structure and morphology of mussel shells and calcium oxide obtained from shells, scanning electron microscopy (SEM) was performed at different magnifications as represented in Figure 4-6 (a), (b) and (c). i.e., 2 μm, 5 μm, and 10 μm, respectively. The microstructures of natural shell experienced a considerable change when the calcination temperature increased from 700 to 900 °C, shifting from layered architecture to porous structure. The calcined waste mussel shells had an amorphous semi-spherical shape, and some of them formed aggregates when they linked together. During the decomposition of CaCO₃ to CaO, the release of gaseous CO₂ and water may have caused the porous structure after calcination [11,15]. The released water and gaseous CO₂ acted as porogens. The presence of porosity on the surface of the catalyst increased the BET surface area that led to an increase in the catalytic activity [11]. The smaller size of the grains and aggregates could provide higher specific surface areas. Since all samples were less porous or even nonporous, the size of the particle should directly respond to the surface area. The EDS spectrum represented the elemental composition of CaO with 41% w/w Ca and 52.80% w/w oxygen in Figure 4-6(d).

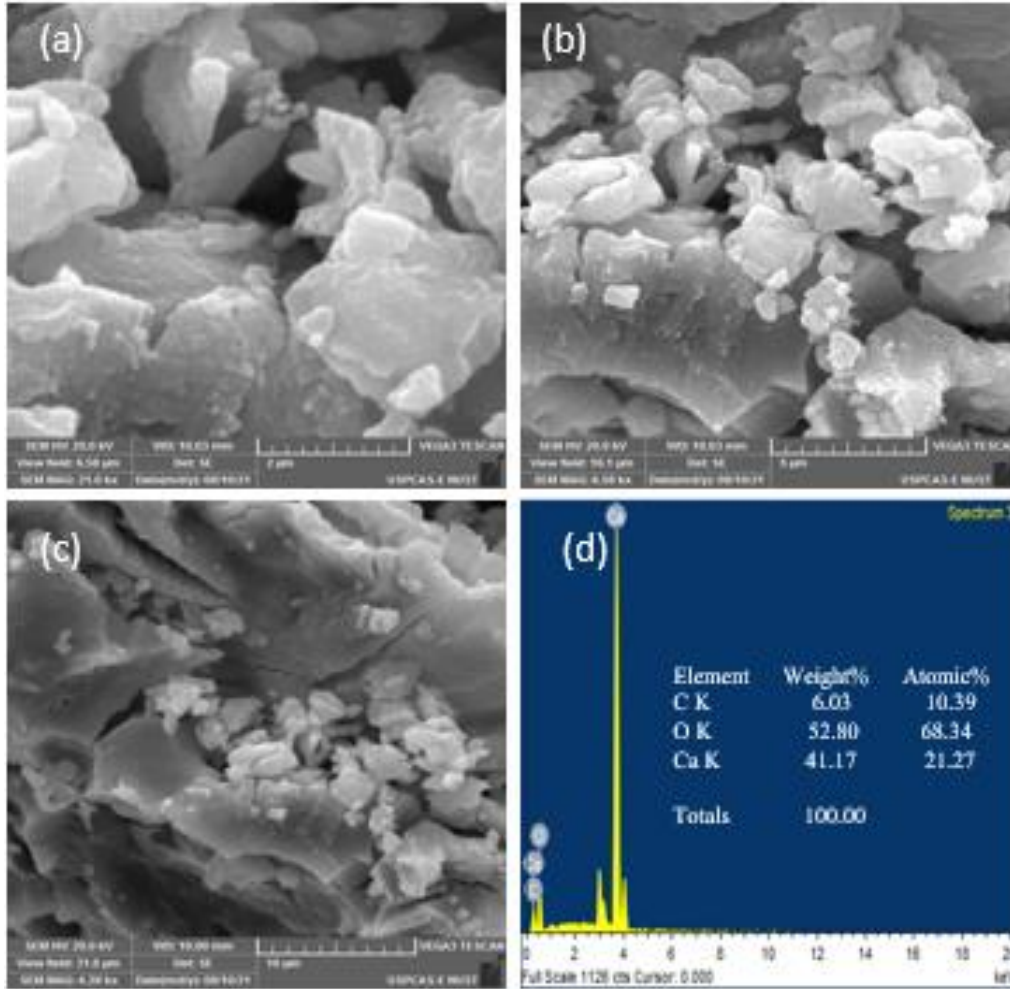


Figure 4-6: SEM images of Calcined CaO at (a) 2 μm (b) 5 μm (c) 10 μm (d) EDS with % weight of elements.

Scanning electron microscopy (SEM) was also performed to analyze the surface structure and morphology of the doped, calcined catalyst at 2 μm , 5 μm , and 10 μm in Figure 4-7 (a), (b) and (c), respectively. The 7% Pr-CaO mixed oxides were observed as dense, flower like crystalline particles of irregular shape. A very little accumulation of nanoparticles was observed in this micrograph. The agglomerates were almost uniform and were formed due to the unsuitable drying process or calcination [21]. A change in the morphology of the particles was observed by the addition of the rare earth dopant as the size of the particles substantially increased by increasing the calcination temperature which showed an obvious sintering of crystallinity [14]. The EDS spectrum shown in Figure 4-7 (d) represented the elemental composition of the nano-

catalyst. Based on the peaks, Pr-CaO with 60.78 % w/w Pr and 9.71% w/w Ca and 23.81% w/w oxygen were observed.

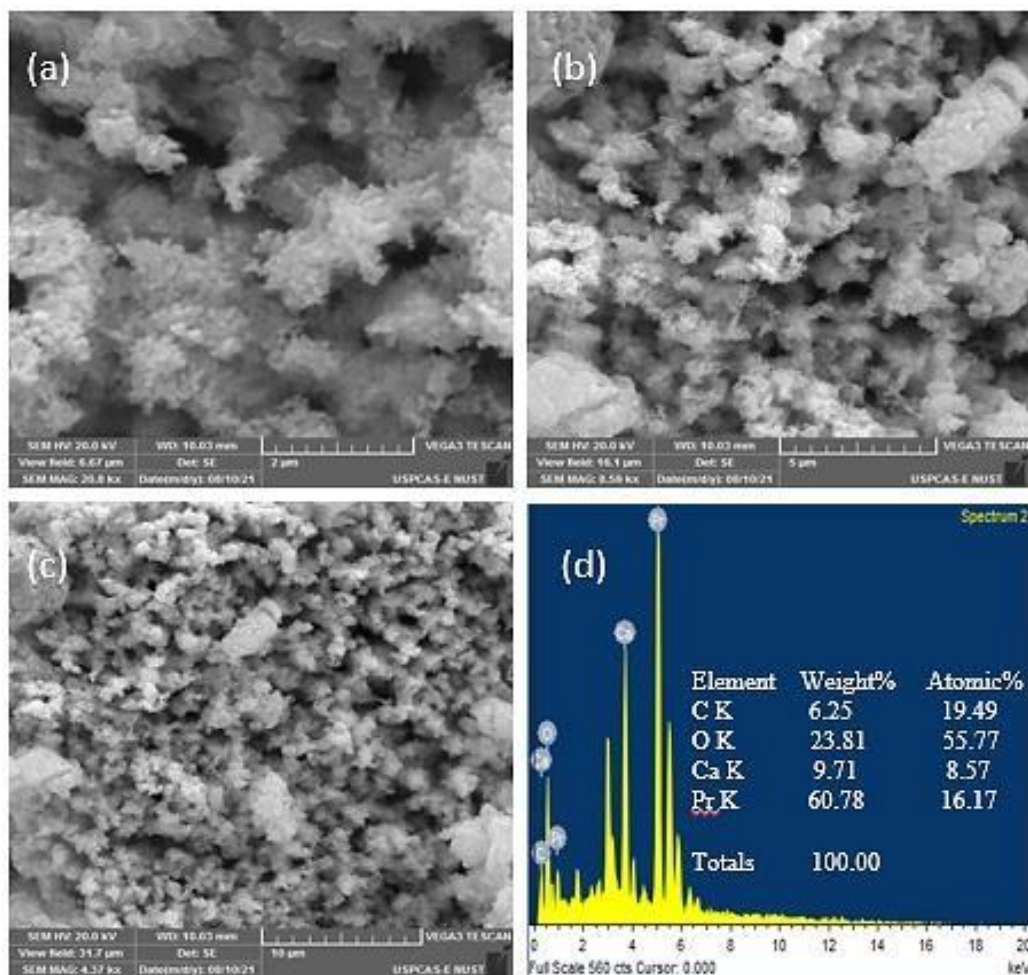


Figure 4-7: SEM images of 7% Pr doped CaO at (a) 2 μm (b) 5 μm (c) 10 μm (d) EDS with % weight of elements.

4.2. Biodiesel analysis

4.2.1. Flash point

Biodiesel is a safer and more cost-effective alternative to conventional diesel since it has a higher flashpoint [22]. Biodiesel must meet the standard value of 130 °C or higher. Hence in case of CaO it is 140 °C and with doped catalyst (7% Pr-CaO) it is 150 °C. The flashpoints measured for biodiesel were in accordance with the biodiesel's standard flashpoint value [23].

4.2.2. Calorific value

To compare fuel characteristics of biodiesel with petroleum diesel properties, calorific value is an essential parameter. Due to biodiesel's low power percentage, important efficiency parameters like torque and horsepower are affected [4]. The standard calorific value for biodiesel is 37.3 MJ/kg, although the energy density of different samples varies depending on the feedstock and production method. The calorific values of the samples being studied in this work are 37.06 MJ/kg for undoped catalyst (CaO) and 37.40 MJ/kg for 7% doped catalyst (Pr-CaO).

4.2.3. GCMS

The assessment of components of FAME in biodiesel was done using Shimadzu GCMS-QP2020 NX (Japan). A 25 mg sample of biodiesel was dissolved in 0.5 mL n-hexane and the solution was then filled in the autosampler vial and injected in Gas Chromatography/Mass Spectrometry (GC-MS) to analyze the composition of FAME. The flow of He gas in the column (HP-5MS column (30 m*0.32 mm*0.25 μ m)) was 1.5 mL/min. The injection was of 1.0 μ L with a 10:1 split ratio and a 150 °C set temperature and initial retention time of 5min for the detection of FAME. The maximum temperature reached was 220 °C with a heating rate of 10 °C/min for a retention time of 15min.

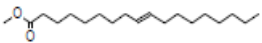
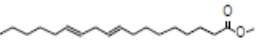
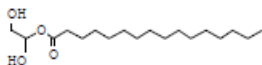
Table 4-1: GCMS Analysis of the Biodiesel Samples.

Peak#	Name	Formula	Area
1	Hexadecenoic acid, methyl ester	C ₁₇ H ₃₄ O ₂	270
2	Heptadecanoic acid, methyl ester	C ₁₈ H ₃₆ O ₂	284
4	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	C ₁₉ H ₃₄ O ₂	294
5	6-Octadecenoic acid, methyl ester, (Z)	C ₁₉ H ₃₆ O ₂	296
9	cis-10-Nonadecenoic acid, methyl ester	C ₂₀ H ₃₈ O ₂	310
10	9-Octadecenoic acid, 12-hydroxy-, methyl ester	C ₁₉ H ₃₆ O ₃	312

To ensure the presence of methyl esters in biodiesel, GC-MS was employed. The biodiesel sample synthesized from castor oil using Pr-CaO as catalyst contained 9-Octadecenoic acid, 9,12-Octadecadienoic acid, 12-hydroxy-methyl ester, Hexadecanoic Acid as the dominant fatty

acids. Other minor methyl esters were also present in the sample. All these constituents of biodiesel samples have been depicted in table 4-3 and 4-4. These methyl esters ensure the conversion of oil to FFAs.

Table 4-2: Methyl esters in Biodiesel.

Component Fatty acids	Molecular Formula	Structure
9-Octadecenoic acid	$C_{19}H_{36}O_2$	
9,12-Octadecadienoic acid	$C_{19}H_{34}O_2$	
Hexadecanoic Acid	$C_{19}H_{38}O_4$	

The GCMS chromatogram of the castor oil biodiesel formed representing the methyl esters is shown in Figure 4-8.

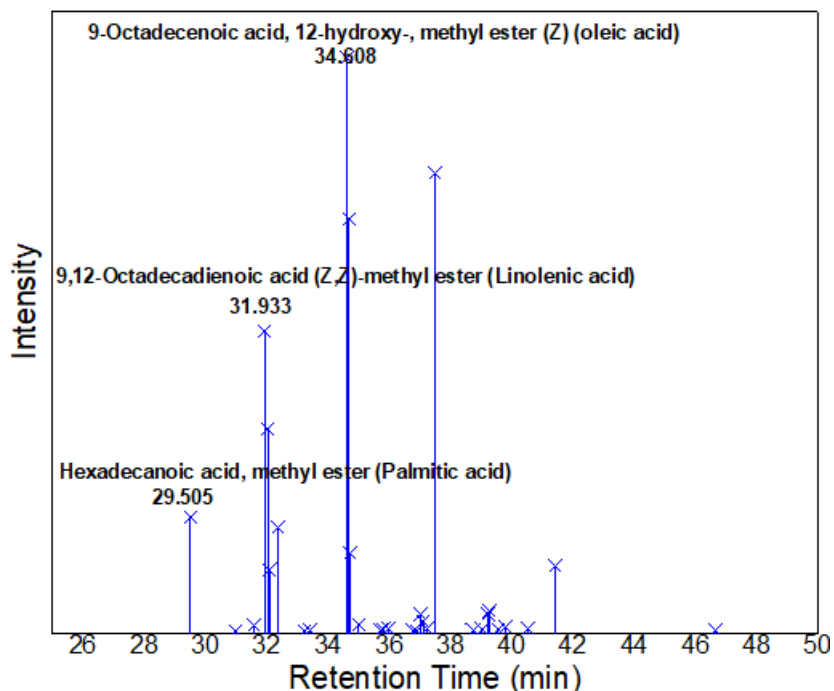


Figure 4-8: GCMS Chromatogram representing the presence of various methyl esters in the castor oil biodiesel.

4.2.4. FTIR

The functional groups present in biodiesel are confirmed through FTIR of the yield. This spectrum in Figure 4-9 indicates the symmetric and asymmetric stretching vibrations of C-H

bond on 2926 cm^{-1} and 2862 cm^{-1} wavenumber respectively. The ester bond ($\text{C}=\text{O}$) is ascribed by the wavenumber at 1732 cm^{-1} . In aliphatic organic compounds, for $\text{C}-\text{O}$ stretching the wavenumbers were found at 1425 cm^{-1} to 1510 cm^{-1} . The functional groups of ester bond $\text{C}-\text{O}$ were also detected at 1173 cm^{-1} to 1200 cm^{-1} . The observations were consistent with the work in literature [24].

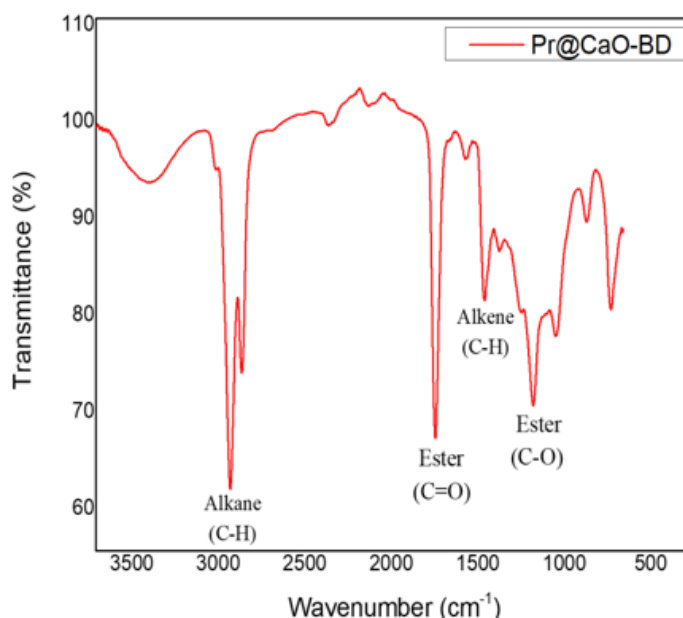


Figure 4-9: FTIR spectrum of synthesized biodiesel (BD) sample for prepared catalyst.

4.2.5. Density

The standard values of densities of diesel and biodiesel are 848 kg/m^3 and $870\text{-}900\text{ kg/m}^3$ respectively. Biodiesel has a higher density (0.88 g/cm^3) than petroleum diesel. For 7% Pr-CaO, biodiesel has a density of 0.87 g/cm^3 . The density of biodiesel enables the optimal air-fuel ratio for thorough combustion in combustion engines.

4.2.6. Saponification value

Poor biodiesel quality and lower yield re attributed due to a major issue of saponification during biodiesel production [25,26]. Standard biodiesel's saponification value is $<312\text{ mg KOH/g}$, while the tested value for 7% Pr doped CaO is 224.4 mg KOH/g . Saponification value can be affected by the method used for the pretreatment of the oil.

4.2.7. Iodine number

Iodine value calculations are used to determine the unsaturation level of biodiesel. It is useful in the investigation of oil stability. Polymerization is caused due to the high degree of unsaturation leading to the creation of epoxy due to the addition of oxygen in dual bonds [16].

The iodine value for 7% Pr doped CaO is 76.14. As the iodine values are nearly half (60 g I₂/100 g oil) of the specified maximum point (120 g I₂/100 g oil), these result showed the improved stability of synthesized biodiesel [23].

4.2.8. Cetane number

The cetane number for biodiesel changes on the concentration of FAME and fuel carbon number. The cetane number for 7% Pr-CaO is recorded to be 53. It was observed that the standard cetane ranges for biodiesel were 46–52 and 40–55. The results show that the product has an appropriate concentration of FAME and carbon number, which is a sign of a higher-quality biodiesel synthesis.

4.2.9. Product Yield

The dependance of biodiesel yield produced in correspondence to the substrate used is mainly on catalyst loading rate, type of feedstock, other reaction factors such as temperature, time and stirring speed. Therefore, the yield of biodiesel varies with the changes in reaction conditions [25]. The maximum yield of biodiesel was 87.42% for Pr-CaO (7%) catalyst while for calcined undoped CaO the yield was 80%. The physical properties of the biodiesel samples were in accordance with the standard values showing improved results presented in Table 4-5.

Table 4-3: Properties of biodiesel produced using 7% Pr-CaO catalyst.

Properties	Unit	BD Standards	Pr-CaO
Flashpoint	°C	>130	140-150
Specific gravity	NA	0.86-0.9	0.87
Calorific value	MJ/kg	>35	37.40
Saponification value	mg KOH/g	<312	224.4
Iodine value	g I ₂ /100 g oil	<120	76.14
Cetane number	NA	>47	53
Yield	Vol%	NA	87.42

Summary

This chapter includes the characteristic analysis of the synthesized CaO and Pr-CaO. The results of TGA, XRD and SEM are compared with the studies done in past, which are in accordance with each other. The results of biodiesel samples have also been compared with the standard values provided. The synthesized nano-catalysts were characterized with TGA, XRD and SEM where the analysis results showed agreement with the literature review being done. XRD results showed sharp characteristics peaks while the crystal size calculated using Scherer Equation was found to be 23.56 nm for CaO while 15.78 nm for Pr-CaO. SEM images showed cubical images of 2, 5 and 10 μm for both CaO and Pr-CaO. TGA results showed that both the materials decomposed at 900 °C. The catalysts were then used for their application in the process of biodiesel production. The process of transesterification was performed for both the catalysts to produce the samples of biodiesel. Further several standard testing analysis techniques were used to compare the produced samples where the results agreed with the samples. Flashpoint of CaO-BD was 140 °C, Pr-CaO-BD was 150 °C and calorific value of 37.06 MJ/kg and 37.40 MJ/kg for each with a conversion of 80% and 87.42% respectively.

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Chapter 5: Conclusion and Future Recommendation

5. Conclusion and Future Recommendations

5.1. Conclusion

- Waste seashells were utilized successfully as raw materials for the efficient and low-cost synthesis of CaO and Pr-CaO mixed oxide catalysts for biodiesel production through calcination and wet impregnation method, respectively.
- To define the morphological and crystallographic properties of the prepared catalyst, detailed characterizations were performed. XRD indicated the formation of CaO and 7% Pr-CaO crystals with crystal size of 23.6 nm and 15.78 nm respectively. TGA depicted the thermal stability of CaO until 781 °C and 7% Pr-CaO until 650 °C which was suitable for biodiesel production.
- To produce biodiesel through transesterification, the synthesized catalysts were employed to the process. The synthesized catalyst subjected to transesterification for the production of biodiesel and the maximum yield of biodiesel was 87.42% for Pr-CaO (7%) catalyst while for calcined undoped CaO the yield was 80%.
- The standard value for biodiesel must be 130 °C or higher. Therefore, in case of CaO it is 140 °C and with doped catalyst (7% Pr-CaO) it is 150 °C. The biodiesel sample synthesized from castor oil using Pr-CaO as catalyst contained 9-Octadecenoic acid, 9,12-Octadecadienoic acid, 12-hydroxy-methyl ester, Hexadecanoic Acid as the dominant fatty acids.

5.2. Recommendations

- The characterization of biodiesel confirmed that the produced biodiesel meets the standards of ASTM in all aspects. This study can be the baseline for the techno-economic analysis of the catalyst and biodiesel yield on pilot scale and to study further development in heterogeneous catalysis validated in catalyst recycling for biodiesel production.
- The work needed in the future which is necessary for the accomplishment of the long-term goal to optimize the process of biodiesel production considered various effective

factors is involved. For future perspective a rather efficient and augmented setup would play a crucial role in the generation of biofuel.

- This study involves the synthesis of the doped catalysts through wet chemistry route. Future work could be aimed for the optimized production and increased percentage yield of the biodiesel using other synthesis methods for the nano-catalysts to study different physical and chemical properties of the synthesized catalysts i.e., surface area, shape and structure, and effect on the obtained yield.
- A detailed analysis of the prepared undoped and doped catalysts can be done through transmission electron microscopy to obtain the highly magnified images of the catalysts as well as information about surface features, shape, size, and structure.
- The efficiency of the synthesized catalysts can also be studied comparatively on oils other than castor oil for biodiesel production.
- This study can be the baseline for the techno-economic analysis of the catalyst and biodiesel yield on pilot scale and to study further development in heterogeneous catalysis validated in catalyst recycling for biodiesel production.

Appendix A



Figure S 1 Bruker's X-ray Diffractometer (D8 Advance)



Figure S 2 Tescan Vega 3 Scanning Electron Microscope

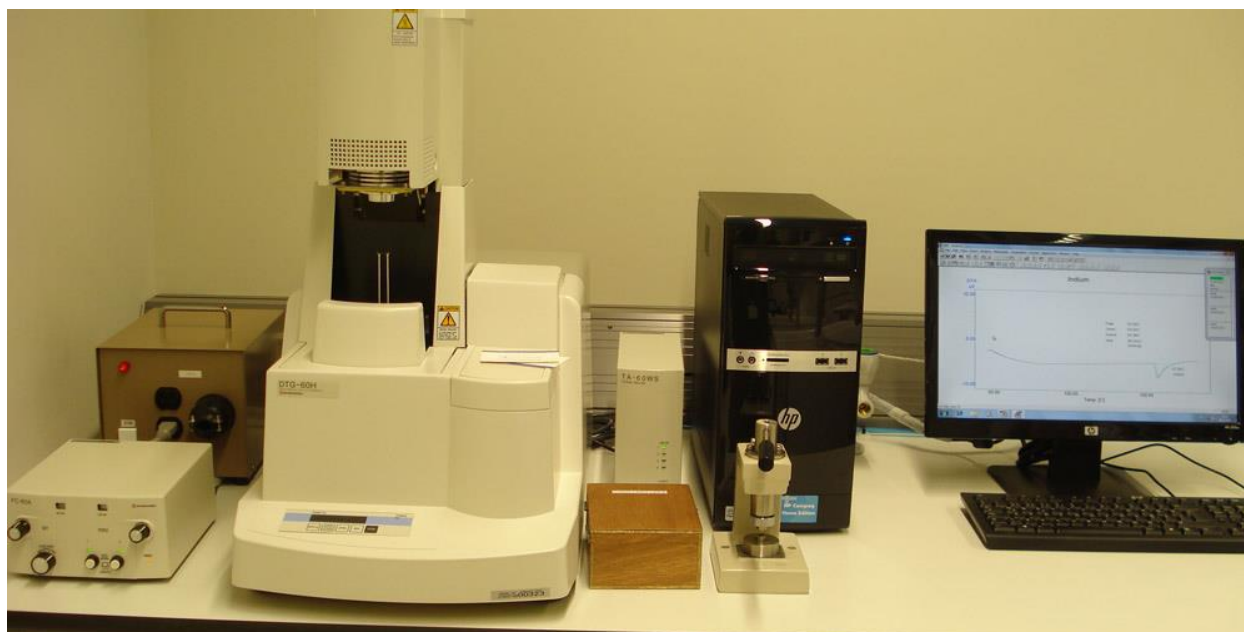


Figure S 3 SHIMADZU-DTG 60H Thermo gravimetric instrument



Figure S 4 HI9829 Multiparameter pH/ISE/EC/DO/Turbidity

Waterproof Meter with optional GPS



Figure S 5 Seta flash Series 3 Active Cool Small Scale Flash Point Tester



Figure S 6 6200 Isoperibol Bomb Calorimeter



Figure S 7 Shimadzu gas chromatograph-mass spectrometer GCMS-QP2020 NX



Figure S 8 Agilent Cary 630 FTIR

