TRIACETIN SYNTHESIS USING HOMOGENEOUS AND HETEROGENEOUS CATALYSTS

A
Thesis Submitted
in partial fulfillment of the requirement for the degree of

MASTER OF SCIENCE
IN
CHEMISTRY

Submitted by:
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JULY, 2011

DEDICATED TO MY

PARENTS…….

CERTIFICATE

This is certify that the thesis entitled ***"Triacetin synthesis using homogeneous and heterogeneous catalysts"*** *being submitted in partial fulfillment of requirements for the award of degree of* ***Master of Science in Chemistry, submitted in the School of Chemistry and Biochemistry, Thapar University, Patiala*** *is a bonafide work carried out under the supervision of* ***Dr. Amjad Ali****, Assistant Professor, School of Chemistry and Biochemistry, Thapar University Patiala and that no part of this project has been submitted for the award of any other degree.*

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CANDIDATE'S DECLARATION

I hereby declare that the work presented in this thesis entitled, " ***Triacetin Synthesis using Homogeneous and Heterogeneous catalysts****" in partial fulfillment in the requirement for the award of Degree of* ***Master of Science in Chemistry****, submitted in the School of Chemistry and Biochemistry,* ***Thapar University, Patiala****, is an authentic record of my own work carried out under the supervision and guidance of* ***Dr. Amjad Ali****, Assistant Professor, School of chemistry and biochemistry, Thapar University, Patiala and refers other researcher's work which are duly listed in the reference section.*

The matter embodied in this thesis has not formed the basis for the award of any other degree of this or any other university.

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This is to certify that the above statement made by the student concerned is correct and true to the best of my knowledge.

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In the end, I wish to express my deep sense of gratitude to my family, for supporting and encouraging me at every step of my work. It is power of their blessings, which has given me the courage, confidence and zeal for hard work.

Date: 15July, 2011

Place: Patiala

Regards,

Jaspreet Kaur

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ABSTRACT

In present thesis, Na ion impregnated CaO catalysts was prepared using wet impregnation method and prepared catalyst was used for the esterification of glycerol with acetic anhydride to produce triacetin. The catalyst was characterized by using powder X-ray diffraction (XRD) and Scanning Electron Microscopic (SEM) studies. The catalyst prepared by impregnating 1.5 wt-% Na in CaO support were found to catalyse the esterification of glycerol with acetic anhydride to yield triacetin using glycerol to acetic anhydride molar ratio 1:4. The complete conversion of the glycerol into triacetin was observed in 4.5h of reaction period at 60 °C. Triacetin is also produced by conventional homogeneous catalyst, triethyl amine, using glycerol to acetic anhydride molar ratio of 1:4. The complete conversion of glycerol to triacetin was observed in 4h of reaction period at room temperature.The production of triacetin was confirmed by Thin Layer Chromatography, FT-IR and proton NMR studies.

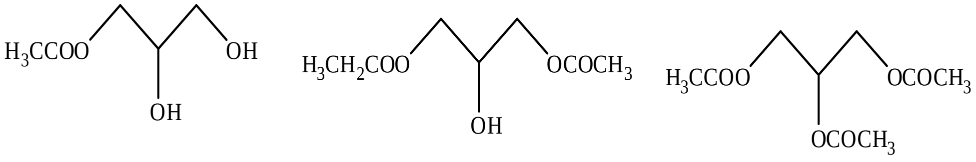
CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1 INTRODUCTION

The transesterification of triglycerides with alcohols leads to the formation of fatty acid methyl ester and glycerol. Global production of glycerol is estimated to reach 1.2 million tons by 2012 [1] and hence, this enormous amount of glycerol must find an industrial application [2-4]. One such example of glycerol application is the chemical transformation of glycerol into glycerol acetates which have major applications in cryogenics [5], plastics [6] and fuel additives[7].

Transesterification of triglycerides with methanol in the presence of alkali, or acid leads to the formation of glycerol and the reaction affords the fatty acid methyl esters, commonly known as biodiesel, and glycerol. Today, one of the most challenging aspects of the biodiesel technology is related with the economical utilization of the glycerol, formed. The major uses of this compound are in personal care products, cosmetics and soaps, but these sectors will not be able to utilize the tons of glycerol coming from biodiesel production. Glycerol is also a good feedstock for the production of other important chemicals viz; 1,2 and 1,3-propanediol [8-10], acrolein using solid catalysts [11-13] butanol and ethanol [14] which can be used as biofuels. Glycerol reforming to synthesis gas, a mixture of carbon monoxide and hydrogen, has been studied over noble metal catalysts [15] and could be a possible pathway for the production of hydrocarbons in the diesel and gasoline. Similarly esterification of glycerol leads to the formation of glycerol acetates viz; mono, di or triacetin as shown in fig.1



Monoacetin Diacetin Triacetin

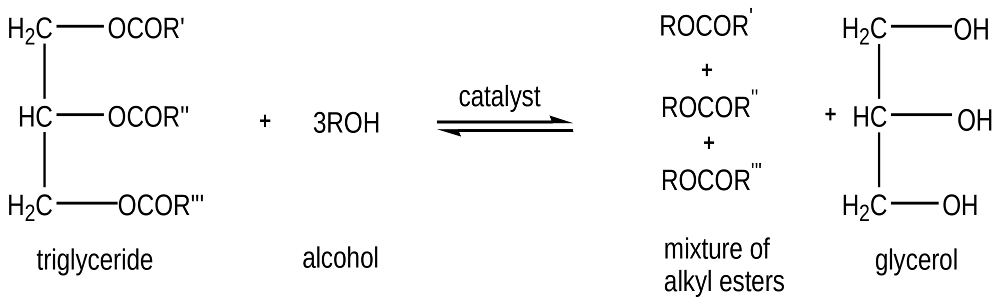
Fig.1 Monoacetin, diacetin and triacetin formed by the esterification of glycerol.

Triacetin is traditionally used as a plasticizer in cigarette filters, but in recent years it has also been tested as a biodiesel additive [16, 17] to improve the cold flow properties. This application is extremely interesting, because the glycerol produced from transesterification could be used in the biodiesel chain, as an additive to improve the properties of this biofuel. Triacetin can be produced in the acid-catalyzed reaction of glycerol with acetic acid. There are many studies [18-21] using different solid acid catalysts and oprerational conditions, but the selectivity to triacetin is limited. The presence of water, shifting equilibrium and weakening the catalyst acid strength, as well as the acetylation of the hydroxyl groups contributes for this result. Calculations suggest [22] that acetylation with acetic acid is an endothermic process, requiring high energy demand for the introduction of the third acetyl group to form triacetin. In comparison, acetylation with acetic anhydride is exothermic, favoring formation of triacetin.

In present work demonstrates the application of Na impregnated CaO as solid catalyst for the esterification of glycerol with acetic anhydride.

1.2 LITERATURE REVIEW

Glycerol is a triol and its all three hydroxy groups can be functionalized. Glycerol is the byproduct of biodiesel produced by transesterification of vegetable oils with methanol or ethanol, under base catalysis conditions[23]. Under base catalyst conditions [23], or even acid catalysis [24], in the presence of methanol, there occurs formation of three methyl esters of fatty acid molecules, which are the biodiesel themselves, releasing glycerol as by-product (Scheme 1).



Scheme1. Biodiesel production from the transesterification of vegetable oil.

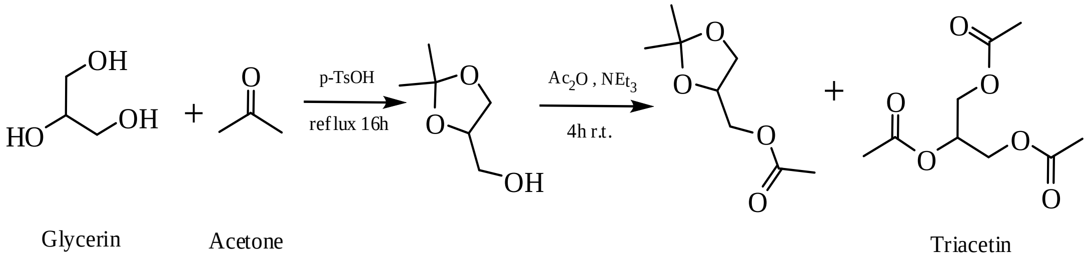
Acetylation of glycerol can also be a good alternative for the glycerol produced from biodiesel. The mono, di and triacetyl esters have great industrial applications. The triacetylated derivative the triglyceride 1,2,3 triacetoxypropane is more generally known as triacetin and glycerin triacetate. It is the ester produced from the esterification of glycerol .The various applications of triacetin are as follow [25-28] :

- Antifungal agent in external medicine.
- Food additive (e.g. butter) - E1518.
- Potential green solvent and fuel additive.
- Component of casting liquor used as a plasticizer and solvent.
- Plasticizer applied to the cigarette filter.
- Flavor and essence fixative and lubricate in cosmetics.
- Excipient in pharmaceutical products as a humectant, a plasticizer and a solvent.
- Fuel additive as an antiknock agent which can reduce engine knocking in gasoline.
- Fuel additive to improve cold flow and viscosity properties of biodiesel.
- It is used as a gelatinizing agent in explosives.

There are various methods, which are used for Triacetin synthesis. A brief description of each method is given below:

Production of triacetin using glycerol,acetone and acetic anhydride

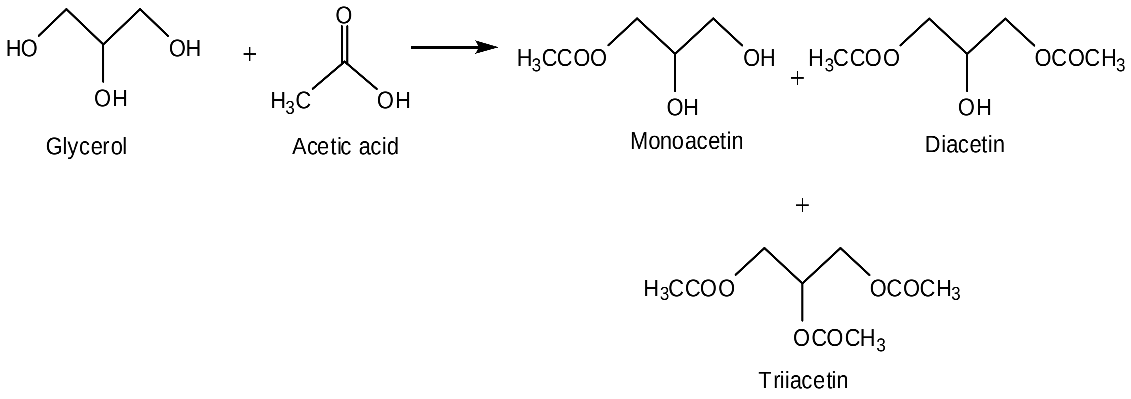
Acetal 1 (2,2dimethyl-1,3-dioxolan-4-yl)methanol was obtained by mixing glycerol, acetone with p-toluene sulphonic acid and refluxing the mixture for 6h.The reaction was stopped by adding Na_2CO_3. Acetal 2 (2,2dimethyl-1,3dioxolan-4-yl) methyl acetate was obtained by reacting 1 with acetic anhydride and triethylamine at room temperature for 4 hours. The reaction yields a mixture of acetal 2 and triacetin **(Scheme 2).**



Scheme 2. In first step: Glycerin is refluxed with Acetone to give Acetal 1 (2,2dimethyl-1,3-dioxolan-4-yl)methanol. In second step Acetal 1 reacts with acetic anhydride and triethyl amine to produce a mixture of Acetal 2 (2,2dimethyl-1,3dioxolan-4-yl) methyl acetate and triacetin. The reaction mixture was dissolved in ethyl acetate and washed with a saturated solution of $NaHCO_3$, water and brine and dried over anhydrous $MgSO_4$, and the solvent was evaporated in the rotary evaporator. The average share of triacetin produced was determined by nuclear magnetic resonance(NMR) spectroscopy[19].

Production of triacetin using glycerol and acetic acid

Glycerol reacts with acetic acid and give multiple products: Monoacetin, Diacetin and Triacetin. This reaction gives water as a byproduct **(Scheme 3).**



Scheme 3. Esterification of glycerol with acetic acid to give monoacetin, diacetin and triacetin.

Production of triacetin using glycerol and acetic acid in the presence of various solid acid catalysts is given in **Table 1**

Table 1. Production of triacetin using glycerol and acetic acid in the presence of various solid acid catalysts

Catalyst	**Triacetin yield**	**Conditions**	**References**
Ion exchange resin (Amberlyst-15 and 35),v $MgSO_4$	87%	temperature~30°C Reaction time, 72h	[29]
Phosphotungstic acid	84.6%	Temperature136-155°C Reaction time 7h	[30]
Amberlyst-15	Above 95%	Temperature 80°C Reactive chromatography	[31]
$Fe_2O_3/S_2O_8^{2-}/La^{3+}$ solid superacid	93%	Glycerol/AA=1:6 Catalyst/reactant=3.3wt%	[32]
heteropolyacid	97.2%	-	[33]
SO_4^{2-} / ZrO^{2-} / TiO_2	93.6%	Temperature 130°C	[34]
H_2SO_4,ion exchange resin (Amberlyst-15 and36)	~100%	Temperature100-140°C Excess AA and acetic anhydride	[35]
Sulphonic acid	Combined diacetin and triacetin yield 80%	temperature125°C	[36]
Amberlyst-15	41%	Temperature100-150°C Pressure 65-100 bar In supercritical CO2	[37]
Niobic acid supported tungstophosphoric acid	98%	Temperature 120°C Reaction time 4h Glycerol to AA ratio 1:5	
without catalyst	triacetin yield 83%	temperature, 100-130 °C, pressure, 20-50 mmHg	[38]
without catalyst glycerol/AA) 1:4	triacetin yield 35%	pressure, 1070 kPa; temperature, 120-160 °C	[39]
dodecamolybdophosphoric acid (PMo) encaged in USY zeolite	triacetin yield very low (4%)	different PMo loading (0.6-5.4 wt %) checked	[40]

Entrainer –Based Reactive Distillation for Esterification of Glycerol with Acetic Acid

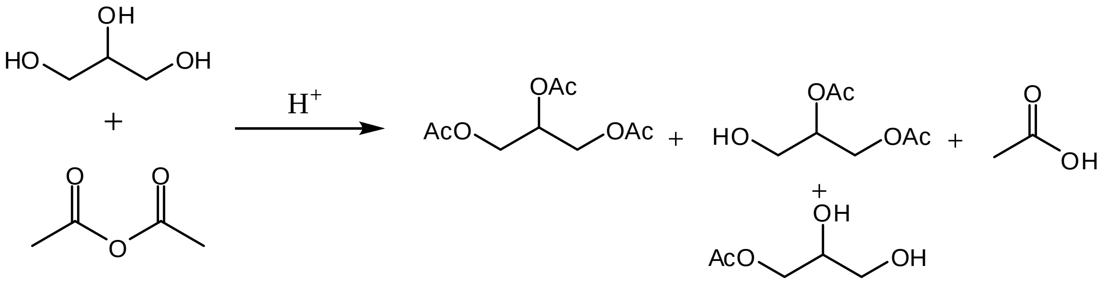
The applicability of reactive distillation for esterification of glycerol with acetic acid in the presence of Amberlyst-15 as catalyst and ethylene dichloride (EDC) as an entrainer is evaluated through experiments and simulation. The reaction is studied in both semibatch and continuous reactive distillation systems. The effect of different parameters such as entrainer amount, catalyst loading, and reboiler duty is studied. The results indicate that entrainer-based semibatch reactive distillation can enhance the selectivity toward triacetin to about 100%, which is much greater than that offered by any conventional reactor with stoichiometric mole ratio of reactants. Simulations for both semibatch and continuous reactive distillation are performed, and results agree reasonably well with those obtained by experiments. The best possible design and operating parameters are obtained through detailed simulation using an experimentally validated model. A column configuration is recommended for a continuous process [41].

Advantages of Entrainer-based semibath reactive distillation

1. It enhances the selectivity towards triacetin to about 100%
2. It keeps the reactive zone temperature below the thermal stability limit of catalyst i.e. reaction temperature below 120°C
3. It increases the efficiency of water removal.

Catalytic Acetylation of glycerol with Acetic anhydride

In this the acetylation of glycerol with acetic anhydride using different solid acid catalysts was studied. The results indicated that at 60 °C, zeolite Beta and K-10 Montmorillonite showed 100% selectivity to triacetin within 20 min, with a molar ratio of 4:1. Amberlyst-15 acid resin yielded 100% triacetin after 80 min, whereas niobium phosphate gave diacetin and triacetin in 53% and 47% selectivity, respectively. All catalysts were more selective to triacetin than the uncatalyzed reaction. By contrast, zeolite Beta gave poor yield of triacetin when acetic acid was used as acetylating agent. The different behavior was explained in terms of the stabilization of the acylium ion intermediate. The reaction of glycerol with acetic anhydride is shown in **Scheme 4** [42].



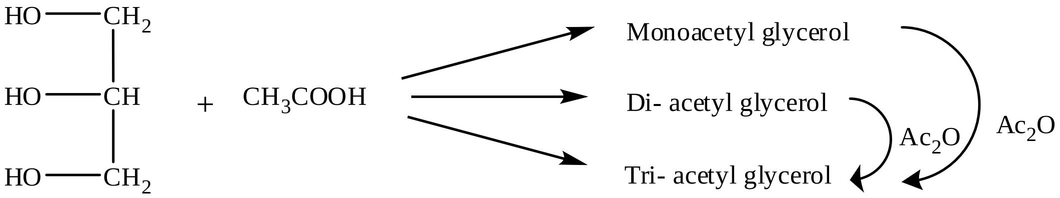
Scheme 4. Acetylation of glycerol with acetic anhidride.

Producing Triacetin with glycerol by two steps: Esterification and acetylation

A two-step method is proposed to obtain high selectivity and high conversion rate for producing additive triacetylglycerol of biofuel from its byproduct glycerol. The esterification of glycerol with acetic acid was carried out over resin and zeolites. Amberlyst-35 was found to be an excellent catalyst. The reaction conditions were optimized by testing catalysts, temperatures, feedstock ratios as well as loads of catalysts.

The esterification reaction was carried out in a round bottomed glass flask (100 cm3) fitted with a water cooled condenser. The temperature was maintained using an oil bath connected to a thermostat. The reactants glycerol and acetic acid were taken directly into the round bottomed ask along with the catalyst. The reaction mixture was continuously stirred during the reaction using a magnetic stirrer. The reaction was carried out for a definite period of time after which the catalyst separated from the reaction mixture by filtration. After the optimal conditions were chosen, the quantitative acid anhydride was added drop by drop when the conversion of glycerol reaches almost 100% in 1 h as shown in **Scheme 5** [43].

The reaction showing the two step process is as follow:



Scheme 5. Reaction for two step process showing the complete conversion of glycerol into Tri-acetyl glycerol.

The optimal conditions are temperature of 105 °C and an acetic acid to glycerol molar ratio of 9:1 with 0.5 g catalyst. After the 4 hour reaction of the optimal condition, the selectivity of triacetyl glycerol reaches almost 100% in 15 min by adding there to acid anhydride. Recycling experiments indicate that no significant deactivation of Amerlyst-35 occurred during the reaction[43].

CHAPTER 2

OBJECTIVES

1. To prepare 1.5wt% Na impregnated CaO as solid catalyst for the esterification of glycerol by wet impregnation method.

2. To synthesize triacetin from glycerol and acetic anhydride using prepared Na/CaO as solid catalyst

3. To synthesize triacetin from glycerol and acetic anhydride using homogeneous catalyst viz; triethyl amine.

CHAPTER 3

MATERIALS AND METHODS

3.1 CHEMICALS

Glycerol , Acetic Anhydride , Sodium Hydroxide , Triethyl Amine(99.5%), hexane, ethyl acetate and silica gel for thin layer chromatography were obtained from Loba Chemie, India and used as such without further purification. Calcium oxide was obtained from Sigma Aldrich. All of them are of AR grade.

3.2 INSTRUMENTS

FTIR spectra were recorded using Attenuated Total Reflectance (ATR) accessories in the range 600-4000cm^{-1} on a Thermo Scientific Spectrophotometer.

Powder X-ray diffraction (XRD) patterns were recorded on a Panalytical’s X’Pert Pro with using monochromatic CuKα radiation (λ=1.54060 Å) in Thapar University, Patiala. Data were collected over a 2θ range of 5–80° with a step size of 0.0260° at a scanning speed of 2°/min. at an accelerating voltage of 45 kV and current of 40 mA.

Field emission scanning electron microscopy (FESEM) was performed on JEOL JSM 6510LV to collect the SEM images of the catalysts.

Fourier transform-nuclear magnetic resonance (FT-NMR) spectra of triacetin was recorded on a Bruker Avance-II (400 MHz) spectrophotometer.

3.3 CATALYST PREPARATION

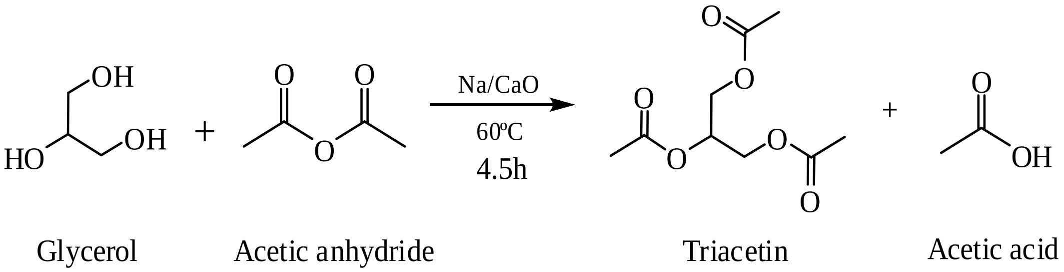
Sodium impregnated CaO as solid catalyst was prepared by the wet impregnation method as reported in the literature [24] with a slight modification. In a typical preparation, 5 g of calcium oxide was suspended in 20 mL of deionized water, and to this 10 mL of aqueous NaOH solution (0.130425g) concentration was added. The resulted slurry was stirred for 3h, then evaporated to dryness, and heated at 200 °C for 24 h. The catalyst so prepared was represented as 1.5-Na/CaO, and characterized by X-ray diffraction and scanning electron microscopic techniques.

CHAPTER 4

ESTERIFICATION OF GLYCEROL USING HOMOGENEOUS AND HETEROGENEOUS CATALYST

4.1 ESTERIFICATION RECTION USING HETEROGENEOUS CATALYST

Esterification of glycerol with acetic anhydride was performed in two necked, 100ml round bottom flask equipped with water cooled condenser, magnetic stirrer and oil bath. Glycerol (2g, 0.0434782mol), acetic anhydride (8.22ml, 0.1739128mol) in a 1:4 molar ratio and 1.5-Na/CaO catalyst (80mg) added to the round-bottom flask and the reaction mixture was refluxed upto 60ºC for 4.5h as shown in **scheme 6**.



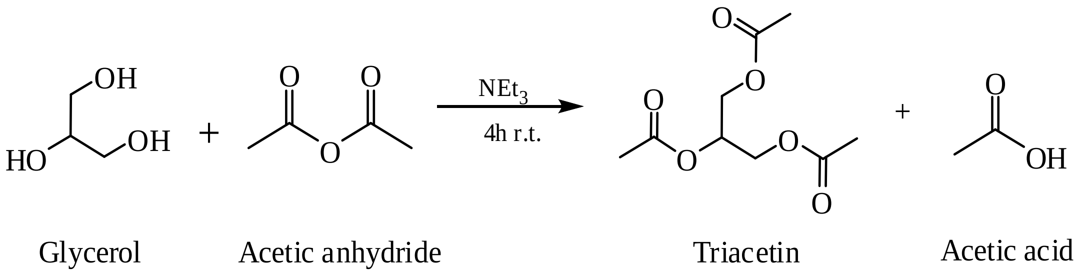
Scheme6. Glycerol reacts with acetic anhydride in the presence of Na/CaO at 60°C for 4h 30 min to give triacetin.

Samples from the reaction mixture were withdrawn after every 30 min with the help of glass capillary and subjected to the thin layer chromatography using Hexane/Ethyl acetate (6:4,v/v) as mobile phase and silica gel on glass plate as stationary phase.

After the completion of the reaction, the catalyst was separated from the reaction mixture by centrifugation at 9000 rpm. The reaction mixture thus obtained was heated at 110ºC to remove the acetic acid and triacetin thus obtained was further characterized by FT-IR and proton NMR techniques.

4.2 ESTERIFICATION REACTION USING HOMOGENEOUS CATALYST

Esterification of glycerol with acetic anhydride was performed in two necked, 100ml round bottom flask equipped with water cooled condenser, magnetic stirrer and oil bath. Glycerol (1g, 0.0434782mol), acetic anhydride (4.11ml, 0.0869564 mol) in a 1:4 molar ratio and triethyl amine (6.244ml, 0.0434784 mol) added to the round-bottom flask and the reaction mixture was refluxed at room temperature for 4h as shown in **scheme 7.**



Scheme 7. Glycerol reacts with acetic anhydride in the presence of triethyl amine for a time period of 4h to give triacetin.

Samples from the reaction mixture were withdrawn after every 30 min with the help of glass capillary and subjected to the thin layer chromatography using Hexane/Ethyl acetate (6:4,v/v) as mobile phase and silica gel on glass plate as stationary phase.

After the completion of the reaction, the reaction mixture was washed with water to remove acetic acid formed and triethyl amine as they are soluble in water. The lower triacetin layer is separated and triacetin thus obtained was further characterized by FT-IR and proton NMR techniques.

4.3 CHARACTERIZATION OF CATALYST

Characterization of the catalyst 1.5-Na/CaO was done by X-ray diffraction and scanning electron microscopic techniques.

4.3.1 XRD STUDIES:

Powder X-ray diffraction studies of CaO and Na impregnated (1.5 wt %) CaO have been performed, and comparisons of XRD patterns are given in Figure 2. The intense peaks at 2θ ~ 37.34, 53.93, and 32.23 correspond to the d-values of 2.39, 1.69, and 2.75, respectively, of calcium oxide in cubic form, while peaks at 2 θ ~34.18, 18.16, and 47.18 correspond to d-values of 2.63, 4.92, and 1.92, respectively, of calcium hydroxide in hexagonal form as shown in Fig. 2.

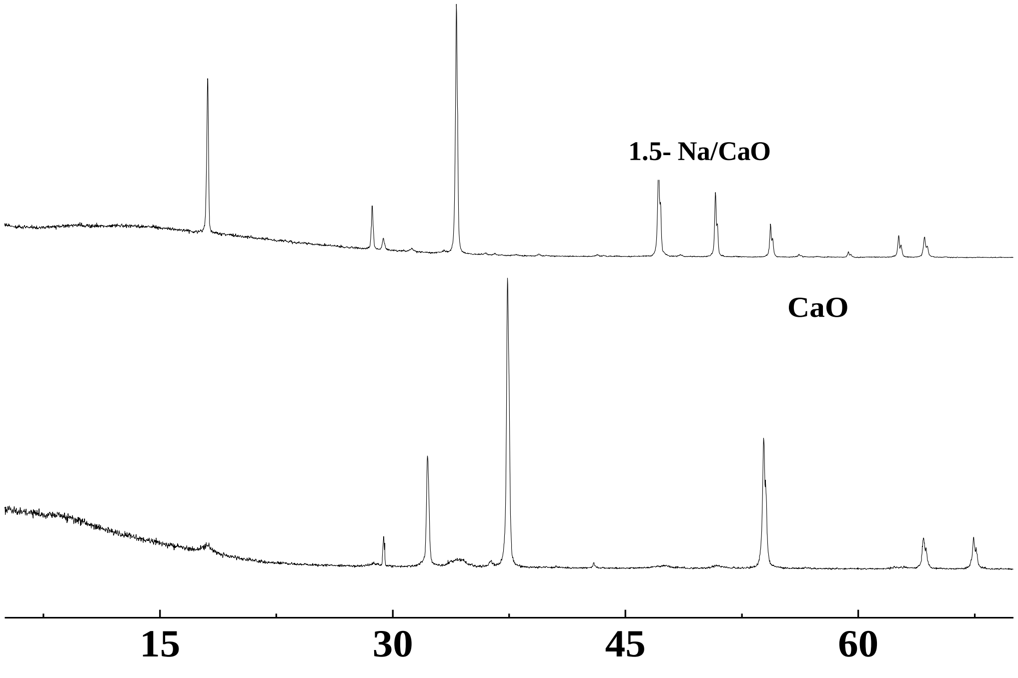


Fig.2 Comparison of powder XRD patterns of commercially available CaO with 1.5-Na/CaO.

4.3.2 SEM STUDIES:

The surface morphology of the 1.5-Na/CaO catalyst has been investigated by scanning electron microscopy shown in **Fig. 3.** The shape of the particles was found to be oval or irregular. The average size of catalyst particles by FESEM studies were found to be ~ 2µm.

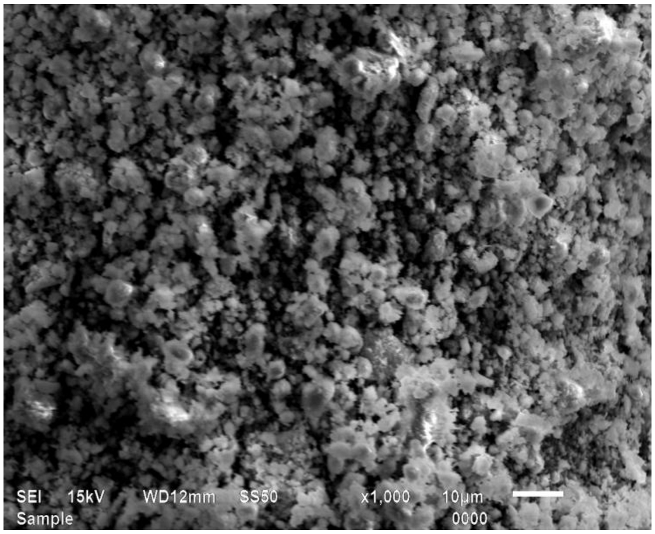


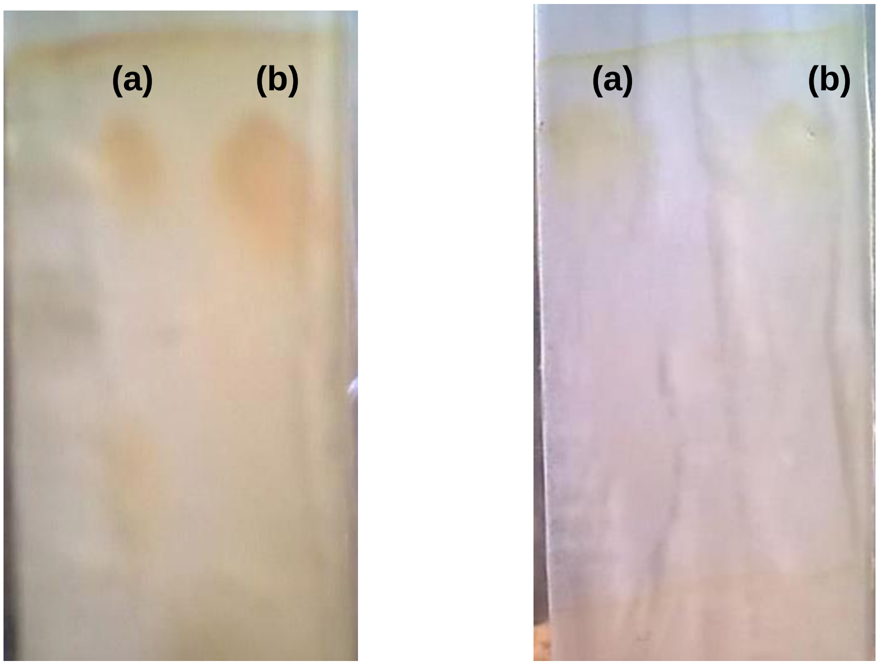
Fig. 3 SEM image of 1.5 - Na/CaO

4.4 CHARACTERIZATION OF TRIACETIN:

Triacetin produced by the esterification of glycerol with acetic anhydride using heterogeneous 1.5 - Na/CaO or homogeneous, triethyl amine catalyst was characterized by thin layer chromatogphy, FT-IR and proton NMR spectroscopic techniques.

4.4.1 TLC STUDIES

The progress of the reaction and primary characterization of the products were carried out by thin layer chromatographic (TLC) technique using hexane/ethylacetate (6:4,v/v) as the mobile phase and silica gel as the stationary phase on glass plate. TLC analysis of triacetin product formed, triacetin standard is as shown in figure 4.



(A) **(B)**

Figure 4. (A) TLC analysis of (a) triacetin formed in the esterification reaction using catalyst 1.5-Na/CaO(b) triacetin standard .**(B)** TLC analysis of (a) triacetin formed in the esterification reaction using catalyst triethyl amine(b) triacetin standard

The appearance of the triacetin spot in the product formed at R_f value 0.81 corresponding to the standard triacetin spot of the standard triacetin spot support formation of triacetin .

4.4.2 FT-IR STUDIES

FT-IR spectra of triacetin synthesized using 1.5-Na/CaO catalyst or triethyl amine were compared with commercial triacetin and shown in Fig.6. The appearance of peak at ~ 1740 cm^{-1} supports the presence of carbonyl group in triacetin.

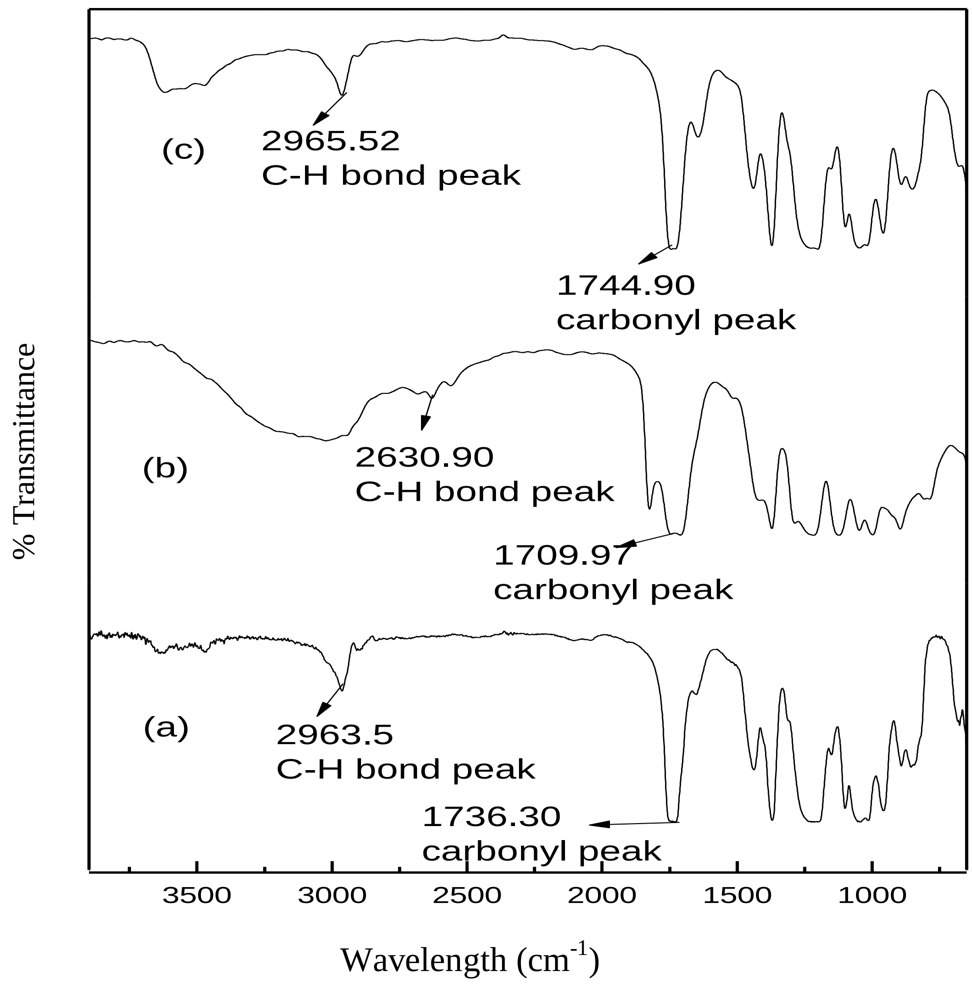


Figure6. FT- IR spectra of: (a) Triacetin pure (b) Triacetin obtained using Na/CaO as catalyst (c) Triacetin obtained using triethyl amine as catalyst

4.4.3 PROTON NMR STUDIES:

Triacetin produced during the esterification reaction of glycerol with acetic anhydride using catalyst 1.5- Na/CaO or triethyl amine was characterized by ^{1}H NMR spectroscopy as shown in fig.7. The peak in ^{1}H NMR spectrum of triacetin at ~ 2ppm is due to methyl ($-CH_3$) protons of triacetin. Multiplet at ~ 4.1ppm is due to $–CH_2$- protons and at 5.1ppm is due to single proton on methine carbon.

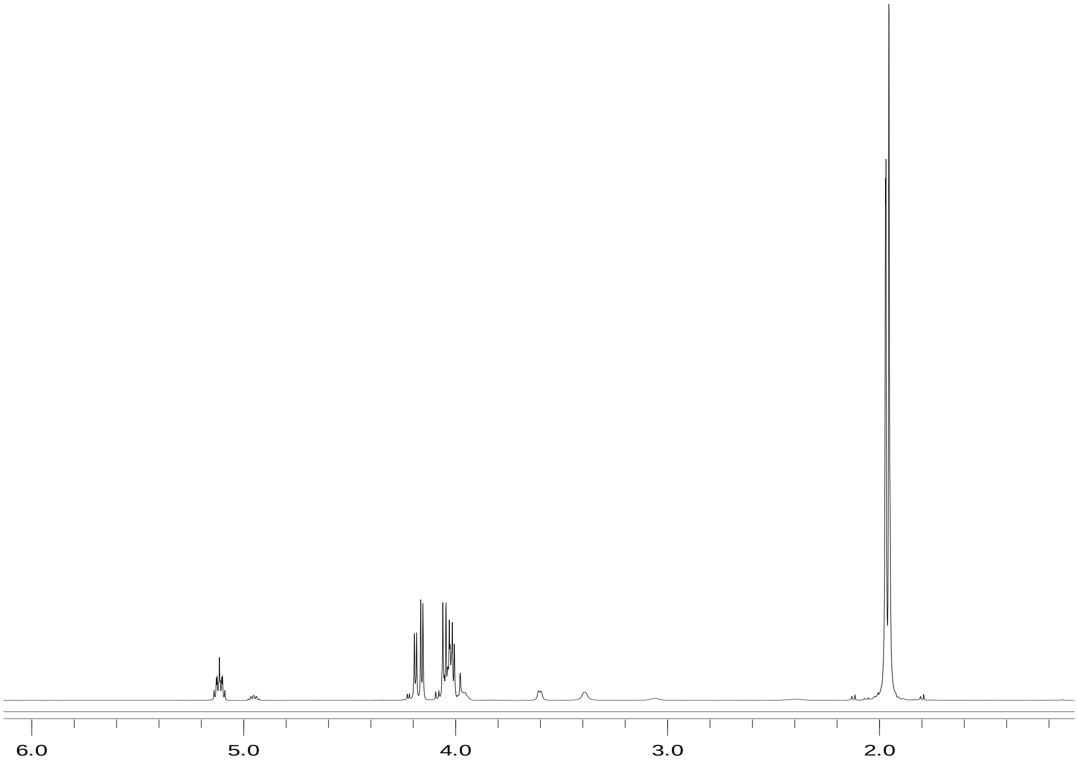


Fig.7 Proton NMR spectra of triacetin produced by the esterification of glycerol with acetic anhydride using triethyl amine or 1.5-Na/CaO as catalyst.

CHAPTER 5

CONCLUSIONS

CONCLUSIONS

The present work demonstrates the preparation of sodium ion impregnated CaO and its characterization by powder investigation and SEM studies. The powder X - ray diffraction study supports the formation of hexagonal calcium hydroxide after wet impregnation of sodium ions. The SEM study support the existence of Na/CaO particles in oval and irregular shape with average particle size of ~ 2µm. The prepared Na/CaO has been used as solid catalyst for the esterification of glycerol to yield triacetin. The catalyst, 1.5-Na/CaO required 4.5 h for the complete esterification of the glycerol utilizing acetic anhydride to triacetin molar ratio of 1:4 at 60 ºC. Same reaction has also been performed in the presence of homogeneous catalyst, triethyl amine, which required 4 h to yield complete conversion of glycerol into triacetin at room temperature. The triacetin synthesized has been characterized by proton NMR and FTIR studies. Although homogeneous as well as heterogeneous catalyst were found to yield the triacetin from glycerol, but solid catalyst could be more promising owing to its ease of separation from the reaction mixture.

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