STUDIES ON CETANE NUMBER AND LUBRICITY OF ADDITIVES FROM VEGETABLE OILS

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by

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मै की हा की हस्ती मेरी आप करे ते मेरा नाम|
अवतार मेरे ते सत्गुर तुट्ठै सुण लेवे बेशक कुल जहा||

|| **सम्पूर्ण अवतार वाणी** ||

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Dinesh Kumar

CERTIFICATE

This is to certify that thesis entitled "STUDIES ON CETANE NUMBER AND LUBRICITY OF ADDITIVES FROM VEGETABLE OILS", being submitted by Mr. Dinesh Kumar, to the School of Chemistry and Biochemistry, Thapar University, Patiala for the award of degree of DOCTOR OF PHILOSOPHY, is a record of bonafide research work carried out by him. Mr. Dinesh Kumar has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results embodied in the thesis have not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

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List of Abbreviations

Abbreviation	Description
ACE	Analysis, Comparison, Evaluation
amu	Atomic mass unit
APcI	Atmospheric pressure chemical ionization
ASTM	American Society for Testing and Materials
BCN	Blending cetane number
BET	Brunauer- Emmett-Teller
BJH	Barret-Joyner-Halenda
Cetol E	2-Ethoxyethyl nitrate
CFAMEs	Fatty acid methyl ester derived from castor oil
CFR	Co-operative Fuel Research
CN	Cetane number
cm	centimetre
cSt.	Centistokes
DRS	Diffuse reflectance solid state
DTBP	di-*tert*-butylperoxide
EDX	Energy Dispersive X-ray
EHN	2-ethylhexyl nitrate
EI-MS	Electron impact mass spectrometry
ESI	Electrospray ionization
FAMEs	Fatty acid methyl esters
FAACO	Fatty acid amide derived from castor oil
FAAML	Fatty acid amide derived from methyl laurate
FAAMM	Fatty acid amide derived from mutton fat derived FAMEs
FAAUC	Fatty acid amide derived from used cotton seed oil
FAEMO	Epoxidized derivative of methyl oleate
FAEUC	Epoxidized derivative of used cotton seed oil
FAEUM	Epoxidized derivative of used cotton seed oil derived FAMEs
FANCM	Nitrate derivative of castor oil derived FAMEs
FESEM	Field emission scanning electron microscope
FFAs	Free fatty acids
FTIR	Fourier transform infra red
FT-NMR	Fourier transform nuclear magnetic resonance
HFRR	High Frequency Reciprocating Rig
IUPAC	International Union of Pure and Applied Chemistry
JCPDS	Joint Committee on Powder Diffraction Standards
KOMe	Potassium methoxide
MeOH	Methanol
MFAMEs	Fatty acid methyl esters derived from mutton fat
mg	Milligram
MHz	Mega hertz

mL	Milli litre
min	minute
MO	Methyl oleate
mol	mole
m/m	Mole by mole
m/z	Mass to charge ratio
N_2	Nitrogen
NaOMe	Sodium methoxide
nm	nanometre
NMR	Nuclear magnetic resonance
NO*x*	Nitrogen oxides
ppm	Parts per million
TEM	Transmission electron microscope
tert	tertiary
TLC	Thin layer chromatography
UFAMEs	Fatty acid methyl esters derived from used cotton seed oil
UV	Ultra violet
v/v	Volume by volume
Vis	visible
w/w	Weight by weight
wt%	Weight percentage
XRD	X-ray diffraction

List of Symbols

Symbol	Description
Å	Angstrom
α	Alpha
°	Degree
K	Principal quantum number 1
K	Kelvin
k	Rate constant
%	percentage
μ	Micro
θ	Theta
R_f	Retention factor
t	Time
W	Watt
ν	Frequency
g	Gram
m	Metre
H_	Basic strength

Abstract

The present work envisaged to synthesize, characterize and evaluate the dual functional diesel additives from the vegetable oils using heterogeneous catalyst. Mainly three different types of solid catalysts have been prepared viz., Li/CaO, Ni/CaO and Ti/SiO_2 and characterized by various spectroscopic and analytical techniques (powder XRD, BET surface area, FESEM, TEM and Hammett indicator studies). The Li/CaO has been used for the transesterification of a variety of triglycerides viz., used cotton seed, soybean, jatropha, castor, karanja oil and mutton fat. The prepared fatty acid methyl esters (FAMEs) of cotton seed, jatropha and karanja oil have been used as substrate for the aminolysis reaction with diethanolamine in order to prepare the fatty acid amide derivatives using Ni/CaO as solid catalyst. The resulted amide derivatives being having long hydrocarbon chain and amide group, are expected to improve the lubricity as well as cetane number of the diesel fuel. The vegetable oil derived fatty acid esters have unsaturation (-CH=CH-) in hydrocarbon chain and in order to prepare lubricity improvers for high temperature applications the -CH=CH- have been epoxidized using Ti/SiO_2 as solid catalyst. All the prepared catalysts have also been reused successfully several times. The fatty acid methyl esters derived from castor oil has –OH group at C-12 position, and same has been nitrated with the help of nitric acid and acetic anhydride. All vegetable oil derivatives have been well characterized by FT-IR, proton NMR and in few cases mass spectroscopic studies.

Finally the nitrate derivative of castor oil derived FAMEs and amide derivative of used cotton seed oil were tested as dual functional diesel fuel additives and their cetane number and lubricity improver properties has been evaluated. The nitrate derivative was found to improve the cetane number of the base diesel fuel from 52.4 to 56.0 and lubricity from 458 to 152 µm. While, the amide derivative was found to improve the cetane number of the base diesel fuel from 52.4 to 56.0 and lubricity from 458 to 143 µm. The epoxidized derivative of used cotton seed oil derived FAMEs has been evaluated as lubricity improver only, and found to improve the lubricity of base diesel fuel from 458 to 115 µm.

Keywords: Transesterification, aminolysis, nitration, triglycerides, cetane number, lubricity improvers, powder X-ray diffraction, BET surface area, N_2 adsorption desorption isotherm, field emission scanning electron microscope, transmission electron microscope, and ^{1}H & ^{13}C nuclear magnetic resonance.

Chapter 1

Introduction and Literature Review

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Abstract

A brief introduction about diesel fuel additives with special emphasis on literature reported cetane number and lubricity improvers has been discussed in this chapter. In order to improve the diesel fuel quality and to achieve the better performance from the diesel engines, the application of diesel fuel additives are necessary. The cetane number improvers which are available at commercial level include 2-ethylhexylnitrate (EHN) and di-*tert*-butylperoxide (DTBP) and lubricity improvers mainly consists long chain hydrocarbons and fatty acid esters. The use of naturally occurring triglyceride derived nitrate and amide derivatives have also been reported in literature as cetane number improvers. The synthesis of vegetable oil derived lubricity improvers utilizes the peracid process, which involve the application of concentrated acids (e.g., formic and sulfuric acid) and hydrogen peroxide. Very few studies have been reported in the literature related with the preparation of dual functional diesel fuel additives from vegetable oils using solid catalysts.

Keywords: Cetane number improvers, lubricity improvers, transesterification, aminolysis, epoxidation, nitration, dual functional diesel fuel additives.

1.1 Introduction

Diesel fuel play an important role in the economy of a country as diesel engines are used in agriculture, transportation and industries and their demand is increasing steadily. It contributes to the prosperity of the worldwide economy since it is widely used due to high combustion efficiency, reliability, adaptability and cost-effectiveness. Diesel engines generally run with fossil diesel fuel and hassle free operation of the engine required premium quality diesel fuel. The five properties that are most commonly associated with premium quality diesel fuel are; energy contents, cetane number, fuel injector cleanliness, low temperature operability and thermal stability (Suppes et al., 2001c). Although lubricity is not listed as one of the five "premium" properties, distributors of diesel products recognize lubricity as a sixth and very important diesel fuel property.

While cetane number improvers increases the ignition quality of diesel fuel, lubricity improvers are extremely important to minimize the wear between close tolerance metal on metal moving parts in diesel fuel injectors. A single compound upon addition with diesel fuel, when improves more than one of these six properties is known as multifunctional diesel additive and is of great value and economic interest (Suppes et al., 2003)**.**

As per BHARAT IV (equivalent to EURO IV and implemented since April 2010) norms for diesel fuel, cetane number should be higher than 51, the wear scar diameter should be less than 460 μm, and sulfur content should also be less than 50 ppm. Formerly, the lubricity was provided by natural components in the diesel fuel viz., sulphur, aromatics and other heterocyclic polar compounds (Kajdas and Majzner, 2003; Spikes et al., 1997). Due to environmental protection and human health reasons, the sulphur contents in diesel should be less than 10 ppm as per the European Union norms implemented in 2010. It has become generally accepted that the reduction of sulfur in diesel fuel is also accompanied by a reduction in polar oxygenated compounds and polycyclic aromatics including nitrogen containing compounds. These compounds are usually responsible for imparting the boundary lubricity to the diesel fuel and hence, desulphurization is also accompanied with reduction of diesel fuel lubricity. Thus, it would be desirable to add appropriate lubricity improver in diesel fuel to attain the prescribed lubricity.

1.2 Diesel fuel additives

1.2.1 Cetane number

Cetane number is a measure of the ignition quality of a diesel fuel, often mistaken as a measure of fuel quality, refers to the time period between the start of injection and start of combustion (ignition) of the fuel (Challen and Barabescu, 1999; Ulrich, 1994). In a particular diesel engine, higher cetane fuels will have shorter ignition delay periods than lower cetane fuels. Improved ignition (shorter ignition delay time) has been directly correlated with faster start up in cold weather, reduced emissions of nitrogen oxides (NO*x*), and smoother engine operation (Bacha, 1998).

Cetane or hexadecane ($C_{16}H_{34}$) as shown in Figure 1a, have been assigned arbitrarily a cetane number of 100 while alpha-methyl naphthalene as shown in Figure 1b was assigned a cetane number of zero.

Figure 1. Chemical structure of (a) cetane and (b) alpha-methyl naphthalene.

All other hydrocarbons in diesel fuel are indexed to cetane as to how well they ignite under compression. Since there are hundreds of components in diesel fuel, with each having a different cetane quality, the overall cetane number of the diesel is the average cetane quality of all the components (Heywood, 1988; Owen, 1995).

1.2.2 Cetane Number Improvers

Cetane number improver is specialty chemical that, when added to diesel fuel, enhance the cetane number of the diesel fuel. Alkyl nitrates having a carbon-to-nitrogen ratio greater than 5 tend to provide best cetane improver performance (Robbins et al., 1951; Ladommatos et al., 1996). The following fuel properties were also found to be improved by the addition of cetane number improvers in trace quantities (50-100 ppm):

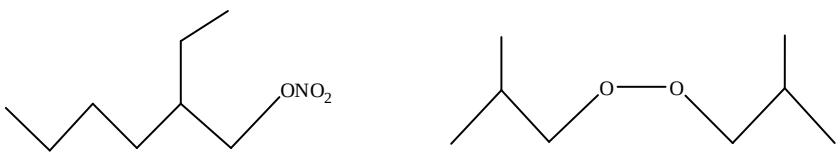
i. High cetane number fuel burn with a shorter ignition delay and lower peak pressure.
ii. High cetane number fuel typically burn with less smoke and odor.
iii. Cold temperature starting is improved with high cetane number fuels.

iv. The emission of CO and NOx were found to reduce in high cetane number fuel.

v. High cetane number fuel increases the engine life and causes the less diesel noise.

The efficiency of the cetane number improver is attributed to their ability to contribute and assist in free radical generation during the ignition (Clothier et al., 1993).

Cetane number improvers are added to diesel fuel at concentrations in the range of 0.1-0.25 % (v/v). They found to decrease the ignition delay time by directly or indirectly affecting the free-radical ignition process (Clothier et al., 1993). Commercially available cetane number improvers either have nitro viz., 2-Ethylhexylnitrate, EHN (Figure 2a) or ether functional group viz., di-*tert*-butylperoxide, DTBP (Figure 2b) as both functional groups are known to yield free radicals quite readily. Addition of 0.1 % (v/v) of these compounds were found to boost the cetane number of diesel fuel by 5 units (Ladommatos et al., 1996).



(a) **(b)**

Figure 2. Molecular structure of (a) 2-ethylhexylnitrate (EHN) and (b) di-*tert*-butylperoxide (DTBP).

1.2.3 Mechanism of cetane improvers

Ignitions being a free radical process, the effectiveness of cetane number improvers are attributed to their ability to contribute and assist in free radical generation during ignition (Clothier et al., 1993). The homolytic cleavage of a nitro bond is thermally induced and followed by a cascade of additional free radicals. The alkyl group disintegrates to generate NO_2 and alkyl radicals that subsequently attack on diesel fuel to initiate the ignition process (Clothier et al., 1993). Within this proposed mechanism, and as observed in practice, the nature of the alkyl group and other functional groups on the alkyl structure tends to have a significant impact on performance. The nitrate groups cleave at a space and time in the stratified injection spray such that the corresponding free radicals, together with the free radicals of the fuel, are sufficient to promote quicker ignition. The nitrates must cleave neither too early (as is the case with molecules such as nitroglycerin) nor too late. In addition, the alkyl group should not have any group that could stabilize the alkyl radical

formed by the cleavage of the nitrate group e.g., aromatic rings are undesirable as they have the ability to stabilize free radicals.

A reported or hypothesized mechanism for improving cetane number of diesel fuel by cetane number additives (Clothier et al., 1993; Suppes et al., 1996) includes the following steps:

i. The decomposition of cetane number improvers into free radicals which react with the fuel-air mixture.
ii. The decomposition of cetane number improvers into gas-phase catalysts such as NO_2.
iii. Reactions between cetane number improvers and free-radical inhibitors found in the fuel to scavenge the later free-radical.

1.2.4 Diesel fuel cetane number improvers

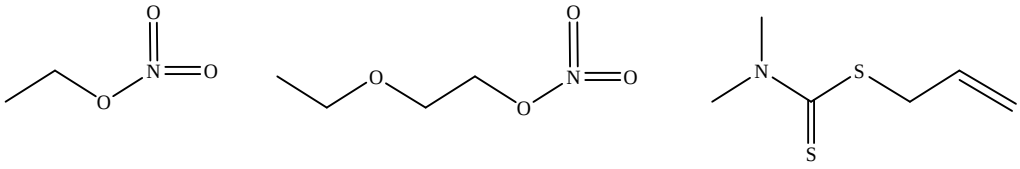
1.2.4.1 Commercially available cetane number improvers

2-Ethylhexylnitrate (EHN) dominates the cetane number improver market and replaced by di-*tert*-butylperoxide (DTBP) when nitrogen content in the fuel is high. However, EHN is corrosive in nature and its vapors are hazardous for human being. EHN volatilizes and explodes because of the combination of its low flash point and nitrate decomposition (Suppes et al., 2001c). On the other hand the application costs of DTBP are typically higher and are only considered when good alternatives are not available (Peckham, 1998).

1.2.4.2 Literature reported cetane number improvers

iso-octyl nitrate, di-nitro propane and isoamyl nitrate are the other organic cetane number improvers reported in literature (Suppes et al., 2001c). Suppes et al. (1997) also reported the cetane number improver properties of tetraethylene glycol and compared it with that of EHN. Jordan (2003) reported that cetane number of a fuel can be increased by mixing a fuel additive comprising beta carotene that was prepared in inert atmosphere. Smith et al. (1984) reported an improvement in the cetane number of diesel fuels by the addition of a small amount of dithiocarbamate or sulfonamide compounds viz., allyl N,N-dimethyldithiocarbamate (Figure 3c) and N,N-dimethyl-*t-butyl* sulfenyldithiocarbamate respectively. A gain in cetane number was achieved in the range of 1.8 to 7.6 depending upon the compound and the amount added in the diesel fuel.

Alkyl nitrites prepared from the byproducts of sugar industries (Chibber et al., 1986) were found to increase the cetane number by 9 units when added 0.6 % (v/v). A 2 % (v/v) addition of ethyl nitrate ($C_2H_5ONO_2$) as shown in Figure 3a could save 25 % fuel and increase the cetane number from 33 to 43-49. 2-ethoxyethyl nitrate (Cetol E) as shown in Figure 3b was derived from 2-ethoxyethanol (Desikan et al., 1979) and used as a cetane number improver. At a level of 0.3 % (v/v), 2-ethoxyethyl nitrate imparted a larger increase in cetane number along with improved cold-starting behavior of diesel fuels.

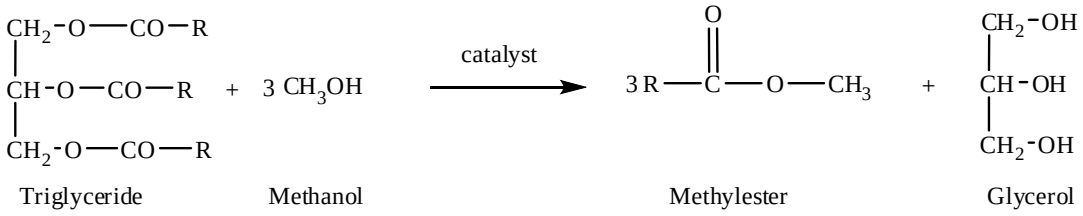


(a) **(b)** **(c)**

Figure 3. Chemical structure of (a) ethyl nitrate, (b) 2-ethoxyethyl nitrate and (c) allyl N,N-dimethyldithiocarbamate.

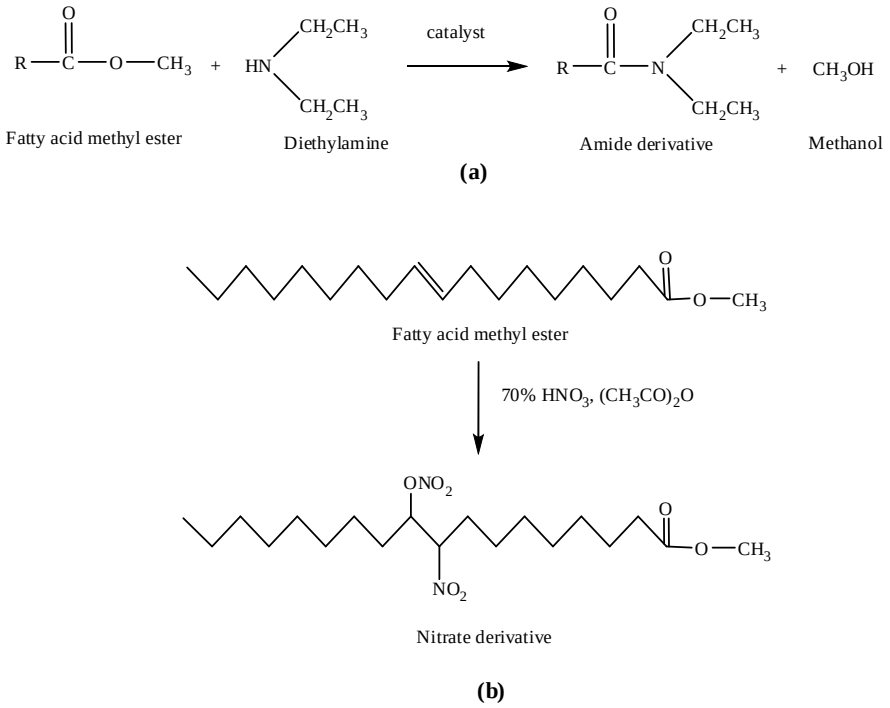
1.2.4.3 Fatty acid methyl esters

Fatty acid methyl esters used as diesel fuel substitute and could be prepared by the transesterification of triglycerides (vegetable oils and animal fat) as shown in scheme 1. Such fatty acid methyl esters also have the potential to act as diesel fuel additives (Sonntag et al., 1982) however, it has been reported that amide and nitrate derivative of such esters are significantly more effective in enhancing the ignition quality of the diesel fuel than pure esters (Stournas et al., 1995; Biermann et al., 1995).



Scheme 1. Transesterification of triglycerides.

The ester as well as –C=C– of the fatty acid methyl esters provide functional groups that can be converted into amides and nitrates (Alcantara et al., 2000; Stournas et al., 1995) groups, respectively, in high yields as shown in scheme 2.



Scheme 2. Reaction schemes of (a) aminolysis of fatty acid methyl ester and (c) nitration of fatty acid methyl ester derived from castor oil.

Fatty acid methyl esters can be prepared from a variety of triglycerides including vegetable oils, animal fats and waste greases in the presence of homogenous or heterogeneous catalyst (Ma and Hanna, 1999; De and Bhattacharya, 1999; Alcantara et al., 2000; Meher et al., 2006; Vicente et al., 2004). Homogenous acid catalysts viz., HCl and H_2SO_4 (Encinar et al., 2002; Rashid et al., 2008; Marinkovic and Tomasevic, 1998; Dorado et al., 2004) and base catalysts viz., NaOH, KOH, sodium methoxide and potassium methoxide (Sun et al., 2010; Serio et al., 2005; Aranda et al., 2008) have been used frequently at industrial scale for fatty acid methyl ester production as they catalyze the reaction at faster rate even at mild reaction condition. However, same catalyst yielded FAMEs and glycerol contaminated with catalyst and leads to the formation of soap if free fatty acids (FFAs) and moisture contents are greater than 0.5% and 0.3% (w/w) (Haas, 2004; Canakci and Gerpen, 1999), respectively. More recently, there has been an increased research activity directed towards the development of heterogeneous catalysts which has several advantages over homogeneous one viz., formation of uncontaminated products, is recyclable, has low sensitivity towards FFAs and moisture contents and not corrode the reaction vessel (Clark and Macquarrie, 1996; Tanabe et al., 1989).

A variety of heterogeneous catalysts for transesterification reactions were reported in literature, including, immobilized enzymes (Shah et al., 2004; Xie and Ma, 2010), calcium carbonate (Suppes et al., 2001a), sodium aluminate (Wan et al., 2009), sodium supported hydrotalcite (Hernandez et al., 2010), sodium loaded silica (Akbar et al., 2009), alkali-earth-metal compounds (Arzamendi et al., 2008), sulphated zirconia (Charusiri et al., 2006), tin compounds supported in ion-exchange resins (Cardoso et al., 2008), solid basic resin (Marchetti and Errazu, 2010), alkylguanidines heterogenized on organic polymers (Schuchardt et al., 1995; Schuchardt et al., 1996), alumina loaded with alkali metal salt (D'Cruz et al., 2007), alkali loaded MgO (Teng et al., 2009), alkali metal based mixed oxides (Singh and Fernando, 2009), potassium loaded TiO_2 (Salinas et al., 2010), potassium supported Ca-Al hydrotalcite (Gao et al., 2010), calcium based mixed oxides (Yap et al., 2011; Kim et al., 2011), calcium oxide loaded with lithium (Watkins et al., 2004; Kumar and Ali, 2010) and mixtures of Li-CaO and $Fe_2(SO_4)_3$ (Endalew et al., 2011).

1.2.4.4 Nitrate derivatives of fatty acid methyl esters

The nitrate derivative of fatty acid methyl esters derived from vegetable oil has the potential to act as cetane number improver and/or lubricity improver (Sonntag et al., 1982). The typical 14-18-carbon alkyl groups of the fatty acids potentially provide the straight-chain alkyl backbone of a nitrate. Poirier et al., (1995) reported cetane improvers comprising nitrate derivatives of tall oil fatty acids as shown in Figure 4.

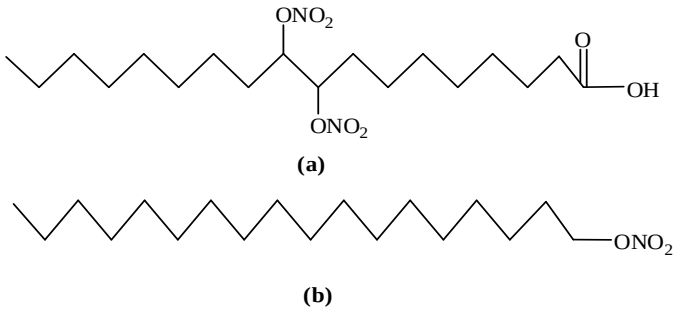


Figure 4. Literature reported nitrated fatty acid derivatives as cetane number improvers.

Anand et al. (2006) synthesized a number of transesterified and alkarylated derivatives of karanja, kusum, mohwa, mustard, castor and ratanjyot oils. Several esters of fatty acids of these vegetable oils were found to show high natural viscosity index, low pour points and high thermo-oxidative stability. The direct nitration of carbon-carbon double bonds in

vegetable oils yields a nitro functional group as shown in Figure 4. Whereas the nitrates promote desired ignition traits, the nitro groups do not promote an increase in the cetane number and potentially reduce the efficacy of the nitrate groups (Mason, 1999). Ricinoleic acid contains one internal alcohol group (Bockish, 1993) and this alcohol group can also be nitrated easily as shown in Figure 5, to yield the nitrate derivative of fatty acid ester.

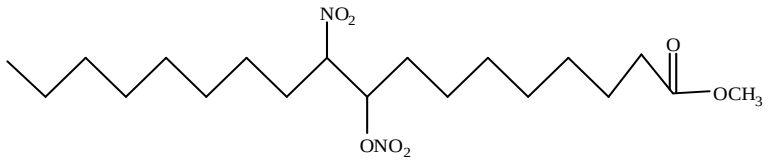


Figure 5. Nitrate derivative of soybean oil.

1.2.4.5 Amide derivatives of fatty acid methyl esters

The fatty acid amides have also been reported in literature (Biermann et al., 1995; Alcantara et al., 2000; Stournas et al., 1995) to enhance the ignition quality and other characteristics of the fuel and hence could be used as multifunctional diesel fuel additive. Alcantara et al. (2000) have reported the synthesis of amide biodiesel using soybean oil, used frying oil and tallow by amidation reactions with diethylamine in the presence of sodium methoxides catalyst. The amide biodiesel thus obtained was blended with petroleum diesel fuel to improve the ignition quality of later (Alcantara et al., 2000). Few methods are reported in literature for the synthesis of fatty acid amides viz., microwave assisted (Awasthi and Singh, 2009), lipase catalyzed (Zoete et al., 1996; Litjens et al., 1999; Levinson et al., 2005; Awasthi and Singh, 2007; Al-Mulla et al., 2010a) and chemically catalyzed (Al-Mulla et al., 2009; Hoidy et al., 2010; Al-Mulla et al., 2010b).

Fatty acid amides were synthesized from fatty acids with urea using *Candida antartica* lipase (Novozyme 435) as a catalyst at 60 °C for 48 h and atmospheric pressure (Awasthi and Singh, 2007). *Pseudozyma* (*Candida*) *antarctica* lipase B has been reported (Levinson et al., 2005) as catalyst for the fatty acid amide synthesis from ricinoleic acid and ammonia. The maximum conversion of 95% was obtained when reaction was carried out at 55 °C for 1 day.

The N, N' carbonyl difatty amides were synthesized by refluxing palm oil and urea using sodium ethoxide as a catalyst in the presence of ethanol at 78 °C for 8 h (Al-Mullah, 2009). Jorden and Port, (1961) reported conversion of *n*-butylamine and methyl stearate to *n*-butyl

stearamide using sodium methoxide as catalyst. Maag et al. (1984) suggested the preparation of desired diethanolamide and amine ester by reacting 2 mol of fatty acid and 1 mol of diethanolamine at 180 °C. Another method is based on the reaction of 2 mol of fatty acid with 1 mol of ethylenediamine at 180-185 °C during 6 h under nitrogen and with continuous removal of water (Mckenna, 1982).

Fatty alkanolamides are prepared from fatty acids or fatty methyl esters and alkanolamines, such as ethanolamine, by heating at 140–160 °C for 6–12 h (Feairheller et al., 1994; Shapiro, 1968). An alkanolamide was synthesized from laurel oil by employing this method; the reaction was completed in 9 h. Although a stronger base such as sodium methylate or sodium methoxide shortens the reaction time to 3 h and 1 h respectively (Monick, 1962; Kolancilar, 2004).

1.2.5 Measurement of cetane number and blending cetane number

The optical method for determining cetane number is ASTM test D-613 and this method requires the use of an industry standards test engine equipped with accepted instrumentation which operated under specific conditions. In this test, the engine compression ratio is varied for the test sample and reference fuels of known cetane number to obtain a fixed ignition delay. The compression ratio of the sample is bracketed by those of two reference fuels. The cetane number of the sample fuel is determined by estimating between the two reference fuel points. Because the ASTM D-613 or D-4737 test is time consuming and expensive, calculated cetane index is often substituted for cetane number. The calculated cetane index is derived from the fuel's density and boiling range. While useful for estimating the cetane number of distillate fuels, this technique cannot be applied to fuels containing additives that raise cetane number. These additives do not change the fuel density or distillation profile, so they do not alter the calculated cetane index.

Glavincevski et al., (1984) have shown the use of carbon type structural composition as derived from ^{1}H-NMR for determining the cetane index of fuels. Selucky et al., (1990) developed a method for calculating the cetane number using ^{1}H and ^{13}C-NMR spectroscopy. In this method, the ^{1}H NMR spectrum is divided into six or seven zones and the ^{13}C NMR spectrum into 13 zones, roughly corresponding to the distribution of various C types in both the aliphatic and aromatic regions. Fifty five fuel blends, prepared from six refinery streams, including syncrudes, were tested by the engine test. Their proton and carbon NMR

spectra were obtained and cetane numbers were correlated with cetane indexes, using conventional multiple regression and so called ACE method (Breiman and Friedman, 1985). Blending cetane number can be defined by the equation below:

$$CN_{fuel\ blend} = (1-x)CN_{neat\ fuel} + xBCN$$

Where x is the mass fraction of cetane improver added to the fuel (for application rates <0.02%).

The BCN of a compound depends on the molecular structure of the compound. Many trends in BCN follow known trends for CN (Suppes et al., 1999). Known impacts of alkyl structure on CN trends include the following:

i. Increased saturation increases the CN.
ii. Aromaticity significantly decreases CN.
iii. Increased branching decreases CN.
iv. Increased straight chain carbon number increases CN through C_{12}.

1.3 Diesel fuel lubricity improver additives

1.3.1 Lubricity

A lubricant (sometimes referred to "Lube") is a substance (often a liquid) introduced between two moving surfaces to reduce the friction and wear between them. A lubricant provides a protective film which allows for two touching surfaces to be separated and smoothed, thus lessening the friction between them. Lubricants contain 90% base oil (most often petroleum fractions, called mineral oils) and less than 10% additives. Diesel fuel lubricity is a term used to characterize the ability of the diesel fuel to lubricate the close-tolerance moving parts that rely on the lubricity of diesel fuel to minimize the maintenance related wear of diesel engine. Lubricity is extremely important to minimize wear between close tolerance metal-on-metal moving parts in diesel fuel injectors (Suppes et al., 2001b).

1.3.2 Lubricity Improvers

Lubricity improvers are substances that are added to carrier fuels for the purpose of lowering friction and/or reducing wearing during sliding (Lang et al., 2001). Lubricant

additives also deliver improved viscosity index, resistance to corrosion and oxidation, aging or contamination, e.g. two-stroke oil (2T oil). Lubricants perform several key functions viz., (i) keep moving parts apart (ii) reduce friction (iii) transfer heat (iv) carry away contaminants & debris (v) transmit power (vii) protect against wear (viii) prevent corrosion (ix) stop the risk of smoke and fire of objects (Inman, 2003). The standards for determining lubricity of fuel and lubricant are CEC F-06-A-96 and ASTM D6079-99 and high frequency test rig (HFRR) is designed to conduct these standards (Ladommatos et al., 1996). These standards recommend that wear scar should not be greater than 460 microns in diameter (Kajdas and Majzner, 2003).

The diesel fuel injector pumps depend on the fuel itself to show lubricity function. The natural components in the diesel fuel viz., sulphur, aromatics and other heterocyclic polar compounds were provided the lubrication function formerly (Kajdas and Majzner, 2003; Kajdas and Majzner 1999; Spikes and Wei, 1997). But due to the human health reasons and environmental protection, the sulphur content of diesel fuels was reduced to 10ppm. With the decrease of sulphur content the lubricity of the diesel fuel also decreased which leads to increase on the moving parts of the fuel pump. Therefore, it is necessary to add lubricity improvers in diesel fuel to reduce the wear of the moving metal parts upto the desired level (Hancsok et al., 2006; Adhvarya and Erhan, 2002).

1.3.3 Mechanism of lubricity improvers

A molecule acting as lubricity improver should have carbon chain length with more than fourteen carbon atoms and polar functional groups (viz., acid, ester, amide, epoxide) in order to form a thin protective film over metal surface to enhance the boundary lubricity and to attach with metal surfaces, respectively (Ladommatos et al., 1996). It is very important to ensure the formation of a cover film, either by physical adsorption or by chemisorptions, in order to reduce the number of metal-to-metal contact points. At normal operating temperature, the lubricity additive forms a thin film on the surface of the inlet system. The formation of stable polymeric film on metal surface through the epoxide functional group cross linking on the metal surface (Adhvarya and Erhan, 2002) and provides the metal surfaces with dispersing/neutralizing protection. The thin film inhibits deposit and provides the metal surfaces with dispersing/neutralizing protection.

1.3.4 Literature reported lubricity improvers

1.3.4.1 Commercially available lubricity improvers

A variety of lubricity additives have been included in literature including alkenyl succinics, alcohols, acids, esters (esters of fatty acids and alcohols, bis-alkenyl-succinic ester (Figure 6)), carboxylic acid amides, reaction products of fatty acids and aromatic triazoles, mixtures of fatty acids and tertiary amines, mixtures of nitrogen-containing compounds and carboxylic acids substituted with polymeric compounds (Adhvaryu et al., 2005; Kajdas and Majzner, 2003; Kajdas and Majzner, 1999; Spikes and Wei, 1997). Esters of dicarboxylic acids with branching have been used as lubricants and hydraulic fluids over wide range of temperature (Kadesch, 1979).

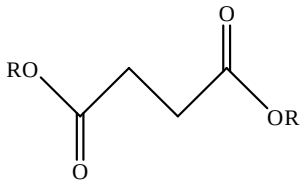


Figure 6. Chemical structure of bis-alkenyl-succinic ester.

Diesel fuel remains in contact with the metal equipment of the diesel engine and hence it must not have any negative effect on these materials. Hydrocarbons do not cause corrosion, but the acidic compounds (i.e. naphthenic acid) and sulphur molecules in the diesel fuel are very aggressive to copper and their alloy and can cause corrosion, especially in case of long-term stand-down. Solid and/or gel materials formed in these reactions can form deposits different parts of the engine and can also cause defects (Haycock et al., 2004; AAMA, ACEA, JAMA, 2002). Some mineral oil-based lubricants, due to their inherent toxicity and non-biodegradable nature pose a constant threat to ecology and vast ground water reserves (Adhvarya and Erhan, 2002).

1.3.4.2 Vegetable oil derived lubricity improvers

Vegetable oils possess excellent frictional properties e.g. good lubricity, low volatility, high viscosity index, solvency for lubricant additives, and easy miscibility with other fluids (Erhan et al., 2006; Gawrilow, 2004; Jayadasa et al., 2007; Steren et al., 1989) and hence could be used as lubricants at modest range of temperature. Rapeseed, castor, lesquerella and sunflower oils were reported in literature (Randles and Wright, 1992; Asadauskas et al.,

1996; Wu et al., 2000; Moser et al., 2008) as substitute for mineral oil based lubricants and synthetic esters. However, due to high degree of multiple –C=C– unsaturations in the fatty acid chain vegetable oils form deposits; show poor thermal and oxidative stability and cannot use at high range of temperature.

Epoxides, also known as oxiranes, are cyclic ethers with highly strained triatomic ring and hence are more reactive. Epoxidized soybean oil was able to provide excellent lubricity with less deposit forming tendency due to the formation of stable polymeric film on metal surface through the epoxide (–CHOCH–) functional group cross linking on the metal surface (Adhvarya and Erhan, 2002). Therefore the epoxidised long chain hydrocarbons are expected to be better lubricity improvers as compared to fatty acid methyl esters at higher temperature (Guidotti et al., 2008; Hwang and Erhan, 2001; Meier et al., 2007; Wua et al., 2000). Reports have discussed the use of epoxidized unsaturated fatty acids as metal working fluids (Watanabe et al., 1988) and epoxy oils as lubricating additives to eliminate corrosion from chlorine containing compounds (Tao et al., 1996). Epoxidized soybean oil has been used in high temperature lubricant applications and results were compared with normal soybean oil and high oleic soybean oil (Adhvaryu and Erhan, 2002; Salimon and Salih, 2009; Abdullah and Salimon, 2010).

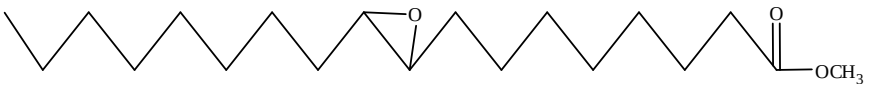


Figure . Epoxide derivative of soybean oil derived fatty acid methyl ester.

In literature several homogeneous catalysts (sulphuric acid, phosphoric acid, nitric acid, hydrochloric acid) have been reported for the synthesis of epoxidized vegetable oil (Dinda et al., 2008). Epoxidized fatty acid derivatives are obtained at industrial scale mainly by the Prilezhajev peracid process as shown in Figure 6.

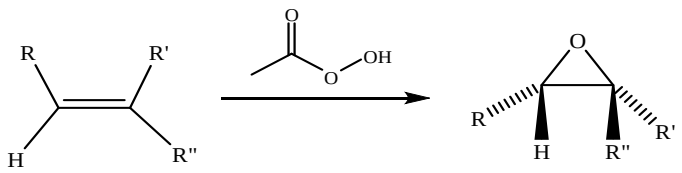


Figure 6. Prilezhajev epoxidation reaction.

However, there exist several drawbacks of the peracid process including, (i) low selectivity to the epoxidised products due to the acid-catalyzed oxirane ring opening, (ii) the separation of acidic by-products is difficult and presence of the same may be a negative impact on further applications of the product, (iii) the handling of highly concentrated hydrogen peroxide and strong acids is dangerous and causes corrosion problems, and (iv) the separation of homogeneous catalyst is cumbersome.

To overcome above mentioned shortcomings related with the homogeneous catalyst, it would be more advantageous to use heterogeneous catalysts for the epoxidation of fatty acid esters (Stern et al., 2002; Schuster et al., 2008; Suarez et al., 2009). In the field of the selective epoxidation of oleochemicals, titanium-silica catalysts showed good stability, versatility and recoverability with respect to conventional systems (Guidotti et al., 2008). It has been found that the incorporation of titanium on an amorphous silica support produces catalysts that are highly effective in epoxidation reactions for 1-octene with hydrogen peroxide (Escrig and Martin, 1999; Sanchez et al., 2000; Sanchez et al., 2003). Few heterogeneous titanium-grafted catalytic systems, already extensively tested in the epoxidation of terpenic substrates (Berlini et al., 2000; Guidotti et al., 2003a; Abdullah and Salimon, 2010), have been applied to the selective epoxidation of unsaturated fatty acid methyl esters (C-18) using a very stable organic peroxide, *tert*-butylhydroperoxide.

Methyltrioxorhenium (Du, et al. 2004; Bouh et al. 2003), and titanium-containing silicas (Guidotti et al., 2003b; Rios et al., 2005; Guidotti et al., 2006; Guidotti et al., 2008) were seemed to be the most promising alternatives as catalysts for the epoxidation of unsaturated fatty derivatives. The epoxidation of soybean oil with dilute solutions of hydrogen peroxide in a polar organic medium in the presence of an amorphous Ti/SiO_2 catalyst and *tert*-butanol diluted reactants were found to produce high reaction yields with selective epoxidation (Campanella et al., 2004).

1.4 Dual functional diesel fuel additives

The combination of a polar head group, long-chain hydrocarbon of the fatty acid with nitrate/amide/epoxide functional group would increase the lubricity (Poirier et al., 1995) as well as cetane number of diesel fuel and hence known as dual functional molecules (Figure 7). Dual functional diesel fuel additives being developed from fat/vegetable oil have the additional advantage of renewability, biodegradability, less volatility and likely to be more

resistant to shock and fire initiated detonation (Suppes et al., 2001c; Poirier et al., 1995) and hence are expected to be less toxic and explosive than EHN.

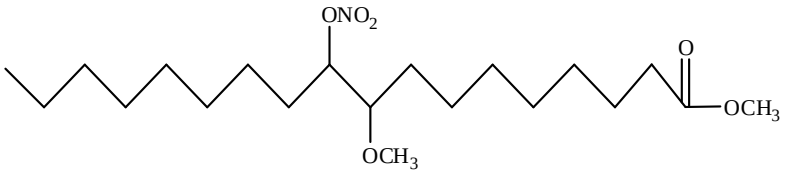


Figure 7. Dual functional diesel fuel additive.

Suppes et al., (2001c) reported the synthesis and performance of nitrates of fatty acid derivatives as cetane number as well as lubricity improvers. These additives exhibit both cetane number as well as lubricity enhancing capabilities thus providing them with distinct performance advantages over commercial products that can enhance only one property either cetane number or lubricity (Suppes et al., 2001c). Poirier et al. (1995) evaluated multiple approaches to the conversion of fatty acids to cetane number improvers. The feedstock of choice was a fatty-acid-rich tall oil mixture, the products of which were predominantly a mixture of primary nitrates of 16-18-carbon *n*-alkanes.

1.5 Conclusions

The literature review given above evidently demonstrates that cetane number improvers should have nitrate or peroxide or amide functional group with hydrocarbon chain and lubricity improver should have more than 12 carbon atoms in hydrocarbon chain. The epoxidation of –C=C– present in hydrocarbon chain could yield the molecules that could be used for high temperature lubrication. The commercially available cetane number or lubricity improvers impart only one property to the diesel fuel and literature reported additives mainly utilizes homogeneous catalysts during their synthesis.

1.6 Objectives

On the basis of research gaps and in order to develop the dual functional diesel fuel additives from naturally occurring triglycerides, the following objectives were defined for the present thesis.

i. To develop heterogeneous catalyst for the transesterification, aminolysis, epoxidation and nitration reactions of vegetable oils viz., used cooking oil, Jatropha, Karanja and Castor oil.
ii. Application of these catalysts to derive nitrate, epoxide and amide derivatives of mono alkyl esters from vegetable oils in order to synthesize dual functional diesel fuel additives.
iii. Testing the cetane number and lubricity improving performance of the synthesized additives.

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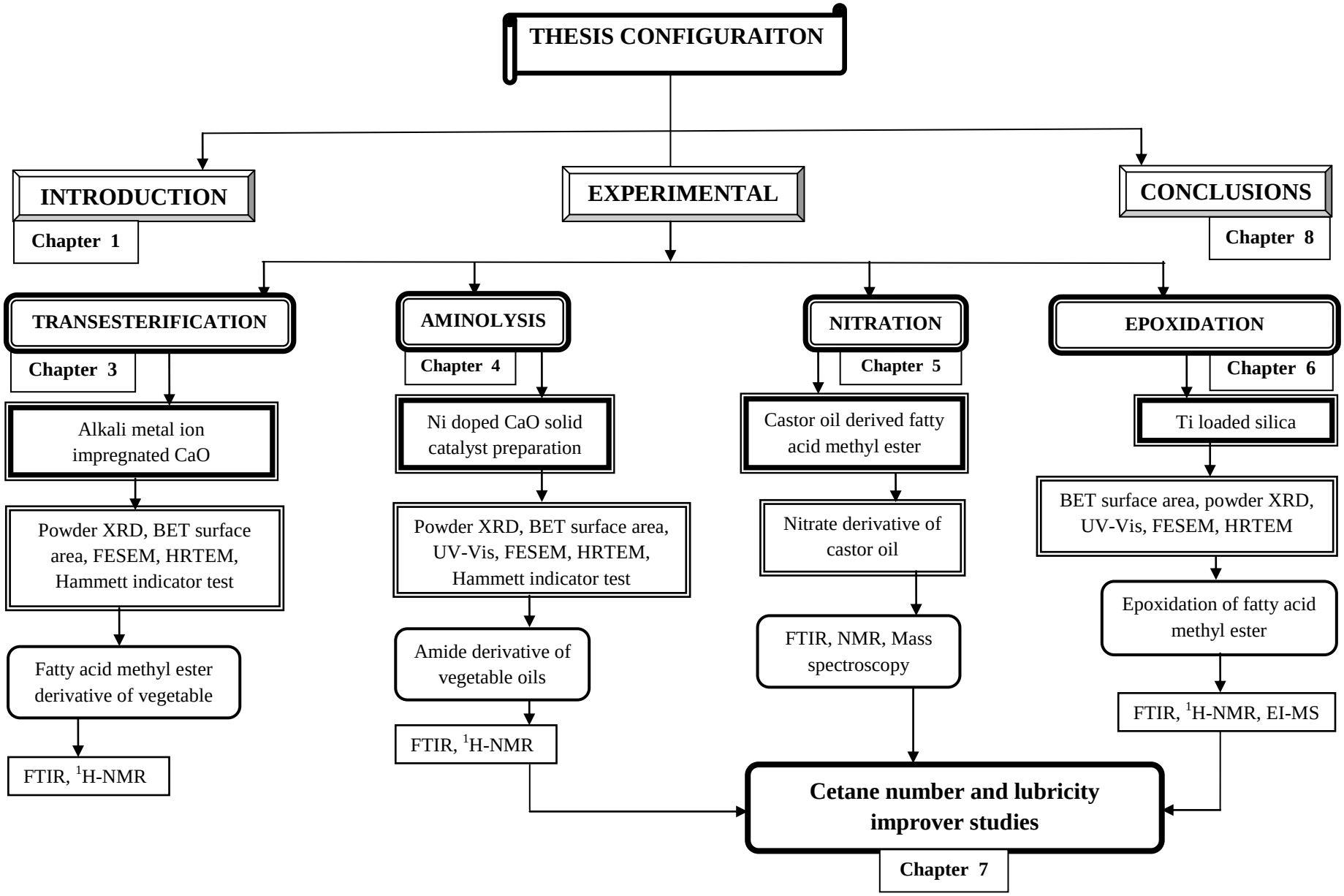
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Chapter 2

Materials and Methods

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2.1 Chemicals

Animal fat, soybean, virgin cotton seed, waste cotton seed, castor, karanja and jatropha oil were purchased from local resources located in Patiala. LiOH, $LiNO_3$, Li_2CO_3, NaOH, $NaNO_3$, Na_2CO_3, KOH, KNO_3, K_2CO_3, $Ni(NO_3)_2$, CaO, and silica gel for thin layer chromatography (TLC) of reagent grade quality were purchased from S. D. Fine Chemicals, India and used as such without further purification. Toluene, acetonitrile, butyronitrile, formic acid, nitric acid, diethanolamine, hydrogen peroxide, hexane, ethyl acetate and acetic acid of analytical grade were purchased from Loba Chemie, India. Methanol (99.8%) used in the present study was obtained from Merck, India. Titanium isopropoxide (99%), methyl oleate (99%), methyl laurate (99%) and silica (Grade 62, surface area: 300 m^2 g^{-1}, pore volume: 1.15 cm^3g^{-1}, pore size: 150Å, particle size: 75-250 µm) were procured from Sigma-Aldrich, USA. The basic strengths of the catalysts (H_) were determined by Hammett indicators test using the following indicators: neutral red (H_ = 6.8), bromthymol blue (H_ = 7.2), phenolphthalein (H_ = 9.3), Nile blue (H_ = 10.1), tropaeolin-O (H_ = 11.1), 2,4-dinitroaniline (H_ = 15.0), and 4- nitroaniline (H_ = 18.4) purchased from Qualigens Fine Chemicals, India.

2.2 Chemical analysis of various vegetable oils and mutton fat

The free fatty acid (FFA) contents, saponification, and the iodine values of the used cottonseed seed oil, karanja oil and jatropha oil were determined by following the methods as reported in literature (Plummer, 1988) and the moisture contents were determined by the Karl Fisher titrimetric method (Table 1).

Table 1. The chemical analysis of used cottonseed oil, karanja oil and jatropha oil.

S. No.	Feedstock	Free fatty acid contents (wt%)	Moisture content (wt%)	Saponification value (mg KOH/g)	Iodine value
1.	Used cottonseed oil	0.8	0.30	190.4	101.7
2.	Virgin cottonseed oil	0.1	0.31	188.7	102.6
3.	Soybean oil	0.2	0.27	190.0	125.4
4.	Mutton fat	0.9	0.32	192.4	46.1
5.	Castor oil	1.8	0.34	180.3	90.7
6.	Karanja oil	4.2	0.35	185.6	96.8
7.	Jatropha oil	8.4	0.28	195.5	101.5

2.3 Fatty acid composition of vegetable oils and mutton fat

The chemical structure of the vegetable oils or fats is dependent on their free fatty acid profile. As most of the vegetable oils contains maximum wt% of mono unsaturated and/or poly unsaturated free fatty acids viz., cottonseed oil contain 35 % oleic (monounsaturated) acid and 42% linoleic (polyunsaturated) acid whereas animal fats contains saturated free fatty acid in maximum wt% as given in Table 2.

Table 2: Fatty acid composition of vegetable oils and mutton fat.

Fatty Acids			Vegetable oils					Mutton fat
			Castor	Cottonseed	Jatropha	Karanja	Soybean	
Fatty Acid Composition (wt% of total fatty acids)	Saturated	Myristic (C14:0)	---	0.4	0.5-1.4	---	0.5*	3
		Palmitic (C16:0)	2	20	12.0-17.0	3.7-7.9	7.0-11.0	24
		Stearic (C18:0)	2	2	5.0-9.5	2.4-8.9	2.0-6.0	19
	Mono unsaturated	Oleic (C18:1)	7	35	37-63	44.5-71.3	22.0-34.0	43
	Poly unsaturated	Linoleic (C 18:2)	5	42	19-41	10.8-18.3	43.0-56.0	3
		Linolenic (C18:3)	---	---	---	---	5.0-11.0	1
	Any other fatty acid	Arachidic (C20:0)	---	---	0.3	2.2-4.7	---	---
		Ricinoleic (C18:1)	86-90	---	---	---	---	---
		9,10-dihydroxy Stearic (C18:0)	0.7	---	---	---	---	---
		Behenic (C22:0)	---	---	---	4.2-5.3	---	---

* trans fatty acid

2.4 Instruments

2.4.1 Flame Photometer

ESICO microprocessor flame photometer model 1382E has been employed for the determination of the alkali metal ion concentrations analysis.

2.4.2 Powder X-ray Diffraction (XRD)

Powder X-ray diffraction (XRD) data has been collected on Panalytical's X'Pert Pro with Cu Kα radiation. The samples were scanned in the range of 2θ = 5-80 º at the scanning speed of 2 º/min.

2.4.3 Nitrogen adsorption desorption isotherm

The surface areas of the catalyst were determined by using the adsorption/desorption method at 77 K by the standard Brunauer-Emmett-Teller (BET) method using Micromeritics Tristar 3000 equipment. All samples were degassed at 473 K for 90 min under nitrogen atmosphere to remove the physisorbed moisture from the catalysts. The pore size distribution and pore volume of nickel doped CaO has been analysed by using N_2 adsorption desorption isotherm.

2.4.4 Field emission scanning electron microscopy (FESEM)

The surface topography of the prepared inorganic material was analyzed with the help of field emission scanning electron microscopy (FESEM). FESEM was performed on JEOL JSM 6510LV to collect the SEM images and Field Emission Scanning Microscopy-Energy Dispersive X-ray Analysis (FESEM-EDX) studies have been performed to analyze the presence of various elements qualitatively.

2.4.5 Transmission electron microscopy (TEM)

The particle size and shape of the prepared inorganic samples have been analyzed by the HITACHI 7500 transmission electron microscopy (TEM).

2.4.6 NMR spectroscopy

For the characterization of organic molecules, Fourier transform-nuclear magnetic resonance (FT-NMR) spectra were recorded on a Bruker Avance-II (400 MHz) spectrophotometer.

2.4.7 Fourier Transform Infrared Spectrophotometer (FTIR)

The presence of functional groups viz., amide, epoxide and nitrate derivatives have been supported with the help of FTIR spectra recorded on Thermo Scientific Nicolet iS10 spectrometer.

2.4.8 Diffuse reflectance solid state Ultra Violet-Visible (UV-Vis) Spectrophotometer

Diffuse reflectance solid state UV-Visible (DRS) spectra of SiO_2, Ti loaded SiO_2, CaO and Ni doped CaO materials were recorded on Shimadzu 2450 Diffuse Reflectance UV-Visible spectrophotometer.

2.4.9 Mass Spectrometer

Mass spectra of methyl laurate, methyl oleate and amide and epoxide derivative of methyl laurate and methyl oleate were recorded on a Waters Micromass Q-ToF Micro mass spectrophotometer equipped with electrospray ionization (ESI) and atmospheric pressure chemical ionization (APcI) sources having mass range of 4000 amu in quadruple and 20000 amu in ToF.

2.4.10 Photochemical reactor

The photochemical reactor equipped with Philips Mercury Vapor lamp H38JA-100/DX (125 W) as a source of UV-Visible radiations has been used for the epoxidation reactions of used cotton seed oil derived fatty acid methyl esters.

2.4.11 Cooperative Fuel Research (CFR) Engine

Cooperative Fuel Research (CFR) engine has been used for the measurement of cetane number of synthesized additives. The ASTM D-613 test method has been followed for the cetane number determination by adding 0.4 wt% of additive in diesel fuel.

2.4.12 High Frequency Reciprocating Rig (HFRR)

High Frequency Reciprocating Rig (HFRR) TE 77 semi dry transfer unit has been used for the lubricity improver measurement study. The test method followed for the lubricity improver study of the epoxidized derivative of used cotton seed oil derived FAMEs (FAEUM), nitrate derivative of castor oil derived FAMEs (FANCM) and amide derivative of used cotton seed oil (FAAUC) was ASTM D6079.

Reference:

Plummer, D. T.; An Introduction to Practical Biochemistry. Tata McGraw-Hill: New Delhi, India. **1988;** pp 195-197.

Alkali Metal Ion Impregnated Calcium Oxide as Nanocrystalline Solid Catalysts: Preparation, Characterization and Application for the Transesterification of Triglycerides

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Abstract

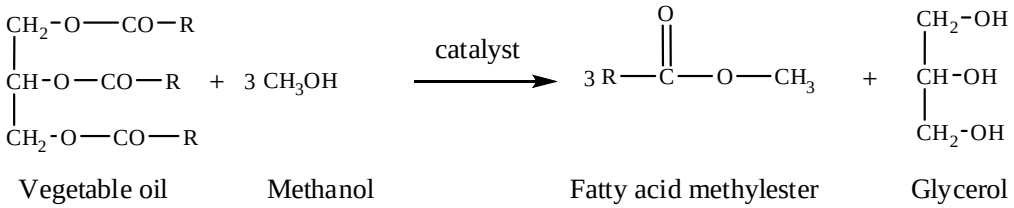
In order to prepare the dual functional diesel fuel additives, cheap and easily available feedstock viz., used cotton seed, jatropha and karanja oil have been used. Used cotton seed oil being the waste oil (recovered after frying the food ~ 10 times) and, jatropha and karanja being non-edible oils, present work would also demonstrates the application of waste and non-edible oil as feedstock for the production of diesel fuel additives.

Present chapter demonstrates the preparation of a series of alkali metal ion (Li, Na and K) impregnated calcium oxide by wet chemical method. These prepared catalysts have been used as solid catalysts for the transesterification of vegetable oils in order to produce fatty acid methyl esters which were used later as substrate for the synthesis of dual functional diesel fuel additives. The prepared catalysts were characterized by flame photometer, powder X-ray diffraction, scanning and transmission electron microscopic studies. The basic strengths of the catalysts were measured by Hammett indicators and were found maximum when the catalyst was prepared by impregnating 1.5 wt% of Li in CaO support (1.5-LiC/CaO). Transesterification of used cotton seed oil with methanol (1:12 molar ratio) at 65 °C, using 5 wt% (oil/catalyst) of the catalyst, required 45 min for the completion (> 99 %, mole/mole) of the reaction. The kinetics of the reaction has also been studied and rate of reaction was found to be effected by the free fatty acid concentration present in feedstock. The same catalyst has been used for the transesterification of a variety of feedstock viz., animal fat, virgin soybean oil, virgin cotton seed oil, used cotton seed oil, castor oil, karanja oil and jatropha oil and complete transesterification has been achieved in all the cases. The same catalyst was able to carry out three successive cycles of the transesterification, and the lixiviation studies shows that the catalyst activity is entirely due to the solid catalyst and not due to any leached species.

Keywords: alkali metal impregnated CaO, transesterification, BET surface area, Hammett indicator test, powder XRD, FESEM, TEM, proton NMR.

3.1 Introduction

Transesterification reaction is the first step in the derivatization of the vegetable oils in order to prepare multifunctional diesel fuel additives. Transesterification of vegetable oils with short chain alcohols (methanol, ethanol etc.) is a well known reaction in literature (Ma and Hanna, 1999) and has a lot of commercial importance as it leads to the formation of the fatty acid methyl esters (commonly known as biodiesel) and glycerol as shown in scheme 1.



Scheme 1. Transesterification of triglycerides.

Fatty acid methyl esters possess viscosity (4-6 cSt.) much lesser than vegetable oil (35-40 cSt.) which is comparable with conventional diesel fuel viscosity (Allen et al., 1999). Fatty acid methyl esters have been used extensively as a blend with conventional diesel fuel substitute in recent past in many countries including Brazil, United States and European countries. Fatty acid methyl esters derived from vegetable oils and its derivatives have the potential to act as diesel fuel additives (Sonntag et al., 1982). But it was reported in literature (Stournas et al., 1995) that fatty acid amides and nitrate derivative of fatty acid methyl ester are significantly more effective than fatty acid methyl esters in enhancing the ignition quality of the diesel fuel. Both the ester groups and the carbon-carbon double bonds of the fatty acid methyl esters provide functional groups that can be converted into nitrates and amides (Alcantara et al., 2000; Stournas et al., 1995) in high yields.

Fatty acid methyl esters can be prepared from a variety of triglycerides including vegetable oils, animal fats and waste greases in the presence of homogenous or heterogeneous catalyst (Ma and Hanna, 1999; De and Bhattacharya, 1999; Alcantara et al., 2000; Meher et al., 2006; Vicente et al., 2004). Homogenous acid catalysts viz., HCl and H_2SO_4 (Encinar et al., 2002; Rashid et al., 2008; Marinkovic and Tomasevic, 1998; Dorado et al., 2004) and base catalysts viz., NaOH, KOH, NaOMe and KOMe (Sun et al., 2010; Serio et al., 2005; Aranda et al., 2008) catalyst has been used frequently at industrial scale for fatty acid methyl ester production as they catalyze the reaction at faster rate even at mild reaction condition. However, same catalyst yielded FAMEs and glycerol contaminated with catalyst

and leads to the formation of soap if free fatty acids (FFAs) and moisture contents are greater than 0.5% and 0.3% (w/w) respectively (Haas, 2004; Canakci and Gerpen, 1999). More recently, there has been an increased research activity directed towards the development of heterogeneous catalysts which has several advantages over homogeneous one viz., formation of uncontaminated products, is recyclable, has low sensitivity towards FFAs and moisture contents and not corrode the reaction vessel (Clark and Macquarrie, 1996; Tanabe et al., 1989).

To prepare fatty acid methyl esters from triglycerides, present chapter demonstrates the preparation of alkali metal ion impregnated calcium oxide as solid catalysts for the transesterification reaction. The same catalysts have been utilized to optimize the reaction condition for the transesterification of the used cotton seed oil and further used for the complete transesterification of a variety of triglycerides (animal fat, virgin soybean oil, virgin cotton seed oil, used cotton seed oil, castor oil, karanja oil and jatropha oil). Selected catalysts was also found to be effective for the transesterification of vegetable oils having upto 8.4 wt% free fatty acid and 15.3 wt% moisture contents. The rate of reaction for the transesterification of used cotton seed oil, karanja oil and jatropha oil have also been evaluated by using pseudo first-order kinetics.

3.2 Experimental Section

3.2.1 Preparation of catalyst

The nanocrystalline alkali metal ion impregnated CaO catalyst was prepared by wet chemical method and in a typical preparation, 10g of calcium oxide was suspended in 40 mL deionized water and to this 10 mL aqueous solution of alkali metal salt of desired concentration was added. The slurry was stirred for 3 h, then evaporated to dryness and heated at 120 $^{\circ}$C for 24 h. A series of alkali metal ion (Li^+, Na^+ and K^+) impregnated catalysts using different salts of alkali metal ions (K_2CO_3, Na_2CO_3, Li_2CO_3, KNO_3, $NaNO_3$ and $LiNO_3$) with varying metal concentration (wt%) ranging from 0.5 to 5.0 wt% (metal ion/CaO) were prepared and characterized by flame photometer, X-ray powder diffraction (XRD), BET surface area measurement, Hammett indicator test, FE-SEM and TEM techniques.

Catalyst prepared in such a manner were designated as *xx*-MA/CaO, where *xx* represents the wt% of impregnation in CaO and MA represents alkali metal salt used for impregnation as described in Table 1.

Table 1. Different alkali metal impregnated CaO catalysts.

S. No.	Catalyst	Alkali metal salt used	Impregnated wt% of metal
1.	1.5-LiC/CaO	Li_2CO_3	1.5
2.	1.5-LiN/CaO	$LiNO_3$	1.5
3.	1.5-NaC/CaO	Na_2CO_3	1.5
4.	1.5-NaN/CaO	$NaNO_3$	1.5
5.	1.5-KC/CaO	K_2CO_3	1.5
6.	1.5-KN/CaO	KNO_3	1.5

3.2.2 Transesterification reaction

All transesterification reaction have been performed in a typical transesterification reaction, vegetable oil and methanol in 1:12 molar ratio and 5 wt% of catalyst were taken in a two neck round bottom flask. The reaction mixture was heated up to the 65 °C with continuous stirring till the completion of the reaction. The samples have been withdrawn from the reaction mixture after every five minutes with the help of glass capillary and diluted with hexane to perform thin layer chromatographic (TLC) studies.

To monitor the progress of the reaction has been monitored by thin layer chromatographic (TLC) technique. Samples from the reaction mixture have been withdrawn with the help of glass capillary after regular intervals of time and subjected to the TLC analysis after diluting the sample with hexane and using hexane/ethylacetate/acetic acid (90:9:1, v/v) as mobile and silica gel as stationary phase. Biodiesel shows higher mobility than vegetable oil with selected solvent system and complete conversion of vegetable oil to biodiesel was supported by the disappearance of vegetable oil spot on TLC plate.

Further fatty acid methyl ester so produced was characterized by ^{1}H, (Figure 4 and 5), ^{13}C-NMR (Figure 6) and FTIR (Figure 7) spectroscopy. The ^{1}H NMR spectra were also used to quantify the FAMEs yield by following the literature reported equation (Gelbard et al., 1995; Knothe, 2001) as given below:

$$\text{Yield} = \{2I_{(\text{methoxy})}/3I_{(\text{methylene})}\}\times 100$$

where $I_{(\text{methoxy})}$ and $I_{(\text{methylene})}$ are the areas of the methoxy and methylene protons, respectively, in ^{1}H NMR spectra of FAMEs.

Methyl esters of used cotton seed oil: FTIR (cm^{-1}): 2925 (ν_{C-H}), 1743 ($\nu_{C=O}$); ^{1}H-NMR ($CDCl_3$, δ ppm): 5.34 (m, -C**H**=C**H**-), 3.6 (s, -OC**H$_3$**), 2.77 (m, -CH=CH-C**H$_2$**-CH=CH-), 2.3 (m, -C**H$_2$**-CO-), 2.03 (m, -C**H**$_2$-$(CH_2)_n$-), 1.6-1.25 (m, -(C**H$_2$**)$_n$-), 0.88 (m, -CH_2-C**H$_3$**); ^{13}C-NMR ($CDCl_3$, δ ppm): 174.09 (–**C**O–CH_2–), 129.9 (–**C**H=**C**H–),77.1 ($CDCl_3$), 51.2 (–O**C**H_3), 34.1 (–CO–**C**H_2–), 31.9 (ω3 -**C**H2–), 29.66–29.08 (-CH=CH–**C**H_2–, –**C**H_2–), 27.2 (–CH=CH–**C**H_2–CH=CH–), 25.6–24.80 (–CO–CH_2–**C**H_2–), 22.70, 22.47 (ω2 –**C**H_2–) and 14.16 (ω1 –**C**H_3).

Methyl esters of karanja oil: FTIR (cm^{-1}): 2925 (ν_{C-H}), 1743 ($\nu_{C=O}$); ^{1}H-NMR ($CDCl_3$, δ ppm): 5.34 (m, -C**H**=C**H**-), 3.6 (s, -OC**H$_3$**), 2.75 (m, -CH=CH-C**H$_2$**-CH=CH-), 2.3 (m, -C**H$_2$**-CO-), 2.03 (m, -C**H**$_2$-$(CH_2)_n$-), 1.61-1.25 (m, -(C**H$_2$**)$_n$-), 0.97 (m, -CH=CH-C**H$_3$**), 0.88 (m, -CH_2-C**H$_3$**).

Methyl esters of jatropha oil: FTIR (cm^{-1}): 2925 (ν_{C-H}), 1743 ($\nu_{C=O}$); ^{1}H-NMR ($CDCl_3$, δ ppm): 5.33 (m, -C**H**=C**H**-), 3.61 (s, -OC**H$_3$**), 2.77 (m, -CH=CH-C**H$_2$**-CH=CH-), 2.3 (m, -C**H$_2$**-CO-), 2.02 (m, -C**H**$_2$-$(CH_2)_n$-), 1.61-1.25 (m, -(C**H$_2$**)$_n$-), 0.89 (m, -CH_2-C**H$_3$**).

Methyl esters of soybean oil: FTIR (cm^{-1}): 2925 (ν_{C-H}), 1743 ($\nu_{C=O}$); ^{1}H-NMR ($CDCl_3$, δ ppm): 5.34 (m, -C**H**=C**H**-), 3.6 (s, -OC**H$_3$**), 2.77 (m, -CH=CH-C**H$_2$**-CH=CH-), 2.3 (m, -C**H$_2$**-CO-), 2.03 (m, -C**H**$_2$-$(CH_2)_n$-), 1.6-1.25 (m, -(C**H$_2$**)$_n$-), 0.88 (m, -CH_2-C**H$_3$**).

Methyl esters of castor oil FTIR: (cm^{-1}): 3422 (ν_{O-H}), 2925 (ν_{C-H}), 1743 ($\nu_{C=O}$). ^{1}H-NMR ($CDCl_3$, δ ppm): 6.5 (-O**H**) 5.51 (m, -CH_2-C**H**=CH-), 5.39 (m, -C**H**=C**H**-), 3.6 (s, -OC**H$_3$**), 3.61 (m, -C**H**-OH), 2.3 (m, -C**H$_2$**-CO-), 2.20 (m, -C**H**$_2$-CH=CH-), 2.03 (m, -C**H**$_2$-$(CH_2)_n$-), 1.61-1.30 (m, -(C**H$_2$**)$_n$-), 0.97 (m, -CH=CH-C**H$_3$**), 0.88 (m, -CH_2-C**H$_3$**).

Methyl esters of mutton fat: FTIR (cm^{-1}): 2925 (ν_{C-H}), 1743 ($\nu_{C=O}$); ^{1}H-NMR ($CDCl_3$, δ ppm): 5.34 (m, -C**H**=C**H**-), 3.6 (s, -OC**H$_3$**), 2.3 (m, -C**H$_2$**-CO-), 2.0 (m, -C**H**$_2$-$(CH_2)_n$-), 1.61-1.25 (m, -(C**H$_2$**)$_n$-), 0.88 (m, -CH_2-C**H$_3$**).

The FAMEs, so produced has also been extensively used as diesel fuel substitute in recent past and commonly known as biodiesel. In order to evaluate the quality of the prepared FAMEs, their few important physicochemical properties have also been studied and

compared with European standards (EN-14214) as given in Appendix 1. Most of the studied properties were found to match with EN specifications.

3.3 Results and Discussion

3.3.1 Catalyst preparation and characterization

The basic strength of the alkaline earth metal oxides and hydroxides increase in the order of Mg < Ca < Sr < Ba (Watkins et al., 2004) and being inexpensive and less toxic, CaO has been chosen for the present work. Further, the basic strength of CaO can be enhanced by impregnating it with alkali metal ions. The series of alkali metal ion impregnated CaO were prepare by wet chemical method and varying the alkali metal concentration in the range of 0.5-5 wt% in CaO. Actual impregnated amount of alkali metal ions was determined by flame photometric method.

3.3.1.1 Hammett indicator test

The basic strengths of the catalysts were determined by using the Hammett indicators (Wan et al., 2009), and summarized in Table 2. The basic strength of 1.5-LiC/CaO was found to be maximum, 15.0<H_<18.4, among the prepared catalysts, probably due to the formation of strong basic sites on CaO surface after Li^+ impregnation. Hence 1.5-LiC/CaO catalyst expected to show better catalytic activity towards the transesterification reaction of vegetable oil among the prepared catalysts.

3.3.1.2 BET surface area measurement

Surface area of Li, Na and K carbonate impregnated (1.5 wt%) calcium oxide catalysts were measured by Brunauer-Emmett-Teller (BET) method. Alkali metal ion impregnated CaO catalysts show high surface area in comparison with pure CaO and highest surface area was found in case of lithium nitrate impregnated CaO as shown in Table 2.

Table 2. Comparison of the basic strengths of alkali metal ion impregnated CaO with that of pure CaO.

Catalyst type	Basic strength (H_)	BET surface area (m^2/g)	Particle size (nm)	
			Debye-Scherrer method	HRTEM method
CaO	9.8< H_<10.1	3.9	104	150
1.5-LiC/CaO	15.0< H_<18.4	6.5	70	50
1.5-LiN/CaO	11.1< H_<15.0	6.9	55	50
1.5-NaC/CaO	10.1< H_<11.1	5.0	45	30
1.5-NaN/CaO	10.1< H_<11.1	4.3	38	25
1.5-KC/CaO	10.1< H_<11.1	4.2	48	70
1.5-KN/CaO	10.1< H_<11.1	3.9	52	35

3.3.1.3 Powder XRD studies

Powder X-ray diffraction studies of CaO and 1.5 wt% Li or Na or K impregnated CaO have been performed and comparisons of XRD patterns are given in Figure 1. The CaO shows peaks at 2θ values of 32.14°, 37.46° and 53.90° due to the presence of calcium oxide in cubic form (JCPDS card no. 821691), as shown in Figure 1. The presence of low intensity peaks at 29.47° and 64.4° (JCPDS 881811) support the presence of calcium carbonate as calcite in the commercial CaO. The powder XRD pattern of alkali metal impregnated CaO support the conversion of CaO to $Ca(OH)_2$ in hexagonal form due to the presence of peaks at 18.20°, 34.17° and 47.17° (JCPDS 841275). The conversion of CaO to $Ca(OH)_2$ upon alkali metal impregnation could be the reason for its higher basic strength and activity towards the transesterification reaction in comparison to pure CaO. The absence of the diffraction patterns of alkali metals could be either due to its high degree of dispersion on the CaO surface or its concentration being smaller than those detectable by the powder XRD technique. The particle size of the alkali metal impregnated catalysts were determined by Debye-Scherrer method (Qadri et al., 1999) using powder XRD data and found in the range of 38-70 nm as shown in Table 2.

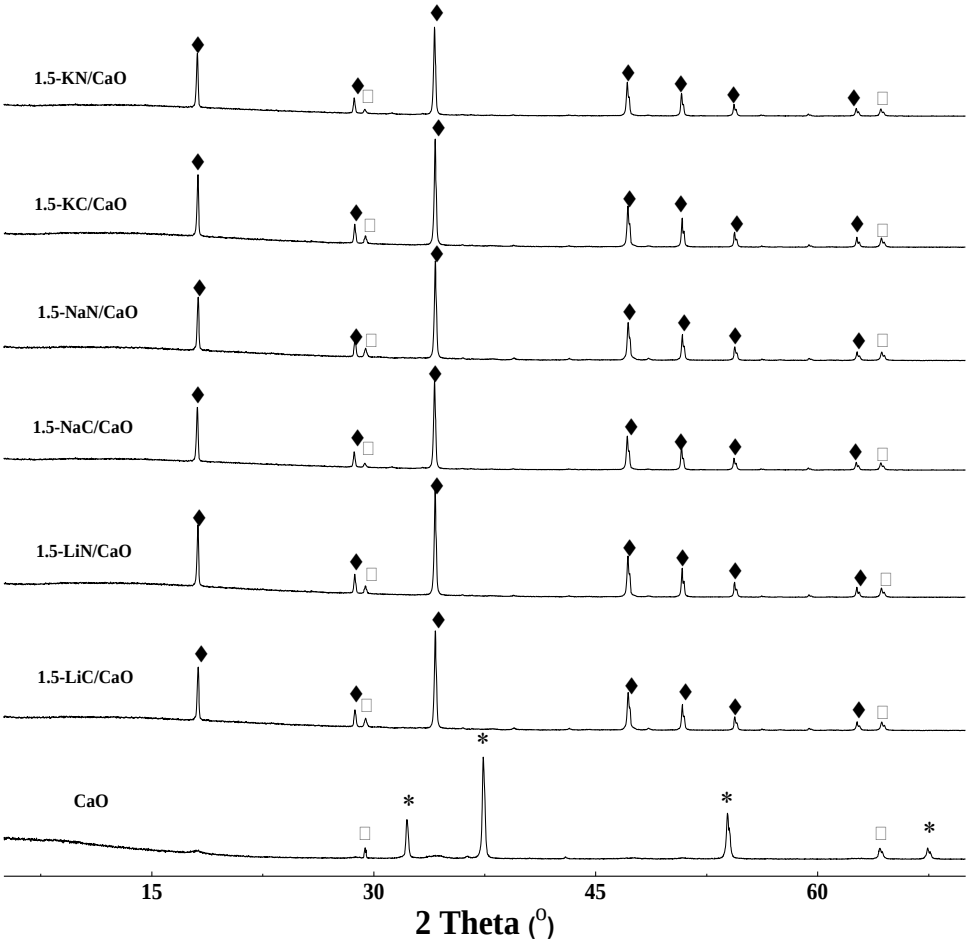


Figure 1. Comparison of Powder XRD patterns of commercially available CaO with 1.5-LiC/CaO, 1.5-LiN/CaO, 1.5-NaC/CaO, 1.5-NaN/CaO, 1.5-KC/CaO and 1.5-KN/CaO. (calcium oxide = *; calcium hydroxide = ♦; and calcium carbonate = □)

3.3.1.4 FESEM analysis

Scanning electron microscopic images of alkali metal impregnated CaO catalysts reveals that the particles are in hexagonal and oval shaped as shown in Figure 2. Average size of particles by FE-SEM studies was found to be ~4-5 µm.

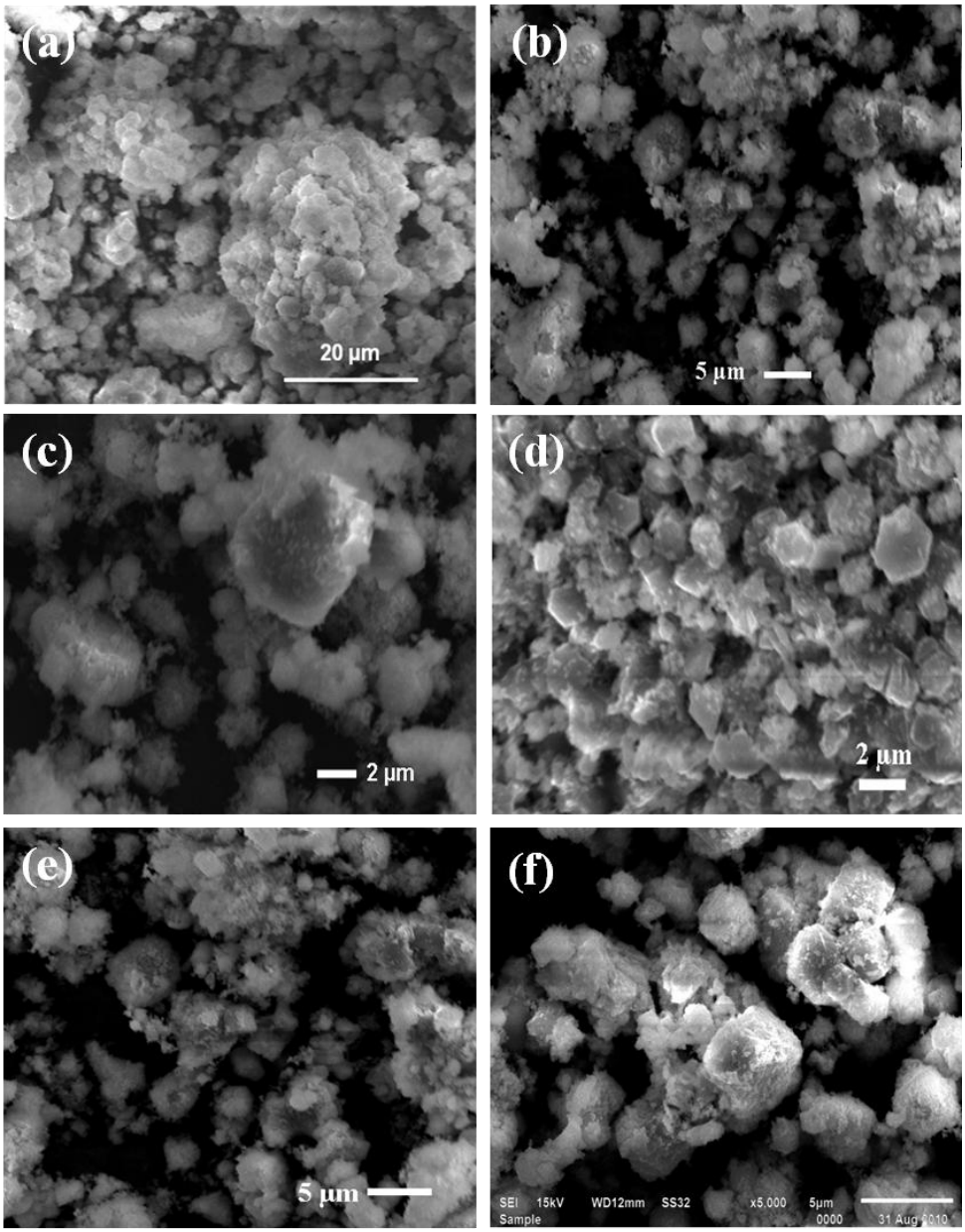


Figure 4. SEM images of (a) 1.5-LiC/CaO, (b) 1.5-LiN/CaO, (c) 1.5-NaC/CaO, (d) 1.5-NaN/CaO, (e) 1.5-KC/CaO and (f) 1.5-KN/CaO.

3.3.1.5 HRTEM analysis

TEM analysis of the same particles shows that these particles are the clusters of further smaller particles. The average particle size of the catalysts varies in the range of 25-70 nm as shown in Figure 3, to support the existence of the catalyst in nanoparticles form. The shape of the catalysts particles as observed by TEM analysis, were either found to be hexagonal (1.5-LiC/CaO, 1.5-NaC/CaO and 1.5-KC/CaO) or oval (1.5-LiN/CaO, 1.5-NaN/CaO and 1.5-KN/CaO).

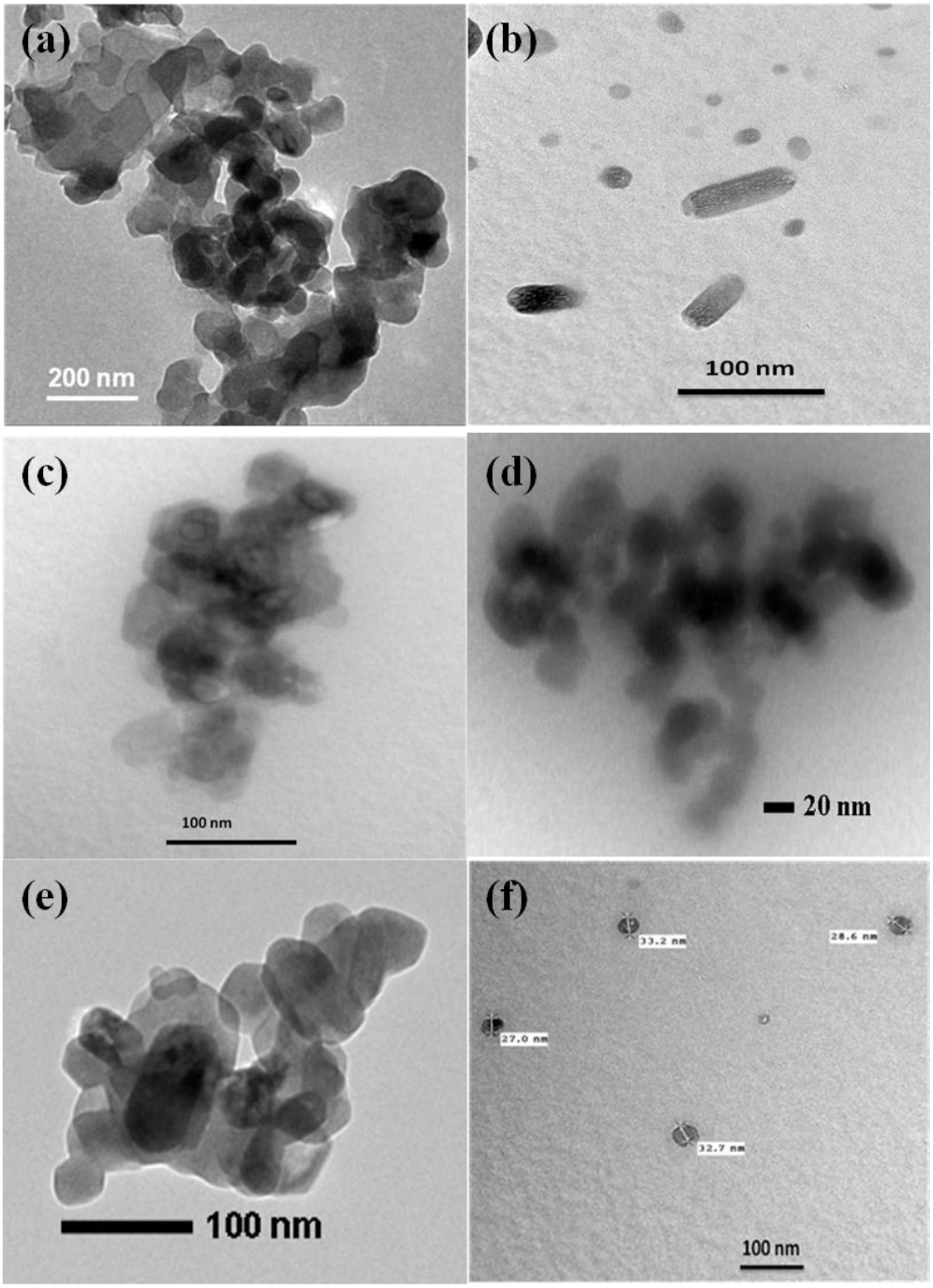


Figure 3: TEM images of (a) 1.5-LiC/CaO, (b) 1.5-LiN/CaO, (c) 1.5-NaC/CaO, (d) 1.5-NaN/CaO, (e) 1.5-KC/CaO and (f) 1.5-KN/CaO.

3.3.2 Transesterification reaction and product characterization

3.3.2.1 Transesterification reaction

The transesterification reactions of a variety of feedstocks (mutton fat, virgin soybean oil, virgin cotton seed oil, used cotton seed oil, castor oil, karanja oil and jatropha oil) with

methanol were employed in the presence of prepared solid catalysts, however, initially the reaction conditions have been optimized using used cotton seed oil as feedstock.

The basic difference in vegetable oil and animal fat (detailed fatty acid composition of individual vegetable oil and fat is provided in material and method section) is the presence of lesser unsaturated FFAs in later as shown in Figure 4 (c). Among vegetable oils castor oil differ from other oils due to the presence of –OH group at C-12 position as shown in Figure 4 (b).

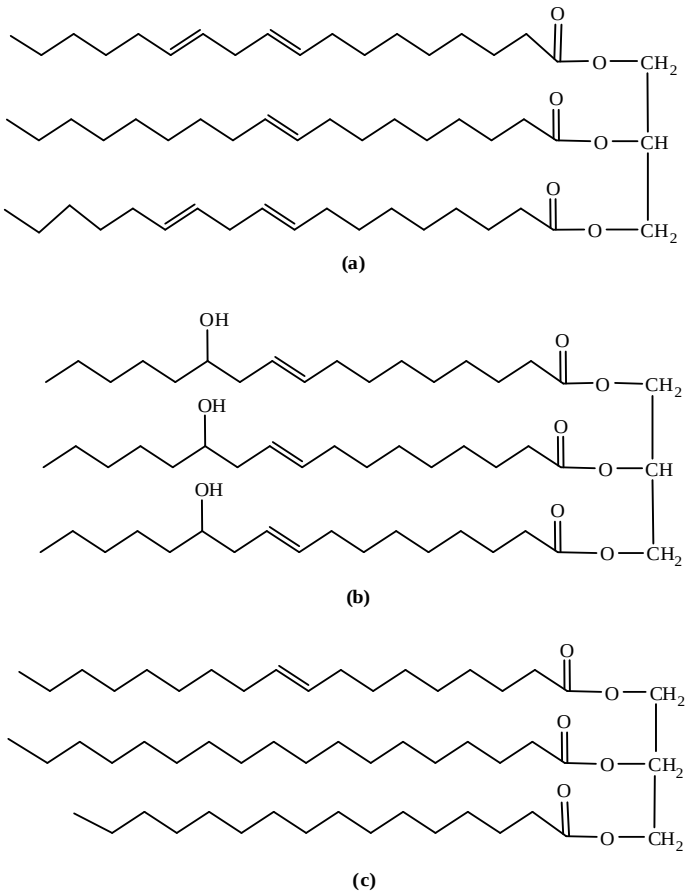


Figure 4. Chemical structure of (a) a typical vegetable oil, (b) castor oil, and (c) mutton fat molecule.

3.3.2.2 Thin layer chromatography

The progress of the transesterification reactions have been monitored by thin layer chromatographic (TLC) technique. The samples from the reaction mixture have been withdrawn with the help of glass capillary after regular intervals of time. The reaction mixture so obtained subjected to the TLC analysis after diluting the sample with hexane and

using hexane/ethylacetate/acetic acid (90:9:1, v/v) as mobile and silica gel as stationary phase. Fatty acid methyl ester shows higher mobility (R_f = 0.65) than vegetable oil (R_f = 0.26) with selected solvent system and complete conversion of vegetable oil to corresponding fatty acid methyl ester was supported by the disappearance of vegetable oil spot on TLC plate. Fatty acid methyl ester, thus obtained, was further characterized by FTIR, ^{1}H NMR and ^{13}C-NMR spectroscopic techniques.

3.3.2.3 FTIR studies

The FTIR spectra of feedstock and corresponding fatty acid methyl esters were found to be almost identical as shown in Figure 5. The characteristic carbonyl peak in vegetable oils was found at ~ 1743 cm^{-1} and same position of the carbonyl peak was observed even after the complete conversion of oil to corresponding FAMEs (Figure 5). Additional peak in case of castor oil and their fatty acid methyl ester was found at ~ 3422 cm^{-1} due to the presence of –OH group at C-12 position in ricinoleic acid as shown in Figure 5c and 5d. Hence, not much information regarding the conversion of triglyceride into corresponding FAMEs could be gained from the IR spectroscopy.

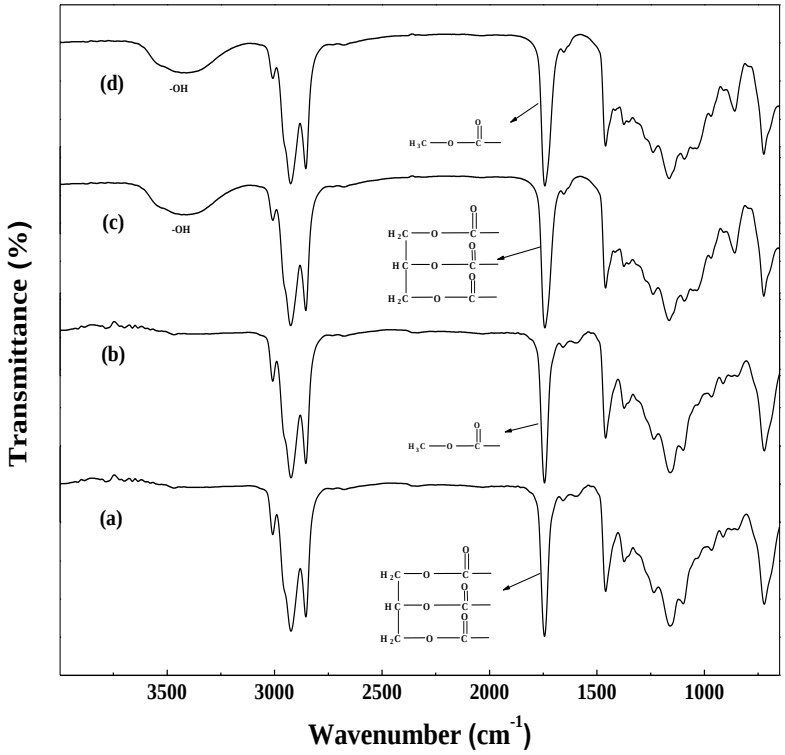


Figure 5. Comparative FTIR spectra of (a) cotton seed oil, (b) fatty acid methyl ester derived from cotton seed oil, (c) castor oil and (d) castor oil derived fatty acid methyl ester.

3.3.2.4 NMR analysis

Fatty acid methyl esters produced in transesterification reaction were further characterized by ^{1}H and ^{13}C-NMR spectroscopy. Proton NMR spectrum of cotton seed oil shows a multiplet at 4.1 and 5.2 ppm due to the presence of glyceridic protons besides other hydrocarbon-proton peaks (Vigli et al., 2003) as given in Figure 6. In transesterified products appearance of a new peak at 3.6 ppm due to $–OCH_3$ protons and disappearance of glyceridic protons support the complete conversion of oil to fatty acid methyl ester as shown in Figure 6. Similar patterns have been obtained in case of fatty acid methyl ester obtained from other oils viz., soybean, karanja and jatropha oil as shown in Figure 6.

Animal fat possess unsaturation mainly in the form of monounsaturated free fatty acids. Due to the absence of poly unsaturated free fatty acids no peaks in proton NMR spectra of fat and corresponding FAMEs was observed at 2.7 ppm due to –CH=CH-C**H**$_2$-CH=CH-. An additional peak in castor oil methyl esters at 3.61 ppm could be due to the proton attach to same carbon where hydroxyl group (-C**H**-OH) is also attached.

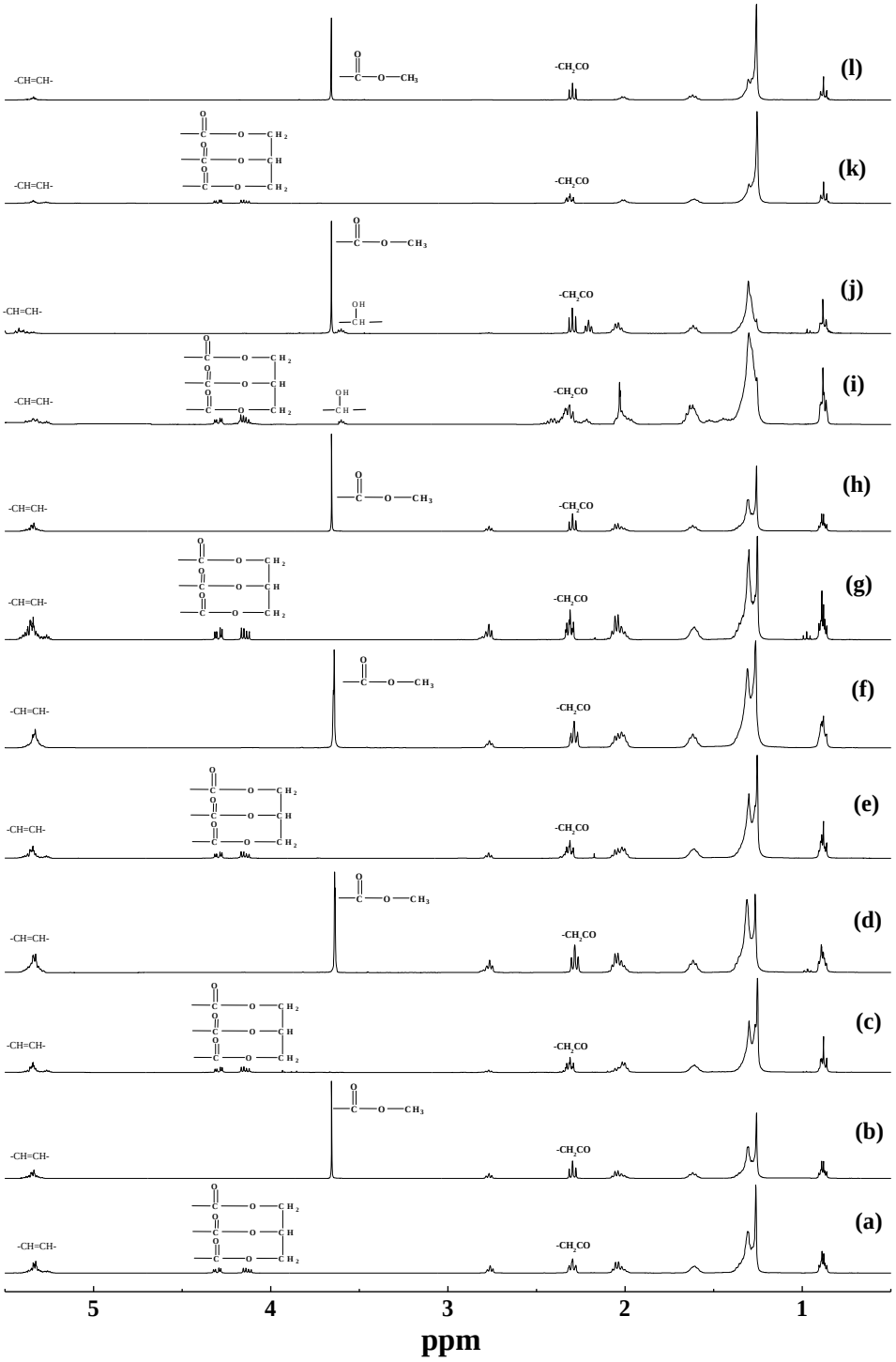


Figure 6. Comparison of ^{1}H-NMR spectra of triglycerides and corresponding methyl ester, (a) cotton seed oil, (b) cotton seed oil derived fatty acid methyl ester, (c) karanja oil, (d) karanja oil derived methyl ester, (e) jatropha oil, (f) jatropha oil derived methyl ester, (g) soybean oil, (h) soybean oil derived methyl ester, (i) castor oil, (j) castor oil derived methyl ester, (k) mutton fat and (l) mutton fat derived methyl ester.

In carbon-13 NMR spectrum of transesterified product appearance of new peak at 51.5 ppm due to –O**C**H_3 carbon and disappearance of glyceridic carbon peaks at 61.9 and 68.7 ppm support the formation of fatty acid methyl ester from used cotton seed oil as shown in Figure 7.

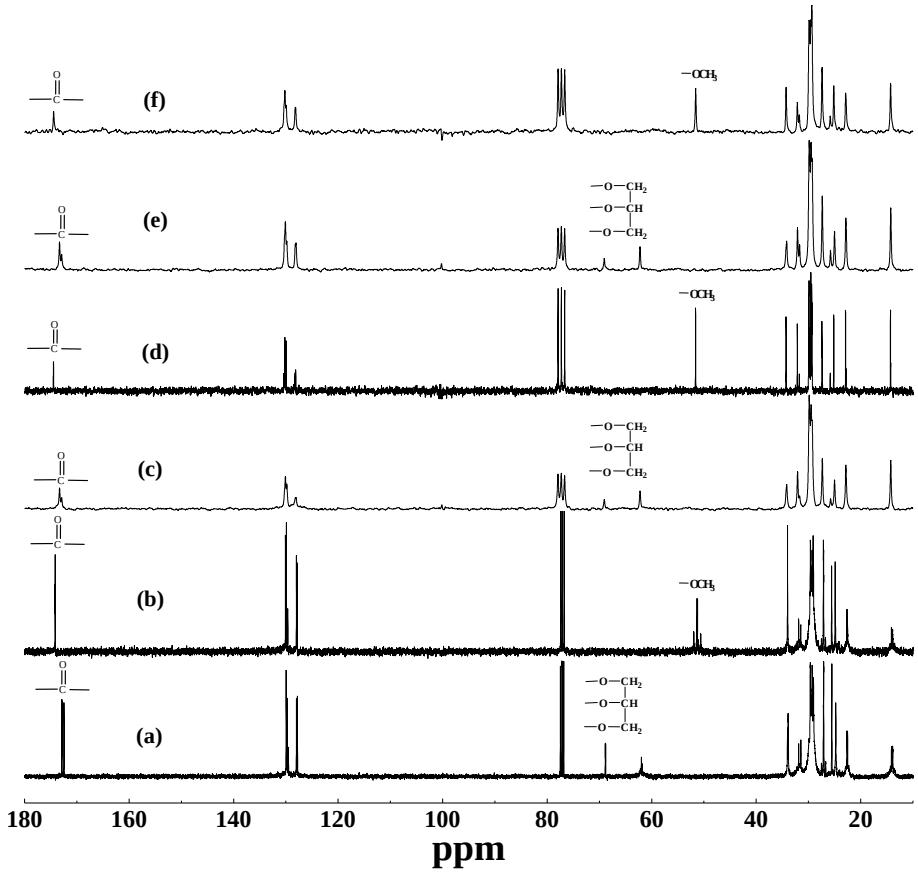


Figure 7. Comparison of ^{13}C-NMR spectra of (a) cotton seed oil, (b) cotton seed oil derived FAMEs, (c) karanja oil, (d) karanja oil FAMEs, (e) jatropha oil and (f) jatropha oil FAMEs.

3.3.3 Catalytic Activity

In order to compare the catalytic activity of the prepared catalysts, used cotton seed oil were used as substrate. Transesterification reactions of used cotton seed oil with desired molar concentrations of methanol were performed in the presence of desired catalyst amount at desired temperature.

During the course of study out of (i) impregnated alkali metal ion, (ii) impregnated lithium ion concentration, (iii) catalyst concentration, (iv) reaction temperature, (v) oil/methanol molar ratio, (vi) moisture content (1-15 wt%), and (vii) free fatty acid content (0.5-6 wt%),

one parameter at a time has been varied in order to establish the most suitable reaction condition for the transesterification reaction.

3.3.3.1 Effect of alkali metal ion on catalyst activity

In order to study the effect of impregnated alkali salts on the catalyst activity, six different catalysts were prepared as given in Table 1. Basic strengths of the prepared catalysts were found to be maximum (15.0 to 18.4) in case of 1.5-LiC/CaO catalyst. As the size of the impregnated alkali metal ion increases, the basic strength of the catalysts were found to decrease as given in Table 2. Smaller sized ions (viz., Li^+) are expected to insert easily in the framework of CaO to create oxygen gaps, which could be responsible for the formation of stronger basic sites in CaO (Barrault et al., 2002).

In order to study the effect of catalyst basic strength on its activity, a series of transesterification reaction of used cotton seed oil was performed with methanol (12:1 methanol/oil molar ratio) at 65 ºC in the presence of 5 wt% prepared catalysts. Reaction time required for the complete transesterification was found to decreased as the basic strength of the catalyst increases and found to be minimum in case of be minimum (45 min) in case of 1.5-LiC/CaO as shown in Figure 8. Being highest in activity towards transesterification reaction 1.5-LiC/CaO was selected for further studies.

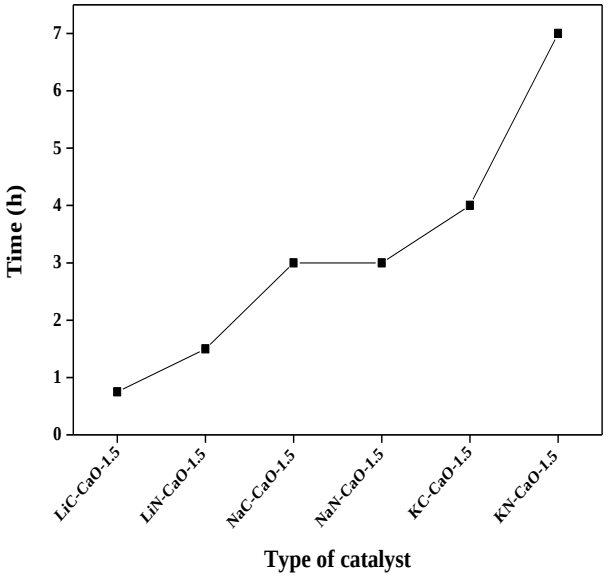


Figure 8. Effect of impregnated alkali metal ion on reaction time required for the complete conversion of used cotton seed oil to fatty acid methyl ester. (Conditions; methanol: feedstock molar ratio = 12:1, catalyst amount = 5 wt% of feedstock, temperature = 65 ºC)

3.3.3.2 Effect of impregnated lithium ion concentration

To determine the optimum lithium ion concentration in CaO to achieve the best catalytic activity, a series of catalyst was prepared by varying the amount of lithium in the range of 0.5-5.5 wt% (Li/CaO). The transesterification reactions of used cotton seed oil were performed with methanol (12:1 methanol/oil molar ratio) at 65 ºC in the presence of 5 wt% prepared catalysts. Reaction time required for the complete transesterification was found to decrease from 3 h to 45 min as the amount of lithium ion in CaO were increased from 0.5 to 1.5 wt%. However, further increase in Li^+ ion concentration does not reduce the reaction time as shown in Fig. 9. Hence, 1.5-LiC/CaO catalyst was selected for optimizing other parameters to achieve the minimum time for the complete transesterification reaction.

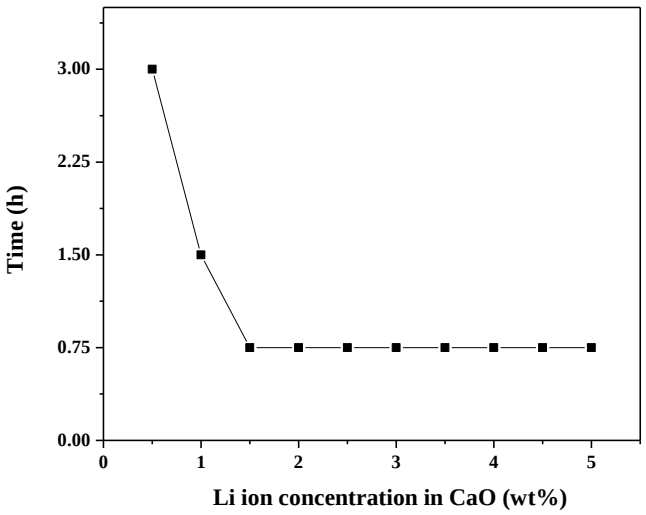


Figure 9. Effect of lithium ion concentration in CaO on the time required for complete transesterification of used cotton seed oil to fatty acid methyl ester. (Conditions; methanol: feedstock molar ratio = 12:1, catalyst amount = 5 wt% of feedstock, temperature = 65 ºC)

3.3.3.3 Effect of catalyst concentration

In order to find the optimum catalyst concentration a series of transesterification reactions of used cotton seed oil with methanol (12:1 molar ratio) at 65 ºC were performed in the presence of nanocrystalline 1.5-LiC/CaO by varying its concentration in the range of 1 to 8 wt% (catalyst/oil). Time required for the complete conversion decreases from 7 h to 45 min as catalyst concentration was increased from 1 to 5 wt%. Further increase in catalyst concentration does not reduce the reaction time significantly as shown in Figure 10. The

transesterification reactions were further studied with catalyst concentration of 5 wt% (catalyst/oil) for optimization the other parameters.

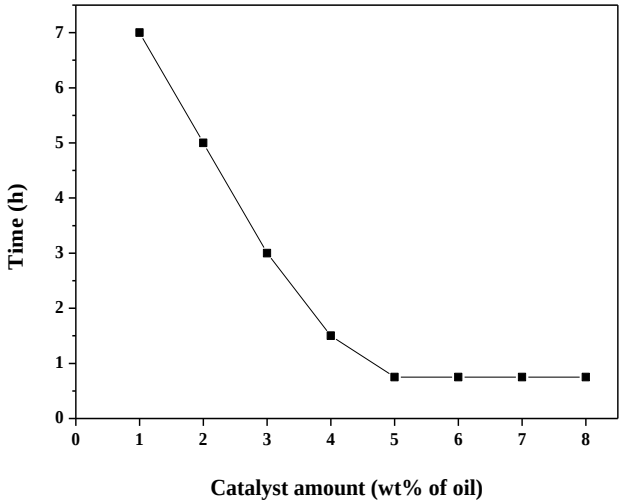


Figure 10. Effect of catalyst concentration on the time required for complete transesterification of used cotton seed oil to fatty acid methyl ester. (Conditions; methanol: feedstock molar ratio = 12:1, temperature = 65 ºC)

3.3.3.4 Effect of reaction temperature

A series of transesterification reactions were conducted in the presence of 5 wt%, (catalyst/oil) nanocrystalline 1.5-LiC/CaO, to find the optimum temperature for transesterification reaction. Time required for the complete transesterification of vegetable oils to FAMEs decreases from 6 h to 45 min as temperature of the reaction was increased from 35 ºC to 65 ºC. Further increase in reaction temperature does not reduce the reaction time significantly as shown in Figure 11 and hence, all transesterification reactions were performed at 65 ºC.

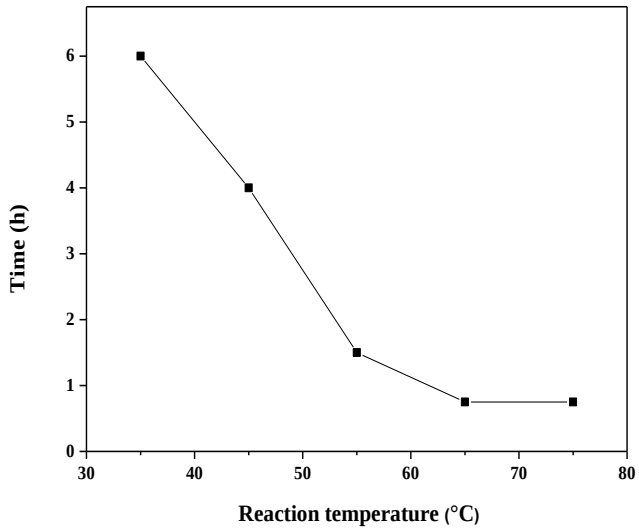


Figure 11. Effect of reaction temperature on the time required for complete transesterification of used cotton seed oil to fatty acid methyl ester. (Conditions; methanol: feedstock molar ratio = 12:1, catalyst, 1.5-LiC/CaO, amount = 5 wt% of feedstock)

3.3.3.5 Effect of methanol/oil molar ratio

The effect of methanol/oil molar ratio on transesterification reaction is one of the important parameter which affects the methyl ester yield as well as its production cost. Theoretical minimum methanol to oil molar ratio should be 3:1 for the complete conversion of vegetable oil to FAMEs. Transesterification being a reversible reaction, nevertheless, usually such reactions were performed with excess of methanol to shifts the equilibrium in forward direction to achieve the maximum fatty acid methyl ester yield. Heterogeneous catalysts usually catalyzed transesterification reaction at slower rate and took more time for the completion of the reaction. The use of higher molar ratios of methanol to oil (even upto 275:1) in heterogeneous catalyzed reactions to improve the yield of transesterified product in lesser time have been well documented in literature (Xie et al., 2005; Furuta et al., 2004; Leclercq et al., 2001).

To determine the optimum methanol/oil molar ratio in present study, the reactions were performed with 3:1 to 18:1 methanol/oil molar ratios at 65 °C using 5 wt% of 1.5-LiC/CaO catalyst. The rate of transesterification reaction increases as methanol/oil molar ratio was increased from 3:1 to 12:1 and reaction were found to be completed in 45 min when 12:1 methanol/oil molar ratio was used. Further increase in methanol/oil molar ratio does not decrease the reaction time as shown in Figure 12.

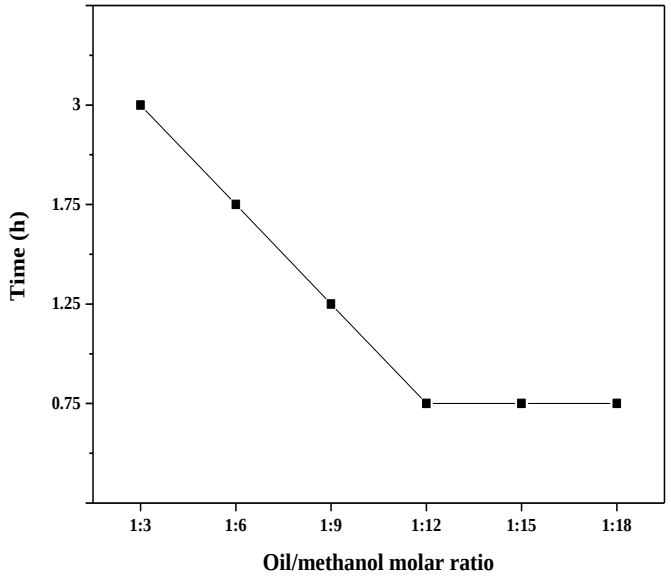


Figure 12. Effect of oil/methanol molar ratio on the time required for complete transesterification of used cotton seed oil to fatty acid methyl ester. (Conditions; catalyst, 1.5-LiC/CaO, amount = 5 wt% of feedstock, temperature = 65 ºC)

3.3.3.6 Effect of moisture content

Presence of > 0.3 wt% moisture contents in feedstock leads to the formation of soap instead of FAMEs when transesterification reaction was catalyzed by homogenous catalyst viz., NaOH or KOH (Canakci and Gerpen, 1999). The used cotton seed oil used in present study were found to have 0.3 wt% moisture contents and transesterification reaction of the same using NaOH or KOH as homogeneous catalyst leads to the saponification of the oil. However, same reaction when catalyzed by 1.5-LiC/CaO catalyst, yielded the complete conversion of oil to FAMEs. In order to determine the maximum moisture resistance of the catalyst, 1.5-LiC/CaO, the transesterification reactions of used cotton seed oil were performed in the presence of 0.3-15.3 wt% (water/oil) water. The same catalyst was found to be effective for the complete transesterification of cotton seed oil in 2.5 h even when 15.3 wt% of moisture contents were present in the reaction mixture as shown in Figure 13. Addition of >15.3 wt% water in the reaction mixture decreases the FAMEs yield and leads to the saponification of oil.

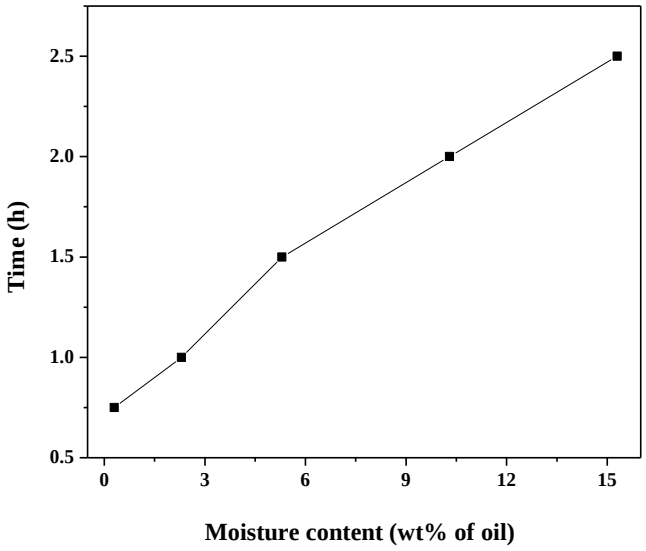


Figure 13. Effect of moisture content on the time required for complete transesterification of used cotton seed oil to fatty acid methyl ester. (Conditions; methanol: feedstock molar ratio = 12:1, catalyst, 1.5-LiC/CaO, amount = 5 wt% of feedstock, temperature = 65 ºC)

3.3.3.7 Effect of free fatty acid contents and varying feedstocks

Like moisture contents, presence of > 0.5 wt% free fatty acids (FFAs) in feedstock leads to formation of soap instead of fatty acid methyl ester when reaction is catalyzed by homogeneous catalyst (Haas, 2004). Used cotton seed oil employed in present study were found to have 0.8 wt% free fatty acid contents and transesterification reaction of the same using NaOH or KOH as homogenous catalyst leads to the formation of soap instead of FAMEs. However, same reaction when catalyzed by nanocrystalline 1.5-LiC/CaO yielded the complete conversion of oil to FAMEs in 45 min. In order to determine the maximum FFA tolerance of the prepared catalyst, the transesterification reactions were performed with a variety of natural feedstocks having different amount of FFAs (wt%) viz., mutton fat (0.9), virgin soybean (0.2), and cotton seed oil (0.11), castor oil (1.8), karanja oil (4.2) and jatropha oil (8.4). As shown in Figure 14, catalyst was found to be effective for the complete transesterification of a variety of feedstocks having upto 8.4 wt% FFAs. However, the activity of the catalyst was found to be effected by the amount of the FFAs present in the feedstock. Relatively lower catalytic activity of the selected catalyst towards the transesterification of karanja and jatropha oil could be due to the partial deactivation of the catalyst by the higher FFAs concentration present in such oils. Transesterification of the same oils in the presence of homogeneous catalyst (KOH or NaOH) leads to the

saponification of the oils instead of FAMEs formation. Hence, the solid catalyst, 1.5-LiC/CaO, used in present study clearly has an advantage over the homogeneous one owing to its application for the transesterification of the high free fatty acid and moisture containing feedstocks.

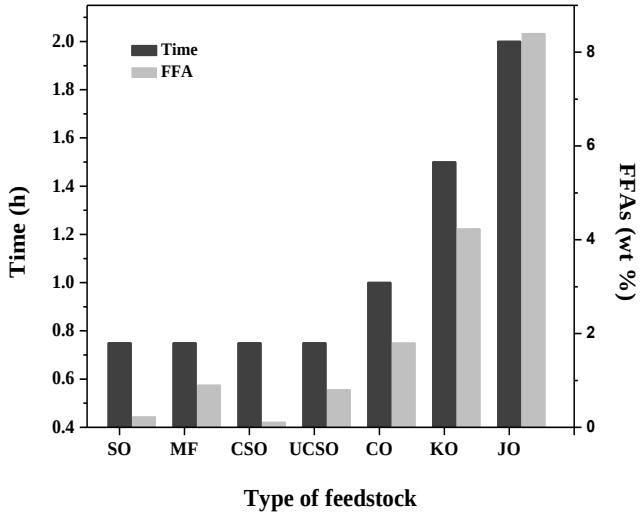


Figure 14. Effect of FFAs on the time required for the complete transesterification of a variety of feedstocks. (Conditions; methanol: feedstock molar ratio = 12:1, catalyst, 1.5-LiC/CaO, amount = 5 wt% of feedstock, temperature = 65 ºC. Acronyms; SO = virgin soybean oil, MF = mutton fat, CSO = virgin cotton seed oil, UCO = used cotton seed oil, CO = castor oil, KO = karanja oil and JO = jatropha oil.)

3.3.3.9 Reusability of the catalyst

An important advantage of the solid catalysts is their reusability as it could reduce the overall processing cost of a chemical reaction. To test the reusability and activity decay of 1.5-LiC/CaO catalyst, it was recovered after transesterification of used cotton seed oil by filtration, washed with hexane and dried at 100 °C. The catalyst thus recovered was used for the second and third catalytic run, respectively, under the same experimental condition and regeneration method. The reused catalyst was also found to complete (100 %) the transesterification of used cotton seed oil though it required 1.25 and 2 h of reaction period when reused for the second and third catalytic cycle respectively as shown in Figure 15. Further reusability (4^{th} cycle onward) of the catalyst leads to the incomplete conversion of the oil to fatty acid methyl ester even after 12 h of reaction period. The lesser activity in 2^{nd}

and 3rd cycle could be due to the partial leaching of Li^+ from the catalyst support or due to the adsorption of the organic molecules on the active sites of the catalyst.

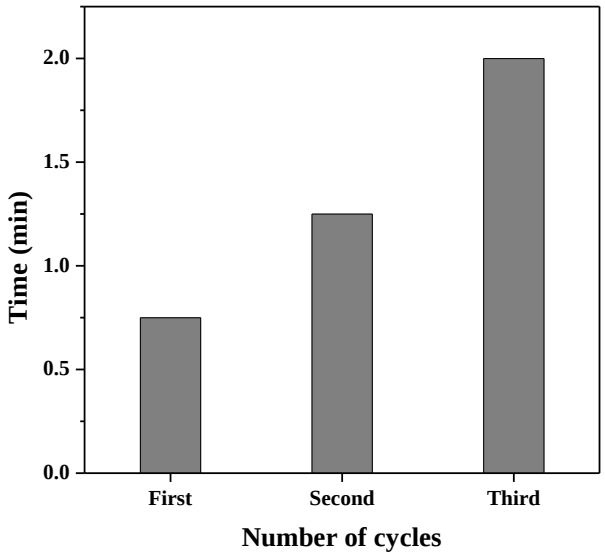


Figure 15. Recyclability studies of the catalyst towards the transesterification of the used cotton seed oil. (Conditions; methanol: cotton seed oil molar ratio = 12:1, catalyst, 1. 5-LiC/CaO, amount = 5 wt% of feedstock, temperature = 65 ºC.)

3.3.3.10 Study of the metal ion leaching and homogeneous contribution

Most of the heterogeneous catalysts reported in literature for the transesterification reactions suffer the drawback of leaching (Gelbard et al., 2001; Lopez et al., 2005; Lotero et al., 2006; Xie et al., 2007) of active species while catalyzing the reaction. The leached species from the catalyst support could catalyze the reaction in a similar manner like homogeneous catalyst can do. In present work to analyze the homogeneous contribution in catalytic activity and to compare the metal ion leaching from the catalyst support, the transesterification reaction of used cotton seed oil with methanol (1:12 molar ratio) has been performed in the presence of 5 wt% of prepared catalysts at 65 ºC as shown in Table 3. After the completion of the reaction, the catalyst was recovered by filtering the reaction mixture through ordinary filter paper, and excess methanol from the same was recovered with the help of rotary evaporator. The reaction mixture thus obtained was kept in separating funnel for 12 h to separate the lower glycerol layer from upper FAMEs layer. The FAMEs thus obtained was investigated for the presence of the metal ion concentration using atomic absorption spectroscopic technique. As given in Table 3, the FAMEs produced by using the 1.5-KC/CaO catalyst was found to have the minimum metal ion concentration.

Table 3. Comparison of the metal ion leaching in FAMEs from the catalysts during the complete transesterification of the used cotton seed oil with a catalyst concentration of 5 wt%, methanol/oil molar ratio of 12:1 and reaction temperature 65 °C.

S. No.	Catalyst	Reaction time (h)	Metal ion leaching (ppm)	
			Li or Na or K	Ca
1.	1.5-LiC/CaO	0.75	7	Not detectable
2.	1.5-LiN/CaO	1.5	2.3	12
3.	1.5-NaC/CaO	3	1.9	1.4
4.	1.5-NaN/CaO	3	6.2	8.4
5.	1.5-KC/CaO	4	1	Not detectable
6.	1.5-KN/CaO	7	1.5	9.6

The metal ions leached from the catalyst support could catalyze the transesterification reaction in a similar manner as homogeneous catalyst can do. In order to quantify the homogeneous contribution involved in the catalyst activity, 500 mg of each catalyst (equivalent to 5 wt% of oil, used later for the transesterification) has been refluxed with the methanol (4.4 g) for desired time at 65 °C. The catalyst was separated from methanol through filtration, and methanol thus obtained has been used for the transesterification of used cotton seed oil (MeOH/oil molar ratio=12:1) at 65 °C. Under the mentioned experimental conditions, no conversion of used cotton seed oil to fatty acid methyl ester has been achieved as shown in Table 4. Thus present study evidently ruled out possibility of the homogeneous contribution due to leached species, and also supports that prepared solid catalyst is responsible for the entire catalytic activity.

Table 4. Homogeneous contribution of the prepared catalysts towards transesterification reaction of used cotton seed oil.

S. No.	Catalyst used (5 wt% of oil)	Refluxing time (h) of catalyst with MeOH	Transesterification reaction time (h) MeOH: oil = 12:1 (m/m)	Conversion due to leached catalyst in MeOH
1.	1.5-LiC/CaO	0.75	0.75	Nil
2.	1.5-LiN/CaO	1.5	1.5	Nil
3.	1.5-NaC/CaO	3	3	Nil
4.	1.5-NaN/CaO	3	3	Nil
5.	1.5-KC/CaO	4	4	Nil
6.	1.5-KN/CaO	7	7	Nil

3.3.4 Kinetic Study

To monitor the progress of the reaction and to evaluate the rate constant, transesterification reactions of jatropha, karanja and used cotton seed oil with methanol have been performed under the optimized reaction conditions viz., using methanol to oil molar ratio of 12:1 in the presence of 5 wt% catalyst (1.5-LiC/CaO) at 65 °C. To monitor the progress of the reaction, samples from the reaction mixture have been withdrawn after every 15 min, centrifuged and rotary evaporated to remove the solid catalyst and excess methanol, respectively and subjected to ^{1}H NMR studies to calculate the fatty acid methyl ester yield in the reaction mixture. As evident from the Figure 16, reaction proceeds at faster rate when used cotton seed oil has been used as feedstock while at slower rate when karanja and jatropha oil have been used as feedstock. The lesser catalytic activity in case of later two oils could be due to the high FFA contents present in them. However, the selected catalyst was found to complete the transesterification of all three feedstock though it required more time (1.5 h and 2 h, respectively) for the complete transesterification of karanja and jatropha oil, in comparison to used cotton seed oil (0.75 h).

The transesterification reaction in the presence of excess methanol is considered to follow the pseudo first-order kinetics (Yan, 2007) and the rate constant (k) for the same could be given as:

$k = -\ln\{(1-y)/t\}$, where y is the FAME yield at time t.

The values of first order rate constant (k) were found to be 0.10, 0.11 and 0.15 min^{-1} for the transesterification of used cotton seed, jatropha and karanja oil respectively, in the presence of 1.5-LiC/CaO catalyst.

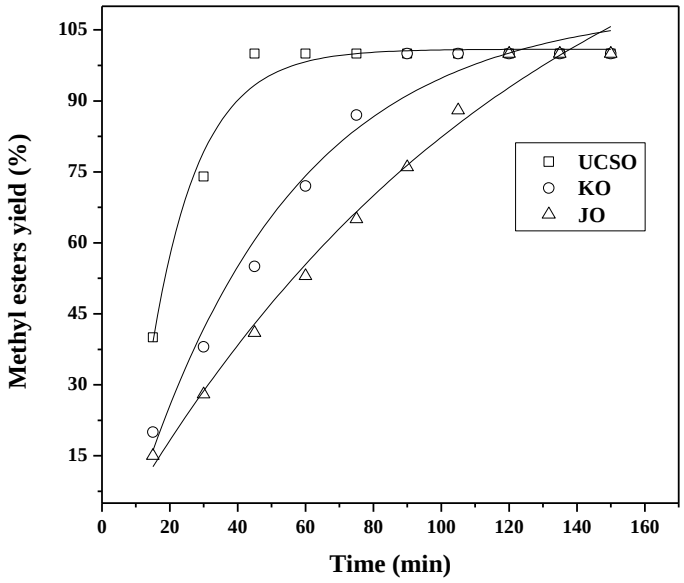


Figure 16. Progress of the transesterification reaction of used cotton seed oil (UCSO), karanja oil (KO) and jatropha oil (JO) with methanol in the presence of 1.5-LiC/CaO catalyst. (Reaction conditions; methanol: feedstock = 12:1 (m/m), catalyst amount = 5 wt%, temperature = 65 ºC.)

3.4 Conclusions

In present work series of alkali metal ion (Li, Na & K) impregnated CaO in nano particle form have been prepared and characterized by the powder XRD, FESEM, TEM, BET surface area and basic strength measurement studies. Calcium oxide impregnated with Li_2CO_3 (1.5-LiC/CaO) was found to have the highest basic strength and surface area and was found to catalyze the complete transesterification reaction of a variety of feedstocks having upto 15.3 wt% moisture and 8.4 wt% of FFA contents. However, the catalytic activity of the same catalyst was found to be adversely affected by the amount of moisture and FFA content present in feedstock. Although, Li and Na impregnated CaO were found to show better activity than K impregnated one, the metal ion leaching in FAMEs was found to be minimum when 1.5-KC/CaO has been used as catalyst. Under optimized reaction condition (methanol: oil molar artio = 12:1; catalyst concentration = 5 wt% and reaction

temperature = 65 ºC), 1.5-LiC/CaO required only 45 min for the complete transesterification of used cotton seed oil. The rate of reaction for the transesterification of used cotton seed oil, karanja oil and jatropha oil have been determined using the pseudo first-order kinetics and found to be 0.10, 0.11 and 0.15 min^{-1} respectively. The lixiviation studies performed with the catalysts suggested that the solid catalyst was responsible for the entire catalytic activity and not any leached species.

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Nickel Doped Calcium Oxide as Nanocrystalline Solid Catalyst: Preparation, Characterization and Application for the Aminolysis of Triglycerides

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Abstract

In present chapter the preparation of amide derivative from vegetable oils and fatty acid methyl esters have been demonstrated using the Ni doped CaO as nanocrystalline solid catalyst. A series of Ni doped CaO as solid catalyst for the aminolysis of vegetable oils and fatty acid methyl ester was prepared by wet chemical method using different amount of nickel and calcinations temperatures. The structure of the prepared catalysts were determined by powder X-ray diffraction studies, and surface morphology and particle size by scanning electron and transmission electron microscopic techniques, respectively. The particle size of the catalysts was found to be in the range of 10-100 nm as supported by transmission electron microscopy and powder XRD studies. Further, the electronic transitions in catalyst in solid state were determined by UV-Vis diffuse reflection spectrum. The N_2 adsorption desorption isotherm was used for pore size distribution and BET surface area measurement of the Ni/CaO particles. The catalyst prepared by doping 0.5wt% of Ni in CaO and calcined at 650 °C (0.5-Ni/CaO-650) was found to show the better activity than others among the prepared catalysts. The same catalyst has been used to carry out the aminolysis of vegetable oil and fatty acid methyl esters with diethanolamine. The variables used for the aminolysis reactions were amount of Ni^{2+} in CaO, catalyst concentration, reaction temperature (35 °C to 150 °C), diethanolamine to oil molar ratio and free fatty acid content (up to 8.4 wt%). The kinetic of the aminolysis reaction has been studied by following the FTIR technique and finally the amide derivative was characterized by proton NMR, and electron impact mass spectroscopic technique.

Keywords: nanocrystalline solid catalyst, aminolysis, N_2 adsorption desorption isotherm, FESEM, TEM, FTIR, proton NMR, EI-MS studies.

4.1 Introduction

In present chapter, the nickel doped calcium oxide as solid catalyst has been employed for the aminolysis of the vegetable oil derived fatty acid methyl esters (as described in chapter 3) and vegetable oils. The fatty acid amides have been reported in literature (Biermann et al., 1995; Alcantara et al., 2000; Stournas et al., 1995) to enhance the ignition quality and other characteristics of the fuel and hence could be used as multifunctional diesel fuel additive.

In literature (Alcantara et al., 2000), aminolysis of soybean oil, used frying oil and tallow with diethyl amine has been reported as shown in Figure 1. In Burton-Coblin autoclave used frying oil with diethyl amine, triethanolamine, sodium methoxide were reacted in an atmosphere of nitrogen at 175 °C for 48 h.

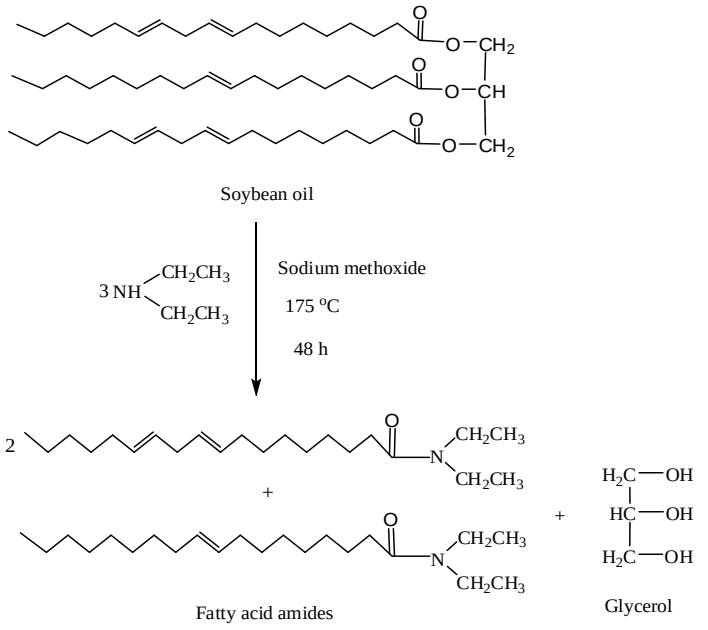


Figure 1. Aminolysis of soybean oil with diethyl amine.

The amide biodiesel thus obtained was blended with petroleum diesel fuel to improve the ignition quality of later (Alcantara et al., 2000). Awasthi and Singh, (2007) reported the fatty acid amide synthesis from erucic acid using lipase (novozym 435) as a catalyst. The reaction was carried out in orbital shaker at 60 °C for 48 h. *Pseudozyma* (*Candida*) *antarctica* lipase B has been reported (Levinson et al., 2005) as catalyst for the fatty acid amide synthesis from ricinoleic acid and ammonia. The maximum conversion of 95% was obtained when reaction was carried out at 55 °C for 1 day.

Other methods of producing fatty acid amides at industrial scale was reported (Feairheller et al., 1994) by heating fatty acids or fatty methyl esters with ethanolamine at 140–160 °C for 6–12 h as shown in Figure 2.

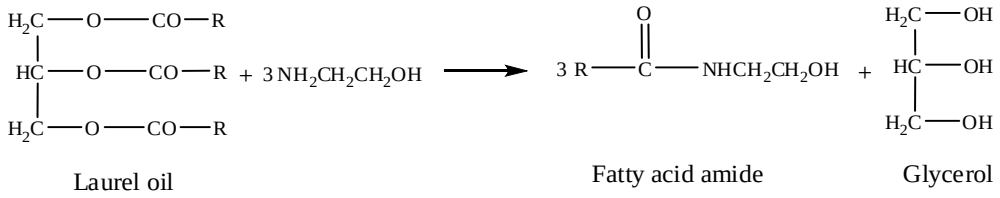


Figure 2. Aminolysis of laurel oil with ethanolamine.

In this reaction amine itself could act as a catalyst, however, when the reaction was catalyzed by stronger base viz., sodium methylate or sodium methoxide, the reaction proceeds at faster rate and leads to the completion of the reaction in 3 and 1h, respectively (Monick, 1962; Kolancilar, 2004).

As discussed above literature reported methods for the preparation of the fatty acid amide derivatives involves either no catalyst or homogeneous catalysts. In former case complete conversion of substrate to fatty acid amide derivative required longer reaction duration and relatively higher reaction temperature, while in later case incomplete conversion and catalyst contaminated products were reported (Alcantara et al., 2000). In order to improve the literature reported methodology for the fatty acid amide derivative preparation form vegetable oils and fatty acid methyl esters, in present chapter efforts have been to prepare the Ni/CaO as solid catalyst for the aminolysis reaction. The Ni doped CaO catalyst has been prepared by wet chemical method and characterized by powder XRD, solid state UV-Vis diffuse reflectance, SEM, TEM, Hammett indicators, BET surface area and pore size distribution studies. The prepared catalyst has been used as solid catalyst for the aminolysis of fatty acid methyl esters derived from cotton seed oil, methyl laurate and fatty acid methyl esters derived from cotton seed oil and animal fat. The prepared amide derivatives have been used later as a dual functional diesel fuel additive to improve the lubricity as well as cetane number of the diesel fuel.

4.2 Experimental Section

4.2.1 Preparation of Ni/CaO catalyst

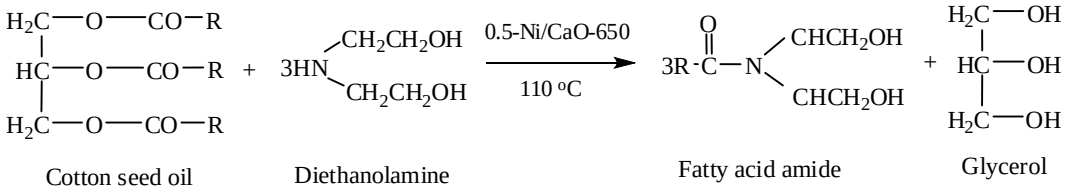
The nanocrystalline Ni/CaO catalysts were prepared by wet chemical method and in a typical preparation, CaO (10 g) was suspended in 40 mL deionized water. A 10 mL aqueous $Ni(NO_3)_2$ solution of desired concentration was added to the CaO suspension to obtain the final nickel concentration 0.25 – 6 wt% in CaO. The slurry so obtained was stirred for 3 h, then evaporated to dryness and heated in the temperature range of 150 to 950 °C for 12 h. The Ni/CaO, so prepared was characterized by powder XRD, UV-visible diffuse reflectance, BET surface area and pore size measurement, a Hammett indicator test, FESEM and HRTEM techniques.

The prepared catalysts were designated as xx-Ni/CaO-T, where xx represents the nickel concentration (wt %) in CaO, and T represents the calcinations temperature e.g. 0.5-Ni/CaO-650 represent the catalyst prepared by doping 0.5 wt % of Ni^{+} in CaO and calcined at 650 °C.

4.2.2 Aminolysis reactions

4.2.2.1 Aminolysis of used cotton seed oil

All aminolysis reactions were performed in a 100 mL, two neck round bottom flask equipped with a water-cooled condenser, oil bath and a magnetic stirrer. In a typical aminolysis reaction, used cotton seed oil and diethanolamine in 1:5 molar ratio and 5 wt% of 0.5-Ni/CaO-650 catalyst were taken in a two neck round bottom flask and heated upto 110 °C for 0.5 h as shown in Scheme 1. After the completion of the reaction, the product was dissolved in 60 mL hexane and placed in a separating funnel. The upper hexane layer was separated from the lower glycerol layer, washed with water, dried over anhydrous sodium sulfate and the hexane was rotary-evaporated to yield the pure fatty acid amide derivative.

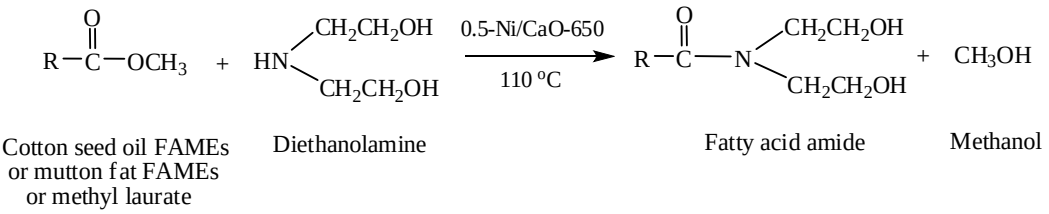


Scheme 1: Aminolysis of cotton seed oil with diethanolamine in the presence of 0.5-Ni/CaO-650 catalyst.

The amide product so obtained was further characterized by FTIR and ^{1}H-NMR techniques and the FTIR technique was also used to quantify the fatty acid amide yield by following the literature reported method (Alcantara et al., 2000).

4.2.2.2 Aminolysis of cotton seed oil derived methyl esters and methyl laurate

In order to test the efficiency of 0.5-Ni/CaO-650 with other substrates, the aminolysis reactions of cotton seed oil and mutton fat derived fatty acid methyl ester (prepared in previous chapter) and commercially available methyl laurate with diethanolamine have been performed in the presence of same catalyst as shown in Scheme 2. In all cases complete conversion (> 99%) of substrate to corresponding amide have been achieved. After the completion of the reaction, the reaction mixture was washed with water to remove the methanol and excess amine and amide product was separated from the aqueous layer with the help of separating funnel. The amide products thus obtained was dried over anhydrous sodium sulfate and finally characterized and quantified by following the same method as mentioned above in case of cotton seed oil derived amide products. In case of amide derivative obtained from the aminolysis of methyl laurate, the product was also analyzed by EI-MS technique.



Scheme 2: Aminolysis of cotton seed FAMEs or mutton fat FAMEs or methyl laurate with diethanolamine in the presence of 0.5-Ni/CaO-650 catalyst.

Fatty acid amide derivative of used cotton seed oil (FAAUC): Yield > 99%. FTIR (cm^{-1}): 3397 (ν_{OH}), 1615 ($\nu_{C=O}$); ^{1}H-NMR ($CDCl_3$, δ ppm): 5.3 (m, -C**H**=C**H**-), 3.77 (m, -C**H$_2$**OH), 3.46 (m, -NC**H$_2$**-), 2.7 (m, -CH=CH-C**H$_2$**-CH=CH-), 2.31 (m, -C**H$_2$**-CO-), 2.0 (m, -C**H$_2$**-$(CH_2)_n$-CH-), 1.6-1.25 (m, -(C**H$_2$**)$_n$-), 0.95 (m, -CH=CH-C**H$_3$**)0.87 (m, -CH_2-C**H$_3$**).

Fatty acid amide derivative of fatty acid methyl ester of used cotton seed oil (FAAUCM): Yield > 99%. FTIR (cm^{-1}): 3398 (ν_{OH}), 1615 ($\nu_{C=O}$); ^{1}H-NMR ($CDCl_3$, δ ppm): 5.3 (m, -C**H**=C**H**-), 3.78 (m, -C**H$_2$**OH), 3.48 (m, -NC**H$_2$**-), 2.7 (m, -CH=CH-C**H$_2$**-CH=CH-), 2.3 (m,

-C**H₂**-CO-), 2.0 (m, -C**H₂**-$(CH_2)_n$-), 1.6-1.25 (m, -(C**H₂**)$_n$-), 0.95 (m, -CH=CH-C**H₃**), 0.87 (m, -CH_2-C**H₃**).

Fatty acid amide derivative of fatty acid methyl ester of mutton fat (FAAMM): Yield > 99%. FTIR (cm^{-1}): 3398 (ν_{OH}), 1615 ($\nu_{C=O}$); ^{1}H-NMR ($CDCl_3$, δ ppm): 5.3 (m, -C**H**=C**H**-), 3.75 (m, -C**H₂**OH), 3.47 (m, -NC**H₂**-), 2.3 (m, -C**H₂**-CO-), 2.0 (m, -C**H₂**-$(CH_2)_n$-), 1.6-1.25 (m, -(C**H₂**)$_n$-), 0.87 (m, -CH_2-C**H₃**).

Fatty acid amide derivative of methyl laurate (FAAML): Yield > 99%. FTIR (cm^{-1}): 3397 (ν_{OH}), 1615 ($\nu_{amide\text{-}C=O}$); ^{1}H-NMR ($CDCl_3$, δ ppm): 3.8 (m, -C**H₂**OH), 3.5 (m, -NC**H₂**-), 2.3 (m, -C**H₂**-CO-), 1.6-1.25 (m, -(C**H₂**)$_n$-), 0.87 (m, -CH_2-C**H₃**); EI-MS (m/z) (Intensity (%), fragment): 287.2 (3, M), 270.3 (100, M-H_2O), 227.22 (10, M-$CH_3(CH_2)_3$), 175.2 (10, M-$CH_3(CH_2)_7$), 132.2 (12, M-$CH_3(CH_2)_{10}$), 114.2 (5, M-$CH_3(CH_2)_{10}OH$).

4.3 Results and Discussion

4.3.1 Catalyst preparation and characterization

As discussed in previous chapter the catalytic activity of the CaO were found to depend on its basic strength. In present work the basic strength of CaO were improved by Ni^{2+} doping. A series of Ni^{2+} doped CaO were prepare by wet chemical method and varying the nickel concentration in the range of 0.25-6 wt% in CaO. The catalysts so prepared were characterized by Hammett indicator test, BET surface area, nitrogen adsorption-desorption, powder X-ray diffraction, solid state UV-Vis, FESEM, and TEM studies.

4.3.1.1 Hammett indicator test

The basic strength of the pres CaO and Ni/CaO were determined by Hammett indicators (Wan et al., 2009), and given in Table 1. The basic strength of the commercial CaO was found to increase from 9.8-10.1 to 15.0-18.4 after 0.5 wt% nickel doping in CaO followed by calcinations at 450 °C. A further change in nickel concentration and/or calcinations temperature either yielded the Ni/CaO of same basic strength (15.0-18.4) or with lesser basic strength as given in Table 1. The highest basic strength of 0.5-Ni/CaO-650 could be due to the formation of strong basic sites on CaO surface after Ni^{2+} doping. Hence 0.5-Ni/CaO-650 catalyst expected to show the better catalytic activity towards the aminolysis reaction among the prepared catalyst.

4.3.1.2 BET surface area studies

The surface area of pure calcium oxide and nickel loaded CaO was measured by BET method and the same was found to be increased after doping the CaO with Ni^{+2} as shown in Table 1. The maximum surface area of 14.66 m^2/g was found in case of 0.5-Ni/CaO-650 material. As the calcination temperature was increased from 150 to 650 °C, the surface area of the catalysts was found to increase regularly form 3.79 to 14.66 m^2/g. A further increase in calcination temperature was found to reduce the surface area due to the sintering, or structural rearrangement (Knozinger et al., 1993), thus leading to lower surface areas and more crystalline material.

Table 1. Comparison of the basic strengths and BET surface area of nickel metal ion doped CaO with that of pure CaO.

Catalyst type	Basic strength (H_)	BET surface area (m^2/g)	Pore Size (Å) BJH Adsorption	Particle size (nm)	
				Debye Scherrer method	HRTEM method
Pure-CaO	9.8< H_<10.1	3.96	----	104	150
0.5-Ni/CaO-150	11.1< H_<15	3.79	----	44.5	35
0.5-Ni/CaO-250	11.1< H_<15	3.80	----	42.2	30
0.5-Ni/CaO-350	11.1< H_<15	4.64	187.89	40.1	20
0.5-Ni/CaO-450	15< H_<18.4	12.88	----	33.4	20
0.5-Ni/CaO-650	15< H_<18.4	14.66	249.78	17.5	10
0.5-Ni/CaO-850	15< H_<18.4	11.70	----	28.1	25
0.5-Ni/CaO-950	11.1< H_<15	3.92	187.79	39.1	35
1-Ni/CaO-650	11.1< H_<15	----	----	44.8	20
2-Ni/CaO-650	15< H_<18.4	----	----	40.1	20
3-Ni/CaO-650	15< H_<18.4	----	----	49.2	20
4-Ni/CaO-650	15< H_<18.4	----	----	49	25
5-Ni/CaO-650	15< H_<18.4	----	----	45.5	30
6-Ni/CaO-650	15< H_<18.4	----	----	26	30

4.3.1.3 Nitrogen adsorption-desorption studies

The N_2 adsorption-desorption isotherms of 0.5-Ni/CaO-350, 0.5-Ni/CaO-650 and 0.5-Ni/CaO-950 are shown in Figure 3. The sharp steps of capillary condensation of N_2 are observed at P/P_0 = 0.8-0.9 in the isotherms of 0.5-Ni/CaO-350, 0.5-Ni/CaO-650 and 0.5-Ni/CaO-950. These isotherms exhibit a typical pattern IV according to the IUPAC classification and H1-type hysteresis loops. In case of 0.5-Ni/CaO-350 and 0.5-Ni/CaO-950, the hysteresis loop becomes narrower and for 0.5-Ni/CaO-650 the loop becomes broad. This observation could explained due to the presence of shortened mesoporous channels and broadened pore size distributions in case of 0.5-Ni/CaO-350 and 0.5-Ni/CaO-950 samples.

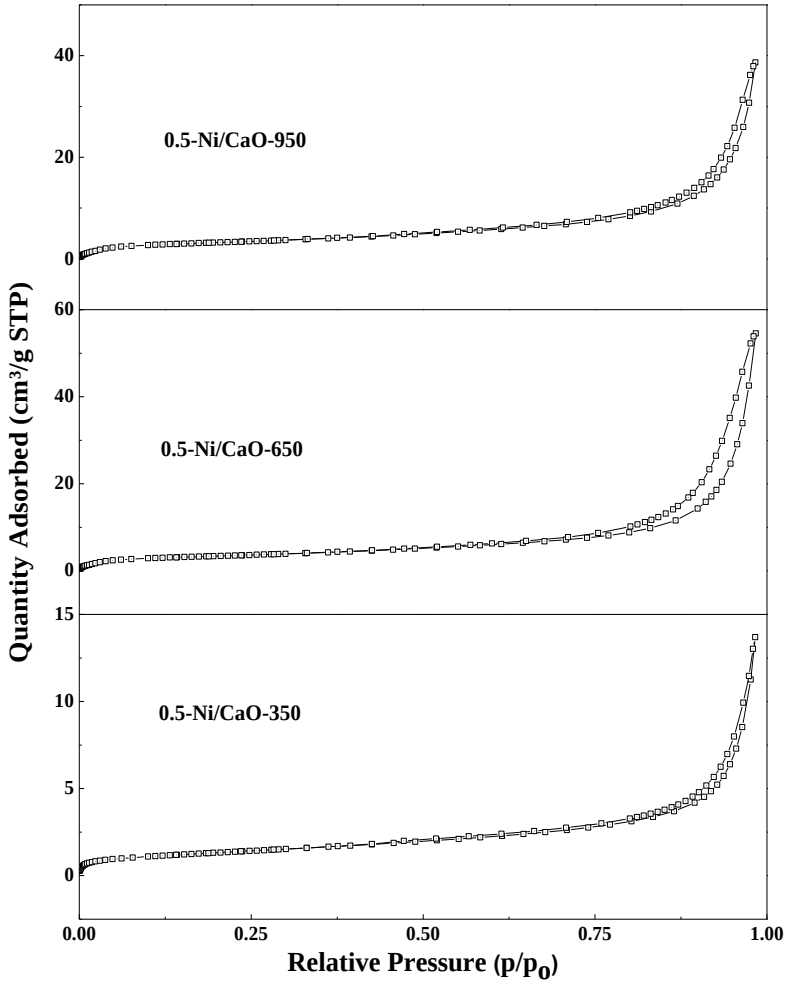


Figure 3. Nitrogen adsorption-desorption isotherms of 0.5-Ni/CaO-350, 0.5-Ni/CaO-650 and 0.5-Ni/CaO-950.

The narrow BJH pore-size distribution curves of 0.5-Ni/CaO-350 and 0.5-Ni/CaO-950 confirm that the pores are uniform in both the cases. However, the BJH pore-size distribution for 0.5-Ni/CaO-650 is much broader than that of 0.5-Ni/CaO-350 and 0.5-Ni/CaO-950 so less uniform as shown in Figure 4.

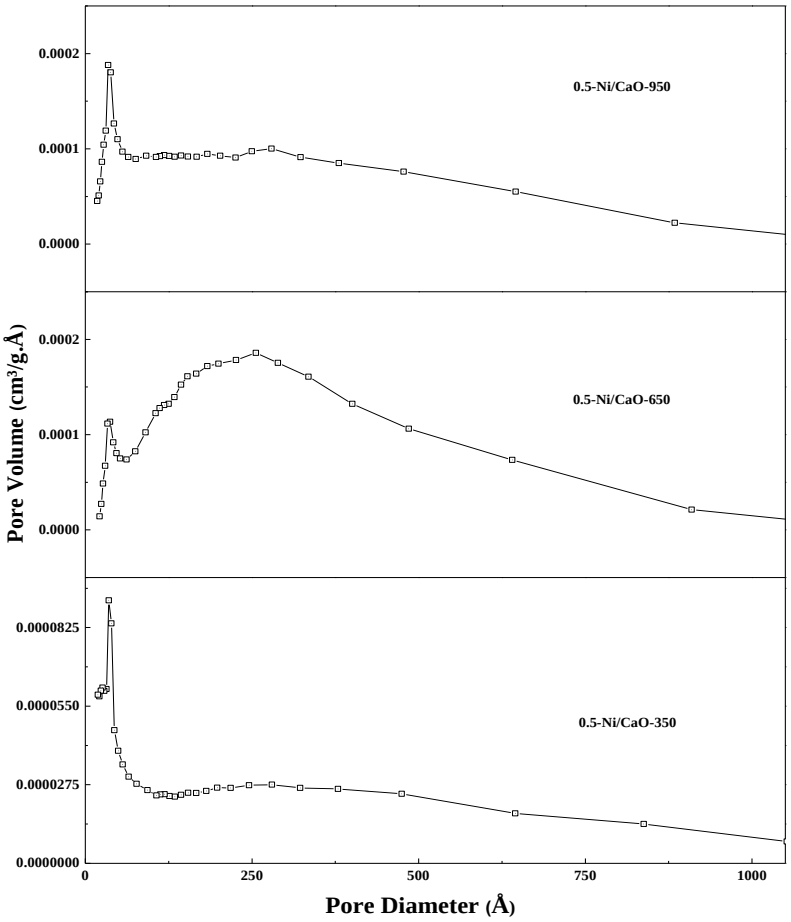


Figure 4. BJH pore-size distribution profile of 0.5-Ni/CaO-350, 0.5-Ni/CaO-650 and 0.5-Ni/CaO-950.

4.3.1.4 Powder XRD analysis

The structure analysis of Ni/CaO, prepared with different Ni^{2+} concentration (0.25-6 wt%) and calcined at different temperatures (150-950 °C), has been done by using powder XRD analysis. The comparisons of the powder XRD patterns of commercially available CaO with 0.5 wt% nickel loaded CaO and calcined at different temperatures are shown in Figure 5. The commercial CaO shows peaks at 2θ values of 37.36°, 54.36° and 32.57° due to the presence of calcium oxide in cubic form (JCPDS card no. 821691) , as shown in Figure 5. The presence of low intensity peaks at 29.4° and at 64.4° reveals the presence of minor

amount of calcium carbonate as calcite in the CaO used as a support (JCPDS 881811). The presence of peaks at 34.12°, 18.06° and 47.15° in the powder XRD pattern of Ni/CaO calcined at 150 and 350 °C supports the existence of $Ca(OH)_2$ in hexagonal form. The XRD pattern of Ni/CaO calcined at 450 °C, shows the peaks at 2θ ~ 34.12°, 18.06° and 47.15° and 2θ ~ 37.36°, 54.36° and 32.57° due to the presence $Ca(OH)_2$ in hexagonal, and CaO in cubic from, respectively. Hence, the transition of $Ca(OH)_2$ to CaO starts at 450 °C and complete conversion of $Ca(OH)_2$ to CaO occurs at 650 °C as shown in Figure 5. The absence of the diffraction patterns of $Ni(NO_3)_2$ or NiO could be either due to its high degree of dispersion on the CaO surface or its concentration being smaller than those detectable by the powder XRD technique.

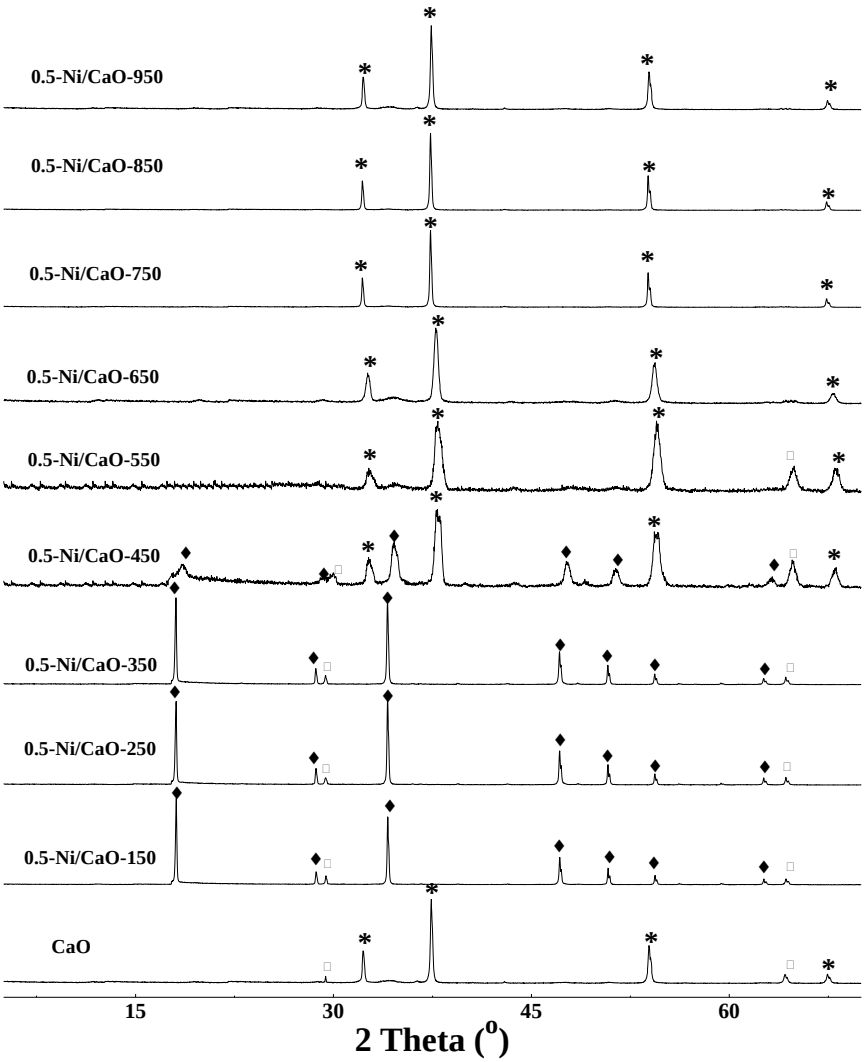


Figure 5. Comparison of XRD spectra of commercially available CaO with 0.5-Ni/CaO-150, 0.5-Ni/CaO-350, 0.5-Ni/CaO-650 and 0.5-Ni/CaO-950. (calcium oxide = *; calcium hydroxide = ♦; and calcium carbonate = □).

In order to check the effect of increasing Ni concentration on CaO structure, the amount of Ni in CaO has been varied in the range of 0.5-6 wt% and resulted Ni/CaO was calcined at 650 °C. In powder XRD spectrum of Ni/CaO, no peaks due to NiO were observed upto 5 wt% loading of nickel in CaO. This could be due to high degree of dispersion of nickel ions on the CaO surface. However, when the nickel concentration was increased upto 6 wt%, the low intensity peaks at 2θ values of 43.2° and 62.7° were observed due to the presence of NiO in cubic phase (JCPDS 780643) as shown in Figure 6. The particle size of the prepared Ni/CaO material was determined by Debye-Scherrer method (Qadri et al., 1999) using powder XRD data and found in the range of 17.5-49.2 nm as shown in Table 1.

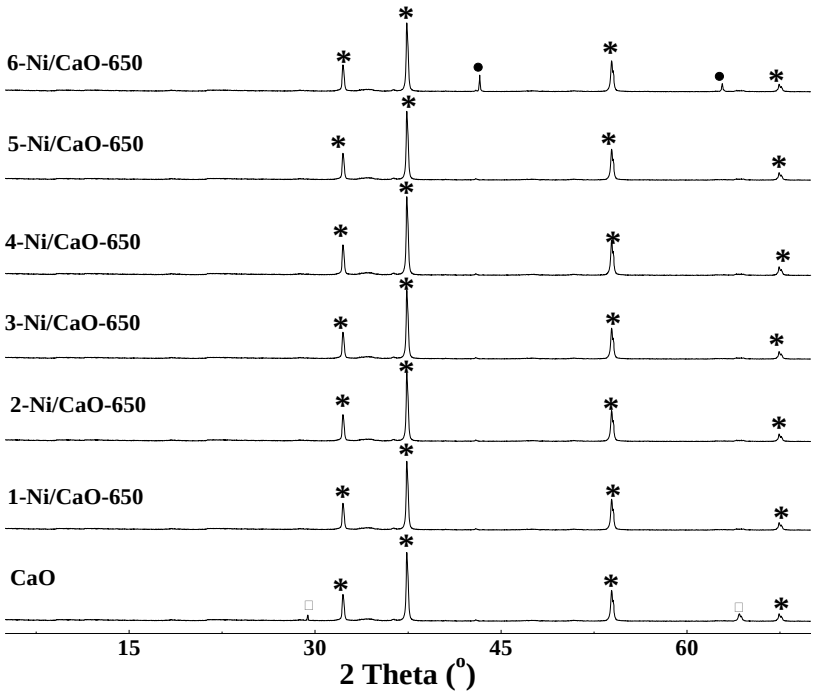


Figure 6. Comparison of XRD spectra of commercially available CaO with CaO doped with 1-6 wt% of nickel. (Calcium oxide = *; nickel oxide = ●; and calcium carbonate = □)

4.3.1.5 FESEM and HRTEM studies

The size and surface morphology of the prepared Ni/CaO catalysts were observed by scanning electron microscope (SEM). There is a mixture of hexagonal and cubic shaped particles in 0.5-Ni/CaO-350, while in case of 0.5-Ni/CaO-650 and 0.5-Ni/CaO-950 the particle shape was found to be cubic and irregular as shown in Figure 7. The average particle size by FESEM studies were found to be in the range of 2-5 μm as shown in Figure 7. The presence of Ni in CaO was also confirmed by Field Emission Scanning Microscopy-

Energy Dispersive X-ray Analysis (FESEM-EDX) studies which show the presence of 0.6 % nickel in 0.5-Ni/CaO-650.

Analysis of the same particles by transmission electron microscope (TEM) shows that the particles of catalysts exist in nanoscale. The average particle size in 0.5-Ni/CaO-350 and 0.5-Ni/CaO-950 is found to be ~20 nm. On the other hand the 0.5-Ni/CaO-650 particles predominantly exists in the form of nanorods having length of ~100 nm and thickness of 8-10 nm as shown in Figure 7.

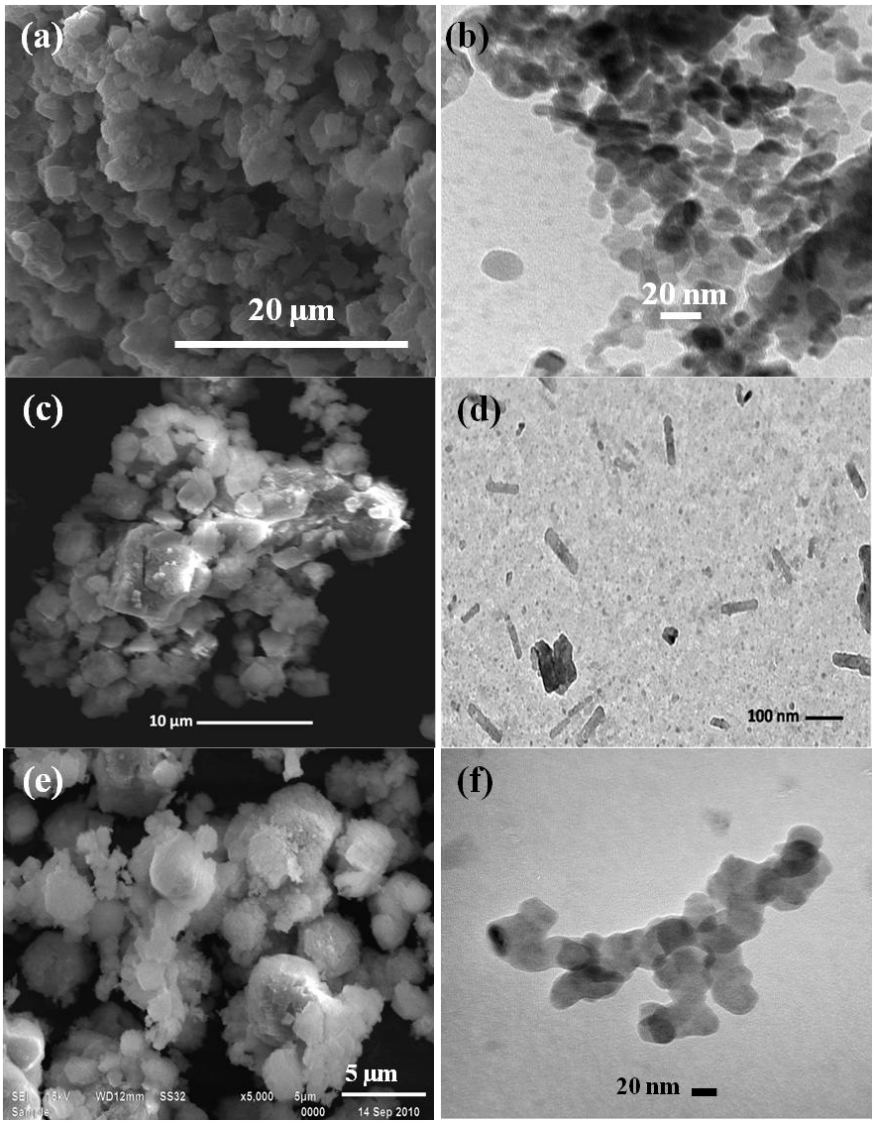


Figure 7. Comparative FESEM images of (a) 0.5-Ni/CaO-350, (c) 0.5-Ni/CaO-650, and (e) 0.5-Ni/CaO-950 and HRTEM images of (b) 0.5-Ni/CaO-350, (d) 0.5-Ni/CaO-650, and (f) 0.5-Ni/CaO-950.

4.3.1.6 UV-visible diffuse reflectance spectroscopic analysis

The solid state UV-visible diffuse reflectance spectra of pure CaO and 0.5 wt% nickel doped CaO and calcined at different temperatures are shown in Figure 8. The Ni/CaO calcined above 350 °C, shows a peak at 254 nm, to support the presence of Ni^{2+} in octahedral coordination environment.

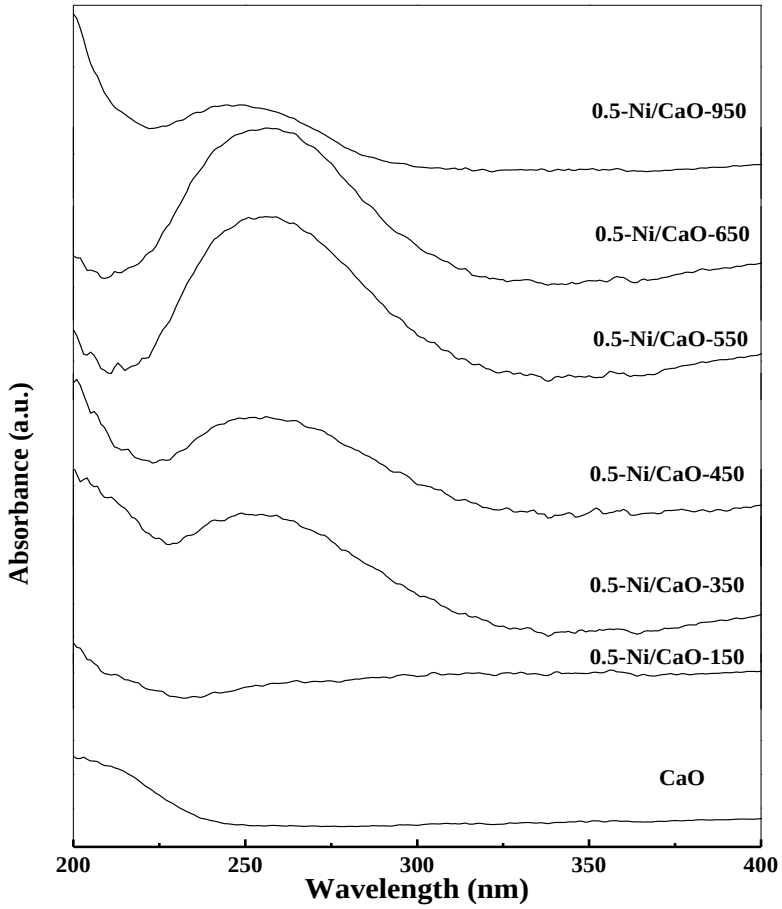


Figure 8. Comparative solid state UV-Visible spectrum of CaO and Ni/CaO and calcined in the temperature range of 150-950 °C.

4.3.2 Aminolysis reaction

The aminolysis reactions of a variety of feedstocks (methyl laurate, mutton fat FAMEs, used cotton seed oil and used cotton seed oil derived FAMEs) with diethanolamine were employed in the presence of prepared Ni/CaO solid catalysts. However, initially the reaction conditions have been optimized using used cotton seed oil as feedstock.

The progress of the aminolysis reactions have been monitored by FTIR spectroscopic technique. The samples from the reaction mixture have been withdrawn with the help of glass dropper after regular intervals of time and subjected to FTIR analysis. The complete

conversion of used cotton seed oil or fatty acid methyl ester to corresponding amide have been supported by the disappearance of the ester carbonyl band at 1743 cm^{-1} and the appearance of a new band at 1615 cm^{-1} due to amide carbonyl.

4.3.3 Product characterization

The purified fatty acid amides, derived from used cotton seed oil, used cotton seed oil derived FAMEs, mutton fat derived FAMEs and methyl laurate were characterized by FTIR and ^{1}H NMR spectroscopic techniques. Amide derivative of methyl laurate was also characterized by mass spectroscopic studies.

4.3.3.1 FTIR analysis

The FTIR spectra of vegetable oils, fat and fatty acid methyl esters show the ester carbonyl peak at 1743 cm^{-1}. After the aminolysis reaction of these esters formation of the amide products was supported by the disappearance of the ester carbonyl band at 1743 cm^{-1} and the appearance of a new band at 1615 cm^{-1} due to amide carbonyl as shown in Figure 9. The presence of –OH group in all amide products was also supported by an additional peak at ~3398 cm^{-1} in FTIR spectra. The FTIR technique has also been used to monitor the progress of the reaction and quantify the amide products formed by following the literature reported procedure (Alcantara et al., 2000).

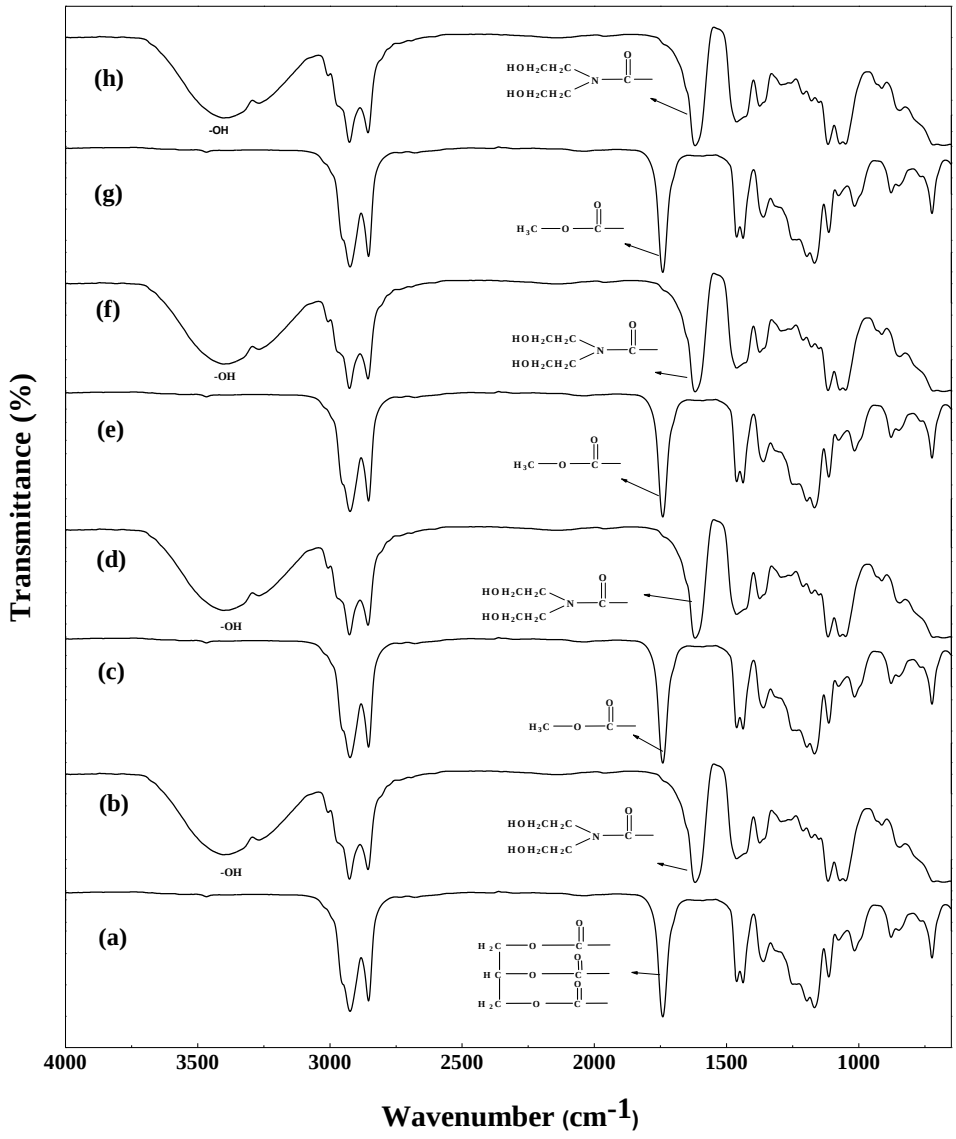


Figure 9. Comparative FTIR spectra of (a) cotton seed oil, (b) fatty acid amide of cotton seed oil, (c) cotton seed oil derived FAME, (d) fatty acid amide of cotton seed oil derived FAME, (e) mutton fat derived FAME, (f) fatty acid amide of mutton fat FAME, (g) methyl laurate, and (h) amide derivative of methyl laurate.

4.3.3.2 ^{1}H-NMR studies

Fatty acid amides produced during the aminolysis reaction of used cotton seed oil with diethanolamine were further characterized by ^{1}H NMR spectroscopy. Proton NMR spectrum of cotton seed oil shows a multiplet at 4.1 and 5.2 ppm due to the presence of glyceridic protons besides other hydrocarbon peaks as given in Figure 10. In aminolyzed product, appearance of multiplet at 3.5 and 3.8 ppm due to -NC**H$_2$**- and -C**H$_2$**OH protons,

respectively and disappearance of glyceridic protons support the conversion of oil to corresponding fatty acid amide as shown in Figure 10. Similarly proton NMR spectra were observed in case of the amide products obtained from the aminolysis of fatty acid methyl esters of cotton seed oil, fatty acid methyl esters of mutton fat and methyl laurate with diethanolamine as shown in Figure 10. The absence of peaks at 5.3 ppm in case of methyl laurate (Figure 10 g) and amide derivative of methyl laurate (Figure 10 h) was due to the absence of unsaturation (-CH=CH-) in same.

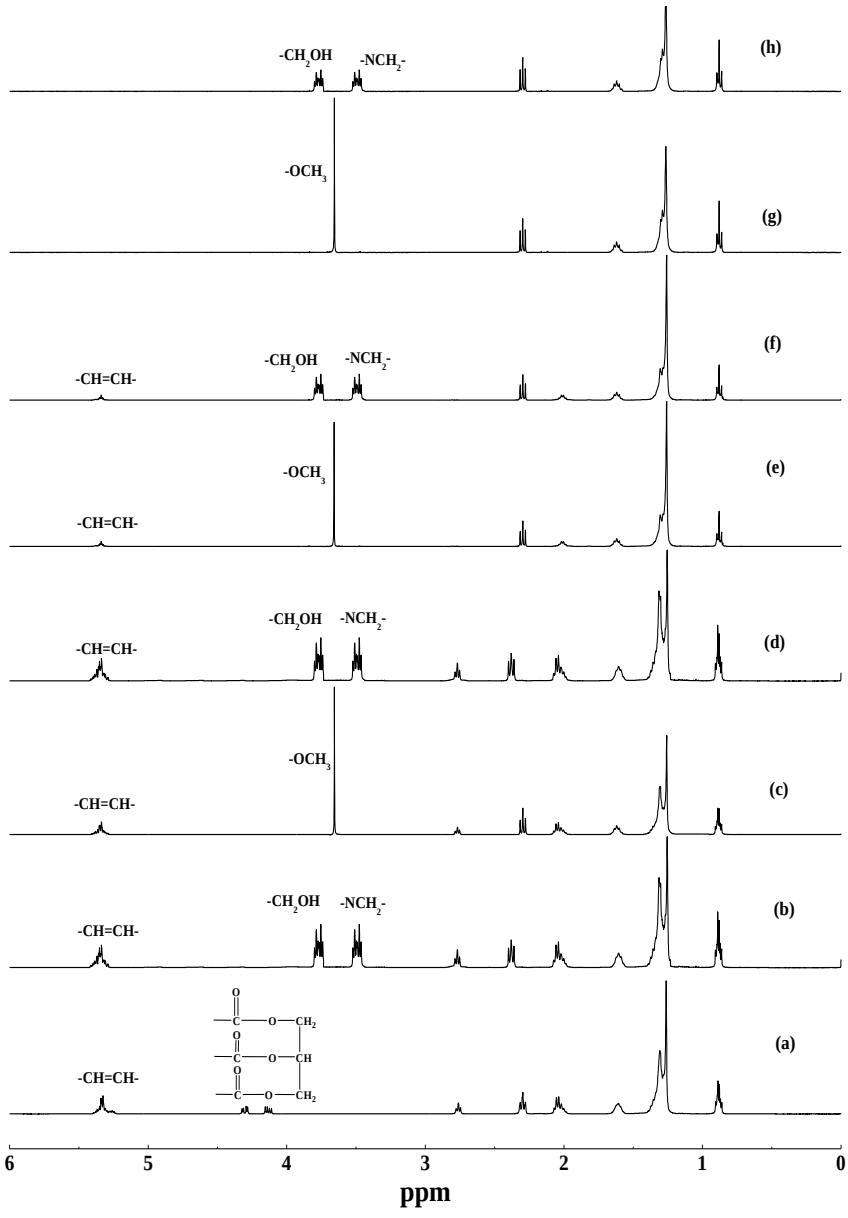


Figure 10. Comparison of ^{1}H-NMR spectra of (a) cotton seed oil, (b) fatty acid amide of cotton seed oil, (c) cotton seed oil FAME, (d) fatty acid amide of cotton seed oil FAME, (e) mutton fat FAME, (f) fatty acid amide of mutton fat FAME, (g) methyl laurate, and (h) amide derivative of methyl laurate.

4.3.3.3 EI-MS studies

Amide derivative of methyl laurate (N,N-diethanoldodecylamide) was further analyzed for mass spectroscopy technique as shown in Figure 11, besides FTIR and proton NMR technique. The EI-MS spectrum of N,N-diethanoldodecylamide shows a very low intensity molecular ion peak at m/z ratio of 287. The base peak was observed at m/z value of 270, showing the loss of water molecule from the laurate amide.

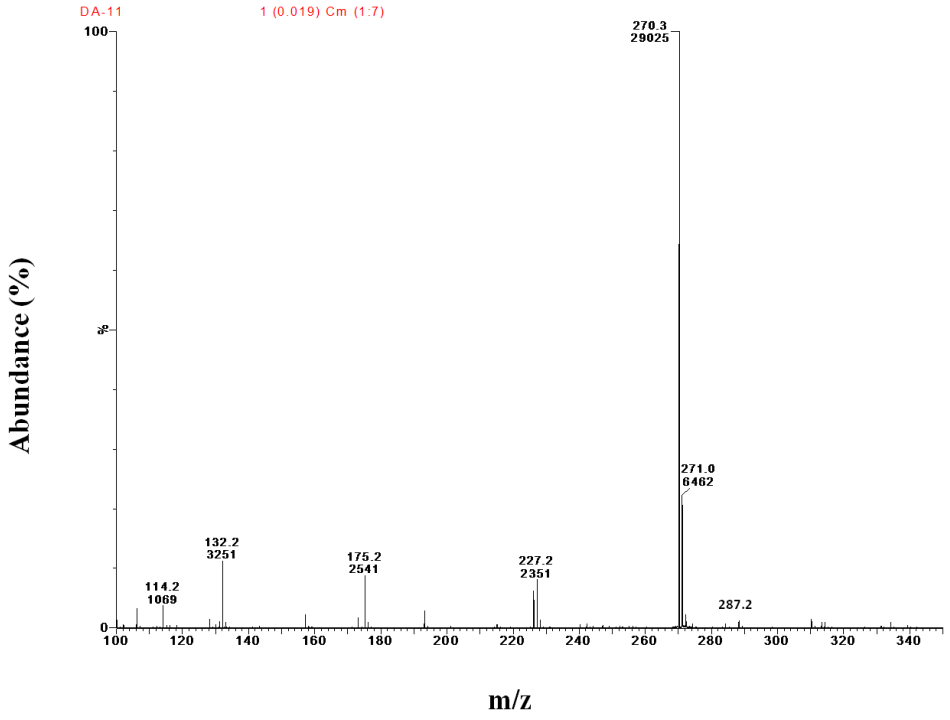


Figure 11. Mass spectra of N,N-diethanoldodecylamide.

4.3.4 Catalytic activity

In order to compare the catalytic activity of the prepared catalysts, used cotton seed oil was used as substrate. Aminolysis reactions of used cotton seed oil with desired molar concentrations of diethanolamine were performed in the presence of desired catalyst amount at desired temperature.

During the course of study out of (i) doped nickel ion concentration in CaO (ii) calcination temperature, (iii) catalyst concentration, (iv) reaction temperature and (v) diethanolamine/oil molar ratio, one parameter at a time has been varied in order to establish the most suitable reaction condition for the aminolysis reaction.

The reusability of the selected catalyst and its homogeneous contribution in the catalyst activity has also been studied.

4.3.4.1. Effect of nickel ion concentration

To determine the optimum nickel ion concentration in CaO to achieve the best catalytic activity, a series of catalyst was prepared by varying the amount of nickel in the range of 0.25-6 wt% (Ni/CaO). The aminolysis reactions of used cotton seed oil were performed with diethanolamine (5:1 diethanolamine/oil molar ratio) at 110 ºC in the presence of 5 wt% prepared catalysts. Reaction time required for the complete aminolysis was found to decrease from 1 h to 30 min as the amount of nickel ion in CaO were increased from 0.25 to 0.5 wt%. However, further increase in Ni^{+2} ion concentration does not reduce the reaction time as shown in Figure 12. Hence, 0.5-Ni/CaO-650 catalyst was selected for optimizing other parameters to achieve the minimum time for the complete aminolysis reaction.

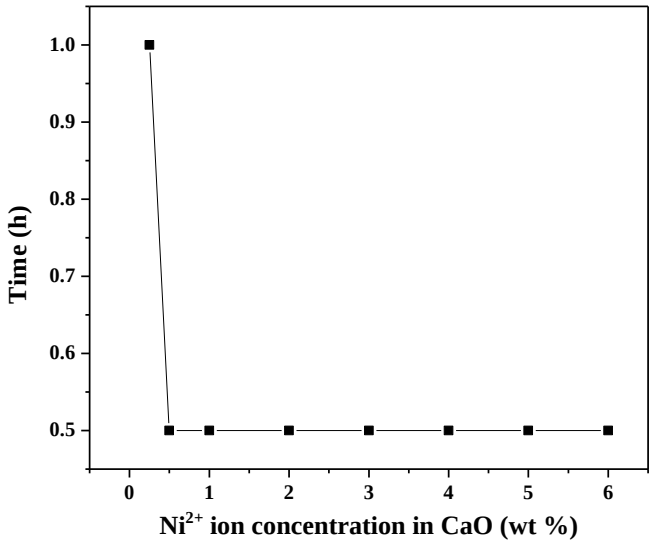


Figure 12. Effect of nickel ion concentration in catalyst on the time required for the complete aminolysis of used cotton seed oil. (Reaction conditions; diethanolamine: feedstock = 5:1 (m/m), catalyst amount = 5 wt% of feedstock, temperature = 110 ºC.)

4.3.4.2. Effect of calcination temperature

In order to determine the optimum calcinations temperature for the best catalytic activity, a series of catalyst was prepared by doping 0.5 wt% Ni in CaO and calcining the same in the temperature range of 150-950 ºC. A 5 wt% amount of the catalysts with respect to oil have

been used for the aminolysis reaction of used cotton seed oil with diethanolamine (1:5 molar ratio) at 110 ºC. Reaction time required for the complete aminolysis was found to decrease from 2.5 h to 0.5 h as the calcination temperature increases from 250 to 650 ºC. However, a further increase in calcination temperature was found to increase the required time for the completetion of the reaction as shown in Figure 13. Hence catalyst prepared by doping 0.5 wt% of Ni^{2+} in CaO and calcining at 650 ºC was selected for optimizing other parameters for the complete aminolysis of used cotton seed oil.

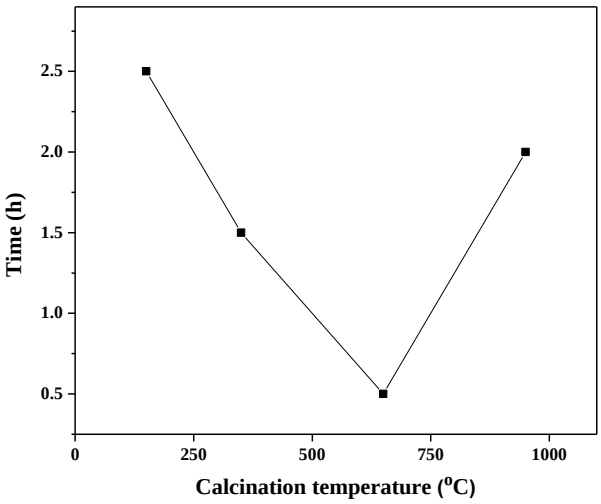


Figure 13. Effect of calcinations temperature on the time required for the complete aminolysis of used cotton seed oil. (Reaction conditions; diethanolamine: feedstock = 5:1 (m/m), catalyst amount = 5 wt% of feedstock, temperature = 110 ºC.)

4.3.4.3 Effect of catalyst concentration

In order to find the optimum catalyst concentration a series of aminolysis reactions of used cotton seed oil with diethanolamine (5:1 molar ratio) at 110 ºC were performed in the presence of nanocrystalline 0.5-Ni/CaO-650 by varying its concentration in the range of 2-7 wt% (catalyst/oil). Time required for the complete conversion decreases from 2.5 h to 0.5 h as catalyst concentration was increased from 2 to 5 wt%. A further increase in catalyst concentration does not reduce the reaction time significantly as shown in Figure 14. The aminolysis reactions were further studied with 5 wt% (catalyst/oil) catalyst concentration for optimization the other parameters.

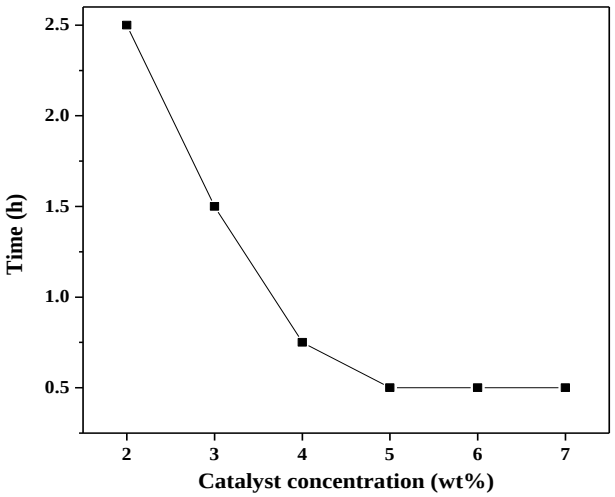


Figure 14. Effect of catalyst concentration on the time required for the complete aminolysis of used cotton seed. (Reaction conditions; diethanolamine: feedstock = 5:1 (m/m), temperature = 110 ºC.)

4.3.4.4 Effect of reaction temperature

A series of aminolysis reactions were conducted in the presence of 5 wt%, (catalyst/oil) nanocrystalline 0.5-Ni/CaO-650, to find the optimum temperature for aminolysis reaction. Time required for the complete aminolysis of vegetable oils to fatty acid amides decreases from 3 h to 30 min as temperature of the reaction was increased from 35 ºC to 110 ºC. Further increase in reaction temperature does not reduce the reaction time significantly as shown in Figure 15 and hence, all aminolysis reactions were performed at 110 ºC.

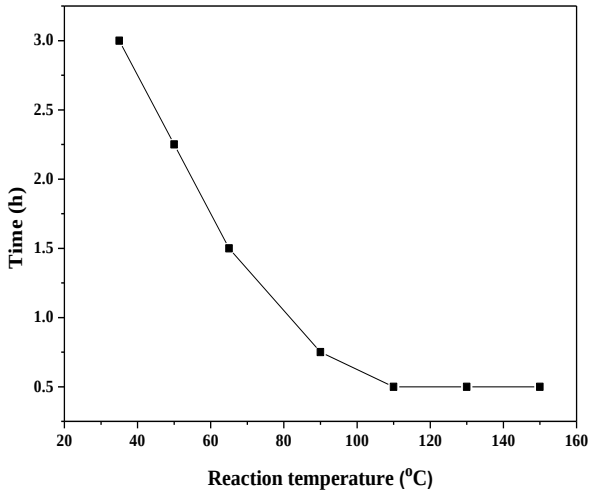


Figure 15. Effect of reaction temperature on the time required for the complete aminolysis of used cotton seed oil. (Reaction conditions; diethanolamine: feedstock = 5:1 (m/m), catalyst amount = 5 wt% of feedstock)

4.3.4.5 Effect of diethanolamine/ used cotton seed oil molar ratio

To determine the optimum diethanolamine/oil molar ratio in present study, the reactions were performed with 3:1 to 7:1 diethanolamine/oil molar ratios at 110 °C using 5 wt% of 0.5-Ni/CaO-650 catalyst. The rate of aminolysis reaction increases as diethanolamine/oil molar ratio was increased from 3:1 to 5:1 and reaction were found to complete in 30 min when 5:1 diethanolamine/oil molar ratio was used. Further increase in diethanolamine/oil molar ratio does not decrease the reaction time as shown in Figure 16.

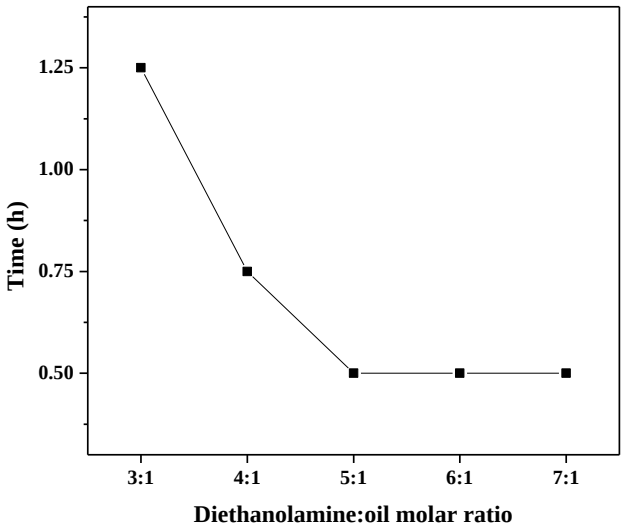


Figure 16. Effect of diethanolamine/oil molar ratio on the time required for the complete aminolysis of used cotton seed oil. (Reaction conditions; catalyst amount = 5 wt% of feedstock, temperature = 110 ºC.)

4.3.4.6 Effect of free fatty acids and varying feedstocks

In order to determine the maximum FFA tolerance of the prepared catalyst, the aminolysis reactions were performed with a variety of natural feedstocks having different amount of FFAs (wt%) viz., mutton fat (0.9), virgin soybean (0.2), and cotton seed oil (0.11), used cotton seed oil (0.8), castor oil (1.8), karanja oil (4.2) and jatropha oil (8.4). As shown in Figure 19, catalyst was found to be effective for the complete aminolysis of a variety of feedstocks having upto 8.4 wt% FFAs. However, the activity of the catalyst was found to be effected by the amount of the FFAs present in the feedstock as shown in Figure 17. Relatively lower catalytic activity of the selected catalyst towards the aminolysis of karanja and jatropha oil could be due to the partial deactivation of the catalyst by the higher concentration of FFAs present in these oils.

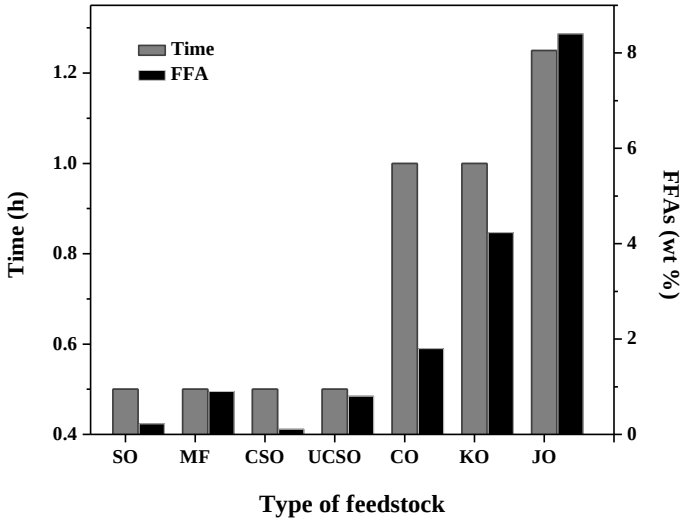


Figure 17. Effect of FFAs on the time required for the complete aminolysis of a variety of feedstocks. (Reaction conditions; diethanolamine: feedstock = 5:1 (m/m), catalyst amount = 5 wt% of feedstock, temperature = 110 ºC. Acronyms; SO = soybean oil, AF = animal fat, CSO = virgin cotton seed oil, UCSO = used cotton seed oil, CO = castor oil, KO = karanja oil and JO = jatropha oil.)

4.3.4.7 Reusability and homogeneous contribution of the catalyst

An important advantage of the solid catalysts is their reusability as it could reduce the overall processing cost of a chemical reaction. To test the reusability and activity decay of 0.5-Ni/CaO-650 catalyst, it was recovered after aminolysis of used cotton seed oil by filtration, washed with hexane and dried at 100 °C. The catalyst thus recovered was used for the seven catalytic runs under the same experimental condition and regeneration method. The reused catalyst was also found to complete (100 %) the aminolysis of used cotton seed oil though it required 7.25 h of reaction period when reused for the seven catalytic cycles as shown in Figure 18. The lesser activity in each recycle could be due to the partial leaching of Ni^{2+} from the catalyst support or due to the adsorption of the organic molecules on the active sites of the catalyst.

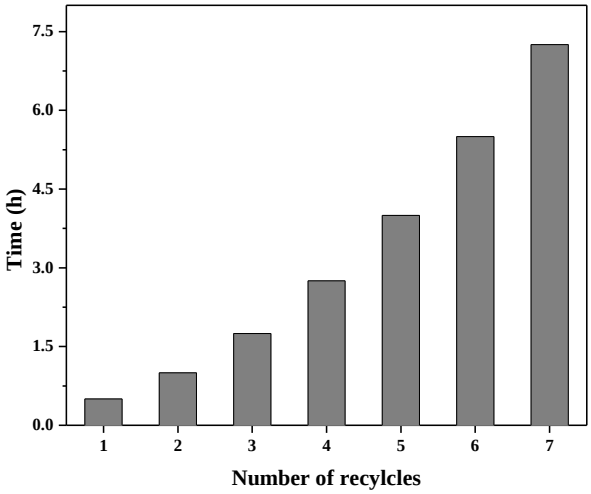


Figure 18. Recyclability studies of the catalyst towards the aminolysis of the used cotton seed oil. (Reaction conditions; diethanolamine: cotton seed oil = 5:1 (m/m), catalyst amount = 5 wt% of feedstock, temperature = 110 ºC.)

The metal ions leached from the catalyst support could catalyze the aminolysis reaction in a similar manner as homogeneous catalyst can do. In order to quantify the homogeneous contribution involved in the catalyst activity, 500 mg of 0.5-Ni/CaO-650 catalyst (equivalent to 5 wt% of oil, used later for the aminolysis) has been refluxed with the diethanolamine (8.3 g) for desired time at 110 °C. The catalyst was separated from diethanolamine through filtration, and diethanolamine thus obtained has been used for the aminolysis of used cotton seed oil (diethanolamine/oil molar ratio=5:1) at 110 °C. Under the mentioned experimental conditions, no conversion of used cotton seed oil to fatty acid amide has been achieved. Thus present study evidently ruled out possibility of the homogeneous contribution due to leached species, and also supports that prepared solid catalyst is responsible for the entire catalytic activity.

4.3.5 Kinetic study

To monitor the progress of the reaction and calculate the rate, aminolysis of used cotton seed oil with diethanolamine have been performed under the optimized reaction conditions viz., using diethanolamine to oil molar ratio of 5:1 in the presence of 5 wt% catalyst (0.5-Ni/CaO-650) at 110 °C. The samples from the reaction mixture have been withdrawn after every 10 min, centrifuged and rotary evaporated to remove the solid catalyst and excess diethanolamine, respectively and subjected to FTIR studies to calculate the fatty acid amide

yield in the reaction mixture. As the reaction progresses due to the conversion of oil to amide, the intensity of the ester carbonyl band at 1743 cm^{-1} regularly decreases, while the intensity of amide carbonyl peak at 1619 cm^{-1} increases, as shown in Figure 19.

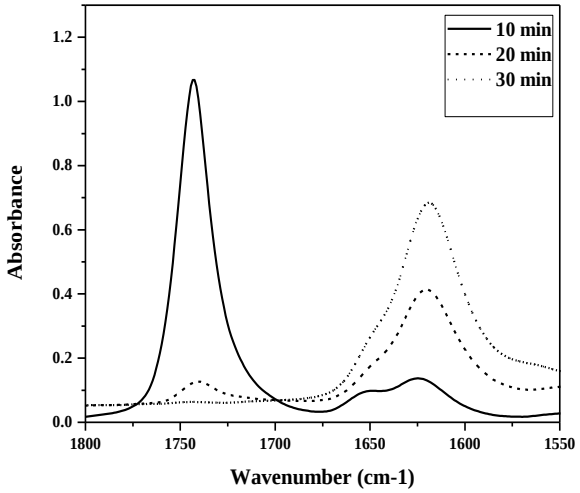


Figure 19. Progress of the aminolysis of used cotton seed oil with diethanolamine, followed by FTIR spectroscopy. (Reaction conditions; diethanolamine: cotton seed oil = 5:1 (m/m), catalyst amount = 5 wt%, temperature = 110 ºC.)

The plot shown in Figure 20, represent the % amide product formed (calculated from Figure 19) at various time intervals. The aminolysis reaction of used cotton seed oil in the presence of 0.5-Ni/CaO-650 was found to follow the pseudo first-order kinetics and the rate constant (k) for the same reaction could be given as:

$k = -\ln\{(1-y)/t\}$, where y is the fatty acid amide yield at time t.

The value of the first order rate constant (k) was found to be 0.10 min^{-1} when 0.5-Ni/CaO-650 was used as a catalyst for the aminolysis of used cotton seed oil.

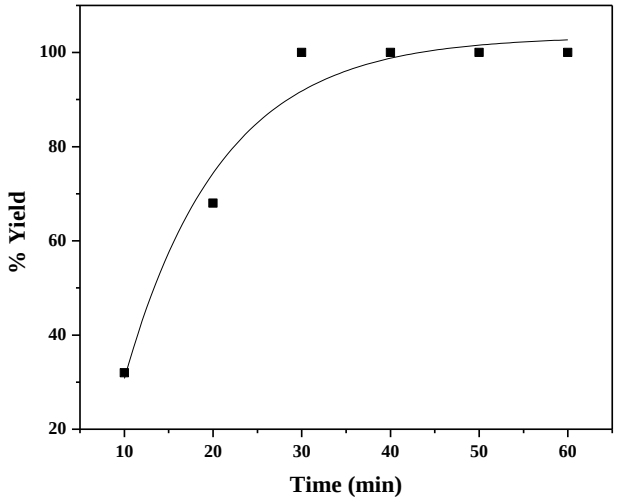


Figure 20. Progress of the aminolysis reaction of used cotton seed oil (UCSO) with diethanolamine in the presence of 0.5-Ni/CaO-650 catalyst. (Reaction conditions; diethanolamine: used cotton seed oil = 5:1 (m/m), catalyst amount = 5 wt%, temperature = 110 ºC)

4.4 Conclusions

In present work a series of Ni^{2+} (0.25-6 wt%) doped CaO were prepared by wet chemical method and Ni/CaO were calcined in the range of 150-950 ºC. The Ni/CaO was found to exist in nano particle form as supported by powder XRD and TEM studies. The catalyst was further analyzed by UV-Vis diffuse reflectance, FESEM, N_2 adsorption-desorption isotherm, BET surface area and Hammett indicator test. Nickel (0.5 wt%) doped CaO and calcined at 650 ºC (0.5-Ni/CaO-650) was found to have the highest surface area and basic strength among the prepared Ni/CaO catalysts as supported by BET surface area and Hammett indicator test respectively. The N_2 adsorption-desorption isotherm exhibit that it has H1-type hysteresis loops and a typical pattern IV according to the IUPAC classification. The solid state UV-Visible diffuse reflectance spectroscopic studies suggested that doped Ni^{2+} exist in octahedral coordination environment in Ni/CaO. The TEM study reveals that 0.5-Ni/CaO-650 catalyst existed in nanorods form. The catalytic activity of the selected catalyst (0.5-Ni/CaO-650) towards the aminolysis of used cotton seed oil, cotton seed oil derived FAMEs, mutton fat FAMEs and methyl laurate has been tested. Under optimized reaction condition (diethanolamine: oil molar artio = 5:1; catalyst concentration = 5 wt% and reaction temperature = 110 ºC), 0.5-Ni/CaO-650 required only 0.5 h for the complete aminolysis of used cotton seed oil. The rate of reaction for the aminolysis of used cotton

seed oil has been determined using the pseudo first-order kinetics and found to be 0.10 min^{-1}. The catalyst has been recycled and reused seven times and found to complete the aminolysis of used cotton seed oil each time. The lixiviation studies performed with the catalysts suggested that the solid catalyst was responsible for the entire catalytic activity and not any leached species. The fatty acid amide derivatives being possessing long chain hydrocarbon and amide functional group are expected to show the lubricity as well as cetane number improving property upon addition in diesel fuel.

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Chapter 5

Nitration of Castor Oil Derived Fatty Acid Methyl Esters

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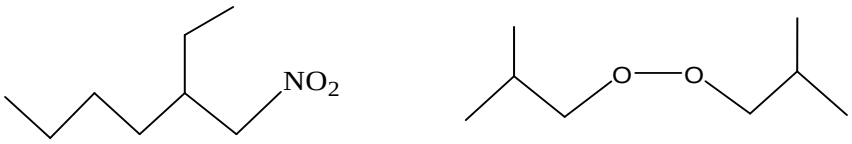
Abstract

Castor oil possesses 89% ricinoleic acid, which has –OH group at C-12 and same hydroxyl group nitrated easily. The nitrate group has been known to impart the cetane number improving property to the diesel fuel additive. In order to synthesize the nitro group based dual functional diesel fuel additive, in present chapter fatty acid methyl ester of castor oil were nitrated with the help of formic acid and acetic anhydride. The nitrate derivative of fatty acid methyl ester was characterized by FTIR and proton NMR spectroscopic techniques.

Keywords: castor oil derived FAMEs, nitration, FTIR, proton NMR.

5.1 Introduction

The nitrate group has been known to impart the cetane number improving property to the diesel fuel additive. As ignition is a free-radical process, the effectiveness of cetane improvers is attributed to their ability to contribute to and assist in free-radical generation during ignition. 2-Ethylhexylnitrate (EHN) and di-*tert*-butylperoxide (DTBP), as shown in Figure 1, are commercially available cetane number improvers as both the functional groups are known to yield free radicals quite readily. Although the application costs of DTBP are typically higher and are only considered when other alternatives are not available (Peckham, 1998). Addition of 0.1 % (v/v) of these these compounds were found to boost the cetane number of diesel fuel by 5 units (Ladommatos et al., 1996).



(a) **(b)**

Figure 1. Molecular structure of (a) 2-ethylhexylnitrate (EHN) and (b) di-*tert*-butylperoxide (DTBP).

Although the nitrate group has been specifically attributed with the ability to promote ignition, (Clothier et al., 1993) there is large impact of the alkyl group on the effectiveness of an alkyl nitrate cetane improver. The homolytic cleavage of a nitro bond is thermally induced and followed by a cascade of additional free radicals. The alkyl group disintegrates to generate NO_2 and alkyl radicals that subsequently attack on diesel fuel to initiate the ignition process (Clothier et al., 1993).

The nitrate derivative of fatty acid methyl esters derived from vegetable oil has the potential to act as cetane number improver and/or lubricity improver (Sonntag et al., 1982). The typical 14-18-carbon alkyl groups of the fatty acids potentially provide the straight-chain alkyl backbone of a nitrate. Both the ester groups and the carbon-carbon double bonds of the fatty acids provide functional groups that can be converted into nitrates in high yields (Suppes et al., 2003). Poerier et al., (1995) reported cetane improvers comprising nitrate derivatives of tall oil fatty acids as shown in Figure 2.

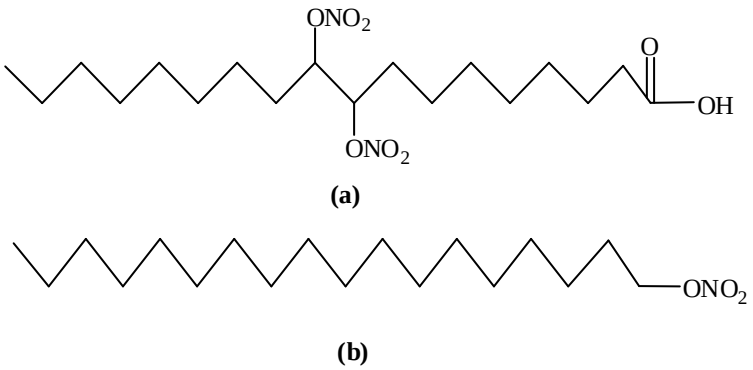


Figure 2. Literature reported nitrated tall oil fatty acid derivatives as cetane number improvers.

The direct nitration of carbon-carbon double bonds in vegetable oils yields a nitro functional group as shown in Figure 3. Whereas the nitrates promote desired ignition traits, the nitro groups do not promote an increase in the cetane number and potentially reduce the efficacy of the nitrate groups (Topchiev, 1959; Mason, 1999).

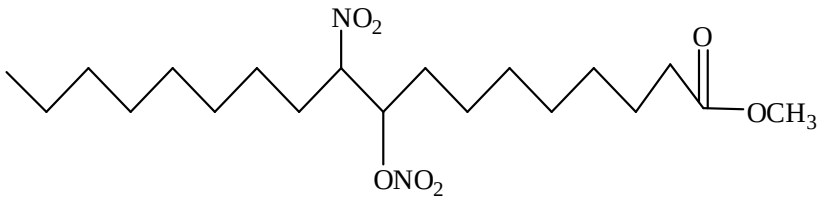


Figure 3. Nitrate derivative of soybean oil.

Due to this reason the castor oil has been selected for the nitration as it has fatty acid profile of about 89% of ricinoleic, 5% linoleic, 3% oleic, 1.5% stearic, and 1% palmitic acids. As ricinoleic acid contains one internal alcohol group (Bockish, 1993) so the secondary alcohols provide for easy nitration with a high degree of repeatability. Castor oil tends to polymerize in the presence of mineral acids, and an excess of solvent is often necessary to prevent this polymerization. The secondary alcohol groups on castor oil can be directly nitrated to form secondary nitrates; however, high viscosity necessitates the use of costly solvent-based methods. Transesterification with methanol to form fatty acid methyl ester is a useful approach to reducing viscosity.

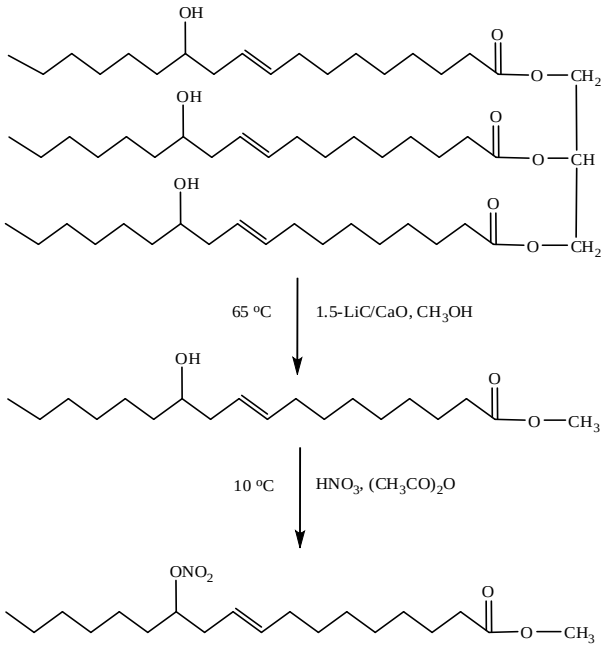
In this chapter, the nitration of castor oil derived fatty acid methyl ester with nitric acid and acetic anhydride has been demonstrated. The final product has been characterized by FTIR

and proton NMR. The prepared nitrate derivative has been used later as a dual functional diesel fuel additive to improve the lubricity as well as cetane number of the diesel fuel.

5.2 Experimental section

5.2.1 Nitration of castor oil derived fatty acid methyl ester

The fatty acid methyl ester from castor oil has been prepared by using 1.5-LiC/CaO catalyst and following the procedure as mentioned in chapter 3. Nitration of thus obtained methyl ester was performed in a 100-mL three-necked round-bottom flask equipped with a thermometer, dropping funnel, ice bath and magnetic stirrer. The round bottom flask was charged with castor oil derived fatty acid methyl ester (25 g) and acetic anhydride (16.4 g) and the temperature of the mixture was maintained at 10 °C. To this reaction mixture nitric acid (5.1 g, 70% (v/v)) was added dropwise and the reaction mixture was stirred for 4 h at 10 °C. The reaction was quenched after 4 h with ice water, and organic product was separated from the aqueous phase with the help of separating funnel. The product so obtained were washed several times with deionized water and dilute sodium bicarbonate solution and finally dried over anhydrous sodium sulphate. The yellow coloured product so obtained was analyzed by ^{1}H NMR and FTIR spectroscopic studies.



Scheme 1: Nitration of castor oil.

Nitrate derivative of castor oil FAMEs: FTIR data (cm^{-1}): 2925 (ν_{C-H}), 1742 ($\nu_{C=O}$), 1627 ($\nu_{>CONO2}$); ^{1}H-NMR ($CDCl_3$, δ ppm): 5.51 (m, -CH_2-C**H**=CH-), 5.39 (m, -C**H**=C**H**-), 4.87-5.01 (m, >C**H**-ONO_2), 3.61 (s, -OC**H**$_3$), 2.3 (m, -C**H**$_2$-CO-), 2.20 (m, -C**H**$_2$-CH=CH-), 2.03 (m, -C**H**$_2$-$(CH_2)_n$-CH-), 1.61-1.30 (m, -(C**H**$_2$)$_n$-), 0.97 (m, -CH=CH-C**H**$_3$) , 0.88 (m, -CH_2-C**H**$_3$).

5.3 Results and discussion

5.3.1 Nitration of castor oil methyl ester

The nitration of castor oil derived fatty acid methyl ester with nitric acid was employed in the presence of acetic anhydride.

The progress of the nitration reaction has been monitored by FTIR spectroscopic technique. The samples from the reaction mixture have been withdrawn with the help of glass dropper after regular intervals of time and subjected to FTIR analysis. The complete conversion of used cotton seed oil or fatty acid methyl ester to corresponding amide have been supported by the disappearance of the hydroxyl band at 3422 cm^{-1} and the appearance of a new band at 1627 cm^{-1} due to nitrate group.

5.3.2 Characterization of nitrated product

The purified fatty acid nitrate, synthesized from castor oil derived fatty acid methyl esters was characterized by FTIR and ^{1}H NMR spectroscopic techniques.

5.3.2.1 FTIR analysis

The FTIR spectra of castor oil, castor oil derived fatty acid methyl esters show the ester carbonyl peak at 1743 cm^{-1} and hydroxyl band at 3422 cm^{-1}. After the nitration reaction of castor oil derived fatty acid methyl esters formation of the fatty acid nitrate product was supported by the disappearance of the hydroxyl band at 3422 cm^{-1} and the appearance of a new bands at 1627 cm^{-1}, 1272 cm^{-1} and 869 cm^{-1} due to nitrate group as shown in Figure 4.

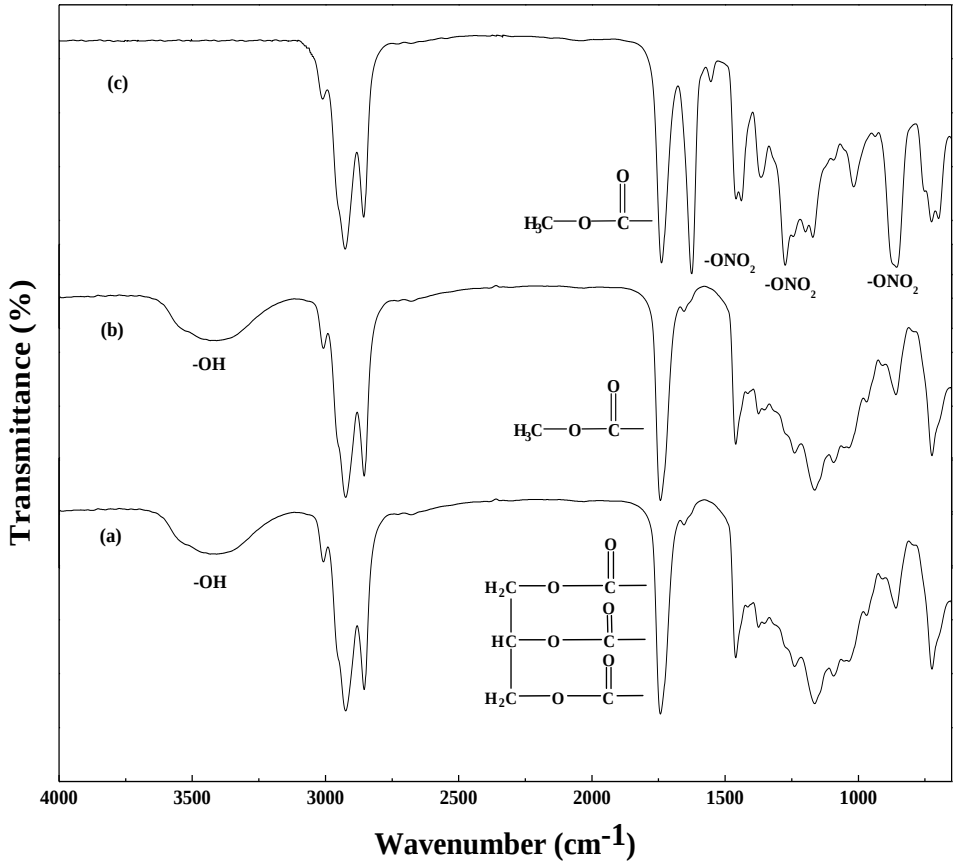


Figure 4. Comparative FTIR spectrum of (a) castor oil, (b) castor oil derived fatty acid methyl ester and (c) nitrate derivative of castor oil derived fatty acid methyl ester.

5.3.2.2 ^{1}H-NMR studies

Fatty acid nitrate produced during the nitration of castor oil derived fatty acid methyl ester was further characterized by ^{1}H NMR spectroscopy. Proton NMR spectrum of castor oil shows a multiplet at 4.1 and 5.2 ppm due to the presence of glyceridic protons besides other hydrocarbon peaks a given in Figure 5a. The appearance of a new peak at 3.6 ppm due to –OCH_3 protons and disappearance of glyceridic protons support the complete conversion of oil to fatty acid methyl ester as shown in Figure 5b. The appearance of low intensity multiplet at 3.61 ppm is due to the proton attach to same carbon where hydroxyl group (-C**H**-OH) is also attached. In nitrated product, appearance of multiplet at 4.87-5.01 ppm due to >C**H**-ONO_2 protons and disappearance of hydroxyl protons at 3.61 ppm support the conversion of castor oil derived fatty acid methyl ester to corresponding fatty acid nitrate as shown in Figure 5c.

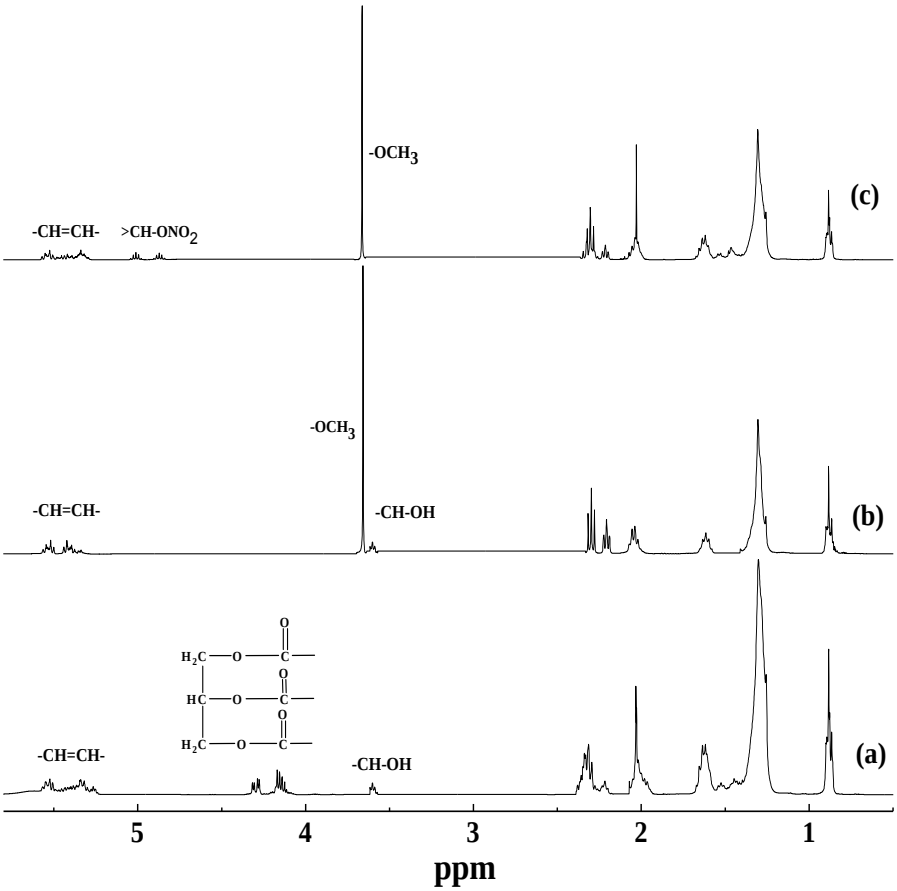


Figure 5. Comparative ^{1}H-NMR spectrum of (a) castor oil, (b) castor oil fatty acid methyl ester and (c) nitrate derivative of castor oil fatty acid methyl ester.

5.4 Conclusion

The nitration of fatty acid methyl ester derived from castor oil has been performed with the help of nitric acid and acetic anhydride. The nitrate derivative was analyzed by FTIR and ^{1}H-NMR to support the conversion of fatty acid methyl ester derived from castor oil to corresponding nitrate derivative. The nitrate derivative being possessing long hydrocarbon chain and nitrate functional group is expected to show the lubricity as well as cetane number improving property upon additive in diesel fuel.

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Chapter 6

Titanium Loaded Silica as Nanosized Solid Catalyst: Preparation, Characterization and Application for the Epoxidation of Triglycerides

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Abstract

In present chapter the preparation of epoxide derivative from fatty acid methyl esters have been demonstrated using Ti loaded SiO_2 as solid nanocatalyst. A series of titanium loaded silica has been prepared in nanoparticle form by loading 1.7 wt% of Ti in SiO_2 and calcined in the temperature range of 550-950 °C. The prepared catalysts were characterized by BET surface area, diffuse reflectance solid state (DRS) UV-Vis, powder X-ray diffraction, field emission scanning electron microscopic and transmission electron microscopic techniques. The prepared catalysts were used as a catalyst for the epoxidation of fatty acid methyl esters derived from used cotton seed oil. The catalyst prepared by loading 1.7 wt% Ti in SiO_2 and calcined at 750 °C (1.7-Ti/CaO-750) was found to show the better activity than others among the prepared catalysts. The epoxidation reaction was performed by varying calcination temperature (550-950) of catalyst, catalyst concentration (1-15 wt% of feedstock) and reaction temperature (35-65 °C) in order to achieve the complete epoxidation in minimum possible time. Complete epoxidation of used cotton seed oil derived fatty acid methyl ester in the presence of 1.7-Ti/SiO_2-750 catalyst required (i) 3 h when hydrogen peroxide and formic acid were used as reagents, and (ii) 6 h when hydrogen peroxide, acetonitrile and butyronitrile were used as reagents in the presence of UV-Visible radiation. Epoxidized fatty acid methyl esters thus obtained were characterized by FTIR, proton NMR, and electron impact mass spectroscopic technique.

Keywords: Ti loaded silica, epoxidation, photochemical reaction, BET surface area, powder XRD, FESEM, TEM, FTIR, proton NMR, EI-MS studies.

6.1 Introduction

Vegetable oils and fatty acid methyl esters derived from vegetable oils possess certain excellent frictional properties e.g. good lubricity, low volatility, high viscosity index, solvency for lubricant additives, and easy miscibility with other fluids. However, a high degree of multiple –C=C– unsaturations in the fatty acid chain of many vegetable oils causes poor thermal and oxidative stability and confines their use as lubricants to a modest range of temperature (Randles and Wright, 1992; Asadauskas et al., 1996; Wu et al., 2000). Reports have discussed the use of epoxidized unsaturated fatty acids as metal working fluids (Watanabe et al., 1988) and epoxy oils as lubricating additives to eliminate corrosion from chlorine containing compounds (Tao et al., 1996). Epoxidized soybean oil has been reported as a potential candidate for the high temperature lubrication (Adhvarya and Erhan, 2002).

Epoxidized fatty acid compounds are obtained at industrial scale mainly by the peracid process. (Rangarajan et al., 1995; Kirk and Othmer, 1984; Fiser et al., 2001; Hill, 2000; Biermann et al., 2000; Knothe, 1999). The peracid in same process is obtained *in situ* by reacting carboxylic acid (usually acetic acid) with hydrogen peroxide in the presence of a catalyst (mineral acids). There exist several drawbacks in peracid process viz., (i) the low selectivity to epoxidized products due to acid catalyzed oxirane ring-opening, (ii) the separation of acidic byproducts is cumbersome, (iii) the handling of highly concentrated hydrogen peroxide and strong acids is dangerous and causes corrosion problems. Thus, in recent years emphasis has been given to develop the catalytic processes which could overcome the above mentioned disadvantages by using more sustainable compounds and technologies viz., application of greener chemical H_2O_2, in place of peracid and solid catalyst in place of mineral acids (Knothe, 1999; Ishii et al., 1988; Herrman et al., 1991; Herrman et al., 1996; Debal et al., 1993; Guidotti et al., 2003; Camblor et al., 1997; Suarez et al., 2009; Schuster et al., 2008).

The incorporation of titanium on amorphous silica support has been reported in literature (Escrig and Martin, 1999; Sanchez et al., 2000; Sanchez et al., 2003) as a catalyst for the epoxidation of –C=C– present in fatty acid chain with the help of hydrogen peroxide. In recent years the focus has now been shifted on titanium-substituted zeolites as catalyst, including TS-1 (Taramaso et al., 1983), Ti-β (Saxton et al., 1997) and Ti-incorporated mesoporous silica (Reddy et al., 1997), for epoxidation of olefins with hydrogen peroxide. Furthermore, the ease in catalyst recovery and the use of acid free reaction conditions make

these catalytic systems promising alternatives for the epoxidation of oleochemicals and substrates derived from renewable sources (Guidotti et al., 2008).

Present work demonstrates the preparation of titanium supported silica as solid catalyst for the epoxidation of used cotton seed oil derived fatty acid methyl ester and methyl oleate using hydrogen peroxide as an oxidizing agent.

6.2 Experimental section

6.2.1 Ti/SiO_2 Catalyst Preparation

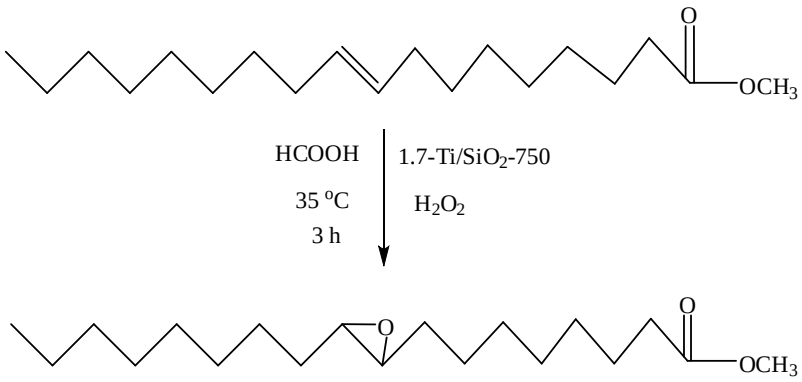
The titanium loaded silica catalyst was prepared as following the procedure as reported by Martin and Frutos, (1999) with slight modification. Titanium isopropoxide (0.50 g) was dispersed in 75 ml of the solvent (toluene) and heated at 150 °C under stirring. To this suspension, 5 g of silica was added and resulting mixture was stirred at 150 °C for 4 h. The solid product thus obtained was filtered using Whatman filter paper (no. 42), washed twice with 150 ml of hot toluene and subsequently dried at 100 °C and calcined at different temperatures (550, 750 and 950 °C) for 6 h. The Ti/SiO_2 thus obtained was characterized by BET surface area measurement, diffuse reflectance solid state (DRS) UV-Vis spectroscopic, powder XRD, FESEM and TEM studies. The Ti/SiO_2 thus prepared were expected to have 1.7 wt% titanium and designated as 1.7-Ti/SiO_2-T, where T represent the calcination temperature.

6.2.2 Epoxidation of fatty acid methyl ester

Cotton seed oil contains ~ 80% unsaturated fatty acid in the form of oleic and linoleic acids. Used cotton seed oil derived fatty acid methyl esters, used as substrate for the epoxidation in present study, were prepared by following the procedure as given in chapter 3. The epoxidation reactions of used cotton seed oil derived FAMEs were performed by two different methods. In first method hydrogen peroxide and formic acid were used as reagents and in second method hydrogen peroxide, acetonitrile and butyronitrile were used as reagents in the presence of UV radiation to carry out the epoxidation.

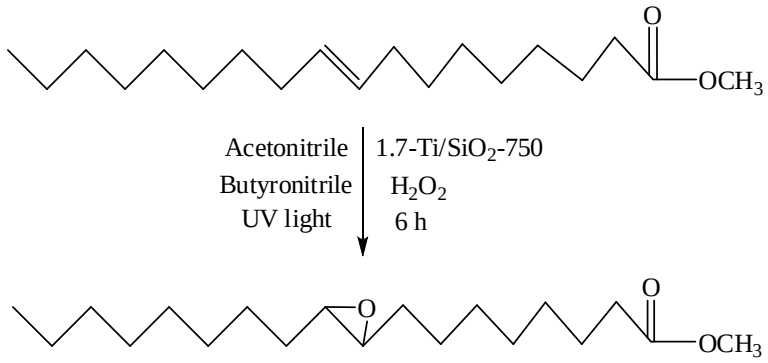
Method I: The epoxidation reactions were performed in a 100 mL, two neck round bottom flask equipped with a water-cooled condenser, oil bath and a magnetic stirrer. In a typical epoxidation reaction, used cotton seed oil derived FAMEs (10 g), formic acid (2 ml), 50% hydrogen peroxide (3 ml) and 5 wt% (of FAMEs) 1.7-Ti/ SiO_2-750 catalyst were taken in a

two neck round bottom flask at 35 °C, and stirred for 3 h as shown in scheme 1. After the completion of the reaction, the product was dissolved in 60 mL hexane and placed in a separating funnel. The upper hexane layer was separated from the lower aqueous layer, washed with water, dried over anhydrous sodium sulfate and finally the hexane was rotary-evaporated to yield the pure fatty acid epoxide derivative. The epoxide product thus obtained was characterized by FTIR, and ^{1}H-NMR techniques.



Scheme 1: Epoxidation of fatty acid methyl ester in the presence of formic acid and hydrogen peroxide in the presence of 1.7-Ti/SiO_2-750 catalyst at 35 °C.

Method II: The epoxidation reactions were performed in a 50 mL, two neck round bottom flask equipped with magnetic stirrer. This complete set up was placed in a photochemical reactor which could provide the UV radiation of 125 W. Used cotton seed oil derived FAMEs (10 g), acetonitrile (3.6 g), butyronitrile (3 g), 50% hydrogen peroxide (0.5 g) and 10 wt% 1.7-Ti/SiO_2-750 catalyst were added to round bottom flask at 35 °C and reaction mixture was stirred in the presence of UV radiation (125 W) for 6 h as shown in scheme 2. After the completion of the reaction, the product was dissolved in 60 mL hexane and placed in a separating funnel. The upper hexane layer was separated from the lower aqueous layer, washed with water, dried over anhydrous sodium sulfate and finally the hexane was rotary-evaporated to yield the pure fatty acid epoxide derivative. The epoxide product so obtained was further characterized by FTIR and ^{1}H-NMR techniques.



Scheme 2: Photocatalytic epoxidation of fatty acid methyl ester in the presence of 1.7-Ti/SiO_2-750 catalysts at 35 °C.

Besides used cotton seed oil derived FAMEs, methyl oleate (C18:1) has also been employed for the epoxidation by following method I and II separately. The epoxidized derivative of methyl oleate was further characterized by mass spectrometry besides FTIR and ^{1}H-NMR techniques.

Fatty acid epoxide derivative of used cotton seed FAMEs: FTIR data (cm^{-1}): 915 (ν_{epoxy}), 872 (ν_{epoxy}) and 840 (ν_{epoxy}); ^{1}H-NMR ($CDCl_3$, δ ppm): 3.6 (s, -OC**H**$_3$), 3.1-2.9 (m, -C**H**OC**H**-), 2.3 (m, -C**H**$_2$-CO-), 2.0 (m, -C**H**$_2$-$(CH_2)_n$-CH-), 1.6-1.25 (m, -(C**H**$_2$)$_n$-), 0.87 (m, -CH_2-C**H**$_3$).

Fatty acid epoxide derivative of methyl oleate: FTIR data (cm^{-1}): 915 (ν_{epoxy}), 872 (ν_{epoxy}) and 840 (ν_{epoxy}); ^{1}H-NMR ($CDCl_3$, δ ppm): 3.6 (s, -OC**H**$_3$), 3.1-2.9 (m, -C**H**OC**H**-), 2.3 (m, -C**H**$_2$-CO-), 2.0 (m, -C**H**$_2$-$(CH_2)_6$-CH-), 1.6-1.25 (m, -(C**H**$_2$)$_n$-), 0.87 (m, -CH_2-C**H**$_3$); EI-MS (m/z) (Intensity (%), fragment): 313.3 (15, M), 299.3 (17, M-CH_3), 281.3 (24, M-OCH_3), 263.3 (24, M-$OOCH_3$), 245.3 (20, M- $CH_3(CH_2)_4$), 209.2 (5, M-$(CH_2)_3COOCH_3$), 175.2 (4, M-$C(CH_2)_5COOCH_3$), 155.2 (3, M-$(CH_2)_7COOCH_3$), 109.2 (5, M-$CHOCH(CH_2)_7COOCH_3$).

6.3 Results and Discussion

6.3.1 Catalyst preparation and characterization

A series of 1.7 wt% titanium loaded SiO_2 were prepared by chemical method and resulted 1.7-Ti/SiO_2 was calcined at the different temperatures viz., 550, 750 and 950 °C. The catalysts so prepared were designated as 1.7-Ti/SiO_2-550, 1.7-Ti/SiO_2-750 and 1.7-Ti/SiO_2-

950, respectively and characterized by BET surface area, powder X-ray diffraction, solid state UV-Vis, FESEM, and TEM studies.

6.3.1.1 BET surface area studies

The surface areas of catalysts were measured by the Brunauer-Emmett-Teller (BET) method. There is slight decrease in the surface area of the prepared 1.7-Ti/SiO_2 when it was calcined at 550 °C and 750 °C. The surface area of Ti/SiO_2 were found to reduce from 300 m^2/g (pure SiO_2) to 291.7 and 277.7 m^2/g after calcinations at 550 and 750 °C, respectively. However, a sharp decrease in surface area (172.2 m^2/g) of Ti/SiO_2 was observed when calcination temperature was increased to 950 °C as shown in Figure 1. The lesser surface area after calcination at 950 °C could be due to the sintering of Ti/SiO_2 particles, or structural rearrangement (Knozinger et al., 1993) in Ti/SiO_2 at high clacination temperature.

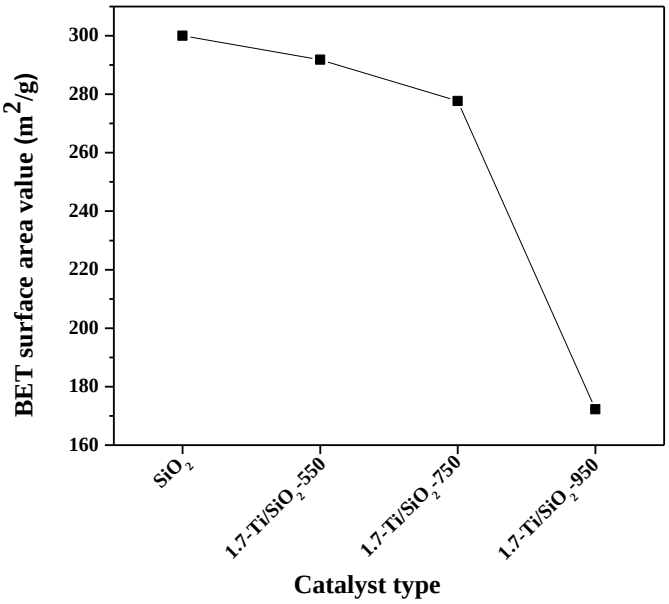


Figure 1: Comparative BET surface area values of silica with Ti loaded silica.

6.3.1.2 Powder XRD analysis

The structure analysis of Ti/SiO_2, prepared at different calcination temperatures (550-950 °C), has been performed by powder XRD analysis. The comparison of the powder XRD patterns of commercially available SiO_2 with 1.7 wt% titanium loaded SiO_2 and calcined at different temperatures are shown in Figure 2. The pure SiO_2 shows peaks at 2θ values of

9.6°, 13.7°, and 21.7° due to the presence of silicon dioxide in monoclinic form (JCPDS 891666), as shown in Figure 5a. The presence of less intense peaks at 25.4°, 37.8°, 47.8°, 54.7° and 62.7° in the powder XRD pattern of Ti/SiO_2 supports the existence of titanium oxide in tetragonal form (JCPDS 891157) in silica support as shown in Figure 5b-d.

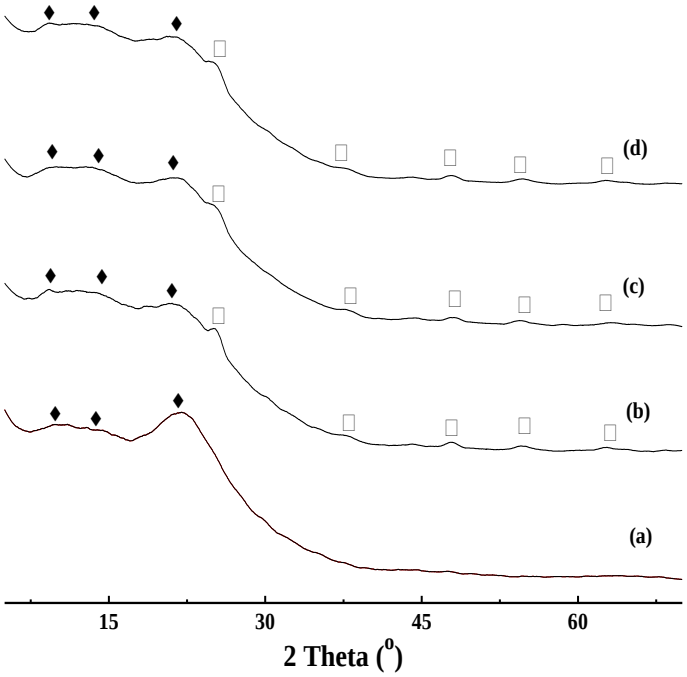


Figure 2: Comparative powder XRD patterns of (a) SiO_2, (b) 1.7-Ti/SiO_2-550, (c) 1.7-Ti/SiO_2-750 and (d) 1.7-Ti/SiO_2-950. (silicon dioxide = ♦; and titanium oxide = □).

6.3.1.3 FESEM and HRTEM studies

The size and surface morphology of the prepared Ti/SiO_2 were observed by scanning electron microscope (SEM). There are irregular shaped particles in all the prepared catalysts having particle size in the range of 20-50 μm as shown in Figure 3a-c. Hence the calcinations temperature has not any significant impact on the macro structure of the catalyst particles. However, when the same particles were observed by TEM, the impact of calcinations temperature on the Ti/SiO_2 particle shape and size could be seen clearly as shown in Figure 3d-f. The Ti/SiO_2 calcined at 550 °C and 950 °C were found to exist in oval shape particles with average size of ~10 nm. However, Ti/SiO_2 particles calcined at 750 °C, were found to exist as nano rods of ~ 100 nm length as observed by TEM studies and shown in Figure 3e. The TEM analysis suggested that the prepared catalysts exist in nanoparticles form. The presence of titanium in silica was also confirmed by Field Emission

Scanning Microscopy-Energy Dispersive X-ray Analysis (FESEM-EDX) studies and ~ 1.8 wt% titanium was found in silica support by the same study.

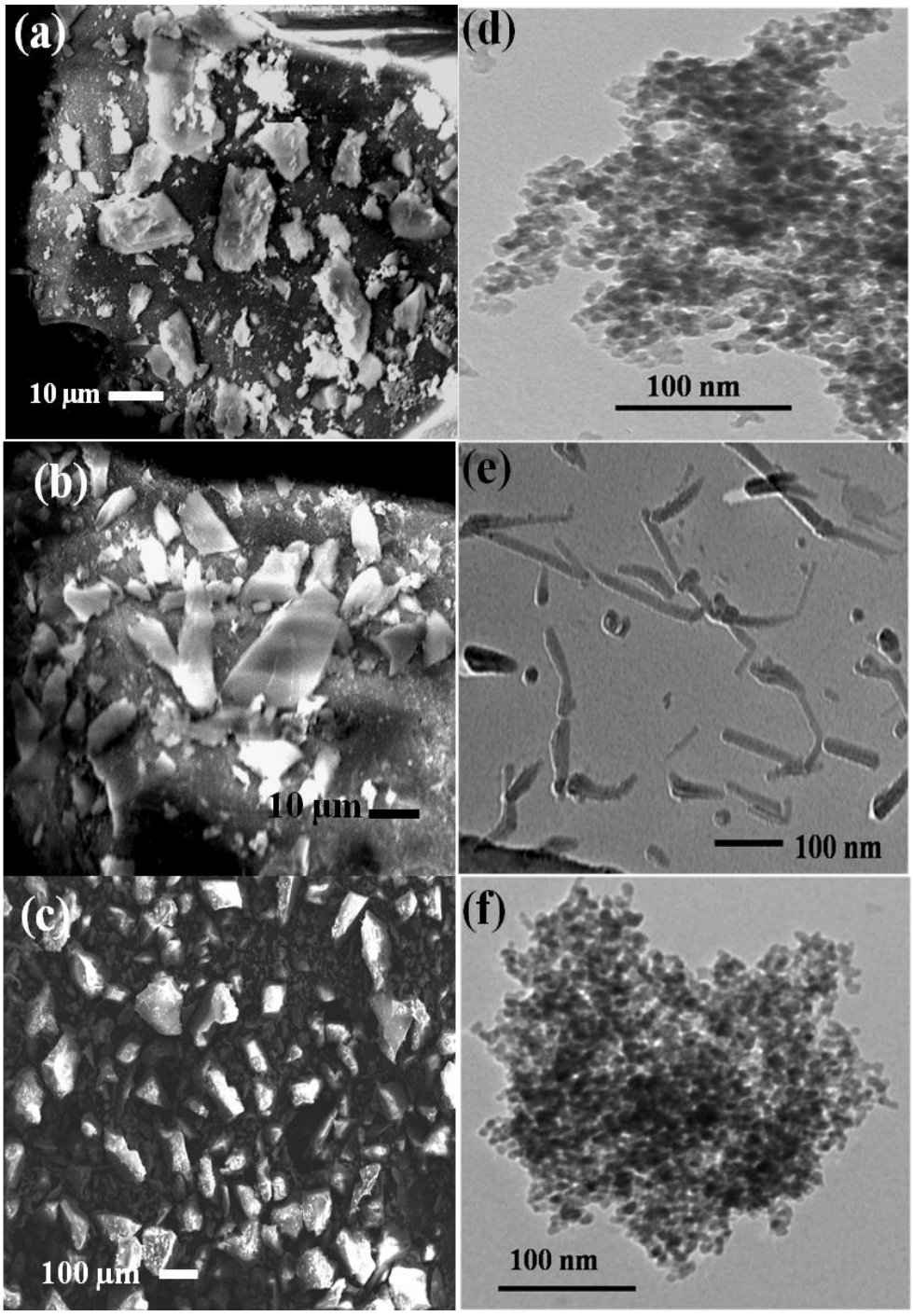


Figure 3. Comparative FESEM images of (a) 1.7-Ti/SiO_2-550, (b) 1.7-Ti/SiO_2-750 and (c) 1.7-Ti/SiO_2-950 and HRTEM images of (d) 1.7-Ti/SiO_2-550 (e) 1.7-Ti/SiO_2-750 and (f) Ti-SiO_2/950.

6.3.1.4 Diffuse reflectance solid state UV-Visible spectroscopic analysis

The coordination environment of the titanium in silica was observed by recording the diffuse reflectance solid state UV-Vis spectra (DRS) in the range of 200-550 nm using $BaSO_4$ as reference material. The peak observed at 250 nm in DRS of 1.7-Ti/SiO_2-550 as shown in Figure 4b, supports the existence of hydrated titanium in tetrahedral coordination environment. A shoulder at ~ 305 nm supports the presence of few titanium atoms in octahedral coordination environment. As the calcinations temperature of Ti/SiO_2, was increased from 550-950 °C, the intensity of the peak at 305 nm was also found to increase and at 950 °C the peaks at 250 nm and 305 nm become almost equally intense as shown in Figure 4b-d. This observation supports the presence of almost equally populated titanium in tetrahedral as well as in octahedral geometry in Ti/SiO_2, prepared at 950 °C calcinations temperature. However, the absence of peak in the range of 370–410 nm rules out the presence of free TiO_2 in all the catalysts (Geobaldo et al., 1992).

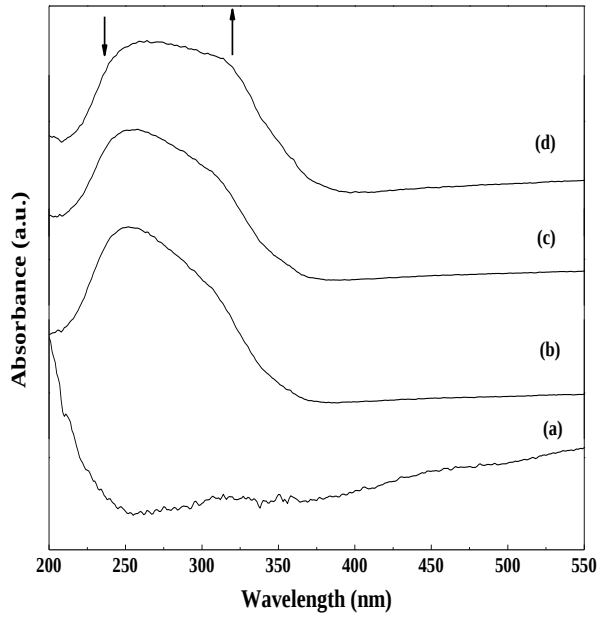


Figure 4. Comparative diffuse reflectance solid state UV-Vis spectra of (a) silica, (b) 1.7-Ti/SiO_2-550, (c) 1.7-Ti/SiO_2-750 and (d) 1.7-Ti/SiO_2-950.

6.3.2 Epoxidation reaction

The epoxidation reactions of methyl oleate and used cotton seed oil derived FAMEs were performed in the presence of Ti/SiO_2 catalyst using (i) hydrogen peroxide and formic acid (method I), and (ii) acetonitrile, butyronitrile and hydrogen peroxide (method II) under UV

radiation. The reaction conditions have been optimized using used cotton seed oil derived FAMEs as feedstock.

The progress of the epoxidation reaction has been monitored by FTIR spectroscopic technique. The samples from the reaction mixture have been withdrawn with the help of glass dropper after regular intervals of time and subjected to FTIR analysis. The appearance of new bands at 914 cm^{-1}, 871 cm^{-1} and 840 cm^{-1} confirm the conversion of –C=C– into corresponding epoxide group.

6.3.3 Product characterization

The purified fatty acid epoxides derived from fatty acid methyl esters of used cotton seed oil and methyl oleate were characterized by FTIR and ^{1}H NMR spectroscopic techniques. Epoxide derivative of methyl oleate has also been characterized by mass spectroscopy.

6.3.3.1 FTIR analysis

The conversion of double bonds to epoxide groups could be monitored by FTIR spectroscopy. The appearance of three bands at 914, 871 and 840 cm^{-1} in the FTIR spectra of epoxidized fatty acid methyl esters supports the conversion of fatty acid methyl ester double bond into corresponding epoxide group as shown in Figure 5C. Similarly, the conversion of double bonds into epoxide group is supported by the decrease in the intensity of the peak at 3008 cm^{-1} as shown in Figure 5B.

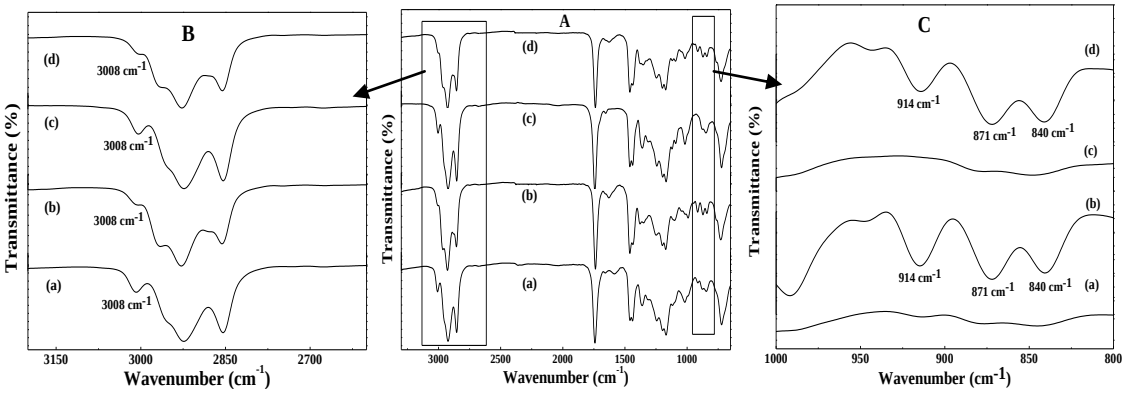


Figure 5. Comparison of FTIR patterns of (a) used cotton seed oil derived FAMEs, (b) epoxidized used cotton seed oil derived FAMEs, (c) methyl oleate and (d) epoxidized methyl oleate. The spectra **B** and **C** represent the magnification of 2600-3200 and 800-1000 cm^{-1} region, respectively.

6.3.3.2 Proton NMR studies

Fatty acid epoxides produced from the epoxidation of used cotton seed oil derived FAMEs and methyl oleate were further characterized by ^{1}H NMR spectroscopy. Proton NMR spectrum of used cotton seed oil derived FAMEs and methyl oleate shows a multiplet at 5.3 ppm due to the presence of protons attached with unsaturated carbons (–CH=CH–), besides other hydrocarbon peaks as given in Figure 6a and 6c, respectively. In epoxidized (–CHOCH–) used cotton seed oil derived FAMEs, appearance of multiplet at 2.9-3.1 ppm due to epoxide protons (–CHOCH–) and disappearance of the proton signal at 5.3 ppm due to–CH=CH–support the conversion of FAMEs into corresponding epoxidized product as shown in Figure 6b and 6d.

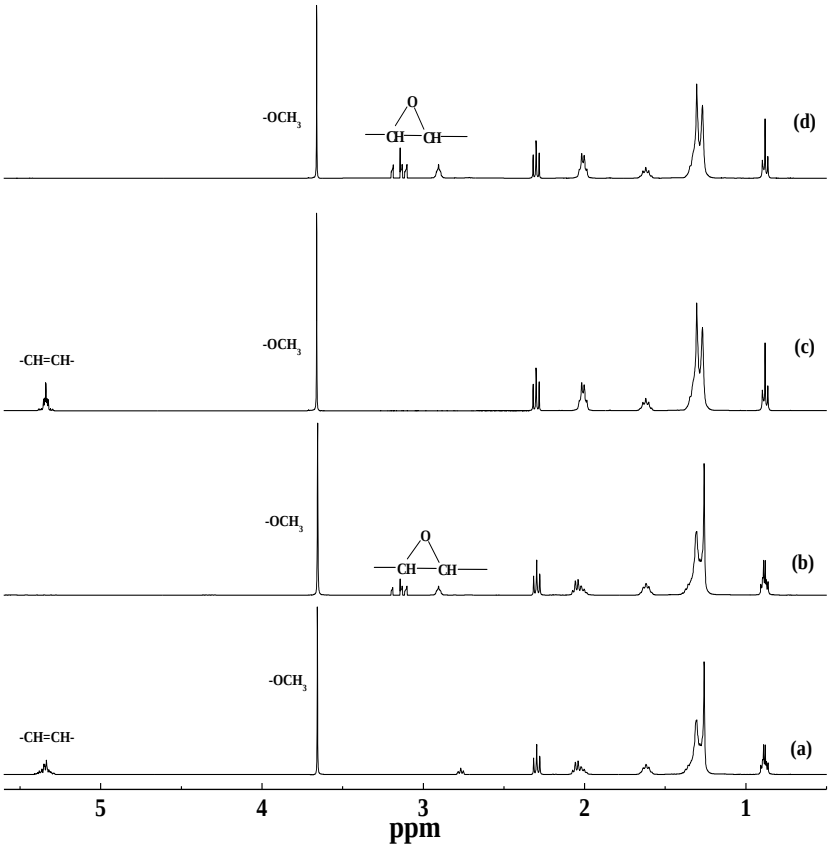


Figure 6. Comparative ^{1}H-NMR spectrum of (a) used cotton seed oil derived FAMEs (b) epoxidized derivative of used cotton seed oil derived FAMEs, (c) methyl oleate, and (d) epoxidized methyl oleate.

6.3.3.3 EI-MS studies

Epoxide derivative of methyl oleate (methyl epoxyoleate) has also been characterized by mass spectroscopic technique as shown in Figure 7, besides FTIR and proton NMR technique. The EI-MS spectrum of methyl epoxyoleate shows a molecular ion peak at m/z ratio of 313.3. The base peak was observed at m/z value of 281, showing the loss of methoxy (-OCH_3) molecule from the methyl epoxyoleate.

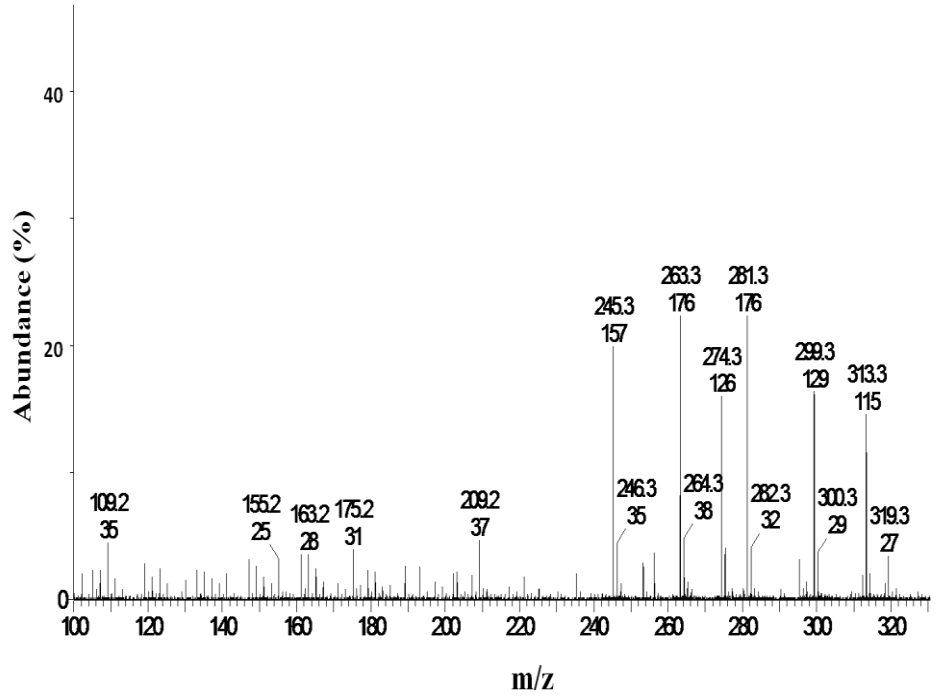


Figure 7. Mass spectra of epoxidized methyl oleate.

6.3.4 Catalytic activity

In order to compare the catalytic activity of the prepared catalysts, used cotton seed oil derived FAMEs were used as substrate for the epoxidation reactions. Epoxidation reactions of used cotton seed oil derived FAMEs were performed in the presence of desired catalyst amount at desired temperature using (i) hydrogen peroxide and formic acid (method I), and (ii) acetonitrile, butyronitrile and hydrogen peroxide under UV radiation (method II).

During the course of study out of (i) calcination temperature of catalyst, (ii) catalyst concentration, and (iii) reaction temperature, one parameter at a time has been varied in order to establish the most suitable reaction condition for the epoxidation reaction. The reusability of the selected catalyst has also been studied.

6.3.4.1 Effect of calcination temperature

In order to determine the optimum calcination temperature for the best catalytic activity, a series of catalyst was prepared by impregnating 1.7 wt% Ti in SiO_2 by chemical method. The Ti/SiO_2 so prepared was calcined at the different temperature viz., 550, 750 and 950 ºC. A 5 wt% of the catalysts for Method I and 10 wt% of the catalysts for Method II with respect to FAMEs have been used for the epoxidation reaction of used cotton seed oil derived fatty acid methyl ester at 35 ºC. Reaction time required for the complete epoxidation was found to decrease from 5 h to 3 h in Method I and 8 h to 6 h in Method II as the calcination temperature increases from 550 to 750 ºC. However, a further increase in calcination temperature were found to increase the reaction time as shown in Figure 8 and hence, the catalyst prepared by loading 1.7 wt% Ti in SiO_2 and calcined at 750 ºC (1.7-Ti/SiO_2-750) was selected for optimizing other parameters for the complete epoxidation of used cotton seed oil derived FAMEs.

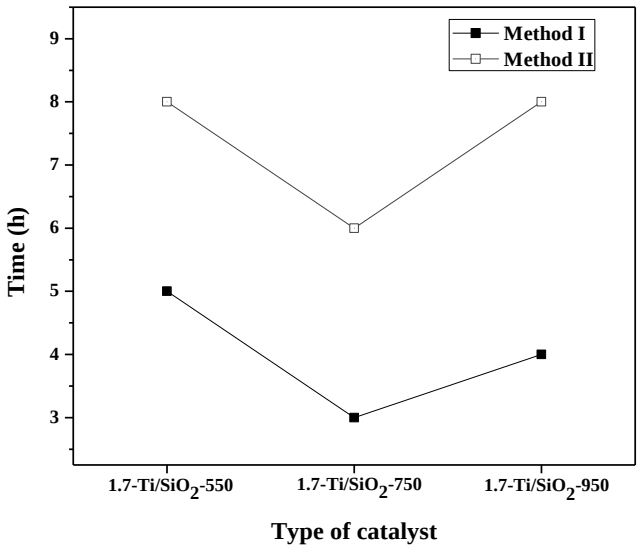


Figure 8. Effect of calcinations temperature on the time required for the complete epoxidation of fatty acid methyl ester derived from used cotton seed oil. (Reaction conditions; (i) hydrogen peroxide and formic acid in method I, and (ii) acetonitrile, butyronitrile and hydrogen peroxide under UV radiation in method II).

6.3.4.2 Catalyst concentration

In order to find the optimum catalyst concentration a series of epoxidation reactions of used cotton seed oil derived FAMEs were performed in the presence of nanocatalyst 1.7-Ti/SiO_2-750 by varying its concentration in the range of 1-15 wt% (catalyst/FAMEs) at 35 °C. Time

required for the complete conversion decreases from 5.5 h to 3 h as catalyst concentration was increased from 1 to 5 wt% in Method I and 18 h to 6 h as catalyst concentration was increased from 1 to 10 wt% in Method II. Further increase in catalyst concentration does not reduce the reaction time significantly as shown in Figure 9. The epoxidation reactions were further studied using catalyst concentration of 5 wt% (catalyst/FAMEs) in method I and 10 wt% in method II for optimization the other parameters.

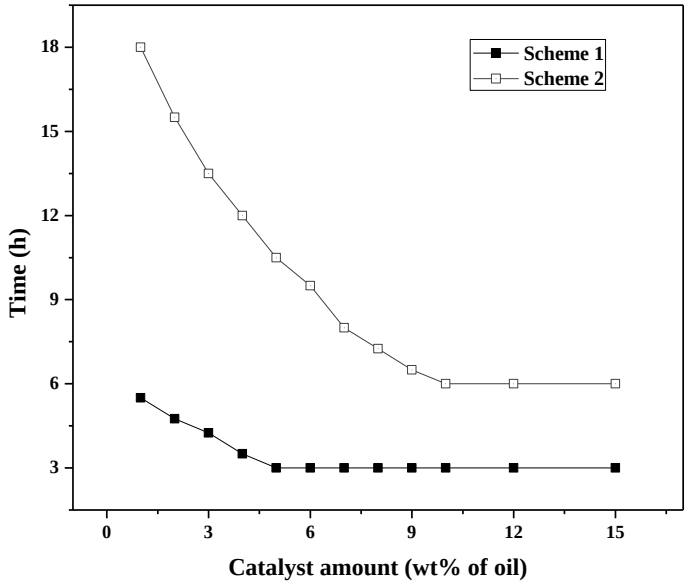


Figure 9. Effect of catalyst concentration on the time required for the complete epoxidation of fatty acid methyl ester derived from used cotton seed oil. (Reaction conditions; (i) hydrogen peroxide and formic acid in method I, and (ii) acetonitrile, butyronitrile and hydrogen peroxide under UV radiation in method II).

6.3.4.3 Reaction temperature

A series of epoxidation reactions were conducted in the presence of 5 wt% (catalyst/FAMEs) of 1.7-Ti/SiO_2-750 catalyst in Method I and 10 wt% of catalyst in Method II, to find the optimum temperature for epoxidation reaction. Time required for the complete epoxidation of FAMEs to corresponding epoxide were found to decreases from 5 h to 3 h in Method I and 7.5 h to 6 h in Method II as temperature of the reaction was increased from 20 ºC to 35 ºC. Further increase in reaction temperature does not reduce the reaction time significantly as shown in Figure 10 and hence, further all epoxidation reactions have been performed at 35 ºC.

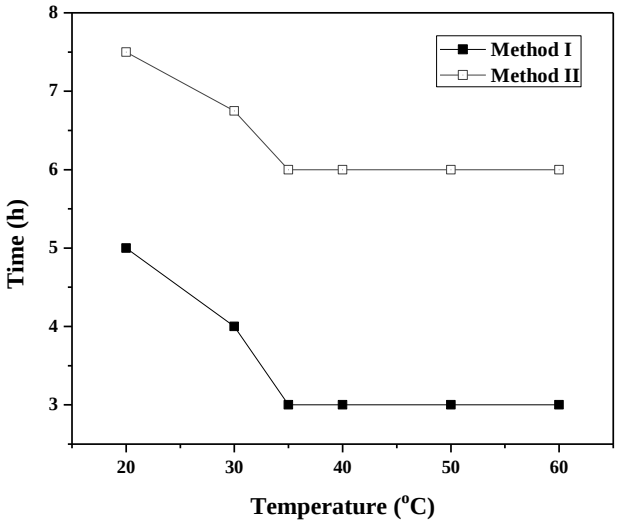


Figure 10. Effect of reaction temperature on the time required for the complete epoxidation of fatty acid methyl ester derived from used cotton seed oil. (Reaction conditions; (i) hydrogen peroxide and formic acid in method I, and (ii) acetonitrile, butyronitrile and hydrogen peroxide under UV radiation in method II).

6.3.4.4 Type of feedstock

A series of epoxidation reactions with different feedstocks viz., used cotton seed oil, fatty acid methyl ester and methyl oleate were conducted in the presence of 5 wt% (catalyst/feedstock) 1.7-Ti/SiO_2-750 in Method I and 10 wt% (catalyst/feedstock) 1.7-Ti/SiO_2-750 in Method II Ti-SiO_2/750, to study the effect of change of feedstock on the catalyst activity. When method I was followed, the epoxidation of FAMEs derived from used cotton seed oil and methyl oleate were found o be completed in 3h, while in case of used cotton seed oil the catalyst required 5 h for the completion of the reaction. On the other hand when method II was followed, the catalyst required 6 h for the complete epoxidation when FAMEs derived from used cotton seed oil and methyl oleate and 10 h in case of the used cotton seed oil as shown in Figure 11.

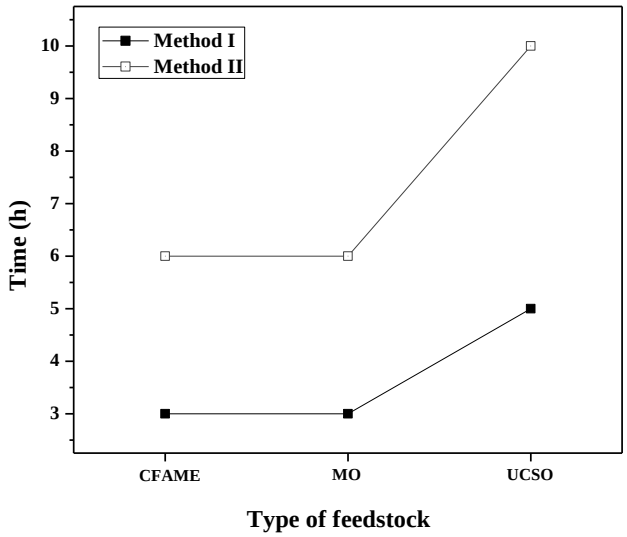


Figure 11. Effect of feedstock on the time required for the complete epoxidation of a variety of feedstock with a catalyst concentration. (Reaction conditions; (i) hydrogen peroxide and formic acid in method I, and (ii) acetonitrile, butyronitrile and hydrogen peroxide under UV radiation in method II). (Acronyms; CFAME= used cotton seed oil derived FAMEs, MO = methyl oleate and UCSO = used cotton seed oil.)

6.3.4.5 Reusability of catalyst

The epoxidation reaction of the FAMEs derived from the used cotton seed oil has been performed in the presence of 1.7-Ti/SiO_2 by following method I and II. In both methods, to test the reusability, the catalyst was recovered from the reaction mixture by filtration, washed with hexane followed by deionized water and finally dried at 100 °C. The catalyst thus recovered was used for the five catalytic runs in both methods, under the same experimental condition and regeneration methods. The reused catalyst was also found to epoxidized the used cotton seed oil derived FAMEs though the reaction time for the complete epoxidation was found to increase after every successive catalytic cycle as shown in Figure 12. The decrease in catalytic activity after every cycle could be due to the partial leaching of titanium from the silica support.

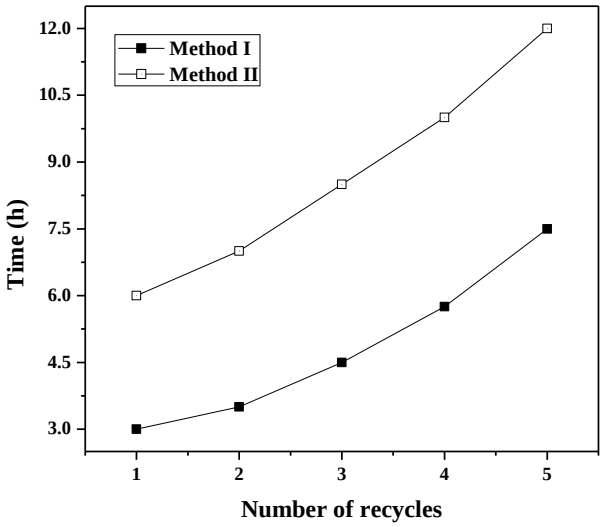


Figure 12. Recyclability studies of the catalyst towards the epoxidation of the used cotton seed oil derived FAMEs. (Reaction conditions; (i) hydrogen peroxide and formic acid in method I, and (ii) acetonitrile, butyronitrile and hydrogen peroxide under UV radiation in method II).

6.4 Conclusions

In present work a series of 1.7 wt% Ti loaded SiO_2 were prepared by chemical method and calcining the Ti/SiO_2 at three different temperatures viz., 550, 750 and 950 ºC. The catalysts were further analyzed by diffuse reflectance solid state UV-Vis spectroscopy, BET surface area, powder XRD, TEM and FESEM techniques. The TEM analysis of the Ti/SiO_2 calcined at different temperatures, reveal that particle size, shape and surface area was found to be effected by the calcination temperature and Ti/SiO_2 calcined at 750 ºC existed in nanorod form while others exist in nanoparticles form. The diffuse reflectance solid state UV-Vis spectroscopic studies suggested that titanium in silica support exist in octahedral and tetrahedral coordination environment. Powder XRD analysis of Ti/SiO_2 material support that the prepared mixed oxide is amorphous in nature having silica in monoclinic phase. The catalytic activity of the selected catalyst ($1.7\text{-}Ti/SiO_2\text{-}750$) towards the epoxidation of used cotton seed oil, used cotton seed oil derived FAMEs and methyl oleate has been tested using two different methods. Under optimized reaction conditions the catalyst $1.7\text{-}Ti/SiO_2\text{-}750$ required only 3 h for the complete epoxidation of used cotton seed oil derived FAMEs when formic acid and hydrogen peroxide were used and 6 h when

acetonitrile, butyronitrile, and hydrogen peroxide were used in the presence of UV-Visible radiation. The catalyst has been recycled and reused successfully five times for the complete epoxidation of used cotton seed oil derived FAMEs. The epoxide derivative of fatty acid esters have been characterized by FTIR, proton NMR and mass spectroscopic techniques. The fatty acid epoxide derivatives being possessing long chain hydrocarbon and epoxide functional group are expected to show the lubricity improving property upon addition in diesel fuel.

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Chapter 7

Diesel Fuel Cetane Number and Lubricity Improver Studies of the Vegetable Oil Derived Additives

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Abstract

The vegetable oil derived transesterified, amide, nitrate and epoxide derivatives of vegetable oils as discussed in chapter 3, 4, 5 and 6, respectively have the potential to improve the lubricity as well cetane number of the diesel fuel. Out of the prepared molecules, nitrate derivative of castor oil derived FAMEs (FANCM) being having long hydrocarbon chain and nitrate group was found to improve the lubricity from 458 to 152 µm as well as cetane number from 52.4 to 56.0 of the base diesel fuel. Similarly amide derivative of used cotton seed oil (FAAUC) being having amide group as well as long hydrocarbon chain were found to improve the cetane number from 52.4 to 56.0, and lubricity from 458 to 143 µm of the base diesel fuel. Hence, both the molecules were found to act as dual functional diesel fuel additives as they improve the cetane number as well as lubricity when added individually in 0.4 wt% concentration in diesel fuel. The epoxide of used cotton seed oil derived FAMEs (FAEUM) has been tested as lubricity additive for the diesel fuel and same molecule was found to improve the lubricity of the diesel fuel from 458 to 115 µm.

Keywords: amide derivatives, nitrate derivatives, epoxides, dual functional diesel fuel additives.

7.1 Introduction

7.1.1 Cetane number

Cetane number is a measure of the ignition quality of a diesel fuel, often mistaken as a measure of fuel quality, refers to the time period between the start of injection and start of combustion (ignition) of the fuel (Challen and Barabescu, 1999; Ulrich, 1994). In a particular diesel engine, higher cetane fuels will have shorter ignition delay periods than lower cetane fuels. Improved ignition (shorter ignition delay time) has been directly correlated with faster startup in cold weather, reduced emissions of nitrogen oxides (NO*x*), and smoother engine operation (Bacha, 1998).

Cetane (also called hexadecane as shown in Figure 1) is an alkane hydrocarbon with the chemical formula $C_{16}H_{34}$ and has 10,359 constitutional isomers.

Figure 1. Chemical structure of cetane.

Cetane also used as a short-hand representation for cetane number and it was assigned a cetane number of 100, while alpha-methyl naphthalene was assigned a cetane number of zero. All other hydrocarbons in diesel fuel are indexed to cetane as to how well they ignite under compression. Since there are hundreds of components in diesel fuel, with each having a different cetane quality, the overall cetane number of the diesel is the average cetane quality of all the components (Heywood, 1988; Owen, 1995).

7.1.2 Lubricity

A lubricant (sometimes referred to "Lube") is a substance (often a liquid) introduced between two moving surfaces to reduce the friction and wear between them. A lubricant provides a protective film which allows for two touching surfaces to be separated and smoothed, thus lessening the friction between them. Lubricants contain 90% base oil (most often petroleum fractions, called mineral oils) and less than 10% additives. Diesel fuel lubricity is the ability of the diesel fuel to lubricate the close-tolerance moving parts in diesel engines so that wear between metal-on-metal moving parts could be minimized (Suppes et al., 2001).

The HFRR lubricity test have been used for the lubricity analysis of fluids which uses a hardened steel ball vibrating in loaded contact with a hardened steel plate immersed in the test fuel. Results from the HFRR lubricity test is based on comparison of the wear scar diameter with that of a reference fuel. The smaller the scar diameter, the better the lubricating ability of the fluid.

In present chapter, the cetane number as well as lubricity improving property of the selected synthesized vegetable oil derived additives have been evaluated.

7.2 Synthesis of dual functional diesel fuel additives

The transesterified, amide, epoxide and nitrate derivatives of vegetable oils, mutton fat, methyl laurate and methyl oleate were prepared as described in chapter 3, chapter 4, chapter 5 and chapter 6, respectively. The chapter wise description of prepared molecules is given below.

7.2.1 Fatty acid methyl esters

Fatty acid methyl esters have been prepared by transesterification of mutton fat and variety of vegetable oils viz., used cotton seed oil, karanja oil, jatropha oil, castor oil and soybean oil with methanol by using alkali metal impregnated CaO solid catalysts as described in chapter 3. The chemical structure of vegetable oil and mutton fat derived fatty acid methyl esters are given in Figure 2.

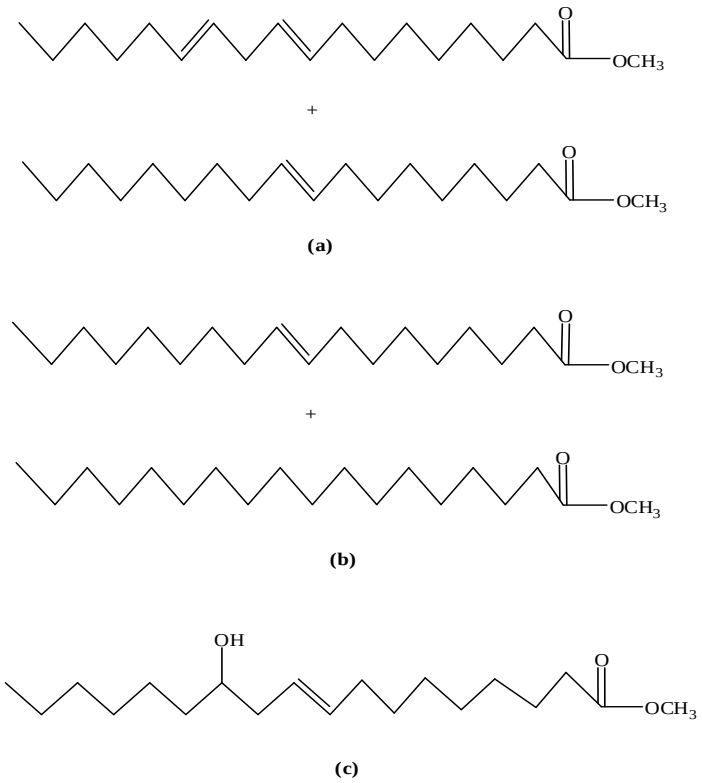

Figure 2. The chemical structures of (a) Fatty acid methyl esters derived from used cotton seed oil (UFAMEs), (b) Fatty acid methyl esters derived from mutton fat (MFAMEs), and (c) Fatty acid methyl ester derived from castor oil (CFAMEs).

7.2.2 Fatty acid amide derivatives

Fatty acid amides have been prepared directly from (i) vegetable oils, (ii) vegetable oil and mutton fat derived FAMEs, and (iii) methyl laurate. All category of substrate, separately, has been treated with diethanolamine in the presence of, 0.5-Ni/CaO-650, catalyst as described in chapter 4. The chemical structure of the resulted amide derivatives are given in Figure 3.

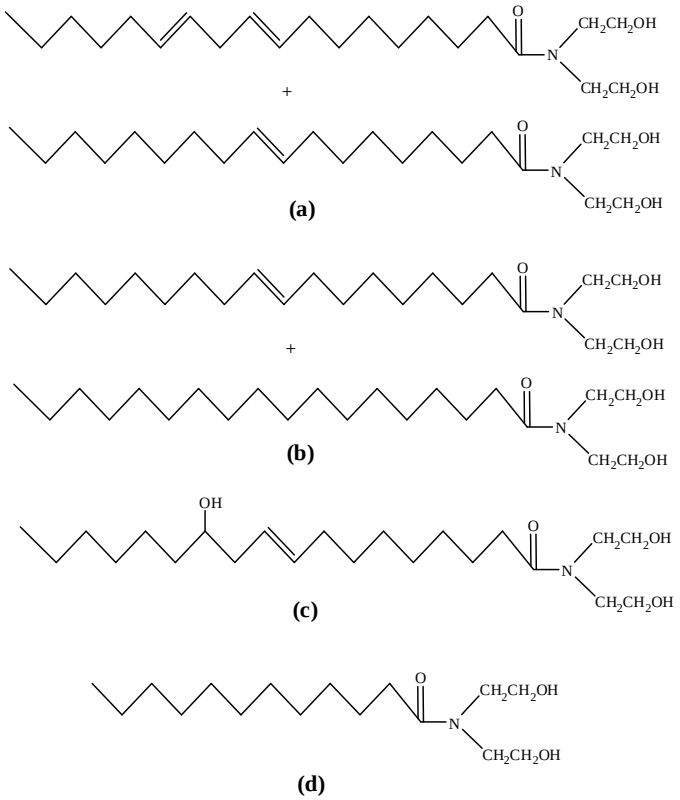

Figure 3. The chemical structures of synthesized dual functional diesel fuel additives (a) fatty acid amide derived from used cotton seed oil (FAAUC), (b) fatty acid amide derived from mutton fat derived FAMEs (FAAMM), (c) fatty acid amide derived from castor oil (FAACO), and (d) fatty acid amide derived from methyl laurate (FAAML).

7.2.3 Nitrate derivative of castor oil derived FAMEs

Nitrate derivative of castor oil derived FAMEs has been prepared by using nitric acid and acetic anhydride as described in chapter 5 and structure of the resulted molecule is given in Figure 4.

Figure 4. Nitrate derivative of castor oil derived FAMEs (FANCM)

7.2.4 Epoxidized derivatives from used cotton seed oil derived FAMEs

Epoxidized derivative of used cotton seed oil, used cotton seed oil derived FAMEs and methyl oleate were prepared by using 1.7-Ti/SiO_2-750 as catalyst and following two

different methods, viz., (i) using hydrogen peroxide and formic acid (method I), and (ii) using acetonitrile, butyronitrile and hydrogen peroxide (method II) under UV-Vis radiation as described in chapter 6. The chemical structure of the resulted epoxide derivatives are given in Figure 5.

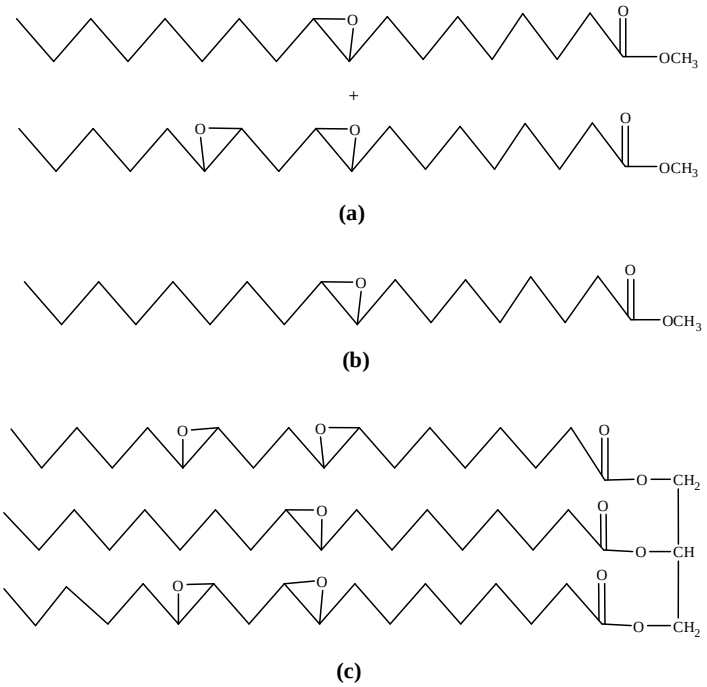

Figure 5. The chemical structures of (a) epoxidized derivative of used cotton seed oil derived FAMEs (FAEUM), (b) epoxidized derivative of methyl oleate (FAEMO), and (c) epoxidized derivative of used cotton seed oil (FAEUC).

7.3 Sample selection for cetane number and lubricity improver study

Although in present thesis as discussed above, all vegetable oil derived amide or nitrate molecules being having long hydrocarbon chain and amide or nitrate functional group has the potential to act as dual functional diesel fuel additives. However, due to financial constrain, out of the prepared molecules nitrate derivative of castor oil derived FAMEs (FANCM) as shown in Figure 4 and amide derivative of used cotton seed oil (FAAUC) as shown in Figure 3a, being having long hydrocarbon chain as well as nitrate and amide group, respectively, were selected to test their cetane number and lubricity improver properties upon addition in diesel fuel.

Whereas epoxide of used cotton seed oil derived FAMEs (FAEUM) as shown in Figure 5a, was selected to test lubricity improving property of diesel fuel.

7.4 Cetane number and lubricity improver study

7.4.1 Cetane number measurement

Cooperative Fuel Research (CFR) engine manufactured by Waukesha Motor Company was used for the cetane number measurement by following the literature reported ASTM D-613 method. In a typical experiment, 0.4 wt% of either FANCM or FAAUC was added in diesel fuel having cetane number of 52.6.

7.4.2 Lubricity measurement

Lubricity improver study has been performed with the help of HFRR TE 77 instrument by following ASTM D6079 method. In a typical experiment, 0.4 wt% of desired prepared additive has been added to diesel fuel having lubricity of 458 μm. The HFRR is currently the internationally accepted and standardized method to evaluate the lubricating ability of the fluids. This method uses a ball bearing, immersed in the test fluid, moving back and forth on a metal surface at a very high frequency for the duration of 90 minutes as shown in Figure 13. The ball bearing is examined under a microscope and the "wear scar" on the ball bearing is measured in microns. The larger the wear scar, the poorer the lubricating ability of the fluid.

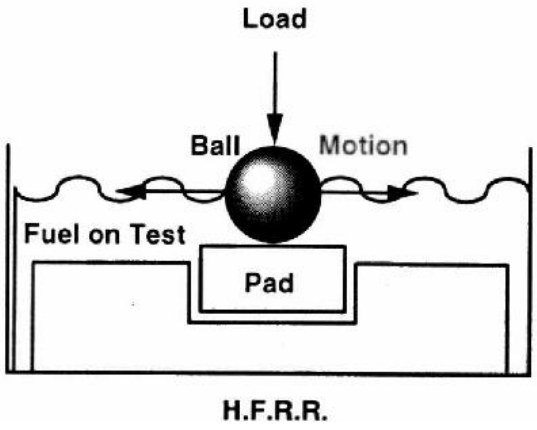

Figure 13. The schematic diagram of HFRR lubricity test uses a hardened steel ball vibrating in loaded contact with a hardened steel plate immersed in the test fuel.

7.4.3 Analysis of the synthesized additives as cetane number and lubricity improvers

The amide derivative of used cotton seed oil derived FAMEs and nitrate derivatives of castor oil derived FAMEs have been tested as dual functional diesel fuel additives viz., for their cetane number and lubricity improving properties. The epoxide derivative of used

cotton seed oil FAMEs has been tested for the lubricity improving property of the diesel fuel. All experiments have been performed with the diesel fuel having cetane number of 52.4 and lubricity 458 µm. As given in Table 1, the diesel fuel additive derived from the nitration of castor oil derived FAMEs was found to improve the cetane number of the base diesel fuel from 52.4 to 56.0 and lubricity from 458 to 152 µm. While, the diesel fuel additive derived from the aminolysis of used cotton seed oil derived FAMEs was found to improve the cetane number of the base diesel fuel from 52.4 to 56.0 and lubricity from 458 to 143 µm. The epoxidized derivative of used cotton seed oil derived FAMEs tested as lubricity improver only, and found to improve the lubricity of diesel fuel from 458 to 115 µm as shown in Table 1.

Table 1: Diesel fuel additive analysis of the prepared vegetable oil derived additives as cetane number and lubricity improvers for diesel fuel.

S. No.	Additive samples	Additive dose (wt %)	Cetane number	Lubricity (µm)
1.	Base fuel	--	52.4	458
2.	FANCM	0.4	56.0	152
3.	FAAUC	0.4	56.0	143
4.	FAEUM	0.4	------	115

7.5 Conclusions

This chapter has demonstrated the application of vegetable oil derived transesterified, amide, nitrate and epoxide derivatives, as given in chapter 3-6, as lubricity and cetane number improver for the diesel fuel. Out of the prepared molecules three have been selected for the evaluation as diesel fuel additive. The nitrate derivative of castor oil derived FAMEs being having long hydrocarbon chain as well as nitrate group was expected to show the lubricity as well as cetane number improving property of the diesel fuel. Similarly amide derivative of used cotton seed oil being having amide group as well as long hydrocarbon

chain was expected to show the lubricity as well as cetane number improving property of the diesel fuel. The evaluation results demonstrates that both molecules could act as dual functional diesel fuel additive as they can improve the lubricity as well as cetane number of the diesel fuel. The epoxide derivative of used cotton seed oil derived FAMEs has been tested as lubricity improver for the diesel fuel and same was found to improve the lubricity of diesel fuel from 458 to 115 µm.

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Chapter 8

Conclusions and Futuristic Aspects

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Abstract

The results given in chapter 3-7 have been concluded, compared and correlated in this chapter. Future studies possible with the synthesized vegetable oil derived additives have also been discussed in this chapter.

8.1 Introduction

In order to improve the diesel fuel quality and to achieve the better performance from the diesel engines, the application of diesel fuel additives are necessary. The cetane number improvers which are available at commercial level include 2-ethylhexylnitrate (EHN) and di-*tert*-butylperoxide (DTBP) and lubricity improvers mainly consists long chain hydrocarbons and fatty acid esters. In present thesis the synthesis of dual functional diesel fuel additives from vegetable oils and animal fat has been demonstrated mainly using prepared heterogeneous catalysts. The prepared diesel fuel additives have been evaluated for their cetane number and lubricity improver properties.

8.2 Conclusions from the present studies

i. **In chapter 3**, the preparation of alkali metal (Li, Na & K) ion impregnated CaO by wet chemical method have been reported. The resulted materials were characterized by powder XRD, BET surface area, flame photometer, FESEM, TEM and Hammett indicator studies.

ii. The prepared catalysts were found to exist in nanocrystalline form as suggested by powder XRD and TEM studies. Among the prepared catalysts 1.5-LiC/CaO was found to be most efficient solid catalyst for the complete transesterification of various feedstocks viz., animal fat, virgin soybean, virgin cotton seed oil, used cotton seed oil, castor oil, karanja oil and jatropha oil.

iii. The lixiviation studies show that the catalytic activity was entirely due to the solid catalysts and not due to any leached metal ions from the catalyst support. The catalyst has been reused for three successive catalytic cycles for the complete transesterification of used cottonseed oil.

iv. The fatty acid methyl esters thus obtained was analyzed and quantified by ^{1}H-NMR and ^{13}C-NMR spectroscopy. The prepared fatty acid methyl esters (biodiesel) have also been analyzed for few physico-chemical properties and values were found within the acceptable limits of the European and American standards.

v. **In chapter 4,** the preparation of Ni doped CaO by wet chemical method has been demonstrated for the aminolysis reaction of vegetable oils. The prepared catalysts were characterized by powder XRD, BET surface area, N_2 adsorption desorption isotherm, FESEM, HRTEM and Hammett indicator studies.

vi. The catalyst was found to exist in nanosized form and particle size and shape was found to be dependent on the calcination temperature of the catalyst. The catalyst prepared by doping 0.5 wt% Ni in CaO and calcined at 650 °C was found to exist in nanorod form and found to be most effective among the prepared catalysts for the aminolysis of various feedstocks viz., methyl laurate, animal fat, virgin soybean, virgin cotton seed oil, used cotton seed oil, castor oil, karanja oil and jatropha oil.

vii. The fatty acid amide derivatives thus obtained were characterized by FTIR and ^{1}H-NMR studies and quantified by FTIR analysis. The amide derivative of methyl laurate has also been analyzed by electron impact mass spectroscopy (EI-MS). The aminolysis reaction has been followed by FTIR technique and kinetic studies suggest that the reaction was following the pseudo first order kinetic model.

viii. The catalyst has been reused for seven catalytic cycles and found to complete the aminolysis of used cotton seed oil each time. The lixiviation studies performed with the catalysts suggested that the solid catalyst was responsible for the entire catalytic activity and not any leached species.

ix. **In chapter 5,** the –OH group present at C-12 position in castor oil derived fatty acid methyl ester have been nitrated with the help of nitric acid and acetic anhydride.

x. The nitrate derivative of fatty acid methyl ester was characterized by FTIR and proton NMR spectroscopic techniques and these studies support the nitration of –OH group.

xi. **In chapter 6,** the titanium loaded silica has been prepared by chemical method and calcining the Ti/SiO_2 at three different temperatures viz., 550, 750 and 950 ºC. The catalysts were characterized by BET surface area, diffuse reflectance solid state UV-Vis, FESEM and TEM techniques. The TEM analysis of the Ti/SiO_2 particles prepared at different calcination temperature revealed that particle size, shape and surface area was found to be effected by the calcination temperature and Ti/SiO_2 calcined at 750 ºC existed in nanorod form while others exist in nanoparticles form.

xii. The solid catalyst, 1.7-Ti/SiO_2-750, was found to be most effective towards the epoxidation of various feedstocks viz., used cotton seed oil, used cotton seed oil derived FAMEs and methyl oleate. Under optimized reaction conditions the catalyst 1.7-Ti/SiO_2-750 required only 3 h for the complete epoxidation of used cotton seed oil derived FAMEs utilizing formic acid and hydrogen peroxide were used and 6 h

when acetonitrile, butyronitrile, and hydrogen peroxide were used in the presence of UV-Visible radiation.

xiii. The catalyst has been recycled and reused successfully five times for the complete epoxidation of used cotton seed oil derived FAMEs. The epoxide derivative of fatty acid esters have been characterized by FTIR, proton NMR and mass spectroscopic techniques.

xiv. **In chapter 7**, out of the prepared molecules nitrate derivative of castor oil derived FAMEs as shown in Figure 1a and amide derivative of used cotton seed oil as shown in Figure 1b, being having long hydrocarbon chain as well as nitrate and amide group, respectively, were selected to test their cetane number and lubricity improver (dual functional diesel fuel additive) properties upon addition in diesel fuel.

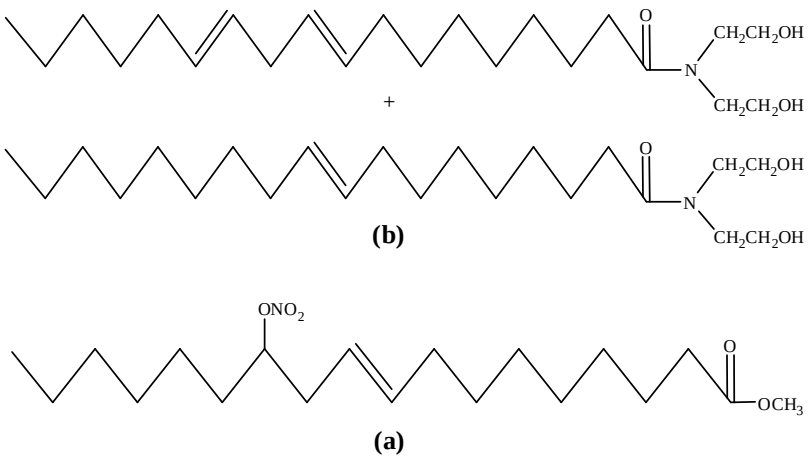


Figure 1. The chemical structures of synthesized dual functional diesel fuel additives, (a) nitrate derivative of castor oil derived FAMEs, and (b) amide derivative of used cotton seed oil.

xv. Whereas epoxide of used cotton seed oil derived FAMEs as shown in Figure 2, was selected to test lubricity improving property of diesel fuel.

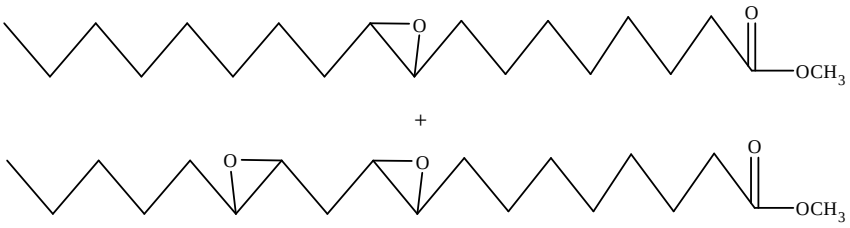


Figure 2. The chemical structures of synthesized epoxide of used cotton seed oil derived FAMEs tested as lubricity improver.

xvi. The diesel fuel additive derived from the nitration of castor oil derived FAMEs was found to improve the cetane number of the base diesel fuel from 52.4 to 56.0 and lubricity from 458 to 152 µm. While, the diesel fuel additive derived from the aminolysis of used cotton seed oil derived FAMEs was found to improve the cetane number of the base diesel fuel from 52.4 to 56.0 and lubricity from 458 to 143 µm. The epoxidized derivative of used cotton seed oil derived FAMEs tested as lubricity improver only, and found to improve the lubricity of diesel fuel from 458 to 115 µm.

8.3 Futuristic aspects

i. In present thesis, naturally occurring triglycerides have been used as feedstock to prepare dual functional diesel fuel additives. As mentioned above only three molecules have actually been tested as diesel fuel additives. The efficacy of other prepared derivatives, as shown in Figure 3, could also be tested in near future.

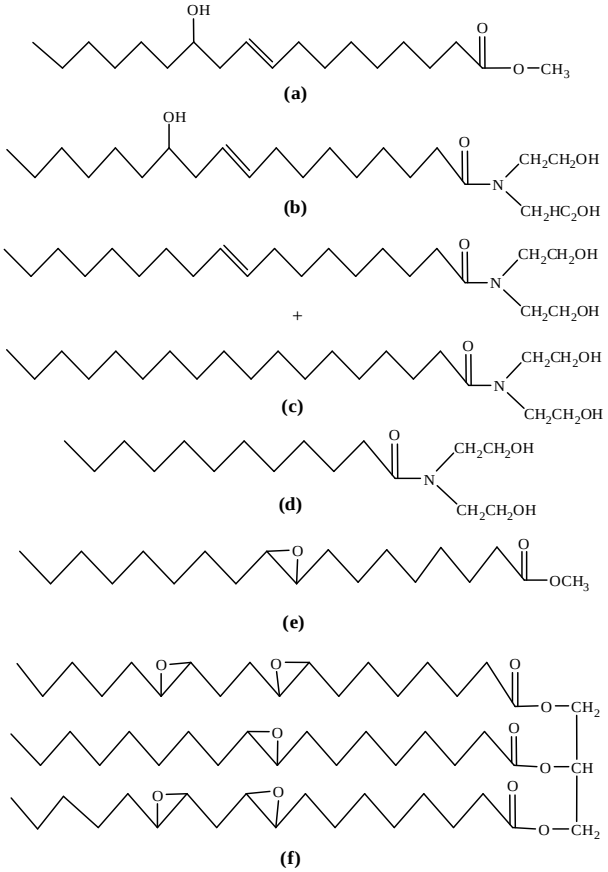
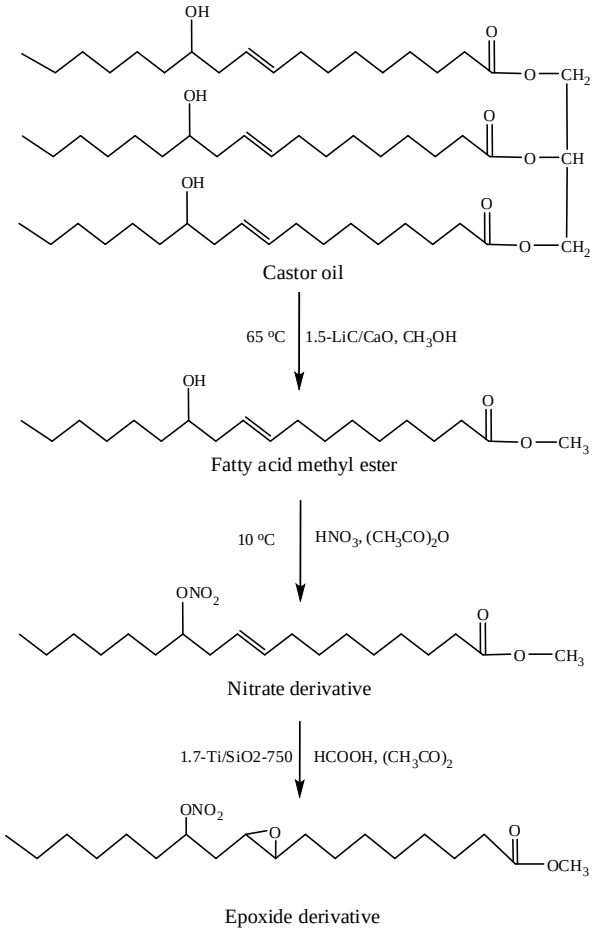
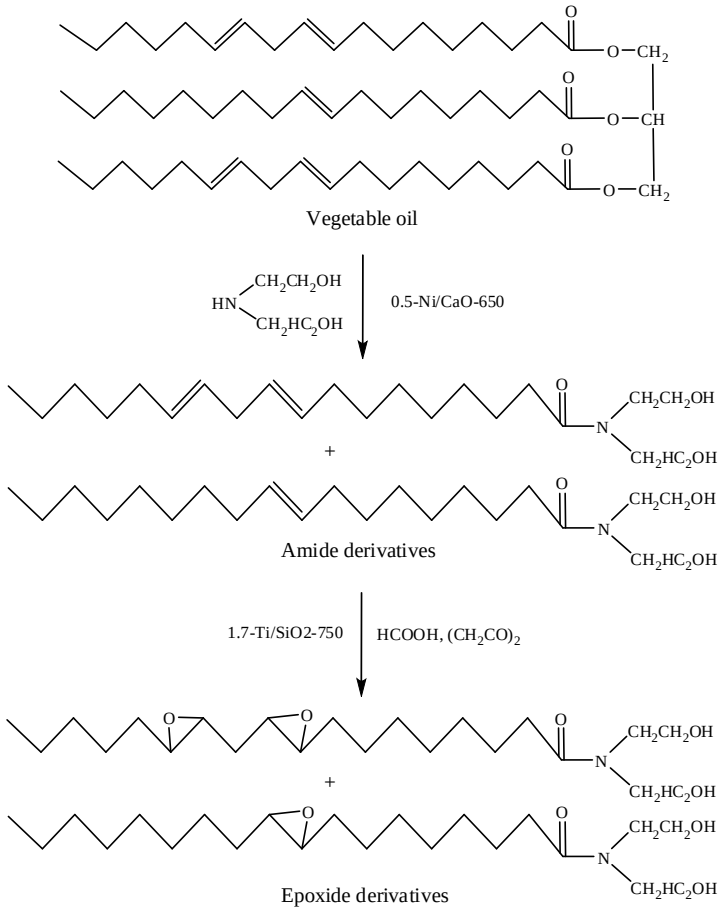


Figure 3. The chemical structures of prepared molecules, (a) castor oil derived FAMEs, (b) amide derivative of castor oil derived FAMEs, (c) amide derivatives of mutton fat derived FAMEs, (d) amide derivatives of methyl laurate, (e) epoxide of methyl oleate, and (f) epoxide of used cotton seed oil.

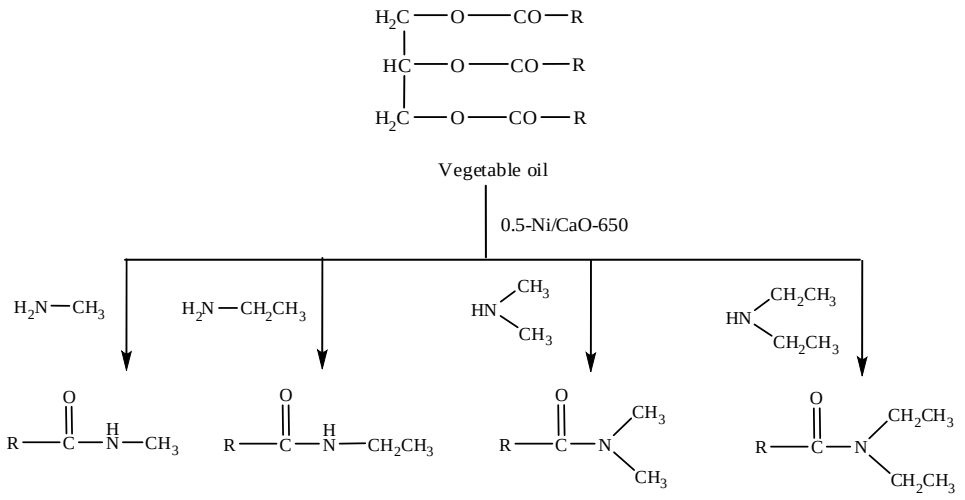
ii. A variety of other vegetable oil derived, nitrate, amide and epoxide derivative could also be synthesized using the proposed scheme 1, 2 and 3. Already prepared catalysts, Ni/CaO, could be used for aminolysis reaction and Ti/SiO_2 for epoxidation reactions.



Scheme 1. Castor oil derived fatty acid methyl ester, nitrate derivative, amide derivative and epoxide derivative.



Scheme 2. Vegetable oil derived amide and epoxide derivatives.



Scheme 3. Aminolysis of vegetable oil using different amines.

iii. The efficiency of these proposed molecules could be tested as lubricity and cetane number improver and compared with those of already reported in present thesis and in literature.

iv. In present work suitable heterogeneous catalyst could not be developed for the nitration of –OH group. This challenging task i.e. development of solid catalyst for the nitration of –OH group could also be taken in coming future.

Appendix-1

Table 1. Physico-chemical properties of fatty acid methyl esters (biodiesel) derived from cotton seed oil (CBD), karanja oil (KBD), jatropha oil (JBD) and mutton fat (MBD) in comparison with European standards (EN-14214).

S. No.	Parameters	CBD	KBD	JBD	MBD	EN-14214	Test method
1.	Ester content (%, m/m)	>99	>99	>99	>99	>96.5	^{1}H-NMR
2.	Flash point (°C)	110	116	104	115	>101	ASTM D 93
3.	Pour point (°C)	2.0	4	-1	1	--	ASTM D 2500
4.	Kinematic viscosity at 40 °C	3.94	5.8	4.2	3.8	3.5-5.0	ASTM D 445
5.	Calorific value (MJ/kg)	40.0	27	37	35	--	IS 1350 P:2
6.	Iodine value	85	81	90	----	<120	EN 14111
7.	Ash (%)	0.02	0.02	0.01	0.01	0.02	ASTM D 874
8.	Density at 31 °C (g/ml)	0.80	0.86	0.85	0.82	0.86-0.90	IS 1448 P:32
9.	Water (%)	0.05	0.05	0.5	0.1	0.5	ASTM D 2709
10.	Acid number (mg KOH/g)	0.1	0.6	0.4	0.15	0.5	ASTM D 664
11.	Li/Ca (ppm)	<1/<1	<1/1	<1/1	<1/1	<5 (total metal)	ASTM D 1318

List of publications

Publications in International Journals

1. Dinesh Kumar and Amjad Ali, Nanocrystalline lithium ion impregnated calcium oxide as heterogeneous catalyst for transesterification of high moisture containing cotton seed oil, Energy Fuels (ACS), 2010, 24, 2091–2097.

2. Dinesh Kumar and Amjad Ali, Potassium ion impregnated calcium oxide as nanocrystalline solid catalyst for the biodiesel production from waste cotton seed oil, Energy Sources A (Taylor & Francis), accepted for publication.

3. Amjad Ali, Priyanka and Dinesh Kumar, Sodium impregnated zinc oxide as a solid catalyst for biodiesel preparation from a variety of triglycerides, Energy Sources A (Taylor & Francis), accepted for publication.

4. Dinesh Kumar and Amjad Ali, K/CaO as nanocrystalline heterogeneous catalyst for the transesterification of a variety of feedstocks, Biomass & Bioenergy (Elsevier), under review.

5. Dinesh Kumar and Amjad Ali, Preparation and characterization of nanocrystalline Li/CaO as Solid Catalyst for the Biodiesel Production from Low Quality Feedstocks, manuscript ready for submission.

6. Dinesh Kumar and Amjad Ali, Alcoholysis and aminolysis of waste cooking oil by using nanocrystalline sodium loaded calcium oxide as solid catalyst, manuscript ready for submission.

7. Dinesh Kumar and Amjad Ali, Na/CaO as nanocrystalline solid catalyst for the transesterification and aminolysis of a variety of feedstocks, manuscript ready for submission.

8. Dinesh Kumar and Amjad Ali, Potassium impregnated calcium oxide as a heterogeneous nanocatalyst for transesterification and aminolysis of vegetable oils, manuscript under preparation.

9. Dinesh Kumar and Amjad Ali, Nickel doped calcium oxide as solid nano catalyst for transesterification and aminolysis of vegetable oils, manuscript under preparation.

10. Dinesh Kumar and Amjad Ali, Ti/SiO_2 as solid catalyst for epoxidation of variety of feedstocks, manuscript under preparation.

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1. Dinesh Kumar, Amjad Ali, Vishal Mutreja, Vinod Sharma and Satnam Singh, Biodiesel preparation from used cottonseed oil using alkali metal ion doped calcium oxide as heterogeneous catalyst, Advances in chemical engineering 2009, Macmillan, 1st edition, 2009, 359-365.

2. Mandeep Kaur, Dinesh Kumar, Amjad Ali, Physicochemical properties of the biodiesel prepared from jatropha and used cottonseed oils in the presence of Li/CaO solid catalyst, Advances in chemical engineering 2011, Macmillan, 2nd edition, 2011, 315-323.

Publications in International Conferences

1. Dinesh Kumar, Vishal and Amjad Ali, Biodiesel from low quality feedstock using alkali metal ion doped calcium oxide as heterogeneous catalyst, Presented in 2nd International Congress on Biodiesel: The Science and the Technologies, November, 15-17, 2009 organized by organized by American Oil Chemist's Society (AOCS) and Euro Fed Lipid, The Westin Grand, Munich, Germany.

Publications in National Conferences

1. Dinesh Kumar and Amjad Ali, Biodiesel production from waste cooking oil by using k^+ metal ion doped calcium oxide as a heterogeneous catalyst, presented in National Conference On Advances on Materials and Devices for Renewable Energy Sources (NCAMDRES-10) 25 - 27th February, 2010, organized by Jaipur Engineering College Jaipur (Rajasthan).

2. Vishal, Dinesh Kumar, Satnam Singh and Amjad Ali, Transesterification of non-edible oils using heterogeneous catalyst, Presented in National Symposium on Green Chemistry: Applications in Science & Engineering, February, 5-6, 2009, 200p, Organized by School of Chemistry & Biochemistry, Thapar University, Patiala (Punjab).