Process Intensification of Methyl Esters Synthesis using Castor Seeds by Reactive Extraction Technique

Thesis submitted in partial fulfilment of the

requirements for the degree of

DOCTOR OF PHILOSOPHY

by

Swaroopa Rani Dasari

Department of Chemical Engineering

Indian Institute of Technology Guwahati

Guwahati-781039, India

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For God so loved the world that He gave His one and only Son, that everyone who believes in Him shall not perish but have eternal life. For God did not send His Son into the world to condemn the world, but to save the world through Him....

John 3:16-17

Jesus answered, "I am the way and the truth and the life. No one comes to the Father except through Me.

John 14:6

Whoever does not love does not know God, because God is love. This is how God's love was revealed among us: God sent His one and only Son into the world, so that we might live through Him....

I John 4:8-9

"Watch and pray so that you will not enter into temptation. For the spirit is willing, but the body is weak."

Mathew 26:41

Dedicated with joy

To my God Jesus Christ Holy Spirit who saved me eternally, my mother Amruthamma Dasari who struggled and sacrificed so much to make her 6 daughters to higher level from our child hood, my father Prasad Dasari, my husband Thatigotla Ramamohan Reddy who loves and sacrificed so much for me, all my 5 sisters, my mother in-law, father-in-law and my class mate Venu Babu Borugadda for their constant help.

&

To all my teachers, well wishers, physical and spiritual friends

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STATEMENT

I do hereby declare that the research findings of this thesis is the result of investigation carried out by me in the Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati, India, under the supervision of Dr. Vaibhav V. Goud.

In keeping with general practice of reporting scientific observations, due acknowledgements have been made wherever the research findings of other researchers have been cited in this thesis.

Date: May, 2017

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CERTIFICATE

This is to certify that the thesis entitled **"Process Intensification of Methyl Esters Synthesis using Castor Seeds by Reactive Extraction Technique"** submitted by **Mrs. Swaroopa Rani Dasari (Roll No: 11610724)**, a research scholar in the Department of Chemical Engineering, Indian Institute of Technology Guwahati, for the award of the degree of Doctor of Philosophy, is a record of an original research work carried out by her under my supervision and guidance. The thesis has fulfilled all requirements as per the regulations of the institute and in our opinion has reached the standard needed for submission. The works documented in this thesis have not been submitted to any other University or Institute for the award of any degree.

(Dr. Vaibhav V Goud)

Associate Professor

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Abstract

Biodiesel is an alternative bio fuel for transportation which is renewable and environment friendly. Biodiesel can be produced from animal fat, vegetable oil (edible or non edible) or waste cooking oil. To avoid the food vs. fuel problem, non-edible oils can be the best way to use to produce the biodiesel and they are the focus of this thesis.

The main objective of the PhD research is to check the feasibility of producing biodiesel (methyl ester) from castor seeds directly via reactive extraction technique. Before preceding the reactive extraction, the performance of seed pre-treatment on the oil yield and the suitability of possible extracting and reactive solvent for biodiesel production was also investigated. Further objective includes an investigation on engine performance, emulsification of prepared castor oil biodiesel in order to reduce the emission of pollutants. Further includes storage stability and biodegradability of castor oil biodiesel, the estimation of various properties of the castor oil biodiesel and emulsions.

Initially, pre-treatment of castor seed on oil yield and properties was investigated in this research. Pre-treatment of castor seed was carried out by heating the cleaned seed for 24 h at 50 °C. Extraction of castor oil from castor seed was carried out by Soxhlet method using polar and non- polar commercial solvents at optimum conditions obtained during preliminary oil extraction study. The solvents used were hexane, pentane, petroleum ether, cyclohexane, ethyla cetate, methanol and isopropanol. The effect of different process parameters such as temperature, solute to solvent ratio and extraction time were studied to optimize and compare the extraction efficiency of different solvents. The highest oil yield of 56.07% and 55.22% were obtained with polar solvents ethyl acetate and methanol respectively. The oil was also extracted by vial method using

hexane for the successive extraction from a single castor seed. The yield obtained from this method was comparable to the yield obtained from the Soxhlet method. Physicochemical properties of the oil extracted using different solvents were also estimated to determine its quality potential using ASTM methods. Similarly the performance of seed pre-treatment on oil yield and the suitability of methanol as a possible extracting and reactive solvent for biodiesel production was also investigated. For castor seed, after pre-treatment slight increased in extraction yield was noticed, with significant decrease in both acid value (3.92 to 0.925 mg KOH/g) and pour point (-15 to -21 °C). Apart from that thermal and oxidative stability analysis of oil was estimated using thermo gravimetric analysis (TGA) and differential scanning calorimetry under nitrogen and air atmosphere respectively. The fatty acid profile of castor oil was determined by gas chromatography (GC). The obtained physico-chemical properties indicated that oil meets the prescribed biodiesel feedstock quality standards, further justifying methanol as a capable solvent for simultaneous extraction and transesterification. Therefore, methanol was considered as desirable solvent for further reactive extraction of castor seed in a single step.

Among non-edible feed stocks, castor seed is a cheap feed stock for the production of biodiesel. In this research, reactive extraction was carried out in two approaches i.e. integrated and non-integrated. Integrated reactive extraction includes no direct contact of the seed material with the catalyst. Whereas non-integrated includes the direct contact of the seed material with the catalyst and alcohol. As an optimization of reaction conditions has the capacity to decrease reagent use and raise yields, reactive extraction was optimized by RSM (Response Surface Methodology) design technique based on the preliminary studies in both the approaches. Initially, optimization of

integrated reactive extraction of castor seed was carried out using KOH as a catalyst and methanol as alcohol. Since an alkali catalyst is favourable than acid catalyst due to its higher reaction rates at lower temperatures, same was used in the reactive extraction. The optimum COME conversion of 95% was achieved with oil/methanol molar ratio of 1:400, catalyst concentration of 1.5 wt % and 6.3 h reaction time. The results showed insignificant effect of co-solvent on the conversion but on the properties such as thermal and oxidative stability are slightly inferior compared to that of COME-without co-solvent (hexane). Similarly optimization of reactive extraction of castor seed by non-integrated approach was carried out by using NaOH as a catalyst. A biodiesel conversion of 97% was achieved with oil/methanol molar ratio (1: 200) using NaOH as catalyst (1.19 wt %) within 3 h reaction time at 30 °C temperature. An estimated properties of COME and its blends are within ASTM standards and comparable to the reported literature data. This study suggests that reactive extraction by integrated or non-integrated approach is an effective process for methyl ester production in single step and COME can be a good alternate fuel for petro-diesel.

Even though, the usage of biodiesel has several increasing ecological benefits, deterioration of biodiesel is more severe compared to commercial petro-diesel during storage. Storage stability is a major concern about the flourishing commercialization of biodiesel in the fuel market. Therefore, storage stability of prepared biodiesel was evaluated over a six-month storage period (180 days) under three different storage conditions. The results showed a sharp decrease in fuel stability over time in terms of increase in density from 0.888 to 0.984 g/cm^3, kinematic viscosity (10.59 to 16.18 cSt), acid value (0.52 to 5.15 mg KOH/g) respectively. While, iodine value significantly decreased from 82.5 to 54.57 g I_2/100 g oil over time. The storage stability study of

COME suggests that COME stored in a dark was more stable than other two conditions. Similarly biodegradability of biodiesel is the strongest point for its use at industrial level. Biodegradability means breakdown of complex and probably poisonous substance in to simple and regular forms. Biodegradability of fuels can be evaluated by methods using microorganisms or without using micro-organisms i.e. bio-kinetic model. In the present study, biodegradability was evaluated by method without using microorganisms. Biodegradability of COME test carried out using a model of bio-kinetics was given 51% degradation in 28 days. The lower biodegradation of castor oil biodiesel may be due to the higher viscosity of COME. Recently, biodiesel fuel has been attracting the world as a blending component or direct fuel in diesel vehicle engines. The low level blends do not need any engine modifications and also produce lower NOx emissions than that of higher blends. Engine performance tests were conducted for castor oil methyl ester and its blends of 5%, 10% and 15% with diesel fuel. Among three blends, B10 blend was given the best brake thermal efficiency of engine at maximum load. The exhaust gas emission was found with reduced CO (26-36%), NOx (14-20%) and HC (17.5-50%) gases. This result proves that COME can be an alternative fuel for conventional diesel.

Biodiesel is an oxygenated fuel as generally contains about 10 wt % of oxygen. The high oxygen content in biodiesel results in the enhancement of NOx formation particularly under an elevated temperature burning environment. NOx discharge is detrimental to both humans and the atmosphere. During past few decades, researchers around the world are trying several options to control NOx emissions. Emulsification might be one of the options to be considered. This technique enhances fuel efficiency and reduces emission of hazardous pollutants from diesel engines. Therefore, two phase emulsions were prepared using COME and water. The study used an ultra sonification

method to investigate the emulsion characteristics of two phase emulsion systems i.e. water in oil (W/ME) and oil in water (ME/W). The optimum conditions in terms of higher emulsion stability for both emulsions were found to be HLB 13, 15 vol % water content, 2 vol % surfactant, 10 min sonication, 10 min agitation time, 2500 rpm agitation speed for W/ME and HLB 7, 20 vol % oil content, 2 vol % surfactant and 10 min sonication time for ME/W emulsions respectively. W/ME emulsion showed superior results than ME/W w.r.t droplet size and properties. The effect of sonication time showed positive effect on the droplet size reduction in both emulsions. The findings of the study have demonstrated the feasibility to produce the stable emusified fuel with castor oil methylester as an alternate fuel in diesel engine to minimize the NOx emissions.

As increasing the growth of biodiesel industry, there will be huge amount of glycerol (by-product) obtained during transesterification. It was still increasing due to the increase in replacement of 5.75% petroleum fuels by bio fuel. Therefore, in order to intensify the reactive extraction process with an intention to make use of by-product glycerol, preliminary studies was carried out using synthetic glycerol using purolite resin catalyst. From the preliminary study, the combination of optimum process parameters obtained for the highest solketal yield (74.68%) were 3 h reaction time, 1 wt % catalyst concentration, 1:4 glycerol/acetone molar ratio, at which the glycerol conversion was 96.57%. Comparison of solketal yield obtained for the present system with the reporetd in literature (continuous reactor) using purolite catalyst reveals that the yield of solketal in the present study found to be lower (74.68%) due to the formation of by-product water during the reaction. Therefore, results of the study seggested that irrespective of the catalyst used, removal of water is necessary to achieve higher solketal yield

The outcomes of this study have been published in some scientific journals and presented at national and international conferences. The published articles and conference presentations are listed at the ending of this thesis.

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LIST OF ABBREVIATIONS AND SYMBOLS

AG	Acyl Glycerides
Al	Aluminium
ANOVA	Analysis Of Variance
AOAC	Association of Analytical Communities
AOCS	American Oil Chemist's Society
ASE	Accelerated Solvent Extraction
ASTM	American Society for Testing and Materials
BMEP	Brake Mean Effective Pressure
BOD	Biochemical Oxygen Demand
BP	Brake Power
BSFC	Basic Specific Fuel Consumption
bTDC	Before Top Dead Center
BTE	Brake Thermal Efficiency
CA	Crank Angle
CBN	Dichlorobenzene
CCD	Central Composite Design
$CDCl_3$	Deuterated chloroform
CNT	Carbon Nanotubes
CO	Carbon monoxide
CO_2	Carbon dioxide
COME	Castor Oil Methyl Ester
CR	Compression Ratio

cSt	Centistokes
CV	Calorific Value
DEE	Diethyl Ether
DG	Di Glycerides
DI	Direct Injection
DMC	Dimethyl Carbonate
DMSO	Dimethyl sulfoxide
DOC	Dissolved Organic Carbon
DSC	Differential Scanning Calorimetry
ECB	Effective Composition of Biodegradation
EGT	Exhaust Gas Temperature
EPA	Environmental Protection Agency
FAEE	Fatty Acid Ethyl Esters
FAME	Fatty Acid Methyl Esters
Fe	Iron
FFA	Free Fatty Acid
FID	Flame Ionization Detector
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatography
GC×GC-TOF-MS	Two-Dimensional Gas Chromatography-Time-Of-Flight Mass Spectrometry
GC-FID	Gas Chromatography – Flame Ionization Detector
GC-MS	Gas Chromatography Mass Spectrometer
HC	Hydro carbon

HCl	Hydrochloric acid
HHV	Higher Heating Value
HLB	Hydrophilic Lipophilic Balance
^{1}H NMR	Hydrogen Proton Nuclear Magnetic Resonance
H_2SO_4	Sulphuric acid
ID	Ignition Delay
IC	Internal Combustion
ISO	International Organization for Standardization
KBr	Potassium Bromide
kg	Kilogram
KOH	Potassium hydroxide
ME/W	Methyl ester-in-water
MG	Mono Glycerides
MJ	Mega joule
N	Normality
NaOH	Sodium hydroxide
NHRR	Net Heat Release Rate
NOx	Nitrogen oxides
OECD	Organisation for Economic Co-operation and Development
OOT	Oxidation Onset Temperature
p	Probability
PM	Particulate Matter
PME	Palm Methyl Ester
PTC	Phase Transfer Catalyst

PTSA	Para Toluene Sulfonic Acid
R^2	Regression coefficient
RME	Rapeseed Oil Methyl Ester
RSM	Response Surface Methodology
SFC	Specific Fuel Consumption
SFE	Supercritical Fluid Extraction
TBHQ	Tert-Butyl Hydro Quinone
TBN	Total Base Number
TGA	Thermo Gravimetric Analyzer
THF	Tetrahydrofuran
ThOD	Theoretical Oxygen Demand
U.S	United States
USA	United States of America
VCR	Variable Compression Ratio
vol.	Volume
WFE	Water-in-diesel Fuel Emulsion
WIP	Water In POME
W/ME	Water-in-methyl ester
W/O	Water-in-Oil
wt	Weight
^oC	Centigrade
L	Litre
mm	milli meter
ml	milli litre

%	Percentage
h	Hour
ppm	Parts per million
rpm	Revolutions per minute
ηvol	volumetric efficiency

CHAPTER 1

Introduction and Literature Review

This chapter discusses briefly on the introduction of biodiesel, its need, current scenario and future perspectives of biodiesel. Apart from that chapter also discusses about various feed stocks available, possibilities for biodiesel usage, literature review on various aspects like oil extraction from various feed stocks, biodiesel production by various methods, other aspects of biodiesel usage in engine performance by using its blends, storage stability, biodegradability, emulsification and glycerol acetalization. Finally objectives of the thesis and its organization are summarized.

1.1. Introduction

The usage of vegetable oil as a fuel was started by Dr. Rudolf Diesel in 1985 when he developed the first diesel engine to run on vegetable oil [1]. Biodiesel is produced from vegetable oils and animal fats by a process called the transesterification process. In this process, vegetable oils or animal fats are chemically reacted with alcohol in the presence of a catalyst to produce a fatty acid alkyl ester [2]. Biodiesel is safe, renewable, non-toxic, biodegradable and contains no sulphur [3]. Emissions such as total hydro carbons and CO are usually low with biodiesel compared to petroleum diesel. This may be due to complete combustion caused by the higher oxygen content in biodiesel. Transesterification is the most widely used method for biodiesel production and is the process of removing glycerides and combining oil esters of vegetable oil with alcohol.

The process reduces viscosity to a value comparable to that of diesel and hence improves combustion [4]. Biodiesel production from oil includes several steps such as oil extraction, refining (degumming, deacidification, dewaxing, dephosphorization, dehydration, etc.), and transesterification. This multiple processes for oil refining include 70% of the total cost of biodiesel production when refined oil is used as feedstock [5, 6]. In the other way, reactive extraction is a single step extraction and a transesterification process which involves alcohol as an extraction solvent and reactant simultaneously for transesterification reaction. Elimination of a costly oil extraction process before transesterification is possible with reactive extraction which reduces capital cost [7], biodiesel cost, and process time [8]. Biodiesel also can be blended with diesel fuel directly or after emulsifying with water. The emulsification of biodiesel with water also could reduce the NOx emissions and other pollutants when used in the diesel engine.

In the prospect of biodiesel, enormous research has been carried out on the extraction of vegetable oils using different edible and non-edible oil seeds. The purpose of oil extraction is to find out the oil content and acid value of the oil which are important factors for biodiesel production. Generally, oil can be extracted from seeds by pressing, solvent extraction and supercritical fluid extraction (SFE) [9]. Though there are various methods, they have their own disadvantages such as oil extracted by pressing is not clean even after centrifugation as it contains gums and fibres [10]. Even though oil extracted by SFE method is pure, it is expensive and extracts only non-polar lipids due to lower solubility of super critical fluid (i.e. CO_2) in polar lipids [11]. However, solvent extraction is the most commonly used technique [12] for extraction of oil from oil seeds with advantages like simple to run, complete recovery of oil which will be even cleaner than

oil obtained by pressing [10]. In solvent extraction, compressed seed meal is extracted by solvent in the Soxhlet extractor [13]. This method extracts both polar and non-polar lipids. Extraction capacity of oil depends on the extraction temperature, extraction time, type of oil and solvent etc. [14]. Other factors like seed cleaning, moisture content and heat treatment will have the influence on the oil yield and quality. Seed cleaning improves oil quality and, on the other hand, reduction in moisture content, particle size, and increase in seed heat treatment also increases the oil yield up to definite levels [15]. Olaniyan (2010) observed the increase of castor oil yield from 33.12% to 55.03% with an increase in the pre-treatment temperature of seeds from 30 to 90 °C, respectively [16]. Although many solvents have been used until now, hexane is one of the most effective solvents reported for the extraction of oil from oil seeds [17-20]. Other solvents used till date for oil extraction are ethyl ether, pentane, toluene, chloroform [21], isopropanol [19, 22], acetone [19], petroleum ether [21, 23-28], ethanol [12, 19, 26] and ethyl acetate [22]. From the aforementioned discussion, all these factors are required while proceeding for the oil extraction to find out the acid value and the oil content which are the important for the reactive extraction.

In order to reduce the end product cost, castor seed which is non-edible (crop produced majorly in India) and cheap will be used as feed stock for the production of biodiesel via reactive extraction in the present thesis work. The detailed discussion on castor will be found in further sections. Methanol is selected as solvent as it is cheap and can be used as an extraction solvent and transesterification reagent simultaneously. In addition to this information, next section deals with the current scenario and future perspectives of biodiesel production.

1.2. Current scenario and future perspectives of biodiesel

Fossil fuels are non-renewable and depleting day by day due to their continuous usage. Many experts believe that by the year 2070, the world will be exhausted of fossil fuels and there won't be fuel for use. The use of fossil fuels also pollutes the environment and causes environmental problems like global warming, green - house effect and air-pollution. Moreover, important fossil fuels like oil and gas are concentrated in some of the countries, resulting the remaining countries like India has to completely depend on such countries which are producing oil and gas. As a result, the import bill also increases thus adversely affects the economy of the country. The cost of diesel fuel increases due to increase in the crude oil prices which require taking appropriate policy decisions in the country to fulfil the future demand. Therefore, biodiesel is being considered as a viable alternative for diesel fuel [29]. As of the moment, countries and different regions around the world aim to utilize biodiesel as fuel in transportation at a blend of 2-20% (B2-B20). Germany, Argentina, Brazil, France and Indonesia are among the top biodiesel producing countries. European countries led by Germany top the world production of biodiesel, while only Indonesia among the top potential Asian countries has made it to the top five producing countries. The USA is the top consumer followed by Germany and Spain. Interestingly, not all the top producers of biodiesel are the largest biodiesel consumers with some countries consuming more than their annual production [30].

The energy needs of India are also rising to cope up the growth rate of the 156.1 million tonnes of crude oil that India consumed in 2007-08; it produced only 34.12 million tonnes. Petroleum fuels are the major contributor to the ecological imbalance in India. India's per capita energy use and carbon emissions, while lower than the world

average, results in a substantial percentage of world energy use and carbon emissions, due to the country's large population and heavy reliance on fossil fuels. To solve dual problems of fossil fuel depletion and environmental degradation, the renewable fuels with lower environmental impact are necessary. Nowadays, many new fuels have been used and biomass derived fuels are among them. Some of the well-known biomass derived fuels are ethanol for gasoline engines and biodiesel for compression ignition engines. Indian Railways has set up a biodiesel production unit at Loco Workshops Perambur in Chennai, which is successfully manufacturing biodiesel for the past 8 years. Similar plants are being established at Raipur in Chhattisgarh and Tondiarpet near Chennai. Biodiesel is being used in blends of B5, B10 and B20 for diesel engines of transport vehicles and locomotives. These locomotives have 2600 hp diesel engines and are mostly underutilized [31]. India has great potential for production of biodiesel from non-edible oil seeds. Only 10-12 varieties have been tapped so far from about 100 varieties of oil seeds. The annual estimated potential is about 20 million tonnes per annum. Wild crops cultivated in the wasteland also form a source of biodiesel production in India and according to the Economic Survey of the Government of India, out of the cultivated land area, about 175 million hectares are classified as waste and degraded land. Thus, given a demand-based market, India can easily tap its potential and produce biodiesel on a large scale. Government agencies like the Ministry of Rural Development, Environment and Forestry, Petroleum and Natural Gas, Agriculture, and Non-Conventional Energy Sources can play a leading role in this program [32].

Edible oils are under use in developed nations such as the USA and European nations, but in developing countries the production of edible oils is not sufficient. In a

country like India, there are many plant species whose seeds remain unutilized, while underutilized have been tried for biodiesel production [32]. The various feed stocks available for the biodiesel production are discussed below in brief.

1.3. Feed stocks for the production of biodiesel

Since the cost of raw materials accounts about 60-80% of the total cost of biodiesel production, choosing a right feedstock is very important. The common feed stock for the production of biodiesel in India is palm oil, which is being imported from Malaysia and Indonesia. As palm oil is being used for edible purpose, the price of the crude palm oil fluctuates in the international market. Apart from that some other feedstocks are also being used (i.e. fish oil, used cooking oil) but to a very less extent. Even though the consumption of edible oils in some countries like India is high, the availability of used cooking oil is very small as it is used till the end. In the production of biodiesel more than 95% of feed stocks come from edible oils since they are mainly produced in many regions of the world and the properties of biodiesel produced from these oils are much suitable to be used as a diesel fuel substitute. However, this may cause some problems, such as the competition with the edible oil market, which increases both the cost of edible oils and biodiesel; moreover, it will cause deforestation in some countries because more and more forests have been felled for plantation purposes. In order to overcome these disadvantages, many researchers, scientists, technologists as well as industrialists are interested in non-edible oil sources which are not suitable for human consumption, because of the presence of some toxic components in the oils. Furthermore, non-edible oil crops can be grown in wastelands that are not suitable for food crops and

the cost of cultivation is much lower because these crops can still sustain a reasonably high yield without intensive care. Therefore, it is always recommended to produce biodiesel from the non-edible oils. The availability of different non-edible oil seeds in India along with their oil yields are given in Table 1.1 [4].

Table 1.1: Non-edible oil seeds in India

Oil seed type	**Available place**	**Quantity (Metric tons/Annum)**	**Oil content (%)**
Castor	Over all India	790, 000	46-55
Cotton	Over all India	851, 000	18-25
Jatropha	Over all India	15, 000	40-60
Karanja	Maharashtra, Karnataka, Assam	2, 00, 000	30-40
Lin	Few places in India	150, 000	35-45
Mahua	Maharashtra, Gujarat, West Bengal, Karnataka, Orissa, Tamil Nadu, Kerala and West Bengal	5, 20, 000	35-40
Nahor	North-eastern states of India	-	58-75
Neem	Over all India	5, 00, 000	35±45
Tumba	Few places in India	21, 000	-

Non-edible oil seeds are the potential feedstock for the production of biodiesel in India. Among the various non-edible oil feedstocks, castor is a cheap and major feed stock in India for the production of biodiesel. The details of the castor seed crop, its oil composition and its scenario are discussed below in brief.

1.3.1. Castor oil

Castor plant has the botanical name called *R. communis* of the family Eurphorbiacae. Castor is an herbal plant which is originated from India and Africa, grown in tropical and sub-tropical climatic conditions in the world and has capability to grow in arid and drought conditions for longer period. The blossoming time for the castor plant is about 90-120 days after sowing [16, 33]. The sowing season of castor is from July to October and harvesting season is from October to April [1]. Generally, castor seeds contain 46-55% of oil (on weight basis) [13]. The content of oil in the seed varies depending up on the ecological conditions, cultural practices and harvesting time [34]. Castor oil contains 91-95% ricinoleic acid, 4-5% linoleic acid and 1-2% palmitic and stearic acid [33]. Major percentage of castor oil constitutes ricinoleic acid. Ricinoleic acid contains double bonds which play a main role in oxidation of castor oil [35]. Due to the presence of ricinoleic acid (12- hydroxyl-9-octadecenoic acid) and allergens which are poisonous, the castor seeds are poisonous to human beings and animals. Ingestion of castor seed leads to abdominal pain, vomiting and diarrhea. The uses of castor plant for ornamental purpose are avoided to prevent accidental ingestion of castor seed by the children. One milligram of ricin has the capacity to kill an adult. Castor seed cake is also poisonous and does not fit for animal feed. The people who are working with the meal may get affected by allergy and asthma. Due to this toxicity of castor seed, farmers in U.S do not grow this crop widely. However, these toxic components will not get into oil and also there are several methods available for detoxification of the seed meal [13]. Castor oil is viscous, colourless or pale yellow with pale odour and extremely disagreeable taste [33, 36]. It dissolves simply in alcohol, ether, glacial acetic acid, chloroform, carbon

sulfide and benzene. It is cheap, eco-friendly and non-edible oil which is used as alternative to edible oil in various chemical applications like soaps, paints, lubricants (steel industry), sweetener (tanning industry), vehicle oil and braking liquid (automotive industry) and also in medicinal applications [16, 33, 37].

Castor oil has a large international market. Castor oil is used in more than 700 industrial products and its demand is increasing by 3-5% per annum. Castor is grown in some 30 countries. India, China and Brazil are the major producers and contribute about 65%, 23% and 7% of the world total production, respectively. The castor area in India increased from 678 thousand ha (2002-03) to 1459 thousand ha (2011-12) showing an increase of 115.9% percent [38]. The annual domestic consumption of castor oil in India is only about 80, 000-100, 000 tons. Of this, the soap industry consumes about 25, 000 tons, paint and allied industries about 35, 000 tons and the lubricant and derivative industries about 20, 000 tons [1]. The state wise status (2011-2012) of the growth of castor crop area in India is shown in Figure 1.1 [1].

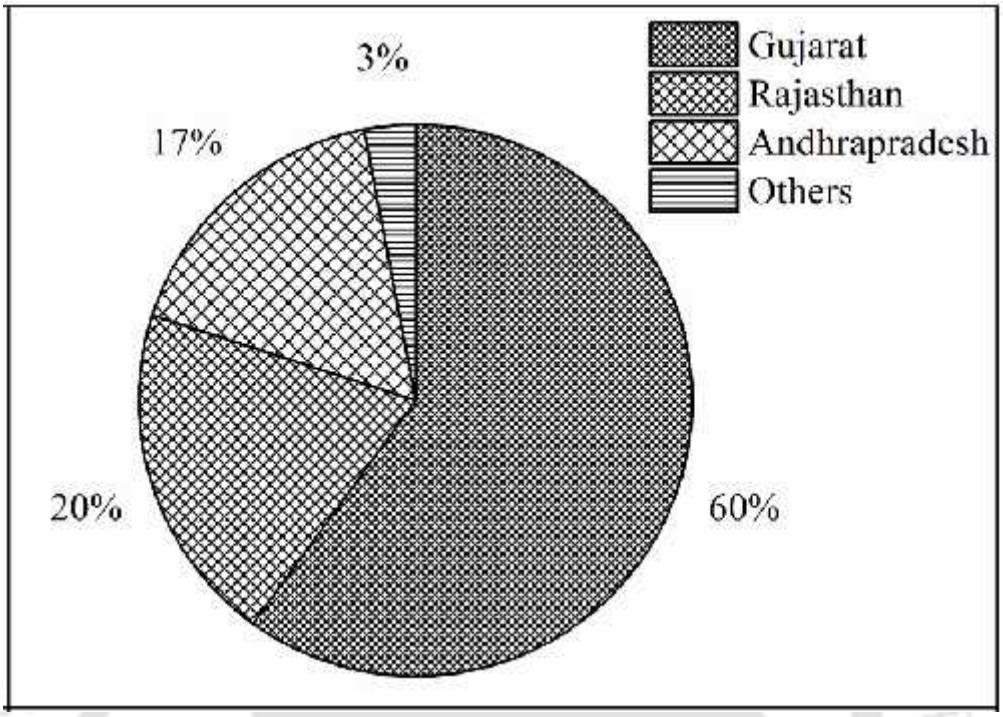


Figure 1.1: State wise castor areas (in '000 hectares) in India 2011-2012

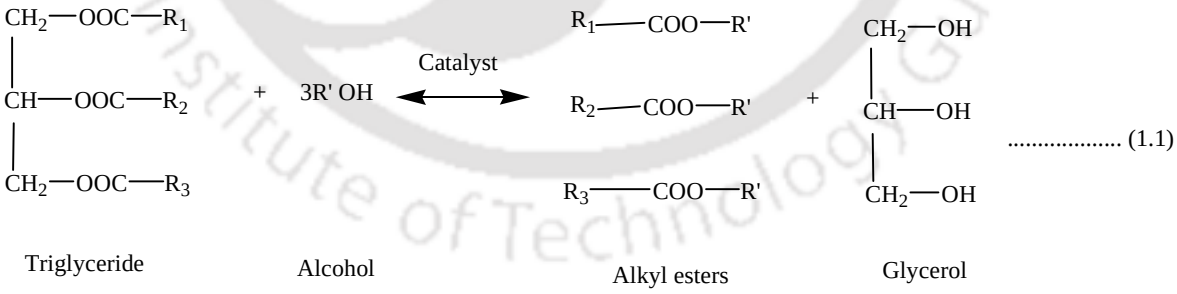
In 1950's, castor was a low value crop and was primarily grown in dry areas of Andhra Pradesh, a state in Southern India. But over the years, the centre of castor production was shifted to Gujarat, a state in Western India. Gujarat alone contributes to 86% of the total castor seed production in India. The increased castor production led to increase exports of castor oil, making India, a major exporter of castor oil. The nearness of Mumbai to Gujarat further contributed to the commercialization of castor seeds till today [39].

The comparative advantage of castor is that it's growing period is much shorter than that of Jatropha and Pongamia, and there is considerably greater experience and awareness among farmers about its cultivation. Being an annual crop, it gives the farmers the ability to rotate or shift away easily depending on market conditions [1]. Therefore,

present research was intended to use castor seed as a feed stock for the biodiesel production. Next section deals with biodiesel production methods, its stability change with environmental conditions and possibility for usage of biodiesel in various means.

1.4. Biodiesel production, stability and its applications

Vegetable oil contain various compounds like free fatty acid (FFA), phospholipids, water, odorants and other impurities which will restricts its use as direct fuel. Therefore, it has to undergo some chemical changes [40]. This chemical modification of oils can be done through transesterification reaction with alcohol in presence of an appropriate catalyst to produce biodiesel [41]. The reaction mechanism for transesterification is shown in the equation (1.1). The mechanism indicates transesterification is the reversible reaction of oil with alcohol to form alkyl esters and glycerol [42].



..... (1.1)

As a substitute, transesterification can be carried out directly from oil bearing materials without prior extraction. This way it is termed as “reactive extraction” or “*In situ* transesterification”. It is a simplification of biodiesel production process and at the same time reduces the production and feed stock cost considerably [5]. Reactive

extraction can be carried out in various ways i.e. by reflux method, super critical, sub critical, micro wave assisted and ultra sound. But in the reactive extraction, separation of residue from catalyst and products is a major concern. However, it can be achieved via filtration of reaction mixture or simultaneous extraction and transesterification (Integrated) [43]. Although, reactive extraction requires about 38 times extra alcohol and 7 times further alkali catalyst compared to the conventional method, but the extra amount of reagents can be reused if needed [44]. In reactive extraction, seed materials are in direct contact with the reactants [i.e. catalyst and alcohol]. On the other hand, it can be also carried out without direct contact between the reaction reagents by integrating the Soxhlet apparatus in the process called integrated system. Apart from that earlier reactive extraction was also carried out by using incubator shaker or centrifuge tubes and non-integrated system (i.e. without using Soxhlet). Different seeds used in reactive extraction are rape seed (non-integrated) [5], castor (non-integrated) [6, 8, 45], jatropha (incubator and integrated) [7, 46], sunflower [47] and soya bean (incubator shaker) [44]. Methanol is commonly used solvent compared to ethanol due to its low cost [48]. Methanol is less toxic and suitable for transesterification. Ethanol is also an environment friendly fuel and obtained from agricultural commodities. Even though solubility of triglycerides in methanol is poor (since methanol is polar and the most of triglycerides are non-polar), it extracts more oil (due to higher solubility of other components of seed like phospholipids, sterols, phenols and vitamins) and transesterify oil into ester instantly in simultaneous extraction and transesterification [5]. Stoichiometrically, a molar ratio of 3:1 (alcohol to oil) is required for the completion of reaction. Since the transesterification is a reversible reaction, an excess of alcohol is used to drive the reaction in the forward direction for

esters formation. The amount of catalyst required is depending on the acidity of oil [47]. For reactive extraction, alkali catalyst is favourable than acid catalyst due to its higher reaction rates at lower temperature [41]. Acid catalyst is a good option for high FFA (Free Fatty Acid) oil feed stock [46]. The feedstock with low FFA is preferred for reactive extraction because high FFA is unsafe for fuel properties of biodiesel. The use of enzymes as a catalyst is rare due to their less effect on the process. The cost of enzymatic catalyst also is very high compared to the other catalysts. So, it is not viable to produce biodiesel commercially using enzymes [49].

An optimization of reaction conditions has the capacity to decrease the reagent consumption, increase the yields, and decrease the contamination by FFA and AG (Acyl Glycerides) [44]. This can be done by the RSM (Response Surface Methodology) design technique which is widely used to optimize the processes in various fields like food industry (food properties), research and development, natural and medical sciences (contamination studies) [50].

Even though, the usage of biodiesel has several increasing ecological benefits [51], its deterioration is more severe compared to commercial petro-diesel during storage [52]. Storage stability is also a major concern about flourishing commercialization of biodiesel in the fuel market. The problem of biodiesel deterioration during storage is due to various factors such as the temperature, unsaturation content, moisture content, microbial contamination, light, metal, nature of the container and nature of fatty acid composition of parent oil. Most of the storage stability studies reported in the literature include an effect of different antioxidants on oxidative stability by using Rancimat method (widely) and by other methods such as Petro OXY method and pressurized

differential scanning calorimetric method. Few studies are available on change in various properties (i.e. acid value, viscosity, peroxide value) of biodiesel during a short or long-term storage period.

Although, biodiesel has several advantages, biodegradability is the strongest point in case it is to be used at industrial level. Biodiesel is easily biodegradable because it consists of alcohol esters of short-chain fatty acids, compounds that exist naturally in the environment [53]. Biodegradability means a breakdown of complex and probably toxic substances in to simple and regular forms in which the elements of carbon, hydrogen and oxygen exist. Management regulators and industries are always concerned about the providence of chemicals and waste products when discarded in to the environment, because toxic substances in the environment eventually affect the ecosystem and humans adversely [54]. The extent of biodegradability of a substance can be determined by measuring CO_2 release as per EPA (Environmental Protection Agency) protocol [53]. Biodegradability of fuels can be evaluated by methods of using microorganisms [55] or without using micro-organisms i.e. bio-kinetic model [56]. There are very limited reports on the biodegradability of biodiesel by using bio-kinetic model.

Recently, biodiesel fuel has been attracting the world as a blending component or direct fuel in diesel vehicle engines. Low level blends do not need any engine modifications. Generally, the blends of biodiesel up to B20 are preferred due to their compatibility in terms of storage and distribution in equipment [57]. Zhihao et al., (2011) studied the emissions of a DI diesel engine fuelled with *Pistacia Chinensis* Bunge seed biodiesel-diesel blends. In their study, they found the reduction in NOx emissions with

lower blends of B10 and B20; while an increase in NOx emissions with increasing the blend to B30 [58].

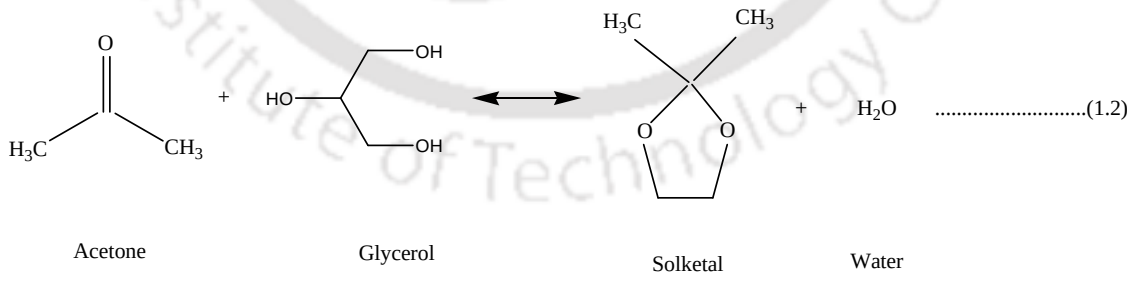
Biodiesel is an oxygenated fuel as generally contains about 10 wt. % of oxygen. The high oxygen content in biodiesel results in the enhancement of its burning efficiency, reduction of particulate matter, CO and other gaseous pollutants, but at the same time results in larger NOx formation particularly under an elevated temperature burning environment. It is estimated that the burning of neat biodiesel would produce about 10% more NOx than that of petroleum-based diesel primarily due to the high oxygen content of the neat biodiesel [59]. NOx discharge is detrimental to both humans and the atmosphere. During the past few decades, researchers around the world are trying several options to control NOx emissions. Emulsification might be one of the options to be considered. This technique enhances fuel efficiency and reduces the emission of hazardous pollutants from diesel engines [60]. Emulsions can be formed by emulsifying oil with water to form a homogeneous distribution of a dispersed phase into another continuous phase with the help of an appropriate surfactant. The surfactant reduces the surface tension between water and oil thus maximizes their superficial contact area and activates their surfaces. This is due to the fact that a surfactant has both a hydrophilic group and a lipophilic group. The lipophilic group in the surfactant will attract the oil phase while the hydrophilic group will attract the water phase [59]. Most of the emulsion studies used Tween 80 (Hydrophilic) and Span 80 (Lipophilic) as surfactants [59]. The largely used emulsified fuels in diesel engine are the emulsions prepared with water and diesel. These emulsions can be prepared in the form of two or three phases. The results of past experiments conducted by various researchers with two phase and three phase

emulsions have shown significant effect on engine performance [60]. Lin et al., (2008) have reported better performance by two phase emulsion W/O (Water-in-Oil) in terms of lower fuel consumption rate, bsfc (break specific fuel consumption), CO and lower black smoke opacity than three phase emulsion (O/W/O). Generally, emulsions can be prepared by mechanical homogenizer or ultra-sonication method. Previous studies reported that ultra-sonication method showed more favourable emulsion characteristics such as lesser droplet size and a lower separation rate of dispersed phase in oil phase than the emulsions prepared by using mechanical homogenizer [61]. The information on the emulsion studies using various methyl esters is very scanty. At present, reported studies include emulsification of methyl esters such as soya bean [59], palm [60], jatropha [62] and castor [63]. It can be done for various other methyl esters. Next section deals with the conversion of glycerol to the value added chemicals.

1.5. Crude glycerol conversion to value added chemicals

Glycerol is the major value-added byproduct produced from transesterification of oil and fat during biodiesel manufacturing processes. Currently, crude glycerol production in the market is about 350, 000 tons per annum (tpa) in USA and 600, 000 tpa in Europe. It is still increasing due to increase in the replacement of 5.75% petroleum fuels by biofuel. Glycerol is a value added product which has potential uses like hydrogen production, citric acid production, cosmetics, eye drops and other chemicals. It can be transformed into many chemicals via catalytic processes such as hydrogenolysis, oxidation, fermentation, dehydration, polymerization and acetalization. At present, greater interest was towards glycerol acetalization. Glycerol acetalization is the

production of acetals and ketals from acetalization of glycerol with an aldehyde or ketone in presence of acid (mineral or solid or metal) catalyst. Acetals are used as surfactants, flavours, disinfectants etc. The present study focus is on ketalization/acetalization with ketone. The reaction mechanism is given in equation 1.2. The reaction parameters in acetalization include temperature, ketone to glycerol ratio and the choice of solvent. The reactant, acetone favours the formation of five member acetal i.e. solketal. Solketal (i.e. glycerol acetal) is produced from acetalization of glycerol with acetone which improves cold properties, flash point and oxidative stability of biodiesel [64, 65]. The homogeneous liquid catalysts used in acetalization are PTSA (para toluene sulfonic acid), hydro chloric acid, sulphuric acid and phosphoric acid. Although, these catalysts are relatively cheap, but corrosiveness of these catalysts causes difficulty in storage, product separation, effluent disposal and most importantly it causes environmental burden. Most of these problems can be addressed by the use of heterogeneous catalysts like amberlyst, zeolite, and montmorillonite etc. [66].



From the aforementioned discussion, it is clear that very few seeds (edible and non-edible) have been used in the reactive extraction for biodiesel production. Apart from that very few authors have mentioned about the use of optimization technique in the areas

of reactive extraction. Hence, more in-depth investigation needs to be done using various other seeds. With this motive, the main objectives of this work are to extract oil from castor seed using various solvents, to produce eco-friendly biodiesel via integrated and non-integrated reactive extraction approaches from non-edible castor seeds, utilization of produced biodiesel for various means and also to seek ways to utilize by-product (crude glycerol) of reactive extraction for the conversion in to glycerol acetal. Therefore, in the next section, a brief summary of the relevant state-of-the-art with respect to the oil extraction, biodiesel production via various methods and other applications of biodiesel have been summarized.

1.6. Literature Review

The following state-of-the-art reveals the research and experimental techniques that relate to oil extraction from various oil seeds using different techniques their merits, demerits, and challenges faced to prepared biodiesel through reactive extraction. Subsequently, the methods used to assess and improve storage stability, biodegradability, engine performance, emulsification of biodiesel and conversion of glycerol to glycerol acetal have also been discussed. This will provide a significant insight on the potential of biodiesel synthesis, utilization of by-product, and about its past and glorious future.

1.6.1. Extraction of oil from various raw materials

As the acid value and oil content of the seeds are the important parameters for the biodiesel production, vast research have been carried out by various researchers in the area of oil extraction using various oil seeds. Oil can be extracted from oil seeds by different methods i.e. aqueous method, hydraulic pressing, supercritical fluid extraction (SFE) [67], screw pressing and solvent extraction [40]. Among these methods, solvent extraction is commonly used (commercial purpose) method as it extracts maximum or complete oil from the seeds [12].

Therefore, the present literature review is focussed on extraction of oil by Soxhlet method. The oil yield obtained at different conditions with different solvents is shown in Table 1.2. From the table, it can be seen that hexane is the most widely used solvent as it gives higher yield. Ajiwe et al., (1994-1995) have studied the oil extraction from three different seeds such as Afzelia africana, Bread fruit nut and Cassava. In their study, they have used petroleum ether as a solvent. They reported that Afzelia africana oil has low

acid value, long shelf life, and it is suitable for the formulation of alkyd resin and shoe polish. Bread fruit oil showed semi-drying properties and can be used for the production of soap, hair shampoo and alkyd resins [19-20]. In another study by Ajiwe et al., (1996) have extracted oil from another three different seeds (i.e. velvet-tamarind, physic-nut and nicker-nut) using petroleum ether by Soxhlet method and recommended that physic-nut and nicker-nut oils are suitable to manufacture elevated quality alkyd resins, paint and polish [25]. Akaranta et al., (1996) have used bio resource solvent for extraction of castor oil. Castor oil was extracted using dry feint (a liquid industrial waste from the distillery) and hexane as solvents. They reported that extraction power of the solvent was dependent on temperature. The results obtained during their study showed that dry feint can act as a suitable solvent for extraction of castor oil which is used in the production of alkyd resin. Especially, extraction coefficients and enthalpy changes were also estimated [14]. Ogunniyi et al., (2006) have extracted castor oil by mechanical pressing and solvent extraction method, and discussed about various applications and refining methods of castor oil. They also reported that castor oil can be used as an alternative to edible oils in chemical industries [13]. Ahmad (2010) has found that methanol also equally extracted higher oil and was comparable with hexane [71]. Ixtaina et al., (2011) have reported the oil yield, fatty acid composition, physicochemical and quality characteristics of chia crude seed oils obtained by pressing and solvent extraction. They found that the extraction method influences the oil yield significantly and oil yield by solvent extraction was 30% more compared to mechanical pressing. They also reported that extraction process has control over the quality and composition of few minor constituents of chia seed oil. The oil extracted using both methods showed similar fatty acid composition.

Further, they studied to improve the oxidative stability by adding normal antioxidants [80].

Saxenaet al., (2011) extracted cotton seed oil using n-hexane and ethanol as solvents at different temperatures: 15, 25, 35 and 45 °C, extraction time: 1-180 min range, particle sizes: 0.6, 1.6 and 2.4 mm and solid to solvent ratio (wt. /vol.): 1:5, 1:10 and 1:15. Their results showed that the highest oil yield was obtained at 45 °C, for lower particle size, reaction time, 180 min and 1:15 solid to solvent ratio [12]. Hamamre et al., (2012) have also extracted oil from grinded coffee material by Soxhlet method using different polar (isopropanol, ethanol, and acetone) and non-polar (toluene, chloroform, hexane and n-pentane) solvents. The yield obtained was higher for n-hexane extracted oil. Other solvents such as pentane, toluene and isopropanol also showed the good extraction yield. They reported that the properties of oil were differed from solvent to solvent. [19]. Akowuah et al., (2012) have extracted jatropha oil from fresh seeds and stored seeds (4 months) by Soxhlet method using petroleum ether as solvent. Storage stability study showed decrease in oil yield from 35.57% to 31.1% and increase in FFA content from 7.83% to 32.1% during storage. They concluded that the storage duration and improper managing of seeds throughout the storage period have negative effects on the oil quality [27]. Solana et al., (2014) have extracted essential oils from fennel by applying Soxhlet and accelerated solvent extraction (ASE) methods. Two variables such as time (4 and 8 h) and solvents were optimized by Soxhlet method. The best results in terms of both qualitative and quantitative analysis were obtained by methanol as solvent and a time period of 4 h. They also reported that Soxhlet technique showed higher performance of extraction and greater amount of compounds extraction compared to ASE, but

similar concentration of estragole [81]. Dutta et al., (2014) have extracted oil from crushed Crotalaria Juncea (or Sunn Hemp) seeds by using a modified Soxhlet apparatus. Parameters such as size fractions of the crushed seeds, extraction time, aging of seeds, choice of solvents and use of co-solvents along with the primary solvent were optimized in order to enhance the yield. Extracted oil was characterized by using Fourier Transform Infrared Spectroscopy (FTIR) and Gas Chromatography Mass Spectrometry. Other physico-chemical properties such as specific gravity, iodine number, saponification value, calorific value, flash point, fire point and kinematic viscosity were also investigated [82].

Based on the overall summary, it was noticed that in recent time, the number of studies has been carried out on extraction of oil from oil seeds using different solvents. However, very concise and un-detailed research was discovered for castor seeds and their oil extraction using various solvents. Therefore, still there is enough scope to conduct research for aforementioned feedstock to prepare biodiesel. As the castor seeds are cheap and non-edible, it can be used for the reactive extraction to produce biodiesel.

Table 1.2: Extraction of oil from different seeds by Soxhlet method (literature data)

Seeds	Extraction conditions	Optimum conditions	Solvent	Oil yield (%)	Reference
Afzelia africana	-	60-80 °C	Petroleum ether	25.80±2.0	68
Bread fruit nut	-	60-80 °C	Petroleum ether	20.83±0.57	24
Cassava	-	60-80 °C	Petroleum ether	23.75	23
Castor	100 g seeds,1:6 solute/solvent, 1-6 h	1:6	Hexane	-	14
Castor	10 g seed sample, 60 °C, each 30 min	-	n-hexane	-	37
Castor	5 g seeds, 55-60 °C	-	n-hexane	43.3	34
Castor	50 g seed sample, 0.4 L n-hexane, 6 h	-	Hexane	-	69
Coffee grounds	60 g seed sample, 30 min	-	Pentane Hexane Toluene Chloroform Ethanol	15.18 15.28 14.32 8.60 9.18	19

			Isopropanol Acetone	10.68 12.92	
Cotton	Extraction temperature:15, 25, 35, 45 °C, Particle size: 0.6, 1.6, 2.4 mm, Extraction time:1-180 min and solvent to solid ratio: 5, 10, 15	Solid ratio:1:10, 0.6 mm particle size, 45 °C	n-hexane Ethanol	- -	12
Coriander	4 g seed sample, 200 mL hexane	12 h	Hexane	19.4	70
Fluted pumpkin	20 g ground seed, solvent amount: 75, 100, 125, 150, 175 mL, extraction temperature: 80, 85, 90, 95 °C, particle size: 2, 2.36, 3.35, 4.75, 7 mm and time: 5, 10, 15, 20, 25, 30, 40 min	20 g grounded seed, 100 °C, 40 min, 100 mL of solvent	n-hexane	46.98	71
Grape	3 g milled seeds mixed with 6 g of sand, d<0.42 mm, 24 h	-	n-hexane	-	72
Grape	-	60 °C, 6 h	Hexane	17.5	20
Grape	Extraction time 10-15 h, 1/15-1/100	1/15 (solid to solvent	Hexane	12.8	26

	solute to solvent ratio,10-40 g seeds, 150-1000 mL solvent, 0.3-0.5 mm mean particle size	ratio) 1/100 (10-15 h, 68-72 °C) 1/20 1/100 1/15 1/100	 Hexane Ethanol Ethanol Ethanol Petroleum ether	 14.8 17.8 18.1 15.1 16.5	
Herba leonuri	3 g sample, 350 mL solvent 6 h, 9 h and 12 h	Highest yield for methanol at 12 h, For hexane at 6 h	Hexane Methanol	6 h (7.25) 12 h (14.18)	73
Jatropha curcas	50 g seeds, 1 mm particle size, 1:7 solute to solvent ratio, 8 h, 75 °C	-	Petroleum ether	-	27
Jatropha curcas from different origins and CPPs	60-70 °C, 6 h	-	Hexane	40 (Malaysia) to 48.4 (Vietnam) among different origins	74

				32.1(CPP-17) to CPP-01(w/w) among CPPs	
Moringa	20 g seed sample, 250 mL solvent, 7 h	-	Hexane Petroleum ether Acetone	33.1 31.8 31.1	75
Pongamia pinnata	100 g seeds, 1:6 solute/solvent ratio (wt. /vol.)	1:6 solute/solvent ratio	n-hexane Petroleum ether Ethyl acetate Isopropanol Ethyl acetate + water Isopropanol + water	33 31 31.5 32 26 28	22

Pomegranate	20 g ground seed, 200 mL solvent, 24 h (with in 3days, 3×8 h)	-	n-hexane	17.94 wt. %	76
Peach	30 g seeds, 200 mL solvent, 24 h, 50 °C	1:6	Hexane, petroleum ether, ethyl ether and chloroform	-	21
Pitaya	3 g seeds, 150 mL solvent	60 °C, 3 h	Hexane	6.13 wt. %	17
Rose hip	100 g seeds, 250 mL solvent, 3 h	3 h, 68.7 °C	Hexane	4.85 g oil	77
Rubber	500 g seed kernels, average dia 1.16, 1.36, 2.36 mm, 40-90 °C, 4 h	70 °C, 1.16 mm	n-hexane	-	9
Soya bean Rice bran	20 g seeds, 10 h	63-65 °C, 73-75 °C 10 h	Hexane Ethanol Hexane Ethanol	18.1±0.07 18.9±0.07 16.05±0.35 20±0.21	78
Tamarind, physic nut, nicker nut	-	60-80 °C	Petroleum ether	17.21±2.09 (Tamarind) 47.40±0.02	25

				(physic nut) 34.00±0.83 (nicker nut)	
Wheat grains	30 g grains	-	Acetone, chloroform, cyclohexane, diethyl ether, ethyl acetate and hexane	-	79

1.6.2. Biodiesel production (Reactive Extraction Technique)

Reactive extraction is an effective approach to produce biodiesel directly from oil bearing feed stocks compared to the conventional transesterification process. As discussed earlier, this method eliminates the costly oil extraction step, reduces capital cost, biodiesel cost, and process time. The present study therefore, focused on the optimization of reactive extraction of castor seeds with the main objective of describing the effects and relationships between the process variables to give the maximum FAME yield from castor seed. An optimization of reaction conditions has the capacity to decrease the use of reagent in the reaction and increase the product yield. Although, there are few reports on the use of reactive extraction and transesterification of non-edible seeds, but very few studies have concentrated on the understanding of the integrated and non-integrated approach of the reactive extraction process. As a result, literature review on reactive extraction have been categorised in various ways. There are some studies which are on reactive extraction using acid catalysts. Amongst them, Marinkovic et al., (1998) have carried out *In situ* transesterification of sunflower oil. The effect of parameters such as oil to methanol molar ratio, amount of acid catalyst, time and temperature of reaction on the yield and properties of esters were studied. They obtained good results at mild reaction conditions (temperature 30 °C) with a strong acidic catalyst and higher molar ratio. They reported that the fatty acid ester composition and properties of the products derived from *In situ* reactions are essentially similar to conventional transesterification [83]. Shuitet al., (2010) have produced biodiesel from *jatropha curcas* seeds in a single step transesterification process. They obtained oil extraction efficiency (91.2%) and biodiesel yield (99.8%) under conditions of seed particle size < 0.355 mm,

n-hexane as co solvent, 60 °C reaction temperature, reaction time of 24 h, 7.5 mL/g methanol to seed ratio and 15 wt. % H_2SO_4. The results showed that higher biodiesel yield was obtained in reactive extraction compared to extraction followed by transesterification. They reported that single step reactive extraction can be a potential route for biodiesel production which reduces processing steps and cost [46]. Khang et al., (2014) have investigated an *In situ* transesterification of coconut oil using mixtures of methanol and tetrahydrofuran with sulphuric acid as a catalyst. The highest biodiesel yield of 96.7% was achieved at 60 °C, THF: methanol volume ratio of 0.4 and methanol: oil molar ratio of 60:1. They found that yield was increased with an increase in the THF: methanol ratio, methanol: oil molar ratio and temperature [84]. Though the conversion achieved was higher with acid catalyst, but the main concern was about the process time required compared to that of alkali catalyst.

Corresponding to alkali catalysts, Haas et al., (2004) have carried out *In situ* experiments with soya beans seeds at room temperature (23 °C) and 60 °C for the production of biodiesel. Experimental conditions used were temperature of 60 °C, alkaline methanol of 7.5 (the minimum to cover 5 g of flakes) - 30.0 mL, NaOH concentrations of 0.05-0.5 N and reaction time about 0.25-7.8 h. For reactions at room temperature, the amount of alkaline methanol was 14.2-36.7 mL, NaOH concentration of 0.02-0.18 N and reaction period of 2.5-10 h. The maximum esterification was obtained at room temperature from ethanol/AG (Acyl glycerol)/NaOH molar ratio of 543:1:2.0 in 8 h compared to 60 °C reaction at methanol/AG/NaOH molar ratio of 226:1:1.6, 8 h incubation [44]. Zakaria et al., (2012) have studied the effect of process parameters on biodiesel yield, conversion and reaction rate of rape seed reactive extraction process. The

rate of ester formation was mainly affected by the catalyst concentration, temperature and particle size. The maximum yield of 82% was obtained at 1:6 molar ratio (oil to methanol). They concluded that *In situ* transesterification needs a high amount of methanol compared to that of conventional transesterification reaction [5]. Qian et al., (2013) have studied the cogeneration of biodiesel and nontoxic rapeseed meal from rapeseed through *In situ* alkaline transesterification. In their study, a conversion rate of 98% was achieved at 0.10 mol/L NaOH in methanol, methanol/oil molar ratio of 180:1, in 3 h and at 40 °C [85]. Madankar et al., (2013) have conducted reactive extraction at different reaction conditions such as oil to methanol molar ratio (1:50-1:250), catalyst concentration (0.5-2 wt. %), temperature (35-65 °C) and rate of mixing (200-800 rpm). The highest yield was obtained at 1% KOH (wt. basis of oil), 65 °C, reaction time of 3 h, methanol to oil molar ratio of 250:1, and mixing speed of 600 rpm. They reported that the cost of biodiesel from castor seed through reactive extraction was estimated to be lower than petro-diesel and soya bean oil biodiesel [86]. El-Enin et al., (2013) have investigated an *In situ* alkaline transesterification of rapeseed and cost indicators for biodiesel production. The effects of parameters studied are molar ratio of methanol to oil in seeds, amount of alkali catalyst, time and temperature on biodiesel yield. The highest conversion of 90% was obtained at 0.02 N catalyst concentration, 720/1 methanol to rapeseed oil molar ratio, 1 h and 65 °C. Thus a techno-economic analysis of the process for production of biodiesel from rapeseed was presented to investigate the profitability indicators of the production capacity [87].

Further reactive extraction was attempted by integrating Soxhlet in to the experimental process. For example, Klaas et al., (2001) have studied reactive extraction

of oilseeds with dialkyl carbonates via lipase catalysed transesterification and reactive extraction by Soxhlet apparatus using rapeseed, linseed and calendula seed as raw materials while dimethyl and diethyl carbonate as extraction solvent, and at the same time transesterification reagent. They reported that the yield of fatty acid methyl esters and ethyl esters obtained with reactive extraction were higher than those achieved by conventional two step transesterification [88]. Lian et al., (2012) have studied the integrated extraction and transesterification of oil from jatropha seeds for biodiesel production using solid catalyst, using methanol and hexane (as co solvent and co-extractant). They studied the effect of catalyst amount, reaction time, reaction temperature, and siphon tube height on the yield. The optimum yield of fatty acid methyl esters (FAME) obtained was 80.2%. They reported that hexane played an important role in the extraction of oil and in facilitating the mass transfer between methanol and oil [89].

In order to assess the effect of co-solvents on *In situ* transesterification, there are few studies available in literature. But considering the aim and objectives of current study, only selected reports have been discussed here. Qian et al., (2008) have studied the *In situ* alkaline transesterification of cottonseed oil for production of biodiesel and nontoxic cottonseed meal. In their study, a conversion rate of 98% was achieved at 40 °C, 0.10 mol/L NaOH in methanol, methanol/oil molar ratio of 135:1, 3 h reaction time and 0.3-0.335 mm particle size. The effect of co-solvents such as petroleum ether and methanol recycling on the cottonseed oil extraction and conversion were also investigated [90]. Similarly, Hincapié et al., (2011) have studied the production of biodiesel from castor oil by conventional and *In situ* transesterification using ethanol and hexane (as co-solvent). Conversions obtained for conventional method were higher than the *In situ*

process. They reported that Hydrogen Proton Nuclear Magnetic Resonance Spectrometer (^{1}H NMR) is a good technique to estimate ethyl ester conversion [45]. Alhassan et al., (2014) have studied the transesterification of cotton seed oil into biodiesel using different mixtures of methanol with Diethyl Ether (DEE), Dichlorobenzene (CBN) or Acetone (ACT) co-solvent systems with Potassium hydroxide (KOH) as a catalyst. The effect of various reaction conditions on biodiesel yield studied were a molar ratio of co-solvent in methanol, reaction temperature, catalyst concentration and time. The result obtained indicates that, 10% (v/v) is the optimal volume of co-solvents i.e. CBN and ACT in methanol. The optimal reaction temperature was 55 °C for 10 min when the catalyst concentration of 0.75% (w/w) was used. They concluded that addition of co-solvent reduced the reaction time and improved some fuel properties of biodiesel [91].

Apart from that reactive extraction process was also optimized by various design techniques and among the available literature only selected reports have been discussed here. Pradhan et al., (2012) have produced biodiesel from castor seeds through reactive extraction using KOH (potassium hydroxide) as a catalyst. They found that catalyst concentration, methanol to oil molar ratio and temperature are the main significant parameters. Optimum conditions at which highest biodiesel yield obtained were methanol to oil molar ratio of 225:1, catalyst concentration of 1.0 wt. %, reaction temperature of 55 °C and mixing intensity of 350 rpm. They concluded that reactive extraction of castor seed is a reasonable process [8]. Kartika et al., (2013) have investigated *In situ* transesterification of jatropha seeds for direct production of biodiesel. The influence of various process parameters on biodiesel yield and conversion were investigated, such as methanol to seed ratio, amount of alkali (KOH) catalyst, stirring speed, temperature and

reaction time. The study was carried out by applying the randomized factorial experimental design with ANOVA. The highest biodiesel yield of 87% with a fatty acid methyl ester purity of 99.7% was obtained at optimum conditions. They reported that stirring speed, temperature and reaction time showed insignificant effect on biodiesel quality [92]. Sulaiman et al., (2013) have investigated reactive extraction of solid coconut waste to produce biodiesel. The effects of catalyst amount such as KOH (0.8-2.0%), temperature (55-65 °C) and mixing intensity (500-900 rpm) were studied to optimize the reactive extraction process. From the RSM study, highest biodiesel yield of 88.5% was obtained at 2.0 wt. % of KOH catalyst, 700 rpm mixing intensity and reaction temperature of 62 °C [93].

There are also few reports in literature on reactive extraction using different methods. Georgogianni et al., (2008) have investigated the comparative studies on biodiesel production from sunflower oil with different alcohols such as ethanol and methanol using mechanical stirring and ultra-sonication process. Similar yield of alkyl esters was obtained by using both ultra-sonication and mechanical mixing. They observed that in case of *In situ* transesterification, both ultra-sonication and mechanical mixing produced methyl esters of equal quality. Whereas, ultra-sonication produced more ethyl esters compared to mechanical mixing. Higher yield of alkyl esters obtained with methanol than ethanol in a short time [47]. Go et al., (2014) have carried out study on *In situ* transesterification of *Jatropha curcas* L. seeds in a subcritical solvent system. A mixture of methanol, acetic acid and water under subcritical conditions was employed. Based on extractable lipids, the yield of about 94-98% was obtained (54-56% based on dry kernel). They reported that the process is capable of tolerating the presence

of moisture up to 10% and free fatty acid up to 5%, thus eliminating the need for pre-treatment steps [94].

Other studies including, Jiang et al., (2013) have reported on *In situ* self-catalyzed reactive extraction of germinated oilseed with short-chained dialkyl carbonates for biodiesel production. Germinated castor seed was used as substrate and catalyst, dimethyl carbonate (DMC) was used as acyl acceptor and oil extractant. The optimum biodiesel yield of 87.41% was obtained with castor seeds germination time of 72 h, DMC/germinated seed ratio of 12.5 mL/g, reaction temperature of 35 °C and water content of 2.11% [95]. Hailegiorgis et al., (2013) have carried out parametric study and optimization of *In situ* transesterification of *Jatropha curcas* L. assisted by benzyl trimethyl ammonium hydroxide as a phase transfer catalyst via response surface methodology. Weight fractions of 89±0.7% fatty acid methyl esters (FAME) yield and 99.4±0.4% fatty acid ethyl esters (FAEE) yield were obtained at optimum reaction conditions. They noticed that the formation of biodiesel was completed in a short time for PTC assisted reaction as compared to reaction without PTC [96]. Zakaria et al., (2014) have developed a kinetic model based on the rape seed reaction/extraction mechanism. The model revealed that at a catalyst concentration of below 0.1 mol/kg-solvent, the reactive extraction rate was controlled by the reaction of triglycerides to esters. Whereas at higher catalyst concentration (>0.1 mol/kg-solvent), the process was controlled by the rate of diffusion of products. They found that external mass transfer does not influence the extraction rate at the conditions used in their study [97].

Among all the studies on reactive extraction, very few studies have reported the use of non-edible oil seeds. Therefore, the present study was aimed at producing biodiesel

from castor seeds via reactive extraction (with and without integration of the Soxhlet in the process). Next section deals with the effect of storage period on stability of biodiesel.

1.6.3. Storage stability of biodiesel

Even though, the usage of biodiesel has several benefits, deterioration of biodiesel is more severe compared to commercial petro-diesel during storage. Thus, the storage stability is a major concern about the flourishing commercialization of biodiesel in the fuel market. The problem of deterioration of biodiesel during storage is due to various factors. Therefore, the latest literature extensively covers the issues which are responsible for biodiesel deterioration and also highlighted the particular areas which should receive more attention. Moreover, a potential identification of these missing and previously-ignored questions in literature will enhance the quality of future research and enable new strategies for biodiesel storage. Das et al., (2009) have studied the long-term storage stability of biodiesel produced from karanja oil. The samples were stored for 180 days under different storage conditions and analysed for various properties at regular intervals. They found a significant increase in the peroxide and kinematic viscosity values, while decrease in the oxidative stability with a storage period. The samples stored under ‘‘open to air inside the room” and ‘‘exposed to metal and air” showed higher peroxide and viscosity value compared to other conditions, hence more susceptible to oxidative degradation. They also studied the effect of three antioxidants on the storage stability of karanja biodiesel and reported an improved stability of KOME by adding different antioxidants [98]. Moser (2011) have investigated the influence of extended storage period on fuel properties of methyl esters prepared from canola, palm, soybean and sunflower oil. They stored samples for 12 months at three different temperatures (15, 22

and 40 °C) and properties such as oxidative stability, acid value, kinematic viscosity, low temperature operability and iodine values were measured periodically. They observed a significant decrease in oxidative stability and relatively little increase in acid value and kinematic viscosity with an extended storage period. They found iodine value and low temperature operability are unaffected by extended storage. Based on the findings, they recommended that acid value or kinematic viscosity can be used as indicators of storage stability and iodine value as predictor of oxidative stability [99]. Ndana et al., (2012) have reported the effect of storage condition on the physico-chemical properties of biodiesel produced from castor, rubber, cotton, neem, soya bean, jatropha and stored in an open air environment for ten months. They observed increase in peroxide value, kinematic viscosity and acid value while decrease in flash point and calorific value. They concluded that these fuels cannot be used as diesel after a long period of storage [52]. Shahabuddin et al., (2012) have investigated the biodiesel stability by means of oxidation and property determination. The biodiesel fuels used were palm methyl ester (PME), jatropha methyl ester (JME), coconut oil methyl ester (COME), 20% blends of PME with diesel fuel and 20% blends of JME with diesel fuel. They evaluated all the samples at regular interval of 180 h for 2160 h (three months). The trend showed increased in density, viscosity and acid value, while the TBN (Total Base Number) decreased due to oxidation. For the flash point, the trend also decreased but the rate was very low. They reported that among all the studied biodiesels, COME was found to be better in respect to oxidation and storage stability [100]. Khalid et al., (2013) have studied the impact of palm biodiesel storage duration on fuel properties and emissions. They stored biodiesel samples in a clinical compartment at different temperatures and monitored at regular interval for 60 days. They

use blends of biodiesel varied from 5 vol. % (B5) ~ 45 vol. % (B45) and storage temperature from 5 °C ~ 30 °C. The analysis of performance parameters showed that the biodiesel density, viscosity and carbon monoxide were affected by the storage duration and storage temperature. Higher blending ratio exhibits a relative variation in emissions due to higher oxygenated fuel [101]. Fernandes et al., (2013) have investigated the storage stability and corrosive character of soybean biodiesel stabilised with tert-butyl hydroquinone (TBHQ) through static immersion corrosion tests for 12 weeks. They concluded that the presence of TBHQ also mitigated biodiesel deterioration even after 12 weeks of the immersion test with both types of steel [102]. Akhabue et al., (2014) have studied the effect of iron (Fe) and aluminium (Al) contaminants on the stability of castor oil methyl ester (COME) for 9 days. During their study, it was observed that as the amount of the metals added to the COME increases from 0.2 to 1.0 g/100 mL COME, the peroxide values of the COME decrease from 1.6 to 0.3 meq/kg and 1.2 to 0.3-0.2 meq/kg for Al and Fe contaminated COME after 24 h. They concluded that the stability of COME was reduced by the presence of metals, and Fe showed detrimental effect on stability than Al [103].

The changes in physic-chemical properties of biodiesel can affect the integrity and stability of the material. Few studies are available in literature on the changes in various properties (acid value, viscosity, peroxide value) of biodiesel during a short or long-term storage period. Studies showed deterioration of biodiesel with the long storage period. Therefore, it is necessary to check the storage stability of any biodiesel. The situation reviewed in the above section, which discuss about the stability of materials could limit the extensive use of biodiesel. Such measures have been proposed in several countries,

and it is a topic of great importance for biodiesel technology. Similarly, the next section discusses the usage of biodiesel in the diesel engines to reduce various pollutants emissions.

1.6.4. Engine performance of biodiesel

Biodiesel fuel can also be used as a blending component or direct fuel in diesel vehicle engines. Low level blends do not need any engine modifications and also reduces NOx emissions. Godiganur et al., (2009) have studied the engine performance and emission tests using methyl ester of mahua (*Madhuca indica*) oil/diesel blends. A Cummins 6BTA 5.9 G2- 1,158 HP rated power diesel engine was run on diesel, methyl ester of mahua oil and its blends at a constant speed of 1500 rpm under variable load conditions. The volumetric blending ratios of biodiesel with conventional diesel fuel were set at 0, 20, 40, 60, and 100. Their results indicated that with the increase of biodiesel in the blends, CO, HC reduced significantly; fuel consumption and NOx emission of biodiesel increased slightly compared with diesel. This increase is mainly due to higher oxygen content of biodiesel [104]. Özcanli et al., (2012) have investigated the performance and emission characteristics of castor bean (*ricinus communis*) oil biodiesel and its blends with diesel fuel. Biodiesel produced from castor oil was blended with diesel fuel at the volumetric ratios of 5% (B5), 10% (B10), 25% (B25), 50% (B50), and 100% (B100). Their performance results showed that blends of castor oil methyl ester with diesel provided an increase in brake specific fuel consumption and a small decrease in brake power output. Compared with diesel fuel, diesel-castor oil methyl ester blends showed reduction in the carbon monoxide and carbon dioxide emissions; but the oxides

of nitrogen emissions observed higher than diesel fuel emission characteristics. Their test results showed B25 as a suitable alternative fuel for diesel engines [105]. Mofijur et al., (2014) have studied the comparative evaluation of performance and emission characteristics of *Moringa oleifera* and palm oil based biodiesel in a diesel engine. The performance of 5% and 10% blends of *Moringa oleifera* and palm oil based biodiesel was assessed in the multi-cylinder diesel engine at various engine speeds and under full-load condition, whereas emissions were assessed under both full-load and half load condition. Engine performance test results indicated that PB5 and MB5 fuels produced slightly lower brake power and higher brake specific fuel consumption values compared to diesel fuel over the entire range of speeds examined. Engine emission results indicated that the PB5, MB5, PB10 and MB10 fuels reduced the average emissions of carbon monoxide and hydro carbons while slightly increased the NOx emissions [106]. Lohith et al., (2014) have carried out experiments using mahua bio fuel. Various blends of mahua methyl ester were prepared and tested on a 4-stroke diesel engine for its performance and emission tests. They found that the emission of harmful gases were low in case of B20 compared to that of other blends and diesel. They concluded that B20 blend can be a viable alternative for diesel as its efficiency was almost comparable with commercial diesel [107]. Palash et al., (2014) have studied the impact of NOx reducing antioxidant additive on performance and emissions characteristics of a multi-cylinder diesel engine fuelled with jatropha biodiesel blends. An experimental study was conducted on a four-cylinder diesel engine to evaluate the performance and emission characteristics of jatropha biodiesel blends (JB5, JB10, JB15 and JB20) with and without addition of N, N'-diphenyl-1,4-phenylenediamine (DPPD) antioxidant. By the addition of 0.15% (m) DPPD additive in

JB5, JB10, JB15 and JB20, the reduction of NOx emissions were about 8.03%, 3.503%, 13.65% and 16.54%, respectively, compared to biodiesel blends without the additive under the full throttle condition [108]. Islam et al., (2014) have studied the emission and performance of diesel engine by using castor biodiesel and its blends from 0 to 40% by volume. Their smoke emission test revealed that B40 (biodiesel blend with 40% biodiesel and 60% diesel) had the least black smoke compared to the conventional diesel. They concluded that B20 can be selected due to its better combustion with lower average percentage of change in PM, CO and HC emissions compared to conventional diesel [109]. Reshad et al., (2015) have conducted an engine performance test for rubber seed oil methyl ester and its blends. They reported that maximum brake thermal efficiency was increased about 28% with RD10 blend compared to diesel. The notable decrease in CO with overall reduction of 30% was achieved. Similarly for blends, NOx also reduced until 80% load and thereafter it showed a higher rise than diesel at maximum load [110]. Abu-Hamdesh et al., (2015) have investigated the emission and performance test of almond and palm biodiesel in diesel engine. Different fuel blends containing about 0%, 10%, 30% and 50% on the volume basis of almond biodiesel with diesel fuel were tested. Another fuel blends consist of 0%, 10%, 30% and 50% on the volume basis of palm oil biodiesel in a palm biodiesel-diesel fuel were also tested. Based on the results, they concluded that almond biodiesel showed better performance compared to palm biodiesel [111].

From the situation reviewed in the above section, it was observed that NOx emissions were reduced with the lower blends of biodiesel with the diesel. Therefore, lower blends of the biodiesel can be used in the diesel engines without any engine

modifications. The next section follows literature review with reference to the biodegradability of biodiesel.

1.6.5. Biodegradability of biodiesel

Biodegradability of any fuel is also one of the important aspects for its use at industrial level because any fuel needs to be biodegradable in order to avoid disposal/spillage problems during its transport. Biodiesel is rapidly biodegradable as it consists of mainly natural compounds which exist in the environment. The biodegradation methods can be carried out by using micro-organisms or without using micro-organisms. Al-Darbi et al., (2005) have investigated the biodegradability of various vegetable and fish oils under the influence of natural bacteria in seawater. They studied the influence of nutrients and microbial environment on changes in the bacterial numbers and the extent and rate of degradation for various oils (olive, mustard, canola and cod liver oils) over time. They observed that different oils responded in different rates and extents to biodegradation depending on their stability, viscosity and compositions. All their results clearly revealed a significant response of the oil-contaminated samples to both the seawater and wastewater environments [112]. Leung et al., (2006) have studied the biodiesel degradation characteristics under different storage conditions. Twelve biodiesel samples were divided into 3 groups and stored in different conditions and monitored at a regular interval over a period of 52 weeks. The results of their study revealed that high temperature together with air exposure greatly increased the biodiesel degradation rate. The temperature or air exposure alone had a little effect on biodiesel degradation [113]. Schleicher et al., (2009) have investigated the biodegradation of rapeseed oil methyl ester

(RME) in pure and in mixtures with diesel fuel. The formation of free fatty acids (FFA) in RME sample was measured according to DIN EN 14214. They observed higher ratio of diesel fuel in the mixture resulted in higher count of bacteria and faster fungal growth was advanced by higher RME contents. The content of FFA in inoculated RME samples increased from 0.08 mass % to 0.344 mass % at the beginning. The oxidation stability of inoculated samples of B20, B5 and pure RME decreased at faster rate than the oxidation stability of blank samples [114]. Luna et al., (2011) have evaluated a rapid method to estimate oxidative stability and biodegradability for mineral, vegetable and synthetic oil samples and reported a lower stability than that of petroleum-based oil. They predicted biodegradability of the synthetic lubricant oil by a bio-kinetic model without using microorganisms. Their studies proved that synthetic lubricant samples were easily degradable (similar to crude castor oil) and showed half-life significantly lower than those of the mineral oil samples [56]. Corseuil et al., (2011) have studied biodegradation of soybean and castor oil biodiesel and implications on the natural attenuation of monoaromatic hydrocarbons in groundwater. They prepared microcosms with unacclimated sediment and groundwater and spiked with 54.8 mg/L of pure soybean or castor oil biodiesel. Approximately 80% of soybean biodiesel was bio transformed in 41 d compared to only 40% of castor oil biodiesel removed in 90 d. They reported that higher persistence of castor biodiesel was attributed to its higher viscosity and lower bioavailability [115]. Silva et al., (2012) have compared the biodegradability of biodiesel and its effect on soil microbial diversity with that of normal diesel using blends of biodiesel with diesel in microcosm experiments with soil obtained from the Atlantic Rain Forest. Degradation was monitored by respirometry and GC analysis of the substrates.

Their results showed that biodiesel is more biodegradable than diesel in contaminated soil and higher concentration of biodiesel in blends also favours the biological breakdown of diesel [53]. Lisiecki et al., (2014) have evaluated the extent of biodegradation of both aromatic and aliphatic hydrocarbon fractions in a saturated sandy microcosm spiked with diesel/biodiesel blends. They evaluated biodegradation kinetics for blends based on measuring the amount of emitted CO_2 after 578 days. Residual aromatic and aliphatic fractions were determined by employing GC-FID and GC-GC-TOF-MS analysis. Their results suggested that an extension of biodegradation for both aliphatic and aromatic hydrocarbon were uninfluenced by the addition of biodiesel regardless of the concentration used. From this observation, they concluded that blending with biodiesel does not impact the long-term biodegradation of specific diesel oil fractions [116].

The survey revealed that biodiesel is more biodegradable than conventional diesel. Some studies stated that biodegradation of fuel vary based on the properties of biodiesel. So far very few studies have reported in the literature. Therefore, biodegradability test could be the aspect which is taken care of once any fuel has been produced. The next section discusses about the usage of various biodiesels for the emulsification to reduce NOx emissions.

1.6.6. Emulsion study using biodiesel

Biodiesel is an oxygenated fuel due to higher oxygen content which leads to the formation of higher NOx when used in a diesel engine. This problem of NOx can be overcome through emulsification of biodiesel with water. Emulsions can be formed by emulsifying oil with water to form a homogeneous distribution of a dispersed phase into another continuous phase with the help of an appropriate surfactant. Emulsions can be

prepared as a two or three phase. Lin et al., (2007) have studied the effects of emulsification variables on fuel properties of two- and three-phase biodiesel emulsions. In their study, the emulsification has been considered to reduce the NOx emission level of fossil fuel. Soya bean biodiesel was emulsified to form two-phase W/O and three-phase O/W/O emulsions. The effects of emulsification variables such as hydrophilic lipophilic balance (HLB) and water content on the fuel properties and emulsion characteristics of W/O and O/W/O emulsions were investigated. Their experimental results showed that the surfactant mixture with HLB = 13 produced the highest emulsification stability while HLB = 6 produced the lowest emulsification stability. The kinematic viscosity, specific gravity and carbon residue of the biodiesel emulsions were larger than that of the neat biodiesel. In their study, W/O biodiesel emulsion was found to have a smaller mean droplet size, lower volumetric fraction of the dispersed phase than the O/W/O biodiesel emulsion [59]. Manjula et al., (2009) have investigated the performance evaluation of a three- phase emulsion of jatropha biodiesel produced by peroxidation**.** By means of high-speed mechanical homogenizer, the biodiesel was emulsified with distilled water and surfactant to produce three phase oil droplets in-water-droplets- in-oil (i.e. O/W/O) biodiesel emulsion and an O/W/O emulsion that contained aqueous ammonia, which is a NOx inhibitor agent. They reported that the existence of aqueous ammonia in the O/W/O biodiesel emulsion curtails NOx formation, thus resulting in the lowest NOx emissions among the four tested fuels in burning the O/W/O biodiesel emulsion that contained aqueous ammonia [117]. Basha and Anand (2010) studied the performance emission and combustion characteristics of diesel engine using carbon nanotubes (CNT) blended water-diesel emulsion fuels. They prepared water-diesel emulsion fuel in the proportion of 5

percent water, 93 percent diesel, and 2 percent surfactants (Span 80 and Tween 80) by volume with a hydrophilic-lipophilic balance of 8. They blended CNT with an aid of a mechanical homogenizer and an ultrasonicator. Their results revealed a considerable enhancement in the brake thermal efficiency and significant reduction in the harmful pollutants due to the incorporation of CNT in the water-diesel emulsion fuel [118]. Debnath et al., (2013) have studied an adjustment of the operating characteristics to improve the performance of an emulsified palm oil methyl ester in a diesel engine. Their objective was to achieve faster combustion, lower ignition delay (ID), improved performance and emission characteristics. They prepared two-phase water in POME (WIP) emulsion and tested in a variable compression ratio (VCR) diesel engine. Their results showed that WIP causes 43% reduction of CO emission than POME. Overall, WIP emits about 17% and 16% lower CO_2 than POME (Palm Oil Methyl Ester) and diesel, respectively. As compared to POME, WIP reduced NOx by 20% by average. They also observed that the WIP produces about 22% higher HC emission than POME [60]. Raheman et al., (2014) have carried out investigation on combustion characteristics and emissions of a compression ignition engine using emulsified jatropha biodiesel blend. An emulsified fuel containing 10% and 15% water by volume was prepared from a diesel blend with 10% Jatropha biodiesel (JB10) to evaluate the combustion characteristics of 10.3 kW single cylinder, 4-stroke and water cooled direct injection (DI) diesel engine. They observed with the increasing percentage of water, ignition delay was longer at higher engine loads. The reduction in emissions such as CO, CO_2, HC and NOx were observed for the emulsified fuel compared to JB10. Therefore, the study concluded that emulsified biodiesel can be recommended for use in place of biodiesel [62]. Basha and

Anand (2014) have investigated the performance, emission and combustion characteristics of a diesel engine using carbon nanotubes blended jatropha methyl ester emulsions. They prepared JME emulsion fuel in the proportion of 93% of JME, 5% of water and 2% of surfactants (by volume) with a hydrophilic-lipophilic balance of 10. The blends of carbon nanotubes with the JME emulsion fuel were prepared in the various dosages systematically. The experimental results revealed an appreciable enhancement in the brake thermal efficiency for the CNT blended JME emulsion fuels compared to that of neat JME and neat emulsified JME fuel. The level of harmful pollutants in the exhaust gases (such as NOx and smoke) was drastically reduced when compared with that of neat JME [119]. Attia et al., (2014) have studied an effect of structure of water-in-diesel fuel emulsion (WFE) on a three cylinder diesel engine performance. Based on membrane emulsification, two different membranes with pore sizes of 0.2 lm and 0.45 lm have been individually used. Their results showed that emulsions with large size of water droplets resulted in a greater reduction in NOx emissions up to 25% [120].

The studies on emulsification of biodiesel are very scanty. From the above literature, it is evident that biodiesel emulsion used in the diesel engines have enhanced the brake thermal efficiency and reduced the NOx as well as other harmful pollutants considerably. In the next section, the value-added utilization opportunities of crude glycerol to glycerol acetal are reviewed.

1.6.7. Conversion of glycerol to glycerol acetal

Glycerol is the major value-added byproduct produced from transesterification of oil and fat during biodiesel manufacturing processes. Currently, crude glycerol production

in the market is about 350, 000 tons per annum (tpa) in USA and 600, 000 tpa in Europe. Glycerol is a value added product which has many potential applications. It can be transformed to various value added chemicals via different methods. Among all methods, the focus is on glycerol acetalization which includes the production of ketals from acetalization of glycerol with a ketone in the presence of acid (mineral or solid or metal) catalysts. Silva et al., (2010) have concluded that addition of 5 vol. % of acetals to biodiesel can reduce the pour point [121]. Agirre et al., (2011) have reported that glycerol can be converted into glycerol acetals and ketals and can be used as diesel additives [122]. From the earlier reports in the literature, it is evident that acetalization reaction can be carried out using either continuous flow reactor or batch reactor. From studies on continuous flow reactor, Royon et al., (2011) have studied ketalization of glycerol in supercritical acetone to produce an oxygenated compound useful as chemical and fuel additive for gasoline, diesel and biodiesel. They observed that below 508 K, the reaction rate of solketal production is very low; but above this temperature reaction rate increases rapidly. The reaction rate is stabilized at 533 K and higher temperatures due to the conversion of glycerol to acrolein and polymeric products as side reactions [123]. Nanda et al., (2014) have designed a new continuous-flow reactor for the conversion of glycerol to solketal through ketalization with acetone. Among all the solid acid catalysts used in the study, maximum solketal yield of 73% and 88% was obtained at 40 °C, 600 psi and WHSV of 4 h^{-1} at the acetone/glycerol molar ratio of 2.0 and 6.0, respectively, with Amberlyst Wet catalyst. Based on the solketal yield and glycerol conversion results, the activity of all catalysts tested follows the following order of sequence: Amberlyst Wet ≈ Zeo-lite ≈ Amberlyst Dry > Zirconium Sulfate > Montmorillonite > Polymax. They

reported that an increase in acetone/glycerol molar ratio or a decrease in WHSV enhanced the glycerol conversion as expected [124]. Nanda et al., (2014) have developed a continuous-flow process using ethanol as solvent and amberlyst-36 as a heterogeneous catalyst for the conversion of glycerol to solketal. The process was optimized using response surface methodology. A model was proposed based on Box-Behnken design. The maximum yield of 94±2% was obtained at 25 °C, acetone-to-glycerol molar ratio of 4 and weight hour space velocity of 2 h^{-1}. They reported that the presence of impurities such as water and salt in glycerol significantly reduced yield at optimum conditions and catalyst could be regenerated and reused for 24 h with an insignificant sign of deactivation [125]. Shirani et al., (2014) have studied an optimization of glycerol ketalization to produce solketal as biodiesel additive in a continuous reactor with subcritical acetone using Purolite® PD206 as a catalyst. A central composite design was used to obtain the optimum conditions for five effective parameters such as temperature, pressure, acetone to glycerol mole ratio, feed flow rate, and the catalyst mass. They achieved yield of 95% at 20 °C, 120 bar, acetone to glycerol mole ratio of 5, feed flow rate of 0.1 $mL \cdot min^{-1}$ and the catalyst mass of 0.77 g [126]. Though the study was carried out in a continuous reactor using Purolite catalyst, there are no reports available by using this catalyst in a batch scale. From the studies on acetalization using batch reactors, Suriyaprapadilok et al., (2011) have synthesised solketal from glycerol and acetone using homogeneous acid catalyst. They observed that reaction progresses successfully when acetone is in excess. In their study, prepared solketal was further used for the synthesis of benzyl solketal ether by performing reaction with benzyl alcohol [127]. Nanda et al., (2014) have conducted heterogeneous ketalization of glycerol with acetone over a solid

acid catalyst of Amberlyst-35 in a batch reactor. They investigated thermodynamics and kinetics of the ketalization reaction for the synthesis of solketal. The effects of various process parameters on the reaction kinetics (glycerol conversion and solketal yield vs. time) were also investigated. A two-parameter kinetic law based on a Langmuir-Hinshelwood rate expression was used. They reported that obtained solketal can be used in applications such as fuel additive and in pharmaceutical industries [66]. Manjunathan et al., (2015) have studied the synthesis of solketal from acetalization of glycerol with acetone over various types of Brønsted solid acid catalysts at room temperature. Among the catalysts screened, they found H-Beta zeolite showed the best performance in a less time with 86% glycerol conversion and 98.5% selectivity to solketal. They reported that glycerol conversion was decreased with decrease in the total acidity of beta catalysts [128].

A comprehensive review of the literature suggests that relatively very few studies have reported the acetalization of glycerol. But, there is still enough scope to find better catalysts and reaction conditions for acetalization of glycerol. Hence in the present study, Purolite resin has been used as a catalyst for acetalization of glycerol in a batch reactor.

1.7. Scope of work

From the thorough literature survey (1.6 section) of the oil extraction, reactive extraction and glycerol usage, it was observed that still lot of technical information is lacking in these fields and those are discussed briefly in this section.

1.7.1. Extraction of oil from various edible and non-edible oil seeds and their respective oil properties were studied. Apart from that extraction of oil after pre-treatment

(i.e. heating) of seeds was carried out only by mechanical extraction. But scanty information is available about solvent extraction of oil before and after pre-treatment of seeds and effect of pre-treatment on oil yield and its properties.

1.7.2. In the vicinity of reactive extraction, few seeds (rape, Jatropha, castor, soya bean, sunflower and grape) have been studied. Among these, optimization of variables by using RSM design technique comprising Central Composite Design was studied only for soya bean and castor seeds. Methods other than CCD can be used for reactive extraction by integrated and non- integrated approach.

1.7.3. Studies on storage stability, engine performance, biodegradability and emulsification using methyl esters are very scanty. Hence, need to be studied in detail.

1.7.4. Simultaneous extraction and transesterification of a lipid with an alcohol to form esters and a by-product, glycerol. Crude glycerol produced during reaction can be purified and re-used as a raw material for glycerol acetal production. Till date very less information is presented on the conversion of crude glycerol to glycerol acetal which needs further investigation.

1.8. Objectives

With the large gap between the biodiesel demand and the current production capacity, there is still enough scope for improvement which requires intensive research in order to meet the demands realistically. Accordingly, following objectives have been formulated for the thesis work.

1.8.1. Studies on extraction of castor oil from castor seeds using various solvents and comparison of their (extracted oil) physico-chemical properties.

1.8.2. Optimization of reactive extraction of castor seeds using base catalysts for the production of castor oil methyl esters (COME) by the non-integrated and integrated approach.

1.8.3. Investigation on emulsion characteristics of two phase castor oil methyl ester-water emulsions (ME/W and W/ME) by ultrasonic technique.

1.8.4. Studies on conversion of glycerol to glycerol acetal using heterogeneous catalyst

1.9. Organization of the thesis

The PhD thesis is organized in seven chapters.

Chapter 1 addresses the state of art literature review, possible scope for further research, objectives and organization of the thesis.

Chapter 2 contains the procedures for oil extraction from castor seeds, methyl esters synthesis by reactive extraction, storage stability and biodegradability of COME, engine performance test of COME and emulsions preparation. Further, this chapter gives main emphasis on various product confirmation methods; correspondingly, physico-chemical characterization techniques used to evaluate the significant product performance properties are reported.

Chapter 3 describes an effect of pre-treatment on castor oil yield and its properties, oil extraction from castor seeds by using polar and non-polar solvents. Further, the chapter

includes estimation of physico-chemical properties of castor oil extracted using different solvents.

Chapter 4 describes an optimization of reactive extraction of castor seeds by an integrated and non-integrated approach, an evaluation of the storage stability of COME for a period of six months, biodegradability of COME, engine performance test of COME and its blends with diesel. Further, chapter includes discussion on the various estimated properties of the methyl ester, its blends and conclusions.

Chapter 5 presents emulsion characteristics of two phase castor oil methyl ester-water emulsions (ME/W and W/ME) by ultrasonic technique and estimated the properties of emulsions.

Chapter 6 addressed the preliminary studies on conversion of glycerol to solketal using acetone

Chapter 7 presents overall conclusions drawn from the research work carried out and the potential directions for future work.

CHAPTER 2

Experimental and Characterization

This chapter gives the information about materials used and detailed experimental procedures carried out for the entire research work. The experimental procedures includes the oil extraction from castor seeds, reactive extraction of castor seeds by integrated and non-integrated approaches [optimization by RSM (Response Surface Methodology) design technique], storage stability and biodegradability of COME (Castor Oil Methyl Ester), engine performance test with COME and emulsion preparation method with methyl ester, and acetalization of glycerol to solketal. Further, this chapter discusses the procedures of product confirmation methods such as ^{1}HNMR, FTIR and various physico-chemical characterization methods.

2.1. Materials

Castor seeds used in this study were procured from Anantapur, Andhra Pradesh, India, and were used for the oil extraction and reactive extraction by integrated and non-integrated approaches. The castor oil methyl ester produced from the reactive extraction via non-integrated approach was used for the storage stability, biodegradability, engine performance test and emulsion study. The chemicals which are analytical grade such as n-hexane, methanol, petroleum ether, pentane, cyclohexane, isopropanol, ethyl acetate, NaOH, phenolphthalein indicator, sodium thiosulfate pentahydrate, starch, Wijs' solution and ethanol were purchased from Merck, India Pvt. Ltd. Pellets of KOH (>85%) were procured from Ranbaxy Fine Chemicals Ltd., India and carbon tetra chloride was

obtained from S. D. Fine Chemicals Ltd., India. The conventional diesel was purchased from Guwahati, Assam, India and used for the engine performance test. The surfactants such as Tween 80 and Span 80 used in the emulsion study were purchased from Merck, India Pvt. Ltd. Glycerol and acetone were purchased from Merck, India Pvt. Ltd. were used for acetalization experiments. Purolite resin was purchased from the Aishwarya Chemicals Ltd, Chennai, India.

2.2. Experimental procedures

2.2.1. Oil extraction from castor seeds

The oil was extracted from castor seeds by using two methods (Soxhlet and Vial) and compared the oil yields obtained. The processing of seeds and detailed procedures are discussed below.

2.2.1.1. Castor seed processing

The collected seeds (Figure 2.1) were divided into two categories as untreated (before heat treatment) and pre-treated (after heat treatment) seeds for oil extraction. Untreated seeds are the seeds which were cleaned manually from dirt and other foreign materials and used directly for extraction without prior heating. Pre- treated seeds were cleaned seeds which were heated at 50 °C in a laboratory oven for 24 h and then used for oil extraction by Soxhlet and vial methods.

Figure 2.1: A. Castor plantation in Andhra Pradesh (South India); B. Matured seeds

2.2.1.2. Oil extraction by Soxhlet method

The oil was extracted by Soxhlet apparatus (Figure 2.2) according to the standard AOAC method. Extraction was carried out at the boiling point of the respective solvent to avoid loss of solvent through evaporation. Extraction time was counted when the first drop of extracting solvent recycled back into the thimble. Solvent was recovered in a rotary evaporator under the vacuum and reused in the next batch of extraction [19]. The residual oil was cooled and weighed. The same procedure was repeated for oil extraction with different solvents at different conditions. The oil yield was calculated using the following expression [9].

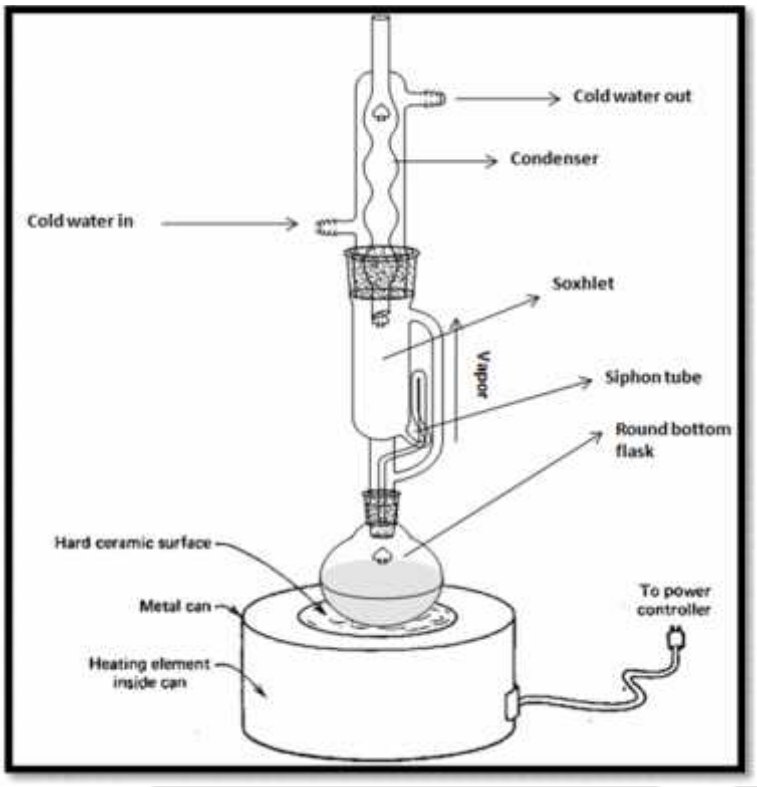


Figure 2.2 : Soxhlet apparatus used for oil extraction

$$\text{Oil Yield} = \frac{\text{Weight of extracted oil}}{\text{Weight of seed sample}} \times 100 \quad \text{.....(2.1)}$$

2.2.1.3. Oil extraction by vial method

Extraction of oil from castor seed was carried out by vial method. Extraction by vial method was carried out using a single castor seed and 2 mL eppendorf vials. From the available seed samples, randomly single castor seed was selected and the weight of the seed was noted. Kernel was grinded manually with a mortar and pestle. The grinded kernel was divided into two halves and transferred into pre weighed two different eppendorf vials. Hexane about 2 mL was added to each vial and centrifuged at 10, 000

rpm for 20 min. The supernatant was decanted into other two pre-weighed eppendorf vials and placed in a fume hood with the lid open in order to evaporate the solvent. Additional 2 mL of hexane was added to the precipitated grinded seed in each vial and the whole process was repeated. The procedure for preliminary tests was followed according to reported literature [129]. The oil content of the castor seed obtained was compared with that of Soxhlet method.

2.2.2. Reactive extraction of castor seeds

Reactive extraction of castor seeds by integrated and non-integrated approaches was optimized using RSM design technique. The detailed procedures are given below.

2.2.2.1. Reactive extraction of castor seeds by integrated approach

Preliminary studies for reactive extraction of castor seeds were carried out in a 500 mL round bottom flask equipped with a Soxhlet apparatus, reflux system, magnetic stirrer and heater (Figure 2.3). The round bottom flask was immersed in an oil bath placed on magnetic stirrer plate. The known amount of KOH (0.5-2 wt % of oil content) was added to the known volume of methanol (oil/methanol molar ratio: 1:400 to 1:550) in a round bottom flask in order to maintain the catalytic activity and to prevent moisture absorbance. The alkali-alcohol solution was heated to a boiling temperature of methanol (65 °C). During extraction, a chamber containing pre-treated castor seeds (20 g) macerated using a mixer grinder were placed between the drops of re-condensed solvent falling from the condenser and the boiling solvent solution.

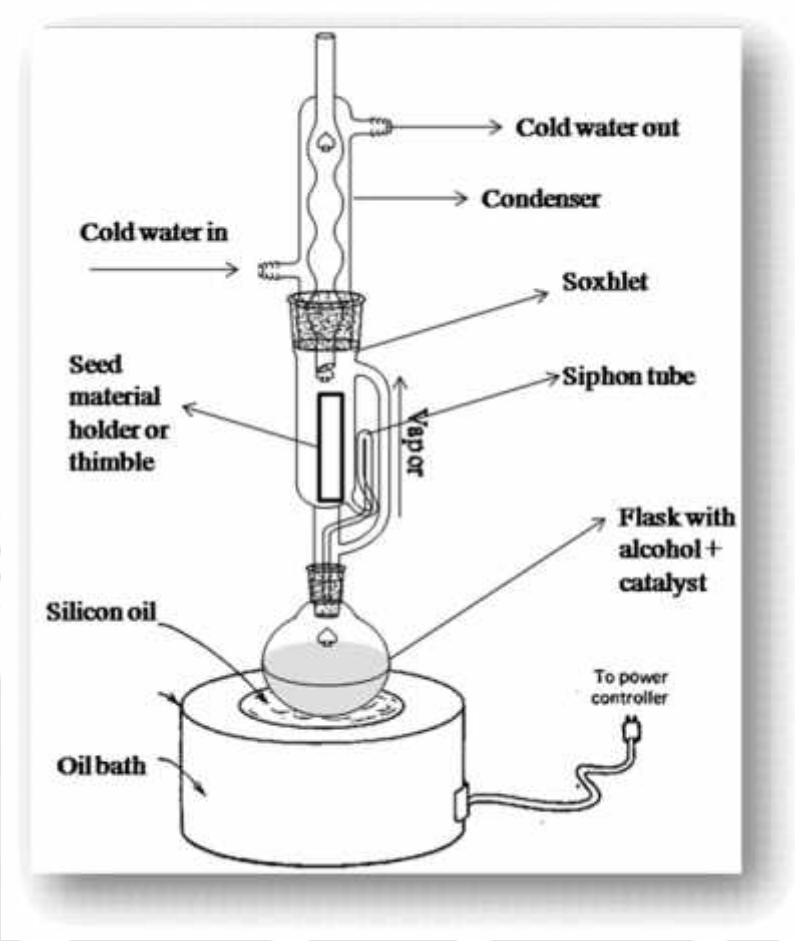


Figure 2.3: Integrated Soxhlet apparatus used for reactive extraction

When the distilled, re-condensed solvent runs through the castor seed material, washing out the oil falls in the reaction flask was considered as a zero reaction time and continued further for desired time duration (6-15 h). Other reaction variables such as, seed quantity (15-25 g), mixing speed (600-1200 rpm) and co-solvent hexane (5-15 vol % of alcohol) were selected to optimise and understand the effect of these variables on reactive extraction of castor seeds. At the end of reaction, the excess methanol was removed from the product using a rotary evaporator. The complete evaporation of methanol leads to the formation of two liquid layers. The upper yellow layer belongs to the biodiesel, while the bottom dark brown layer represents the glycerol. The layers were separated using a

separating funnel. The upper biodiesel layer was washed with warm millipore water (50-60 °C) to remove the catalyst and residual methanol. The moisture was removed from methyl ester by drying at 60 °C under vacuum rotary evaporator. The obtained product weight was recorded for biodiesel yield calculation [92].

A three-level, three-factor central composite design (CCD) was applied for carrying out the optimization studies to maximize the COME conversion. The factorial levels were fixed based on the results of conventional optimization study. The coded and uncoded levels of the independent variables are given in Table 2.1.

Table 2.1: Independent variables and levels for response surface design

			Coded Levels		
Independent Variables	**Symbol**	**Unit**	**-1**	**0**	**+1**
Reaction time	A	h	6	9	12
Oil to methanol molar ratio	B	-	400	450	500
Catalyst concentration	C	wt %	1	1.5	2

The following experimental parameters (or independent variables) have been chosen for optimization: reaction time (A), oil to methanol molar ratio (B) and catalyst concentration (C). The reactions were carried out at varied reaction time (6-12 h), oil to methanol molar ratio (1:400-1:500) and catalyst concentration (1-2 wt % of oil content in seeds). A 2^3 full factorial CCD for three independent variables comprises of 20 sets of experiments. During the optimization study, six axial experiments and eight factorial experiments were carried out with six extra replications at the centre of design were used for the estimation of pure error. In each set, experiments have been done in triplicate (3 runs) so as to assess

the reproducibility of results. The progress of the reaction was monitored by withdrawing the aliquots of reaction mixtures at regular time intervals.

Design-expert software v.8.0.6 trial version was used for the regression and graphical analysis of the data. The response variable, i.e., FAME conversion, was fitted with a full quadratic model (given in Eq. (2.2)) in order to correlate it to the experimental parameters or independent variables. The experimental data obtained by the above procedure was analyzed by the response surface regression using following second-order polynomial:

$$Y = {}_0 + \sum_{i=1}^{n} {}_i X_i + \sum_{i=1}^{n} {}_{ii} X_i^2 + \sum_{i=1}^{n} \sum_{j>1}^{n} {}_{ij} X_i X_j \quad \text{.....(2.2)}$$

Where Y is the response (COME conversion), *i* and *j* are the linear and quadratic coefficients, respectively, β_0 is the regression co-efficient and *k* is the number of factors studied and optimized in the experiment. Statistical analysis of the model was carried out to evaluate the ANOVA (Analysis of Variance). Confirmatory experiments were also carried out to validate the equation. The goodness and best fit of the model were evaluated by regression coefficient R^2. Response surface and counter plots were obtained using the fitted quadratic polynomial equation obtained from regression analysis.

2.2.2.2. Reactive extraction of castor seeds by non-integrated approach

Reactive extraction of castor seeds was carried out in a three-neck 250 mL round bottomed flask equipped with a reflux system, magnetic stirrer, heater and placed in an oil bath (Figure 2.4). Flow sheet for the process was given in Figure 2.5. Initially, sodium methoxide solution was prepared by dissolving known amount of NaOH in methanol and heated to the desired temperature. When a solution reached to the desired temperature, 20

g of macerated castor seed material was transferred into the reaction vessel and then mixing (200-600 rpm) was started. Thus, the reaction was carried out for the desired temperature (30-60 °C) and reaction period.

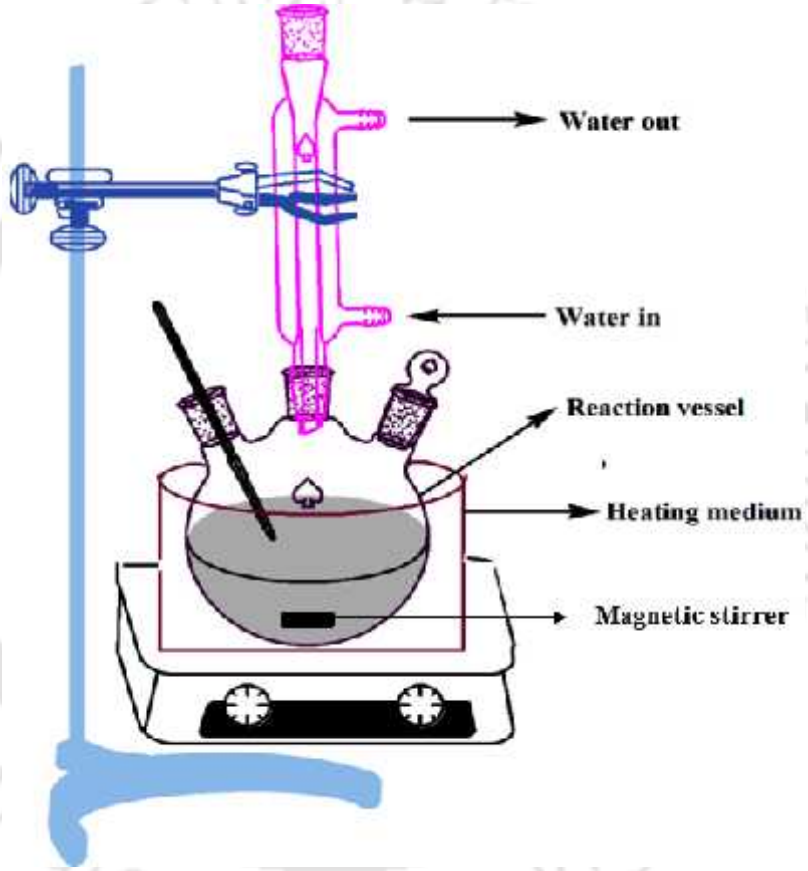


Figure 2.4: Schematic diagram of reactive extraction set up

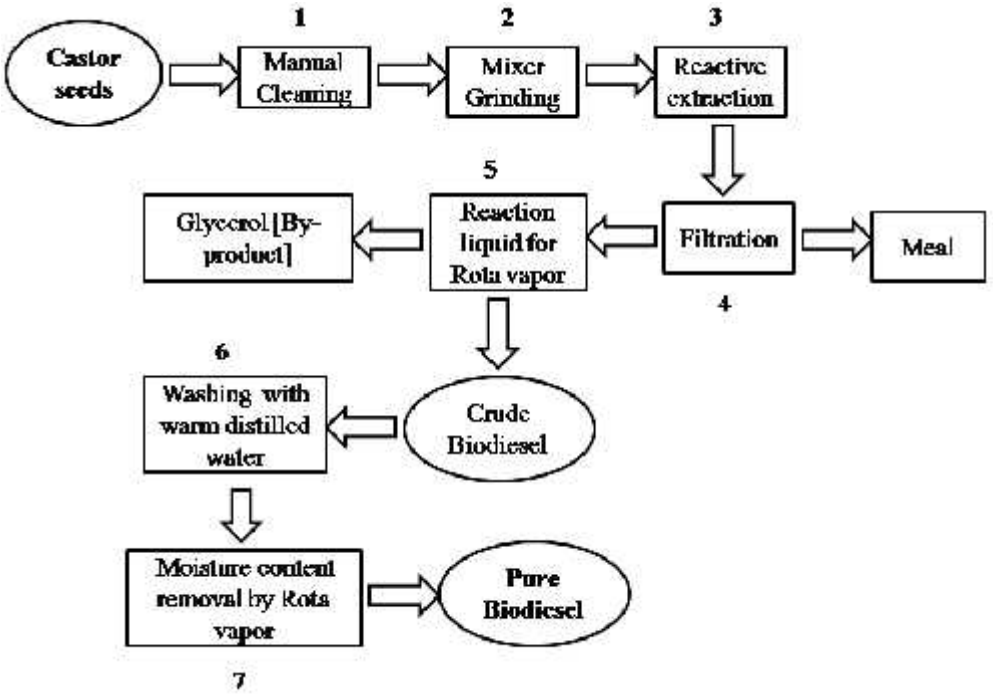


Figure 2.5: Flow sheet of reactive extraction of castor seeds for biodiesel

The optimum reactive extraction condition was obtained by varying process parameters such as reaction time (2, 3, 4, 5 h), oil to methanol molar ratio (1:150-1: 300), catalyst concentration (0.5-2 wt % oil content of seeds) and reaction temperature (30-60 °C). At the optimum condition, reaction was carried out by replacing NaOH with KOH as catalyst and another reaction with hexane as co-solvent using NaOH as catalyst. After the desired reaction time period, 1.5 mL of glacial acetic acid was added to the mixture to neutralize the catalyst and prevent further reaction. The reaction liquid was separated from the seed cake using a normal filtration. The solid residue was washed repeatedly with methanol to recover the product that adhered to the seed and excess methanol was recovered using a rotary evaporator. The complete evaporation of methanol leads to the formation of two liquid layers. The upper layer (yellow) belongs to the castor oil methyl ester while the bottom layer (dark brown) represents the glycerol layer. The layers were further separated

using the separating funnel. The upper biodiesel layer was washed with warm millipore water (50-60 °C) to remove the catalyst and residual methanol. The moisture content of the product was removed using rotary evaporator. The obtained product weight was recorded for biodiesel yield calculation [89]. The biodiesel yield was calculated using the formula below.

$$\text{COME yield (wt \%)} = \frac{\text{Weight of pure biodiesel obtained}}{\text{oil content in seeds used}} \quad \text{.....(2.3)}$$

RSM was employed to evaluate the effect of various process parameters on the conversion of castor oil during reactive extraction. The factorial levels were selected on the basis of our preliminary experiments reported elsewhere [130]. A central composite design has been used to devise the reactive extraction experiments comprising of 30 experiments for four variables [8].

Table 2.2: Independent variables and levels for response surface design

			Coded Levels		
Independent Variables	Symbol	Unit	-1	0	+1
Reaction time	A	h	3	4	5
Oil to methanol molar ratio	B	-	200	250	300
Catalyst concentration	C	wt %	0.5	1	1.5
Temperature	D	°C	30	40	50

The coded and uncoded levels of independent variables are given in Table 2.2. The four independent variables used for the optimization were reaction time (A), oil to methanol molar ratio (B), catalyst concentration (C) and reaction temperature (D). The reactions were carried out at varied reaction time of 2-5 h, oil to methanol molar ratio of 1:150-1:300, catalyst concentration of 0.5-2 wt % (of oil content in seeds) and temperature of 30-60 °C. The lowest and highest levels are assigned to be -1 and +1 while all variables at zero level constitute the centre points, respectively. Value of α (alpha) was fixed at level 2 ($\alpha = 2^{4/4}$). A 2^4 full factorial CCD for four independent variables was used by giving a total number of 30 ($= 2^n+2n+6$) experiments, where 'n' is the number of independent variables. During the optimization study, eight axial experiments and sixteen factorial runs were carried out with six extra replications at the centre of design were used for the estimation of pure error.

Design expert software v.8.0.7.1 trial version was used to predict the response of a process as a function of independent variables and their interactions to understand the system performance. The mathematical relationship between the process variables and response was calculated by the following quadratic polynomial expression:

$$Y = 0 + \sum_{i=1}^{n} iXi + \sum_{i=1}^{n} iiX_i^2 + \sum_{i=1}^{n} \sum_{j>1}^{n} ijXiXj \quad \text{.....(2.4)}$$

Where Y is the response i.e., COME conversion, x_i and x_j represent the independent variables, β_0 is constant, β_i is linear term coefficient, β_{ii} is quadratic term coefficient, β_{ij} is cross term coefficient and 'n' is the number of process variables studied and optimized during the study. Analysis of variance (ANOVA) was carried out to estimate the effects of process variables and their possible interaction effects on the COME conversion in the response surface regression procedure. The best fit of the model was evaluated by

regression coefficient R^2. Response surface and contour plots were drawn based on the obtained quadratic polynomial equation from regression analysis by keeping two of independent variables at central value (0) and by varying other two variables to assess the interaction among the operational factors and to determine the optimal values of each parameter.

2.2.3. Storage stability and biodegradability of COME

Storage stability and biodegradability are important factors for any fuel. Therefore, the analysis was carried to test the produced methyl ester. The detailed procedures are as follows.

2.2.3.1. Storage condition and analysis of COME

Though biodiesel is an alternate fuel to conventional diesel, it is more susceptible to oxidation or autoxidation during long term storage than diesel. As the long term storage study gives better understanding of the effect of an altered storage conditions on the stability of biodiesel [98], present study was carried out to evaluate the long term storage stability of COME. For the storage stability study, COME prepared at optimum condition obtained during the reactive extraction by non-integrated approach with NaOH as a catalyst (without co-solvent) was used. The methyl ester samples (25 mL each) were stored for 180 days at around 23-25 °C at three different storage conditions such as open air (exposed to light), air tight (exposed to light) and dark (not exposed to air and light). All the three methyl ester samples were stored in sealed plastic containers separately. The COME sample stored at air tight condition was prevented from ambient air exposure by wrapping the sealed sample bottle lid with a parafilm tape. The COME sample stored in

the dark condition was stored by covering the whole sample bottle with aluminium foil and kept in the cartoon box without exposure to air and light. During the storage period, samples were withdrawn at definite intervals and analysed to evaluate the properties such as density, kinematic viscosity, acid value and iodine value according to ASTM (American Society for Testing Materials) standard methods.

2.2.3.2. Evaluation of biodegradability of COME

Bio kinetic model, ASTM method D7373-12 was used to predict the biodegradability of COME without using micro organisms. This method was used to evaluate the effective composition of biodegradation (ECB) products and predicts the cumulative biodegradation of prepared esters. The biodegradation test was carried out for COME and the ECB was calculated as per the standard method. The biodegradation tests were repeated twice and average values were recorded.

2.2.4. Engine performance test of COME and its blends with conventional diesel

In this section, engine performance test and emission characteristics of a DI engine fuelled with COME and its blends are investigated. The experimental procedure and measurement techniques are summarized at considerable length in this section.

2.2.4.1. Experimental setup

Engine study experiments were performed on a single cylinder, four stroke, water cooled direct injection diesel engine (Kirloskar make, India) using diesel and blends of COME with diesel. The set-up is equipped with the water cooled eddy current brake

dynamometer for applying a brake load on engine. The schematic diagram of the diesel engine setup is shown in Figure 2.6.

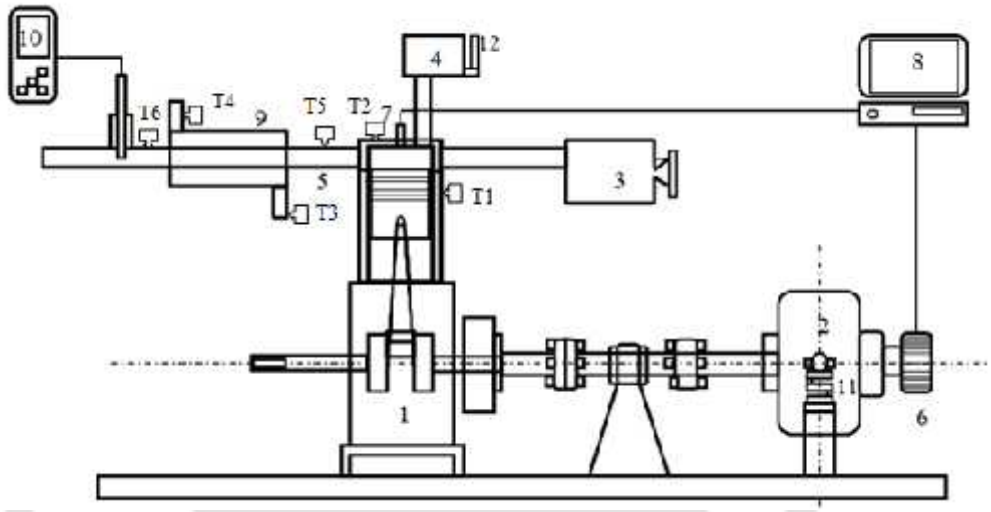


Figure 2.6: Schematic of DI diesel Engine test Bench (1) Engine set up (2) Eddy-current dynamometer (3) Air box with orifice meter (4) Fuel tank (5) Exhaust gas line (6) Crank angle encoder (7) Cylinder pressure transducer with amplifier (8) Computer system with Engine Soft Software (9) Exhaust gas calorimeter (10) Exhaust gas emission analyzer (11) Strain gauge type load cell (12) Fuel measuring tube (13) T1-T6 Temperature measurement using thermocouples

The brief specifications about set up are given in Table 2.3. For combustion related diagnostics, cylinder pressure measurement for each degree of crank rotation was performed using piezo sensor. These signals are then interfaced to a computer through the engine indicator unit to measure the engine speed. The set-up has a standalone panel box containing the air box for air consumption measurement, fuel tank with fuel meter and rota meters for water flow rate measurement required for cooling of the engine as well as exhaust gas calorimeter [131]. The volume of air consumed for a particular load was

found out by measuring the water level difference in mm of water. This will help to find the mass flow rate of air. The coefficient of discharge of an orifice meter was taken as 0.6.

Table 2.3: Specifications of diesel engine

Make and model	**Kirloskar, model TV1**
Engine type	Single-cylinder, four-stroke DI diesel engine
Rated power	5.2 kW (7 BHP) at 1500 rpm
Type of cooling	Water cooled
bore × stroke	87.5 × 110 mm
Swept volume	0.661 L
Compression ratio	17.5:1
Speed	1500 rpm, constant
Injection timing (diesel)	23 ° BTDC
Make, type of sensor, and maximum pressure	PCB, piezo electric (15000 psi)
Resolution and response time	0.1 psi, 2 μs
CA sensor	360° encoder with a resolution of 2°

The liquid fuels were supplied to the engine injection pump from the fuel tank under gravity feed. One minute fuel consumption measurements at a particular load were performed on a volumetric basis using graduated glass burette. This volumetric fuel consumption was converted to gravimetric basis from the fuel density which was evaluated for all fuel blends. All the analogue signals recorded from different locations of the test rig are supplied to the 'Engine soft' software for performance and combustion

analysis. The exhaust gas analysis was performed with the help of Testo-350/M/XL Engine flue gas analyzer. This emission analyzer provides the accurate measurement of five gases i.e. O_2, CO, CO_2, NO_X, and HC. The exhaust gas was ingested by analyzer from exhaust manifold when probe is inserted in the manifold. This process takes place with the help of a pump for fixed time duration under the specified set of operating conditions. The gas then gets analyzed while passing through each sensor one by one. The direct readings of CO, CO_2, NO, NO_2, and hydrocarbon (HC) emissions in ppm and/or percent can be obtained on the digital display. The resolution, accuracy and range of these parameters of the emission analyzer (Make: Testo-350) are shown in the Table 2.4.

Table 2.4: Specifications of exhaust gas analyzer

Emission	Range	Uncertainty
O_2	0-25 vol %	± 5 %
CO	0-10, 000 ppm	± 5 %
CO_2	0-50 vol %	± 5 %
NO	0-3000 pm	± 5 %
NO_2	0-500 ppm	± 5 %
HC	0-40, 000 ppm	± 5 %
SO_2	0-5000 ppm	± 5 %

2.2.4.2. Experimental procedure

The diesel engine was operated using diesel and COME blends. At the beginning engine runs on diesel fuel at standard operating conditions and the test is called as baseline test. Here, the engine runs at a speed of 1500±50 rpm with intake fuel of pressure 190 bars for the fixed compression ratio (CR) of 17.5:1 with fuel injection at an angle of

23 °bTDC under varying loads from 0% to 100% in steps of 20%. At 20% load condition after the start of the engine, when the engine water jacket outlet temperature reaches 30 °C, it is assumed that the steady state has reached for recording the engine data. The increase in load on the engine increases the fuel consumption in order to maintain constant speed and brake mean effective pressure (BMEP). Similarly, the water jacket outlet and exhaust gas inlet to calorimeter temperature increases with the load. For each load condition, up to certain stage the water jacket outlet and exhaust gas inlet to calorimeter temperature rises then become steady. The flow rate of water in the engine jacket and exhaust gas calorimeter were maintained at 300 and 100 L/h, respectively throughout the experiment. After the baseline test with diesel, the engine runs at no load condition for some time using pure diesel fuel. Thereafter, COME blends were used as fuels in a diesel engine and performed each test individually on one test per day basis. The blends of COME with diesel have been carried out using mechanical stirrer in order to get the homogeneous mixture of fuels [132]. After each fuel blend test, the engine was allowed to run at no load condition for some time using pure diesel fuel to flush out the blended fuel through the engine. The engine performance parameters such as brake power (BP), brake thermal efficiency (BTE), specific fuel consumption (SFC), volumetric efficiency (ηvol) and exhaust gas temperature (EGT) were estimated. The details of their calculation are given in Appendix [133-134]. The complete combustion analysis including cylinder pressure, net heat release rate, peak cylinder pressure, ignition delay and emissions like carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NOx) and un-burnt hydrocarbon (HC) were also studied.

2.2.5. Preparation of two-phase emulsions (W/ME and ME/W)

The emulsions prepared in this study are of two types i.e. W/ME and ME/W. Water-in-methyl ester (W/ME) emulsion is mostly used in diesel engines. Methyl ester-in-water (ME/W) emulsion is produced in the first stage of the preparation of the three- phase biodiesel emulsions. The literature reports on ME/W are very less compared to that of W/ME emulsion. A brief overview of emulsion preparation is shown in Figure 2.7.

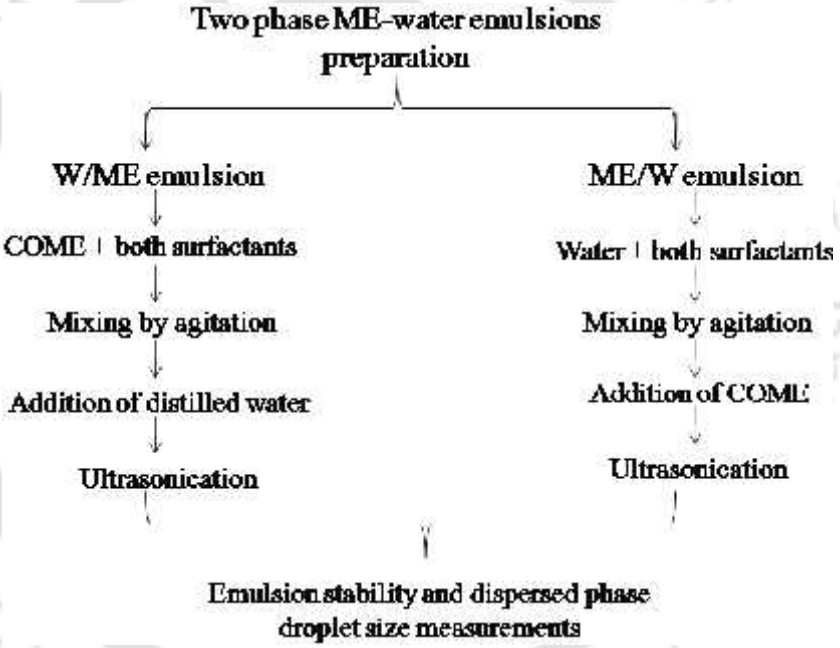


Figure 2.7: Steps followed for the two phase emulsions preparation

An emulsion is a dispersion of small droplets of one liquid (dispersed phase) in another liquid (continuous phase). In W/ME emulsion, the continuous phase is COME with larger volume; whereas, water is the dispersed phase. Similarly, for ME/W emulsion, water is the continuous phase and oil is the dispersed phase. The dispersed phase droplet size measurement has also been carried out for the emulsion samples by varying different

sonication time. The detailed emulsion preparation procedures and estimated emulsion characteristics are discussed below.

The water-in methyl-ester type emulsion (water dispersed in oil phase) was prepared by using two surfactants (i.e. Tween 80 and Span 80). The quantities of surfactants were calculated based on the HLB (Hydrophilic Lipophilic Balance) values using a method reported by Raheman and Kumari (2014) [62]. To determine the desired HLB, six emulsion samples of 40 ml each were prepared for HLB 4.3, 5, 7, 10, 13 and 15 by taking a known amount of castor oil methyl ester (surplus amount based on water and surfactant amount), water (15 vol % of total emulsion) and calculated quantities of both the surfactants. Initially, known amount of methyl ester was mixed with 2 vol % (of total emulsion) surfactants and stirred with the agitator at 2500 rpm. Thereafter, 15 vol % (of total emulsion) distilled water was poured in the beaker and placed into the ultra sonic bath. The mixture was sonicated for 10 min in order to disperse the water phase in to the oil phase. The resultant emulsified sample was transferred into 50 ml measuring cylinder for the observation of emulsion stability or phase separation of unemulsified layer. In order to obtain properly dispersed and stable emulsion, other parameters were also varied such as water content (10, 15, 20 vol %), surfactant volume (1, 2, 3 vol %), ultra-sonication time (10, 30, 60, 120, 180 min), agitation time (10, 20, 30 min) and agitation speed (2500, 3000, 3500 rpm), respectively.

Similarly, ME/W emulsion was prepared using aforementioned surfactants. To find out the desired HLB value, various emulsion samples were prepared (i.e. HLB 4.3, 5, 7, 10, 13 and 15) by taking a known amount of water (surplus amount based on oil and surfactant amounts), 15 vol % (of total emulsion) COME and different calculated

portions of both the surfactants. Rest of the procedure followed was same as mentioned for W/ME emulsification.

To obtain optimum parametric conditions for properly dispersed and stable ME/W emulsion, other parameters were also varied such as COME (10, 15, 20 vol %), surfactant volume (1, 2, 3 vol %) and ultra-sonication time (10, 30, 60, 120, 180 min), respectively. Agitation time (10 min) and agitation speed (2500 rpm) were kept constant as that of W/ME emulsion optimization study.

2.2.6. Emulsion characteristics and properties estimation

The main purpose of this experiment is to study the biodiesel emulsification characteristics such as emulsification stability and droplet sizes of dispersed phase in the emulsions. Further investigation includes an estimation of emulsified fuel properties.

2.2.6.1. Emulsion stability and percentage phase separation

Emulsion stability of both W/ME and ME/W two phase emulsions were measured based on the percentage separation of unemulsified layer from the prepared emulsion over a long duration. The percentage separation is defined as the ratio of an unemulsified layer volume to the total volume of the whole emulsion after it has kept motionless. Larger is the percentage of separation, the more unstable and faster is the separation phenomenon of an emulsion [135]. For this observation, samples were kept motionless for about two weeks.

2.2.6.2. Measurement of droplet size

The droplet size of dispersed phase in W/ME and ME/W emulsions were measured using an optical electron microscope (LEICA DM 2500 M). The microscope has a magnification of 100X. Droplet size measurements for both emulsions were carried out only for the emulsion samples prepared with different sonication time. The samples were analyzed immediately after the preparation of emulsions. After every sonication time intervals of 10, 30, 60, 120 and 180 min, the drops of emulsions prepared are taken on micro slides and analyzed under the microscope accordingly.

2.2.6.3. Estimation of emulsion properties

The properties of optimized W/ME and ME/W emulsion samples were estimated using standard methods described in our earlier paper [130]. The properties estimated include density, specific gravity, kinematic viscosity, pour point, calorific value, flash point, fire point and thermal stability.

2.2.7. Acetalization of glycerol to solketal

In order to intensify the reactive extraction process with an intention to make use of by-product glycerol, preliminary studies on conversion of synthetic glycerol to solketal were investigated over a wide range of parameters. The acetalization of glycerol (synthetic) to solketal was carried out using purolite as catalyst. Experiments were carried out in a two-neck 100 mL round bottomed flask equipped with a reflux system, magnetic stirrer and heater. All the experiments were carried out at room temperature, 500 rpm using 5 g glycerol as constant parameters. From the literature data, it was observed that

reaction at room temperature showed better performance in acetalization of glycerol [136]. Therefore, in this study experiments were carried out at room temperature. In addition, higher quantity of glycerol in the reaction was avoided because high viscosity of glycerol may hamper the homogenization of the reaction medium [136]. Initially, 5 g of glycerol, 1 wt % of catalyst and the calculated amount of acetone (1:4 glycerol/acetone molar ratio) were taken in a reactor and stirred at 500 rpm. The optimum condition was obtained by varying the process parameters such as reaction time (1-4 h), glycerol to acetone molar ratio (1:2-1:6), catalyst concentration (0.5-2 wt % of glycerol) and different catalysts (Purolite, Amberlyst-15, sulphuric acid). After each reaction, acetone and water were removed from the product solketal by using rotary evaporator. The product was analyzed by using GC-MS (Gas Chromatography Mass Spectrometer). Solketal yield and glycerol conversion were calculated using the following equations [66, 137].

$$\text{Solketal Yield (\%)} = \frac{\text{Moles of solketal formed}}{\text{Initial moles of glycerol}} \times 100 \quad \text{.....(2.5)}$$

$$\text{\% Conversion} = \frac{(C_i - C_f)_{\text{(Substrate)}}}{(C_i)_{\text{(Substrate)}}} \times 100 \quad \text{.....(2.6)}$$

Where C_i and C_f are initial and final concentration of the respective species in the reaction mixture.

2.2.8. Product confirmation methods

2.2.8.1. ^{1}H NMR analysis

^{1}H NMR (Nuclear Magnetic Resonance Spectrometer) spectra of castor oil and methyl ester samples were obtained on 400 MHz NMR spectrometer (Oxford, AS400, China) using a 5 mm broad band inverse probe head, equipped with shielded z-gradient accessories. Samples were dissolved in 400 µl deuterated chloroform ($CDCl_3$) and transferred to NMR tube. The deuterated chloroform chemical shift peak at 7.26 ppm was taken as an internal reference. Typical parameters used were: spectral width: 4800 Hz; time domain data points: 32 K; flip angle: 90 °C; relaxation delay: 5 s; spectrum size: 32 K points; and line broadening for exponential window function; 0.3 Hz. The conversion of castor oil was calculated directly from the integrated areas of relevant peaks of methylene and methyl ester protons according to previously reported literature [138]. The equation used for finding the COME conversion is as follows:

$$\text{COME conversion} = \frac{2A_1}{3A_2} \times 100 \quad \text{.....(2.7)}$$

A_1 -Area under the methyl ester singlet peak (3.7 ppm in methyl ester spectrum)

A_2 -Area under the methoxy protons (2.3 ppm in methyl ester spectrum)

2.2.8.2. FTIR analysis

An infrared spectrum analysis of castor oil (CO) and COME samples was performed by FTIR spectroscopy (Make Shimandzu IR Affinity1 Model) using KBr pellets. A sample volume of 0.5 mL was uniformly spread throughout the crystal surface to obtain the spectra. Each spectrum was the result of 20-30 scans performed in the wave number range 4000 to 500 cm^{-1}. The different functional groups present in the castor oil

and COME were identified and compared with the obtained respective individual FTIR spectrum.

2.2.8.3. Analysis of solketal and glycerol by GC-MS

After the separation of acetone and water, all the samples were analyzed by using GC-MS on a Varian 1200 Quadrupole MS (EI) and Varian CP-3800 GC with VF-5 MS column (5% phenyl/95% dimethyl-polysiloxane, 30 m×0.25 mm×0.25 lm), using helium as a carrier gas at a flow rate of 0.5 mL/s. The oven temperature was maintained at 120 °C for 2 min and then increased to 200 °C at 40 °C/min. Injector and detector temperatures were 300 °C. Components were identified by NIST 98 MS library. The procedure was followed according to reported literature [124]. The yield and conversions of all samples were calculated from the peak areas obtained from GC-MS with the help of previously calibrated data of pure solketal and glycerol.

2.2.9. Physico-chemical characterization of product and raw materials

All the physico-chemical properties of extracted castor oil, methyl ester and its blends, diesel, storage stability and emulsion samples were estimated according to the standard ASTM methods. Acid value (AOCS Te 1a-64, 1997), FFA (Free Fatty Acid) content, iodine value (AOCS Tg 1-64, 1997), density (D 4052-91), kinematic viscosity (HAAKE rheometer), specific gravity, refractive index (Abbe- refractometer, Atago Company), saponification value (ISO 3657, 1988) and unsaponifiable matter (U.S Pharmacopeia method) of samples were determined according to respective methods. In addition to that properties such as, pour point (Differential Scanning Calorimetry), flash point and fire point (ASTM D92), moisture content (Karl Fisher Titrator, Switzerland),

thermal stability (Thermo Gravimetric Analyzer, TGA851e/LF/1100, Mettler, Switzerland), oxidative stability and calorific value (Bomb Calorimeter-REICO, Kolkata) were estimated according to ASTM and other methods. The detailed procedures of the some important methods are given below.

2.2.9.1. Density (kg/m^3)

The density (ρ) of a material is defined as its mass per unit volume, densities were determined at 25 °C using a specific gravity bottle according to ASTM D4052 method. The values of density are calculated using the following expression:

$$\text{Density (kg/m}^3\text{)} = \frac{\text{Mass (kg)}}{\text{Volume (m}^3\text{)}} \quad \text{.....(2.8)}$$

2.2.9.2. Viscosity

Viscosity of the samples was determined by using HAAKE rheometer (Rheostress RS1, Thermo Electron Corporation) at 40 °C. All the viscosity measurements were done in triplicate at the shear rates of 50, 100, 150 rpm and the average values are reported.

2.2.9.3. Acid value (AV) and free fatty acid content (FFA)

Acid value is defined as the amount of potassium hydroxide (in mg) required for neutralizing 1 g of sample. Half of the AV is always considered as free fatty acid (FFA) content in the sample. AV and FFA content were evaluated according to AOCS official method (Te TA-64, 1997). The acid value is calculated using the following expression:

$$\text{Acid value} = \frac{\text{Volume of the titrant (mL)} \times \text{N} \times 56.1}{\text{Mass of the sample (g)}} \quad \text{.....(2.9)}$$

Where, N is the normality of accurately standardized sodium hydroxide solution.

2.2.9.4. Thermal analysis

Thermal stability profiles of samples were determined by Thermo Gravimetric Analyzer (TGA851e/LF/1100, Mettler, Switzerland). The sample amount about 6-8 mg was placed in an alumina crucible and heated in an inert atmosphere (nitrogen, 40 mL/min) to determine the thermal stability. Conventional heating rate of 10 °C/min was adopted throughout this study and temperature was programmed from room temperature to 700 °C. The onset temperature (thermal stability, OT, °C) was calculated using weight loss versus temperature (°C) plot for each run.

2.2.9.5. Oxidation onset temperature by DSC

Oxidation onset temperatures (OOT, °C) of samples were determined by Differential Scanning Calorimetry (DSC) (DSC 1 star e-system, Mettler Toledo) associated with computer based controller. Typically, sample of less than 10 mg was placed in an aluminium pan which was sealed with a pinhole lid and the sample was heated to 350 °C from ambient temperature, at a heating rate of 5 °C/min. During the analysis, measuring cell was oxidised with air (100 mL/min) and nitrogen gas (40 mL/min) was used as purging gas. A plot of heat flow versus temperature generated from the obtained data was used to determine OOT graphically.

2.2.9.6. Cold flow properties (Pour point)

Pour point of the samples was determined by using aforementioned Differential Scanning Calorimetric technique. Dynamic DSC measurements were carried out in an aluminium crucible with a small variation in sample mass of approximately 6-10 mg and placed in the DSC module with a similar empty pan as reference. The whole process includes cooling and heating steps. During analysis, initially the sample was heated to 50 °C from room temperature and then held under an isothermal condition for 10 min to allow the dissolution and homogenization of the wax material present in the oil. Then after, the system was cooled from 50 °C to -30 °C at a steady cooling rate of 5 °C/min using a refrigeration system (Huber, TC-45, R290 refrigerant USA). In the heating step, the sample was heated from -30 to 40 °C at a heating rate of 5 °C/min. In all the experiments, nitrogen (40 mL/min) was used as purge gas.

2.2.9.7. Calorific value (CV, MJ/kg)

The calorific value (CV) or higher heating value (HHV) can be defined as the energy released in the form of heat when one gram of testing substance undergoes complete combustion with oxygen under standard conditions. The CV was determined according to ASTM D2015-85 standard method. The calorific value is a characteristic of each substance; higher the calorific value, more is the heat energy produced when the unit amount of oil/FAME is burnt.

2.2.9.8. Fatty acid composition

The fatty acid composition of castor oil methyl esters was determined using Gas Chromatography (GC-5765, Nucon, India). A fused silica capillary column (EC-Wax with 0.25 mm internal diameter, 30 m length, and 0.25 µm film thicknesses) was used. The detection system was equipped with a flame ionization detector (FID). The detector temperature was programmed at 250 °C with a flow rate of 2 mL/min. High purity nitrogen gas was used as a carrier gas. The GC analysis was carried out at column temperature program consisted of initial temperature of 160 °C, 2 °C/min from 160 to 230 °C; increasing at 4 °C/min from 230-250 °C and hold for 5 min. The identification of the peaks was achieved by comparing its retention time to the standards retention time analyzed under the same conditions.

2.3. Summary

Present chapter discussed the detailed experimental procedures for castor oil extraction, preparation of FAME, utilization of COME for various purposes and glycerol conversion to solketal. Further, various product confirmation and physico-chemical characterization techniques are also discussed thoroughly.

CHAPTER 3

Studies on extraction of castor oil from castor seeds using various solvents and comparison of their (extracted oils) physico-chemical properties

This chapter addresses the results of research work carried out on the effect of pre-treatment on castor oil yield and its properties, extraction of castor oil from castor seeds by Soxhlet method using polar and non- polar commercial solvents at optimum conditions obtained during preliminary oil extraction study, apart from that oil was also extracted by vial method, an effect of different process parameters such as temperature, solute to solvent ratio and extraction time on extraction efficiency of different solvents were investigated. Further includes discussion on physico-chemical properties of oil extracted using different solvents and the performance of seed pre-treatment (heating of seeds) on oil yield and their properties.

3.1. Preliminary studies in castor oil extraction

The main objective of preliminary study was to find out the optimum conditions for castor oil extraction with different solvents. In the preliminary study, experiments were carried out to extract oil from untreated castor seeds (50 g) using hexane as solvent for extraction period of 8, 10, 12, 14 h at various solute to solvent ratios of 1:3, 1:6 and 1:9. Hexane was chosen as solvent due to its high oil extraction capacity [9, 14, 19, 34, 37]. Extraction time period and solute to solvent ratio were chosen based on the literature

data [12, 21, 26, 27, 73]. The results of preliminary study on castor oil extraction are reported in Table 3.1.

Table 3.1: Castor oil yields obtained in preliminary study with hexane

S. No	Solid/Solvent ratio (wt/vol)	Extraction time (h)	Yield (%)
1	1:3	08	42.73
2	1:3	10	42.89
3	1:3	12	42.98
4	1:3	14	43.97
5	1:6	08	42.73
6	1:6	10	42.23
7	1:6	12	41.97
8	1:6	14	42.85
9	1:9	08	43.14
10	1:9	10	42.66
11	1:9	12	45.83
12	1:9	14	43.79

The obtained optimum conditions obtained were 1:3 (14 h), 1:6 (14 h) and 1:9 (12 h) with highest yield of 43.97, 42.85 and 45.83%, respectively. The study also noticed some interesting results of increased oil yield with increase in extraction period at 1:3 ratio; whereas for 1:6 and 1:9 ratios, oil yield was not consistent with extraction period. This may be due to the change in oil concentration gradient in the solvent during extraction period [12]. Therefore, from the preliminary study, the optimum condition for castor oil extraction using hexane as solvent was found to be solid to solvent ratio, 1:9 and extraction period of 12 h. Hence, the same optimum condition was applied in the

present study to extract oil using different solvents (i.e. polar and non-polar) such as ethyl acetate, isopropanol, methanol, n-hexane, pentane, petroleum ether and cyclohexane.

3.2. Effect of extraction variables on oil yield

Effect of various extraction variables on castor oil yield was studied using different solvents at the optimized conditions obtained in the preliminary study. Pre-treated castor seeds were used in all the experiments.

3.2.1. Effect of solvents

To know the effect of solvent on the oil yield, seven different solvents i.e. hexane, petroleum ether, pentane, cyclohexane, isopropanol, ethyl acetate and methanol were used in this study. The selection of solvents was done on the basis of available literature data [19, 22, 79, 73]. According to Zarnowskiet al., (2004), cyclohexane and ethyl acetate showed satisfactory results in the extraction of resorcinolic lipids from wheat grains [79]. Saxena et al., (2011) have reported that isopropanol has a property of higher solvency in oil [12]. Therefore in the present study, dissimilar solvents (i.e. polar and non polar) were chosen for the extraction purpose and castor oil yields obtained are reported in Table 3.2. From the table, it can be seen that highest oil yield was obtained with ethyl acetate solvent (56.07%, 1:9, 12 h) followed by methanol (55.22%, 1:9, 12 h), and hexane (52.8%, 1:6, 14 h). Similar oil yield was obtained for isopropanol and cyclohexane (52.73%, 1:9, 12 h). From the table, it is also evident that oil yield was lowr by using petroleum ether (50.49%, 1:9, 12 h) and n-pentane (48.6%, 1:6, 14 h) in comparison with other solvents. The highest oil yield was obtained with polar solvents, possibly because of higher percentage of ricinoleic acid in castor seed which enhances the polarity of castor

oil [139]. The oil content obtained in this study was slightly above the range (30-55%) mentioned in the literature [23, 37]. The oil yield obtained with pentane as solvent at 1:3 (14 h) was very less because extractability of the seed oil depends on the nature of solvent and extraction temperature [14].

3.2.2. Effect of solute to solvent ratio

The effect of solute to solvent ratio on oil yield was studied by conducting the experiments at 1:3, 1:6 and 1:9 solute to solvent ratios (seed weight : solvent volume).

Table 3.2: Yields of castor (pre-treated seeds) oil extracted with different solvents

S. No	Solvent	Solute to solvent ratio (wt. /vol.)	Extraction time (h)	Yield (%)
1	n-hexane	1:3	14	47.68
		1:6	14	52.80
		1:9	12	50.46
2	Petroleum Ether	1:3	14	48.06
		1:6	14	48.30
		1:9	12	50.49
3	n-pentane	1:3	14	24.51
		1:6	14	48.60
		1:9	12	45.02
4	Cyclohexane	1:3	14	45.85
		1:6	14	50.27
		1:9	12	52.73
5	Isopropanol	1:3	14	50.01
		1:6	14	47.74
		1:9	12	52.73
6	Ethyl acetate	1:3	14	51.26
		1:6	14	52.56
		1:9	12	56.07
7	Methanol	1:3	14	54.62
		1:6	14	53.16
		1:9	12	55.22

***Note*:** 20 g of seed sample taken for 1:6 and 1:9 solutes to solvent ratios and 40 g sample for 1:3 ratio

The oil yield was found to be increased with an increase in the solute to solvent ratio for petroleum ether, cyclohexane and ethyl acetate (Table 3.2). The maximum oil recovery was achieved with solvents such as petroleum ether, cyclohexane, isopropanol, ethyl acetate and methanol at 1:9 solute to solvent ratio for 12 h extraction time compared to other two ratios 1:3 (14 h) and 1:6 (14 h). This may be because at lower solute to solvent ratio, the oil extraction might be restricted due to the lower solubility limit of oil in the solvent.

3.2.3. Effect of extraction time

The extraction time is an important parameter for solvent extraction and which helps in deciding the optimum residence time required in extractor. The effect of extraction time on the yield was studied by conducting experiments at optimum extraction time period i.e. 14 h (1:3), 14 h (1:6) and 12 h (1:9). The maximum oil yield was obtained at 1:9 solute to solvent ratio and extraction period of 12 h compared to other extraction conditions for solvents such as petroleum ether, cyclohexane, isopropanol, ethyl acetate and methanol. The higher extraction rate for 12 h may be due to high solubility of oil at the beginning of extraction, since low oil concentration in the fresh solvent. Further increase in the extraction time to 14 h decreased the oil yield, because of slower extraction rate attained with increased concentration in the solvent [12].

3.3. Properties of castor oil extracted with different solvents

The type of solvent used in the extraction influences the properties of extracted oil [24]. The physico-chemical properties of castor oil extracted with different solvents are shown in Table 3.3. Specific gravity of all the oil samples was evaluated using standard

technique. The specific gravity of all the oil samples was in the range of 0.940-0.991 (Table 3.3). Refractive index of the oil extracted with all solvents was found to be 1.475. The refractive index values were well coordinated with the available literature data and indicate the presence of long unsaturated fatty acids in the extracted oil [140]. The refractive index of oil depends on their molecular mass, fatty acid chain length, degree of unsaturation and degree of conjugation. It is a significant parameter for biodiesel during its cloudy state [141]. Density of castor oil was determined according to ASTM standard method as mentioned in previous chapter (Section 2.2.9). Density was found to be higher value of 0.976 g/cm^3 for castor oil extracted with hexane and lower value of 0.925 g/cm^3 for ethyl acetate extracted oil (Table 3.3). Acid value is another important parameter which quantifies the fatty acid content in oil. Acid value is the amount of potassium hydroxide required to neutralize the free acid groups in oil [19]. Acid value was found to be lower (0.925 mg KOH/g) for oil extracted with methanol and higher (4.7 mg KOH/g) for oil extracted by using ethyl acetate compared to that of other solvents. FFA content is the half of the acid value and it has great control over the quality of oil. Oil with lower FFA content is important for the optimal results in transesterification [33]. High FFAs level in the oil increases risk of oil oxidation [19]. The FFA content of oil extracted with all the solvents was found to be lower (<2.5) which is desirable for biodiesel production in a single step using alkali catalyst. The oil with higher FFA content requires purification process or pre-treatment steps to reduce acidity [9, 142].

Table 3.3: Properties of castor oil extracted with different solvents

S. No.	Property	Hexane	Petroleum ether	Pentane	Ethyl acetate	Cyclo hexane	Isopropanol	Methanol
1	Density (g/cm^3)	0.976	0.944	0.937	0.925	0.947	0.959	0.948
2	Specific gravity	0.991	0.959	0.952	0.940	0.962	0.974	0.963
3	Kinematic viscosity at 40 °C (cSt)	230	288	251	207	237	239	259
4	Acid value (mg KOH/g)	2.71	3.08	4.4	4.7	2.76	1.12	0.925
5	FFA (mg KOH/g)	1.35	1.54	2.2	2.35	1.38	0.56	0.462
6	Saponification value (mg KOH/g)	176.38	171.15	175.11	152.87	180.38	176.79	171.04
7	Un saponifiable matter (wt %)	0.39	0.38	1.3	0.19	0.4	0.6	0.59
8	Iodine value (I_2/100g)	84.93	85.55	82.53	73.21	85	70.5	72.86
9	Refractive index	1.475	1.475	1.475	1.475	1.475	1.476	1.475

Thus purification can be avoided for oil with low FFA. Iodine value is the measure of unsaturated fatty acids content in the oil. It gives the drying property of oil [9]. The iodine value range (70.5-85.5 gI_2/100g of oil) obtained in this work was found to less than 100 (Table 3.3). This indicates that castor oil is non-drying oil and can be widely used as lubricant and hydraulic brake fluid [37]. The saponification values of oil samples agrees well with the values reported in literature and found to be in the range of 123-185 mg KOH/g [13, 143]. Saponification of oil is a side reaction during transesterification, which will be favoured at higher temperature and catalyst concentration which leads to soap formation and consequently decreases the biodiesel yield [144]. The formation of unsaponifiable matter is due to the presence of sterols, hydrocarbons, tocopherols and, pigments [145]. The percentage of unsaponifiable matter in the extracted oil samples was within the expected range of below 0.6%.

3.3.1. Viscosity

Viscosity is defined as the fluid offers resistance to flow when a shear stress is applied. It is an important property of oil that represents the flow characteristics of oil [146]. It is a function of temperature which decreases with increase in temperature. Kinematic viscosities of castor oil extracted with all solvents were almost similar and agrees well with the values (240-300 cSt) reported in literature [147]. The higher viscosity of oils is mainly due to the presence of hydroxyl groups. This high viscosity makes the oil suitable as ingredient in blending of lubricants [13].

3.4. Colour and odour of oil

The colour and odour of the extracted oils were determined through physical appearance. The colour of the oil extracted with non-polar solvents is pale yellow which agrees well with the literature [37]. Colour of the oil extracted with polar solvents methanol, isopropanol and ethyl acetate was little darker and disagreeable odour than the oil extracted with non-polar solvents, i.e., hexane, pentane, cyclohexane and petroleum ether (Figure 3.1). Saxenaet al., (2011) reported that cotton seed oil extracted with ethanol was darker than the oil extracted with hexane [12]. This dark colour of oil may be due to the extraction process [69] or due to the presence of hydroxyl groups and natural pigments (carotenoids, tocopherols and its derivatives) [15, 14]. However, it was reported that colour of the oil is not important in any applications except in pigmented coatings [9].

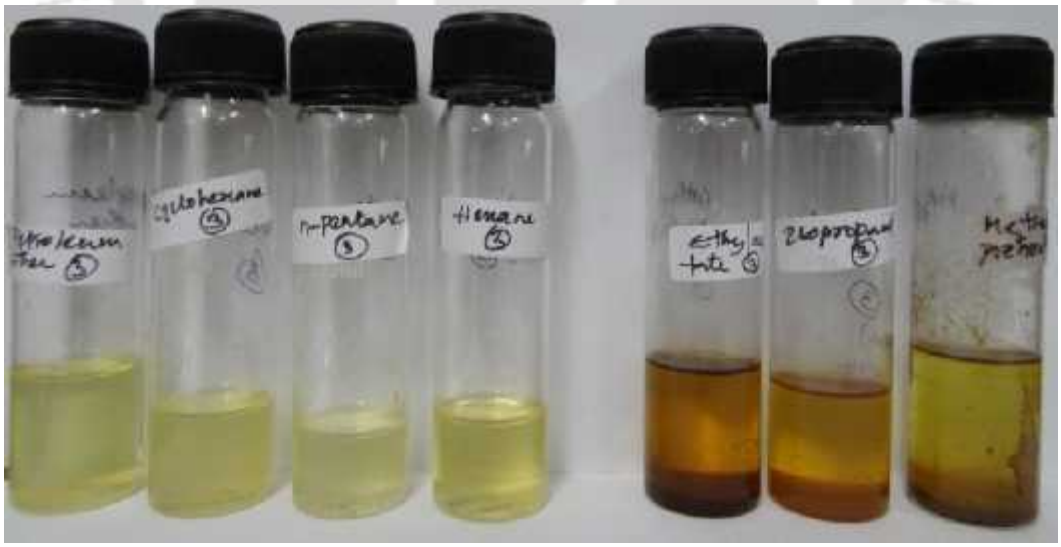


Figure 3.1: Castor oil samples extracted with non-polar (left 4) and polar solvents (right 3)

3.5. Effect of pre- treatment on oil yield and physico-chemical properties

The effect of seed pre- treatment on oil yield and its properties was studied by extracting the oil from untreated and pre-treated castor seeds with methanol as solvent. The oil content of seed was also determined by vial method. The oil content estimated by vial method for a single castor seed was found to be 56.2 % (0.112 g oil/0.199 g single seed) which is comparable to the oil yield of 55.2% (11.04 g oil/ 20 g seed) obtained by Soxhlet method.

3.5.1. Effect of pre-treatment on oil yield

The effect of seed pre-treatment on oil yield was studied by extracting the oil from untreated and pre-treated castor seeds using methanol as solvent (Table 3.3). The oil yield obtained from untreated and pre-treated seeds using methanol as solvent was almost same with difference of only 1%. The results obtained in the present study did not compare favorably with earlier reported literature in oil expression [16]. Olaniyan (2010) during his study on effect of extraction conditions on the yield and quality of mechanically expelled oil from castor bean has reported that castor oil yield was increased from 18.22% to 30.35% when the heating temperature of seed was increased from 30 to 90 °C [14]. The difference in the results may be due to the method of extraction used; in their study oil was expelled mechanically, whereas in the present study Soxhlet method was used for oil extraction.

3.5.2. Effect of pre-treatment on oil properties

The properties of castor oil samples extracted with methanol using untreated and pre-treated seeds are shown in Table 3.4.

Table 3.4: Properties of castor oil extracted by methanol before and after heat-treatment of seeds

S. No	Property	Before pretreatment	After pretreatment
1	Oil yield at 1:9 (12 h)	54	55
2	Density (g/cm^3)	0.945	0.948
3	Specific gravity	0.960	0.963
4	Kinematic viscosity at 40 °C (cSt)	297	259
5	Acid value (mg KOH/g)	3.92	0.925
6	Saponification value (mg KOH/g)	168.52	171.04
7	Unsaponifiable matter (wt %)	0.28	0.59
8	FFA (mg KOH/g)	1.96	0.462
9	Iodine value (g I_2/100 g of oil)	69.74	72.86
10	Moisture content (wt %)	0.12	0.06
11	Refractive index at 23 °C	1.477	1.475
12	Pour point (°C)	-15	-21
13	Flash point (°C)	298	300
14	Fire point (°C)	308	308
15	Calorific value (MJ/kg)	39.67	38.21
16	Thermal stability (°C)	340	340
17	Oxidative stability onset temperature (°C)	200	199.9

The pre-treatment of seeds resulted in slight increase in the iodine value, saponification value of oil, and decrease in its viscosity. These results compare favorably with the reported literature on mechanical oil extraction from castor beans [16]. From the table, it can be also noticed that acid value (0.925) and pour point (-21) were decreased for the oil extracted from pre-treated seeds compared to that of untreated seeds. Olaniyan (2010) in his study reported that increase in the temperature of seeds was resulted in the free fatty acid content increase. However, the results obtained in the present work follows

opposite trend compared to the reported literature. The decrease in FFA content of oil on pre-treatment of seeds may be due to poor interactions of hydroxyl and carboxylic acid groups of the fatty acid molecules with the hydroxyl group in the methanol [14]. Moisture content is another important parameter which influences the storage life of oil. The moisture acts as a medium for microbial growth in oil which may lead to the damage of tank and emulsion formation [140]. The moisture content of castor oil samples extracted using methanol from untreated and after pre-treated seeds was found to be 0.12% and 0.06%, respectively (Table 3.4). This was very low compared to the moisture content (0.15-0.3%) of castor oil extracted by pressing [147]. The minimum moisture content is desirable in transesterification process for biodiesel production. Higher flash point indicates the greater safety during flammable transport and storage [33]. The flash and fire points for the two oil samples are shown in Table 3.4. The obtained calorific values for untreated and pre-treated oil samples were found to be 39.67 and 38.21 MJ/kg (Table 3.4). These values agreed well with the literature value range of 37.2-39.5 MJ/kg reported by Scholz and Silva [147].

3.5.3. Thermal stability

Thermal stability of castor oil samples (extracted with methanol as solvent from untreated and pre- treated seeds) was determined from the onset temperature of thermal decomposition under nitrogen atmosphere (Figure 3.2). From the obtained TGA profiles, it can be observed that thermal decomposition of oil samples took place in three consecutive stages. The first phase of decomposition was started at 340 °C (for both) and the second phase extended up to 515 °C (untreated sample) and 525 °C (pre-treated sample) which lead to rapid weight loss. The final stage of decomposition where

pyrolyzed product of second phase fully decomposed was extended from 515 to 683 °C for untreated sample and 525-690 °C for pre-treated sample, respectively. The starting stage of decomposition was same for the both samples with slight difference in the extension of decomposition and pyrolysis stages. Decomposition of two samples was started at the same temperature may be due to almost equal percentage of moisture content in both the oil samples [140]. The TGA curve for pre-treated sample showed slower degradation compared to untreated sample. From the reported literature, it was noticed that slower degradation was due to higher viscosity of pre-treated oil compared to its untreated oil [140].

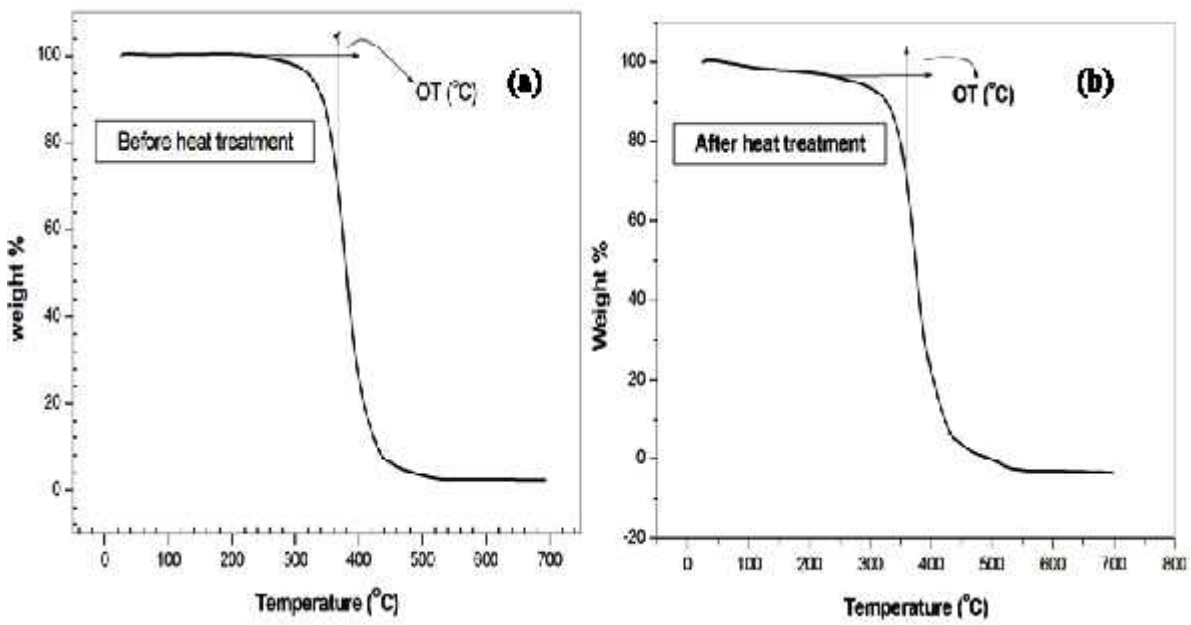


Figure 3.2: TGA curves for castor oil extracted with methanol (a) Before heat treatment of seeds (b) after heat treatment of seeds

3.5.4. Evaluation of oxidative stability

Oxidative stability is defined as the resistance of oil to oxidation. Oxidation decreases the shelf life of oil [148]. DSC is the thermal analysis equipment which gives

the change of physical properties of sample with temperature against heat flow [149]. Most of the reported literature on oxidative stability estimation was carried out using rancimat method which includes oxidation induction time.

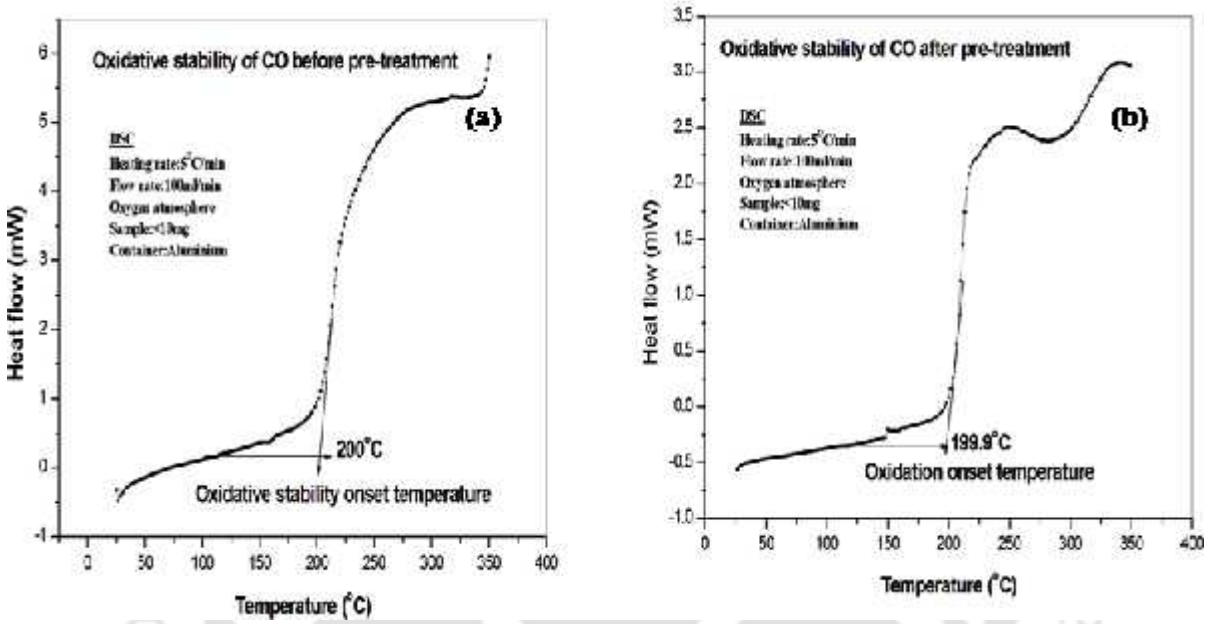


Figure 3.3: DSC -Oxidative stability of castor oil extracted with methanol (a) before heat treatment of seeds (b) after heat treatment of seeds

But in the present work, oxidative stability was determined in air atmosphere by DSC thermal analysis. Oxidation Onset Temperature (OOT) is defined as the temperature at which rapid increase in oxidation rate takes place which is obtained by extrapolation of tangent line drawn to the steepest gradient of the reaction exotherm of heat flow versus temperature plot [150]. DSC plot of castor oil extracted with methanol from untreated and pre-treated seeds are shown in Figure 3.3. The corresponding OOT values were found to be 199 °C and 200 °C, respectively. From the analysis, similar decomposition pattern and equal onset temperatures were noticed for both the samples. Sruthi et al., (2013) found the oxidative stability onset temperature of castor oil as 230 °C using TGA method under air

atmosphere. The value estimated during their study (i.e. 230 °C) was significantly higher than the obtained onset temperature values in the present work (≈200 °C). This can be justified by difference in the viscosity of oil samples. The viscosity of oil in the reported literature [148] was found to be higher than the values obtained in the present work.

3.5.5. Cold flow properties (pour point)

The cold flow properties (cloud point and pour point) of castor oil make the bio fuel an outstanding alternative in the cold climatic conditions [33]. Pour point is the lowest temperature at which oil ceases to flow when it is cooled [151].

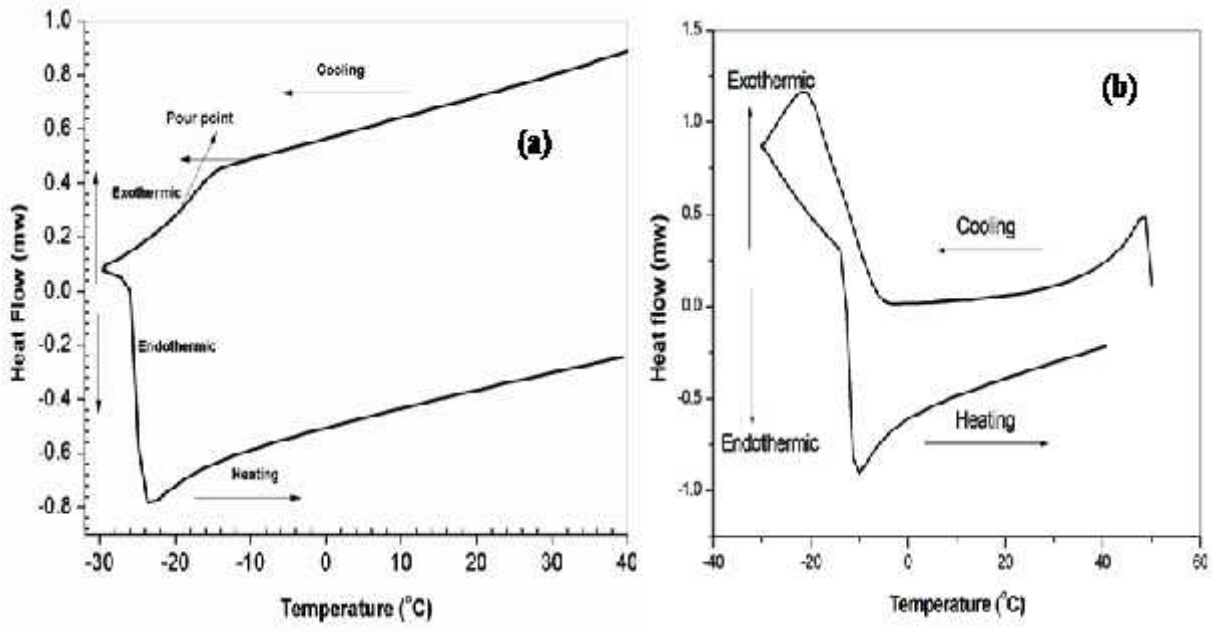


Figure 3.4: DSC –Cooling thermo grams of castor oil extracted with methanol (a) before heat treatment of seeds (b) after heat treatment of seeds

The DSC thermo grams of castor oil samples (untreated and pre-treated) extracted by using methanol are shown in Figure 3.4. The lower pour points of -15 °C and -21 °C were obtained for the untreated and pre-treated samples (Table 3.4). The lowest pour

points were due to less percentage of saturated fatty acid content and high percentage of ricinoleic acid, while the same can be justified by the fatty acid composition reported in Table 3.4. Since ricinoleic acid interrupts the crystallization process, consequently there is a delay in the crystals growth process. Moreover, the pour point obtained for pre-treated sample agrees well with the values reported in the literature [151, 152].

3.6. ^{1}H NMR analysis

^{1}HNMR (Nuclear magnetic resonance) spectroscopy was employed for two castor oil samples extracted using methanol. Figure 3.5 represents the ^{1}H NMR spectra of castor oil extracted using methanol from untreated and pre-treated seeds, respectively. In the ^{1}H NMR spectra of both samples, similar multiple peaks were observed in the region δ 3.4-3.6 ppm (-OH), δ 4.11-4.35 ppm (-CHOCOR), and δ 5.2-5.6 ppm (-CH=CH-) [153]. With the help of literature, region 4.2 ppm was identified as glyceryl protons of triglycerides. The entire castor oil contains 90% triglycerides of ricinoleic acid. It was difficult to differentiate the chemical shifts related to the protons of ricinoleic acid present in oil such as MGs (Mono Glycerides) and DGs (Di Glycerides) which were present in small amount (10%) [142].

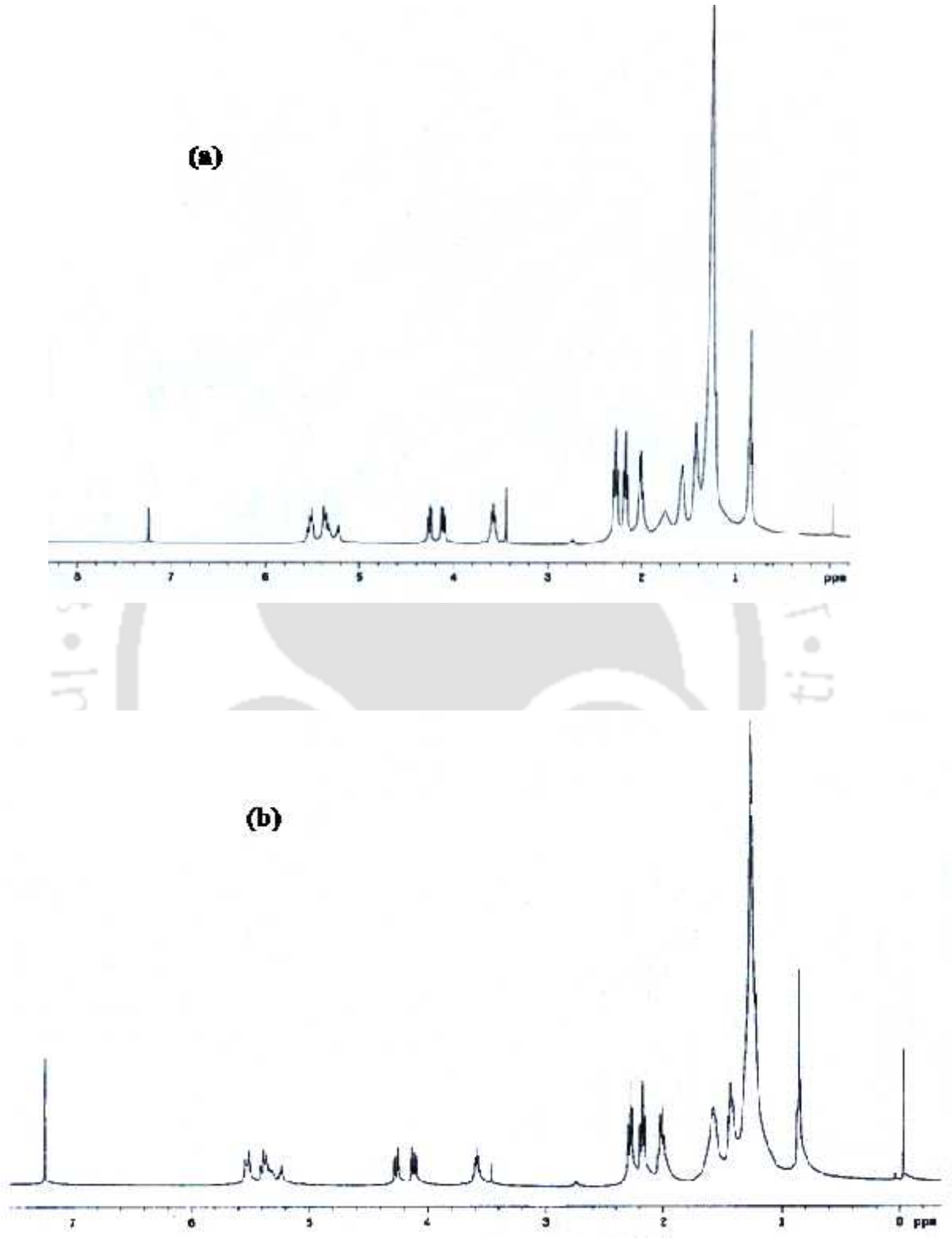


Figure 3.5: ^{1}H NMR spectra of castor oil extracted with methanol (a) before heat treatment of seeds (b) after heat treatment of seeds

3.7. Fatty acid compositions

The fatty acid composition of extracted castor oil was determined by GC and reported in Table 3.5. The major fatty acid present in castor oil composition was ricinoleic acid (84%), this mono-unsaturated acid (ricinoleic acid) has effect on oxidative stability of oil. Unsaturated fatty acids are responsible for oil stability, because chemical reactions mainly occur at double bonds. The rate of oxidation is directly proportional to the number of double bonds present in the carbon chain. The oils with high oleic acid content are more stable and less susceptible to oxidation. [21]. The other fatty acids content of castor oil were palmitic (1.4%), stearic (1.8%), oleic (4%), linoleic (6%) and, linolenic (0.6%). The composition obtained in this work is close to the reported literature data [154, 155, 156].

Table 3.5: Fatty acid compositions of the castor oil

Fatty acid	Content (wt %)
Palmitic (C16:0)	1.4
Stearic (C18:0)	1.8
Oleic (C18:1)	4
Linoleic (C18:2)	6
Linolenic (C18:3)	0.6
Ricinoleic (C18:1-OH)	84

3.8. Summary

In this chapter, an effect of pre-treatment on oil extraction, preliminary studies of castor oil extraction and physico-chemical properties of castor oil extracted using different solvents have been outlined. From the study, it is revealed that polar solvents such as ethyl acetate and methanol gave higher castor oil yield about 55-56% by Soxhlet extraction method and other solvents also extracted appreciable amount of oil. The oil content estimated by vial method for a single castor seed was found to be 56.2 % (0.112 g oil/0.199 g single seed) which is comparable to the oil yield of 55.2% (11.04 g oil/ 20 g seed) found by Soxhlet method. The acid value of an oil extracted using methanol as solvent was found to be low compared to oil extracted with other solvents. Low FFA (0.92 mg KOH/g) and pour point (-21 °C) of the oil were achieved through heat treatment of seeds before extraction. No significant differences were found in the properties of castor oil extracted from untreated and pre-treated seeds. Therefore, from the study on oil extraction and its characterization, it was noticed that low FFA value of castor oil extracted using methanol as solvent indicates that oil can be used for single step transesterification. Since methanol showed higher oil yield with low FFA content, this can be act as a highly desirable solvent for the reactive extraction and transesterification of castor seed in a single step. Therefore, the next chapter deals with direct biodiesel production by *In situ* transesterification of castor seeds using methanol as extracting solvent and transesterification reagent in order to reduce the processing time compared to conventional method.

CHAPTER 4

Optimization of reactive extraction of castor seeds using base catalysts for the production of castor oil methyl esters (COME) by integrated and non-integrated approach

This chapter discusses the results obtained from the work done on optimization of reactive extraction of castor seeds by an integrated and non-integrated approach using base catalysts. The primary section of the chapter discussed ANOVA (analysis of variance) and the impact of process variables to maximize COME (castor oil methyl ester) conversion. Further, the significant physic-chemical properties of COME were estimated at an optimum condition and compared with ASTM standards. As storage conditions have significant effect on COME, an evaluation of the storage stability of COME was carried out for a storage period of 6 months. The biodegradability analysis of COME, engine performance test of COME and its blends with diesel were also investigated. Further includes discussion on the various estimated properties of the methyl ester, its blends and summary.

4.1. Optimization of reactive extraction of castor seeds

Optimization of reactive extraction of castor seed was carried out by a integrated and non-integrated approach using RSM design technique. The results are discussed in the following sections.

4.1.1. Optimization of reactive extraction of castor seeds by integrated approach

4.1.1.1. Preliminary studies in reactive extraction

In order to optimize the reactive extraction process, a single parameter optimisation technique was followed. Madankar et al., (2013) have carried out reactive extraction of castor seeds by a non-integrated approach using KOH as a catalyst [86]. Although, the paper has experimental rigor using non-integrated approach, no attempt has been made by author to explore the reactive extraction by an integrated approach. The current study investigates reactive extraction of castor seeds by a integrated approach using KOH as a catalyst. Castor seed was selected as a feedstock for the study because of its several advantages such as cheap, non-edible and resistant to grow in drought conditions and cultivated mainly in India [86]. Most of the literature published in the area of reactive extraction employs higher oil/alcohol molar ratios to achieve higher conversions. Therefore, in the present study higher molar ratios (1:400-1:550 oil/methanol) are used. Relatively acid catalysed transesterification is slower than alkali catalyst; hence reactions were performed with alkali as a catalyst. The influence of six parameters such as reaction time, oil to methanol molar ratio, catalyst concentration, seed quantity, mixing speed and volume percentage of co-solvent on the reactive extraction of castor seeds were studied and the results of COME yields and conversions are presented in Table 4.1. From the table, it can be observed that among the studied parameters, reaction time, oil to methanol molar ratio and catalyst concentration showed significant effect on the process compared to other variables such as seed quantity, mixing speed and co-solvent percentage. The optimization parameters for the reactive extraction process (integrated) were time 9 h, 1:450 molar ratio, 1.5 wt % catalyst concentration, 20 g seed quantity, 1000 rpm and 5 vol % of co-solvent. At this optimum condition maximum,

COME conversion was found to be 95%. The results of this preliminary study were used as a basis to further optimize the process by RSM design technique.

Table 4.1: COME yields and conversions obtained for the list of preliminary experiments conducted with the respective parameters setting

Reaction time (h)	Oil to methanol molar ratio	Catalyst concentration (wt % of oil content of seed)	Seed quantity (g)	Mixing speed (rpm)	Co-solvent (vol % of alcohol)	COME Yield (%)	COME Conversion (%)
6	1:450	1	20	1000	-	65.15	89.28
9	1:450	1	20	1000	-	67.34	91.8
12	1:450	1	20	1000	-	70.08	87.13
15	1:450	1	20	1000	-	71.15	76.25
9	1:400	1	20	1000	-	64.13	84.75
9	1:450	1	20	1000	-	67.34	91.8
9	1:500	1	20	1000	-	68.13	82.64
9	1:550	1	20	1000	-	70.08	80.25
9	1:450	0.5	20	1000	-	61.82	91.37
9	1:450	1	20	1000	-	65.15	91.8
9	1:450	1.5	20	1000	-	71.36	95.07
9	1:450	2	20	1000	-	72.21	92.76
9	1:450	1.5	15	1000	-	65.61	94.54
9	1:450	1.5	20	1000	-	71.36	95.07
9	1:450	1.5	25	1000	-	74.22	95.36
9	1:450	1.5	20	600	-	65.68	94.7
9	1:450	1.5	20	1000	-	71.36	95.07
9	1:450	1.5	20	1200	-	72.42	93.73
9	1:450	1.5	10	600	5	70.66	95.03
9	1:450	1.5	15	600	10	72.44	94.37
9	1:450	1.5	20	600	15	74.57	93.39

4.1.1.2. Model fitting

According to the central composite design (CCD), total twenty experiments were performed in order to find out the optimum combination and study the effect of process parameters on FAME content using the reactive extraction process and the results are given in Table 4.2.

Table 4.2: Experimental Design matrix by CCD technique for reactive extraction

Run No	A: Time (h)	B:Oil to methanol molar ratio	C: Catalyst Concentration (wt %)	COME Conversion (%)
1	9	450	2.34	85.94
2	9	450	1.5	95.07
3	9	450	1.5	95.07
4	3.95	450	1.5	95.79
5	6	500	1	90.98
6	9	450	0.65	81.22
7	9	365.9	1.5	96.04
8	12	400	1	88.92
9	9	534	1.5	96.48
10	9	450	1.5	95.07
11	14	450	1.5	95.98
12	12	500	2	95.92
13	12	500	1	88.94
14	9	450	1.5	95.07
15	9	450	1.5	95.07
16	9	450	1.5	95.07
17	6	400	1	96.85
18	6	500	2	93.23
19	12	400	2	95.68
20	6	400	2	91.21

The regression mathematical model was tested for statistical significance using the analysis of variance (ANOVA) and results are presented in Table 4.3.

Table 4.3: ANOVA for response surface quadratic model

Source	Sum of squares	df	Mean square	F value	p- value
Model	310.43	9	34.49	28.15	< 0.0001
A-Time	0.45	1	0.45	0.37	0.5562
B-Molar ratio	0.59	1	0.59	0.48	0.5018
C-Catalyst conc.	24.48	1	24.48	19.99	0.0012
AB	2.11	1	2.11	1.72	0.2185
AC	36.67	1	36.67	29.94	0.0003
BC	8.22	1	8.22	6.71	0.0269
A^2	3.58	1	3.58	2.93	0.1177
B^2	5.75	1	5.75	4.69	0.0555
C^2	213.76	1	213.76	174.51	< 0.0001
Residual	12.24	10	1.22		

C.V: 1.18%, R^2_{model}: 0.96, R^2_{adj} : 0.927, predicted R^2_{model}: 0.9

The AOVA of the quadratic regression model has demonstrated that the model is significant with a low probability value ($p < 0.0001$). The coefficient of determination is another (R^2) measure of significance of regression i.e. R^2 = 96%, which indicates that more than 96% of the experimental data were compatible and only 4.0% of the total variation was not explained by the model. A high value of predicted R^2 (0.9) is an indication of accuracy of the fitted model. The more the value of R^2 approaches to 1, the better the model fits an experimental data. The use of an adjusted coefficient of

determination (adj-R^2) is to estimate the model accuracy fitness as well as to correct the coefficient of determination value for the sample size and for the number of terms in the model. The high value of the coefficient of determination (adj-R^2: 0.92) represents the significance of the model. The value of coefficient of variation (CV) was low as 1.18 %, there by indicates the reliability of the fitted model (experimental and predicted values) results [157]. Moreover, p-values are used to check the significance of the corresponding coefficient. Smaller the p-values are, bigger the significance of the corresponding coefficient. In the present study, p-value of the model (found by ANOVA) was 0.001 which indicates that the model terms are significant. In this case, A (reaction time), B (oil to methanol molar ratio), C (catalyst concentration), interaction effects of AC (reaction time with catalyst concentration), BC (oil to methanol molar ratio with catalyst concentration) and quadratic effects of A^2 (time), B^2 (oil to methanol molar ratio), C^2 (catalyst concentration) have shown significant effect on the COME conversion in the range of these parameters considered in this study.The regression equation for the determination of predicted values of output parameter in terms of coded factors are as follows (i.e., COME in this study):

$$\text{COME conversion (\%)} = 95.03 - 0.18A - 0.2B + 1.33C + 0.5AB + 2.14AC + 1BC + 0.49A^2 + 0.63B^2 - 3.8C^2 \quad \text{.....(4.1)}$$

The graph between the predicted versus actual COME conversion (%) and the plot of perturbation given in Figure 4.1 (a) and (b) indicates that the predicted values are quite close to the experimental values and there by confirming the persistence of the model developed for establishing a correlation between the process variables and the COME conversion.

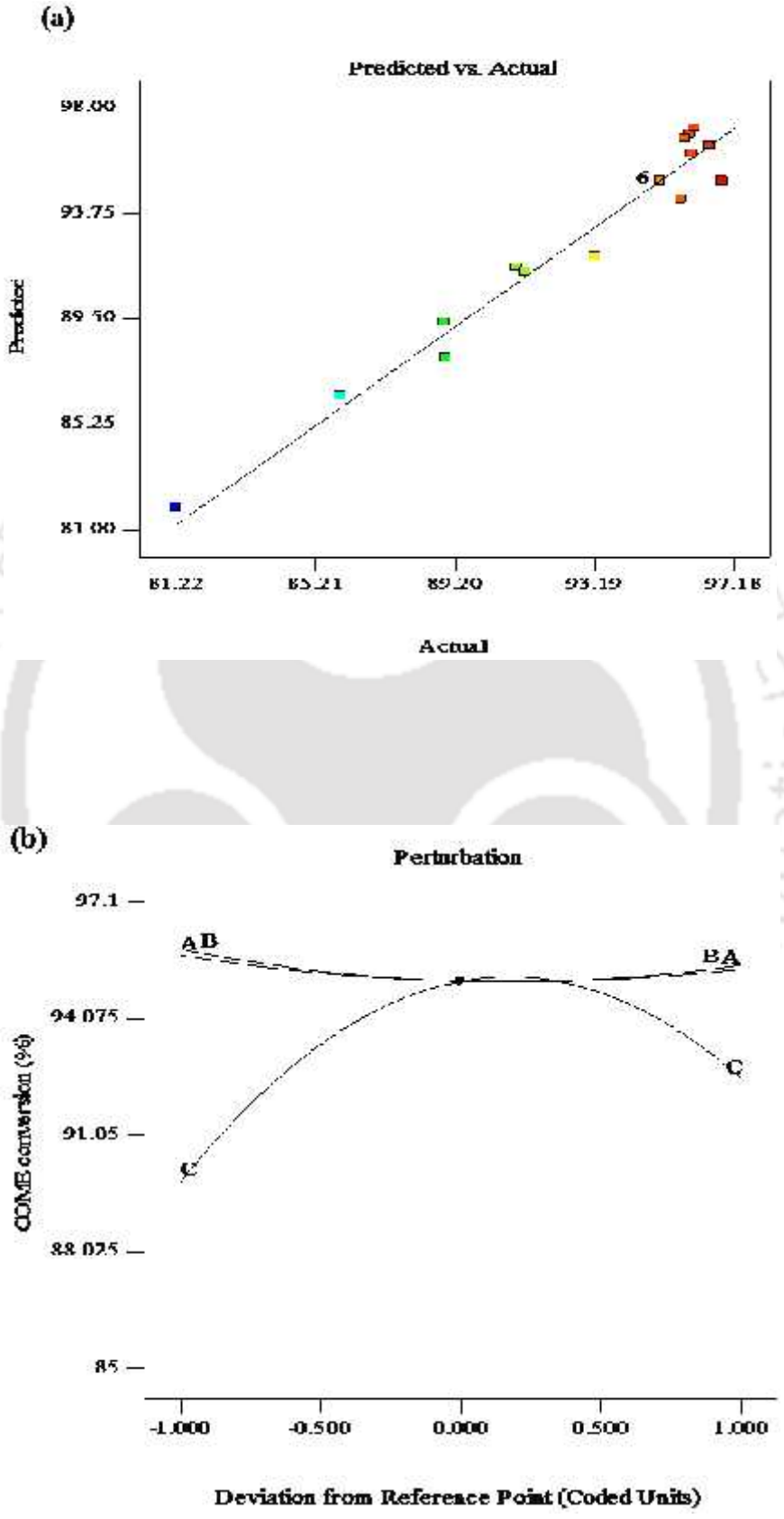
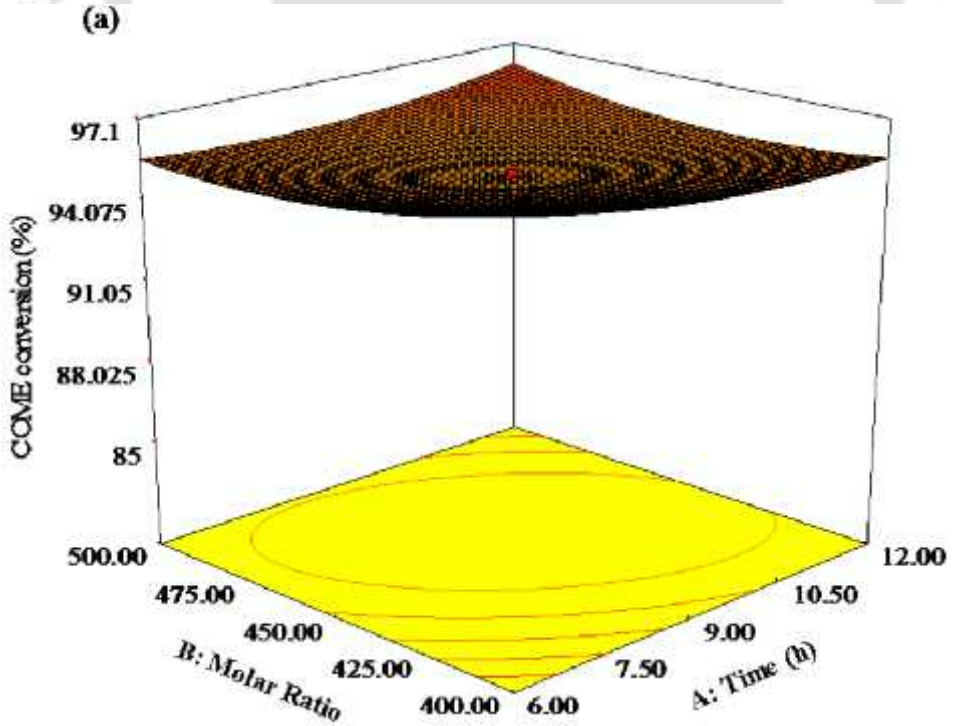


Figure 4.1: (a) Predicted versus actual COME conversion (%) values (b) Perturbation

4.1.1.3. Interactions between process variables

The response surface and contour plot indicates the interactive affect of any two process variables on the COME conversion (Figure 4.2, Figure 4.3, Figure 4.4). The contour plots essentially are graphical representation of the regression equation (4.1). The plots represent interaction effects between the independent and dependent variables for fixed parameters as shown in Figure 4.2, Figure 4.3 and Figure 4.4. The interaction of reaction time and oil/methanol molar ratio on the COME conversion at 1.5 wt % catalyst concentration, 1000 rpm and reaction temperature of 65 °C are shown in Figure 4.2.



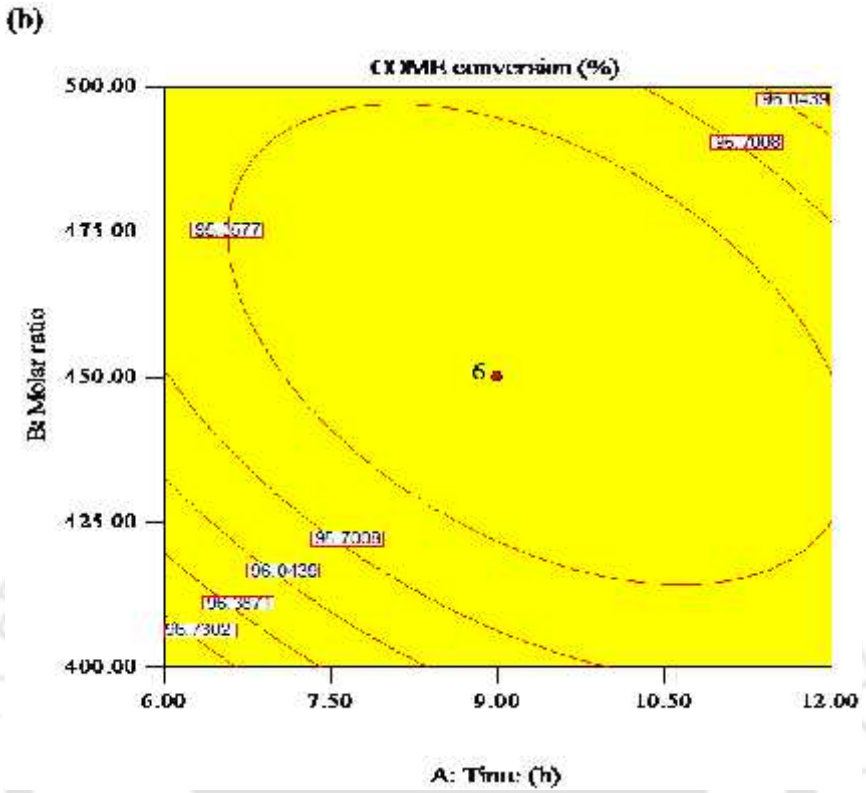
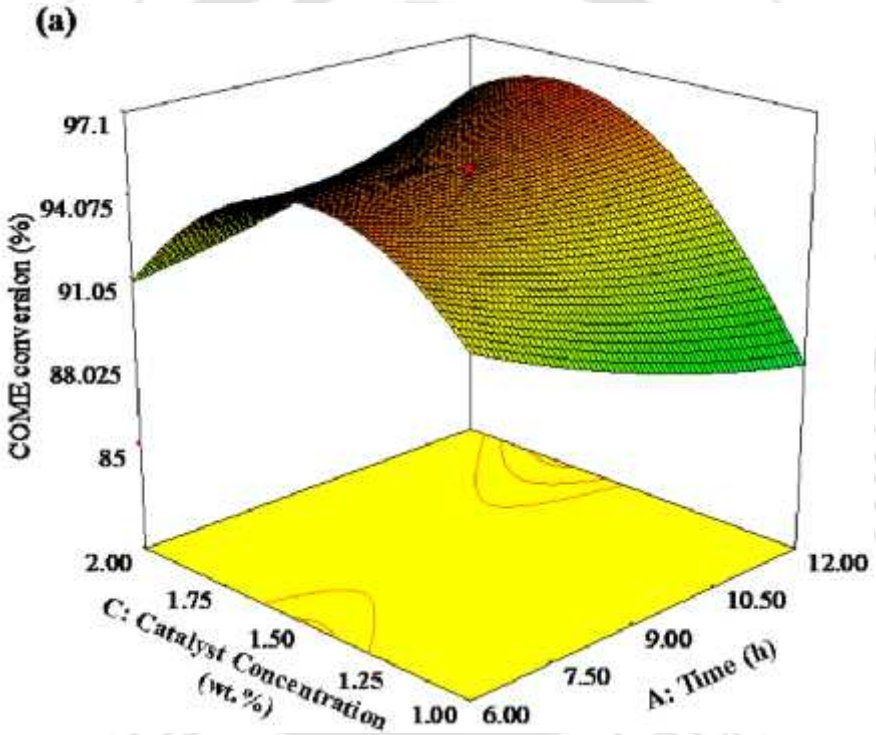


Figure 4.2: Effect of reaction time and oil/methanol molar ratio on COME conversion at 1.5 wt % catalyst and 65 °C temperature: (a) Response surface plot; (b) Contour plot

Increase in the molar ratio and reaction time shown insignificant effect on COME conversion. The optimum conversion of COME was obtained by using oil/methanol ratio of 1:400 for 6.3 h. This shows that reactive extraction can decrease the time required for biodiesel production from oil bearing material compared to the conventional method and thus eventually decrease the price of biodiesel production [158].

Figure 4.3 (a) and (b) establishes the interaction of reaction time and catalyst concentration on the COME conversion at 400 oil/methanol molar ratio, 1000 rpm, 65 °C and indicates that the COME conversion increased with an increase in the catalyst concentration up to 1.5 wt % and decreased thereafter. Whereas, increasing of reaction time results in decreased COME conversion. This may be due to the formation of soap

with increasing reaction time and simultaneous increase in catalyst concentration [130]. The combined interaction effect of catalyst concentration and time shows the saddle trend (raised at front and rear). However, an optimum conversion was obtained at 6.3 h with 1.5 wt % catalyst concentration.



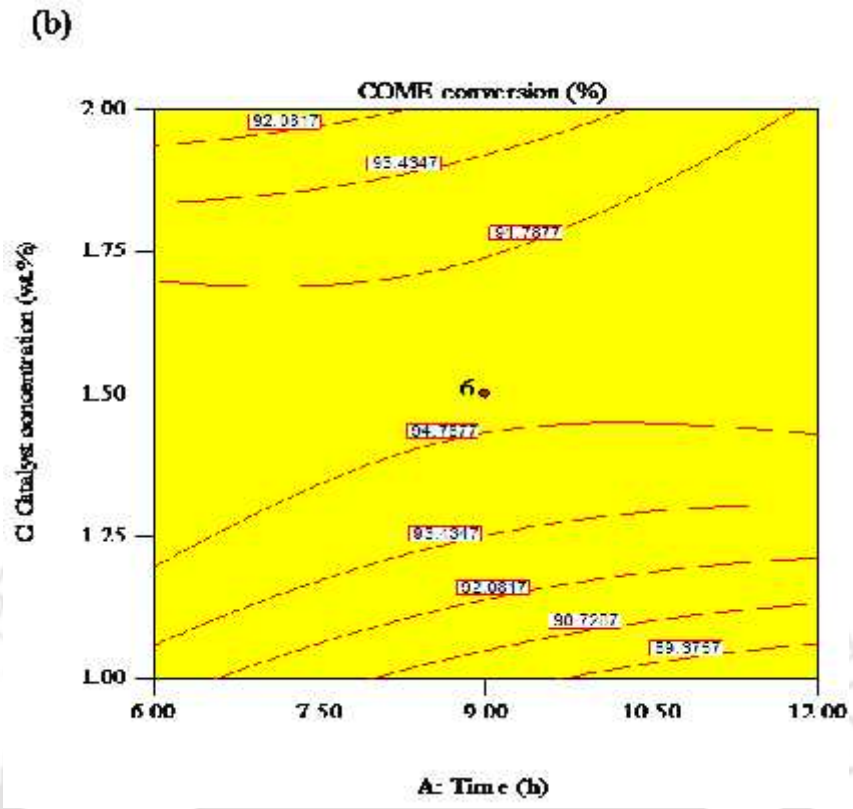


Figure 4.3: Effect of reaction time and catalyst concentration on COME conversion at 1:400 molar ratio and 65 °C temperature: (a) Response surface plot; (b) Contour plot

Figure 4.4 (a) and (b) shows the interaction of oil/methanol molar ratio and catalyst concentration on COME conversion at 6 h, 1000 rpm and 65 °C. From the plot, it can be seen that oil/methanol molar ratio practically had insignificant effect on COME conversion and these results are analogous to the result reported by Goyal et al., (2012), whereas in case of catalyst concentration opposite trend was observed [157]. The conversion of COME substantially increased up to a certain level, beyond which further increase in the concentration of the catalyst results in the formation of soap and gel which significantly reduces the COME conversion.

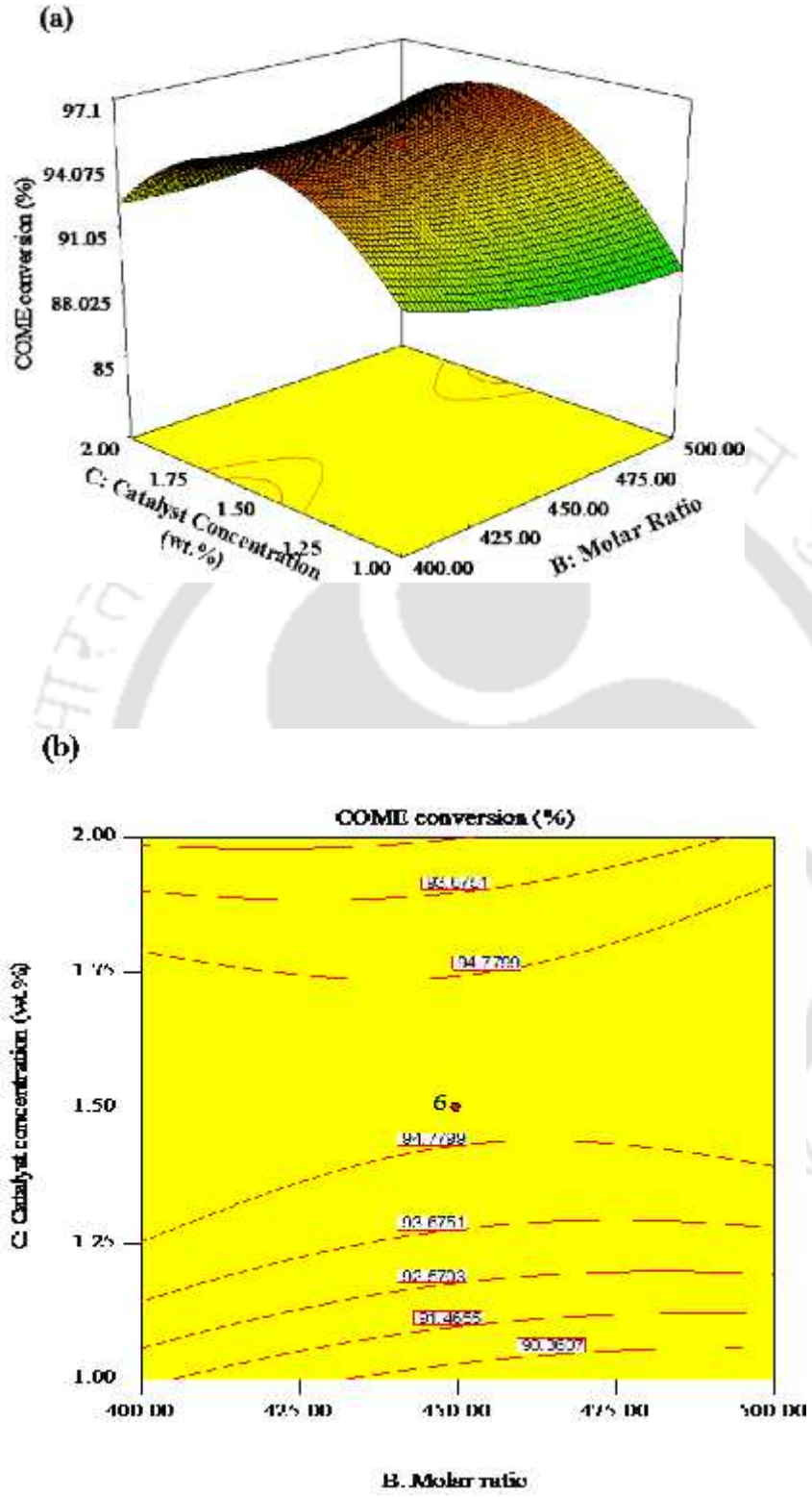


Figure 4.4: Effect of oil/methanol molar ratio and catalyst concentration on COME conversion at 6 h time and 65 °C temperature: (a) Response surface; (b) Contour plot

This is because, side reaction called saponification occurs during reactive extraction in the presence of higher catalyst concentration [7]. The combined effect of oil/methanol molar ratio and catalyst concentration on the COME conversion was found saddle trend which is similar to that of interaction effect of reaction time and catalyst concentration. The optimum conversion was found at 1:400 oil/methanol molar ratio and 1.5 wt % catalyst concentration

4.1.1.4. Optimization of process parameters

After regression analysis, optimization study was performed based on the desirability function to determine the optimal synthesis conditions for maximum COME conversion. The optimum conditions to maximize COME conversion calculated from the equation (4.1) were: reaction time, 6.3 h; oil/methanol molar ratio, 1:400; 1.5 wt %, catalyst concentration. These values have been selected from the optimum solutions proposed from the multiple solutions given by RSM optimization tool. The anticipated maximum COME conversion from the model at this condition is 96%. The model verification was carried out by performing the experiments in triplicate at identical condition and the maximum COME conversion of 95% was obtained. The good agreement between the model predicted and experimental value confirmed that the formulated model believed to be precise and authentic.

4.1.1.5. Characterization of COME

The physico-chemical properties of COME synthesized at optimal condition using KOH as a catalyst (with and without co-solvent) were determined as per ASTM standards and reported in Table 4.4. COME Conversions obtained are also shown in the same table.

From the table, it can be observed that the highest COME conversion of 95% was obtained at optimum condition with KOH as a catalyst. The effect of co-solvent (hexane) has not shown any effect on the COME conversion. Density of castor oil methyl ester was found to be 886 (without co-solvent) and 892 kg/m^3 (with co-solvent) which are within the acceptable range of ASTM standard specification. Density values are also used in the determination of COME viscosity. The kinematic viscosity of methyl ester samples were found to be 10.39 cSt (without co-solvent) and 10.72 cSt (with co-solvent), respectively. The kinematic viscosity of methyl ester obtained is well above the standard limits, but agrees well with that of literature (14.85 cSt) [159]. The higher viscosity of COME may be due to the presence of a free hydroxyl group on its fatty acids chain. This makes COME more advantageous for preparing lubricant over other vegetable oil based methyl esters [86]. But, the higher viscosity of biodiesel leads to poor atomization of the fuel and results incomplete combustion, including formation of deposits in the fuel injector of the diesel engine. Moreover, being more viscous hardware modifications are essential before using in the existing engine [160, 161]. The acid value of COME sample was within the range of standard limits (0.8 mg KOH/g) and signifying that there will not be problems like deterioration or pump plugging during usage [162]. The iodine value of biodiesel implies the un-saturation content. Iodine value can be directly correlated with viscosity, cetane number and cold flow properties [163]. The iodine value of COME found to be 83.24 and 82.94 $gI_2/100$ g oil, which are far lower than the maximum limit prescribed in EN 14214 standards. The saponification values of COME were found to be 103.2 and 102 mg KOH/g, respectively. The flash and fire points of COME (without co-solvent) were found to be 202 °C and 212 °C which are higher than fossil diesel. A higher flash point

guarantees safety during usage and storage [164]. The estimated calorific values of methyl esters were close to the biodiesel standards.

Table 4.4: Physico-chemical properties of COME

Properties	**KOH catalyst**		**Biodiesel standards**	**Standard Method**
	without co-solvent	**with co-solvent**	-	-
COME yield (%)	74.44	74.57	-	-
COME conversion (%)	95	95	-	-
Density (kg/m^3)	886	892	860-900	EN14214-2008
Specific gravity	0.896	0.921	0.860-0.900	ASTM D 4052
Acid value (mg KOH/g)	0.64	0.7	0.8 max.	ASTM D 6751-09
FFA(mg KOH/g)	0.32	0.35	-	-
Refractive Index at 30 °C	1.459	1.459	-	-
Kinematic viscosity (cSt) @ 40 °C	10.39	10.72	1.9-6	ASTM D 6751-09
Kinematic viscosity (cSt) @ 25 °C	18.94	19.36	-	-
Iodine value (g I_2/100g oil)	83.24	82.94	120	EN14214-2008
Saponification value (mg KOH/g)	103.2	102	-	-
Pour point (°C)	-19	-19	-15	ASTM D97
Oxidative stability (°C)	209	182	-	-
Thermal stability (°C)	240	222	-	-
Flash point (°C)	202	-	130-170	ASTM D92
Fire point (°C)	212	-	-	-
Calorific value (MJ/Kg)	39.43	34.43	37.27	-

The lower calorific value of COME than diesel is due to the oxygen content in biodiesel. The presence of oxygen in biodiesel helps for complete combustion of fuel in the diesel engine [165].

4.1.1.6. FTIR analysis

The FTIR spectra of castor oil and its methyl esters with KOH (with and without co-solvent) are compared and shown in Figure 4.5. The bands at a, b, signify OH group of ricinoleic acid (3450 cm^{-1}), -C=C- (3008 cm^{-1}) and –C=O (1742 cm^{-1}), correspondingly. The bands c and d corresponds to CH-stretching at 2928 cm^{-1} and 2855 cm^{-1}, respectively.

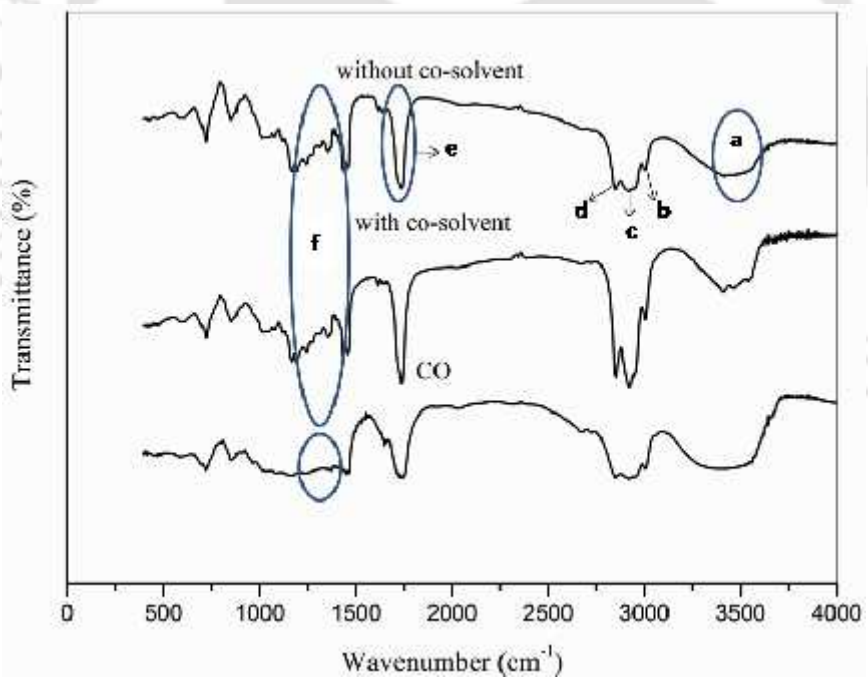


Figure 4.5: FTIR spectra of castor oil and its methyl esters using KOH (with co-solvent and without co-solvent)

From the figure, it can be observed that the bands a, b, c, d and e are general in both castor oil and methyl ester spectra. Whereas, the band peak of 'f' at 1438 cm^{-1} (-O-CH_3 group of methyl ester) indicates the methyl ester spectrum which was absent in the castor oil sample. Islam et al., (2014) reported that castor methyl ester contains oxygen functional group such as C-O and C=O at 400 to 1500 cm^{-1}. But, the conventional diesel does not have the oxygen functional group. The fuel with oxygen group promotes complete combustion with a smaller quantity of black smoke [109].

4.1.1.7. Thermal stability

Thermal stability of prepared COME samples (with co-solvent and without co-solvent) was determined by thermo gravimetric analysis (TGA) technique under nitrogen environment. Figure 4.6 describes TG and DTG thermo gram of both the samples. From the figure it can be seen that both the COME samples followed a similar decomposition pattern. Single step decomposition was noticed in DTG curves of both the COME samples and was in agreement with the reported data [156]. Thermal onset temperatures of the COME samples were found to be 240 °C (without co-solvent) and 222 °C (with co-solvent), respectively. The reason behind the variation in onset temperatures might be owing to the difference in the viscosity or either moisture content of the samples. The samples were stable up to respective onset temperatures, beyond that sample started to decompose which was evident from the weight loss data. The TG curves of the samples showed mass loss in three steps. In the first step, 10% weight loss was observed for COME-without co-solvent at 260 °C, whereas in case of COME-with co-solvent, it was at 226 °C which is due to decomposition of mono, poly-unsaturated fatty acids (oleic, ricinoleic, linoleic and linolenic) [156].

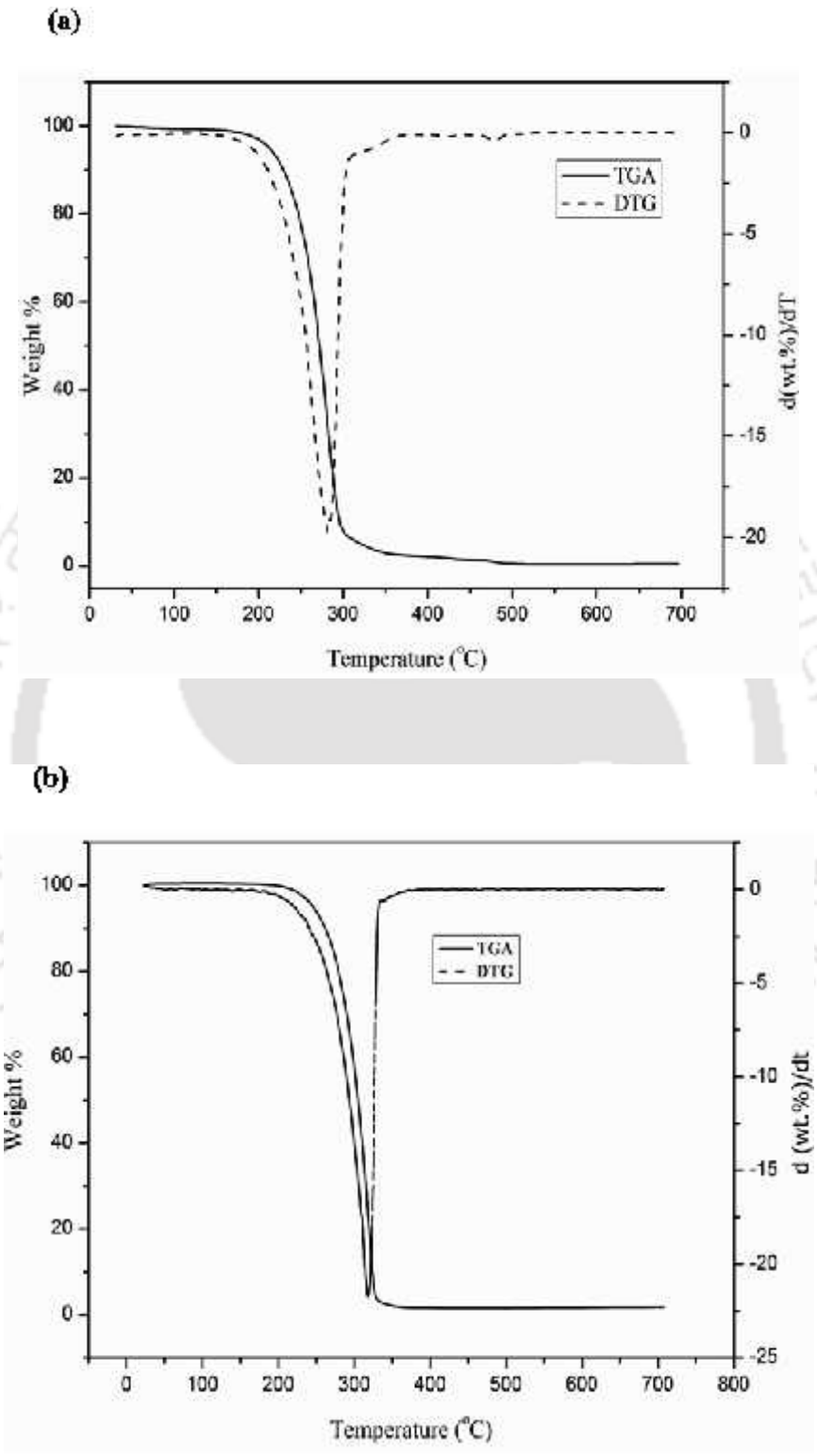


Figure 4.6: TGA and DTG curves of COME using KOH (a) with co-solvent) (b) without co-solvent under inert gas atmosphere

In the second step, 50% weight loss was observed at 304 °C (without co-solvent) and 271 °C (with co-solvent) which was attributed to the breakdown of saturated fatty acids (i.e. palmitic and stearic). Approximately 90% of weight loss was observed at 323 °C for COME- without co-solvent and in case of COME- with co-solvent, it was around 296 °C. In the third step, remaining 10% weight loss was mainly the pyrolysis products which were highly viscous liquids and undergoes secondary decomposition up to 330-700 °C for COME-without co-solvent and 300 °C-700 °C for COME- with co-solvent, respectively. From the above discussion, it can be concluded that thermal stability of COME-without co-solvent was superior to COME-with co-solvent. Thus, it could be authenticate that COME can act as potential fuel alternative to diesel.

4.1.1.8. Evaluation of oxidative stability by DSC

Oxidative stability of COME samples (with co-solvent and without co-solvent) was analyzed by using DSC under air atmosphere in the temperature range of 25-350 °C. Oxidative stability was measured in terms of oxidation onset temperature (OT). The onset temperature is defined as the temperature at which a rapid increase in the rate of oxidation is observed. The DSC thermo grams of COME samples with KOH (with and without co-solvent) are shown in Figure 4.7. The oxidation onset temperature of COME samples prepared with and without the use of co-solvent was found to be 182 °C and 209 °C, respectively. These results indicate that COME- prepared without the use of co-solvent was oxidatively more stable compared to COME-with co-solvent. The end temperatures of oxidative degradation were found to be 240 °C (without co-solvent) and 232 °C (with co-solvent).

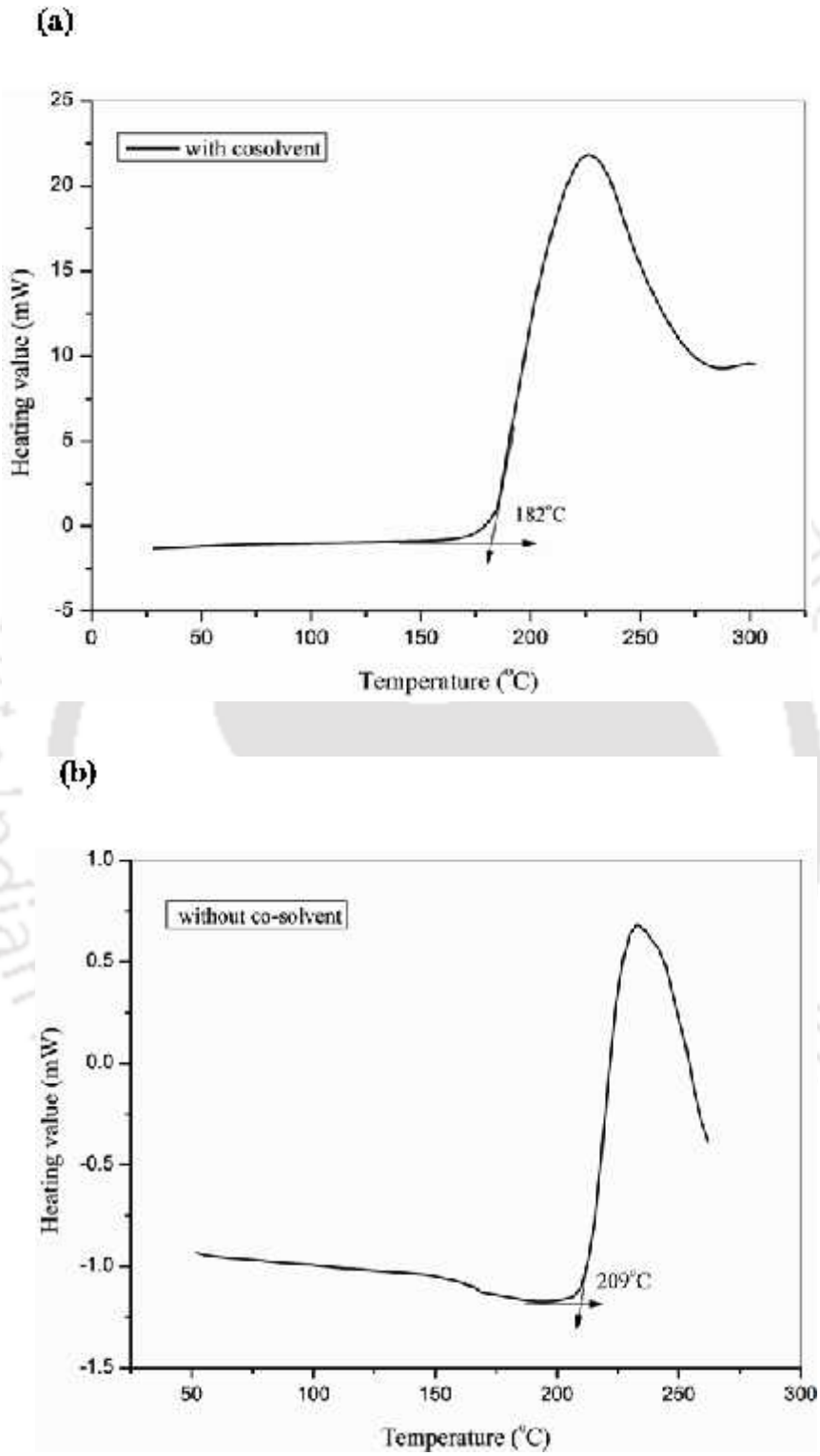


Figure 4.7: Oxidative stability of castor oil methyl ester using KOH (a) with co-solvent (b) without co-solvent under oxygen environment

The oxidative onset temperatures of the castor oil methyl ester obtained in this work are superior to the reported (120 °C) in the literature which was estimated by using TGA [148]. The higher OT values indicate more stability of COME towards oxidation. The higher oxidative stability of COME samples could be attributed to its higher mono-unsaturation content (i.e. ricinoleic acid, 84%). An improvement of oxidative stability can be done by using vegetable oil based antioxidant additives or synthetic antioxidants available in the market [156]. This evaluation reveals that it is possible to estimate the oxidative stability quickly by using a minimum sample amount.

4.1.1.9. Pour point analysis by DSC

Poor low temperature flow properties is one of the major problems associated with the biodiesel/methyl ester and because of that operating engine at cold climate regions is often challenging [166]. The cloud point is the temperature at which the first solids become visible when cooling a fatty acid methyl ester sample; pour point is the temperature at which the fuel ceases to flow. Pour point values of castor oil methyl ester samples prepared with and without the use of co-solvent were estimated by using DSC technique in the nitrogen atmosphere using standard methods described in our earlier paper [156]. The pour point of methyl esters sample has been noticed with a sharp increase in the heat energy flow due to the exothermic nature of increasing reaction. The temperature at which exothermic peak occurs that has been considered as pour point [156]. DSC thermo gram of COME samples are shown in Figure 4.8.

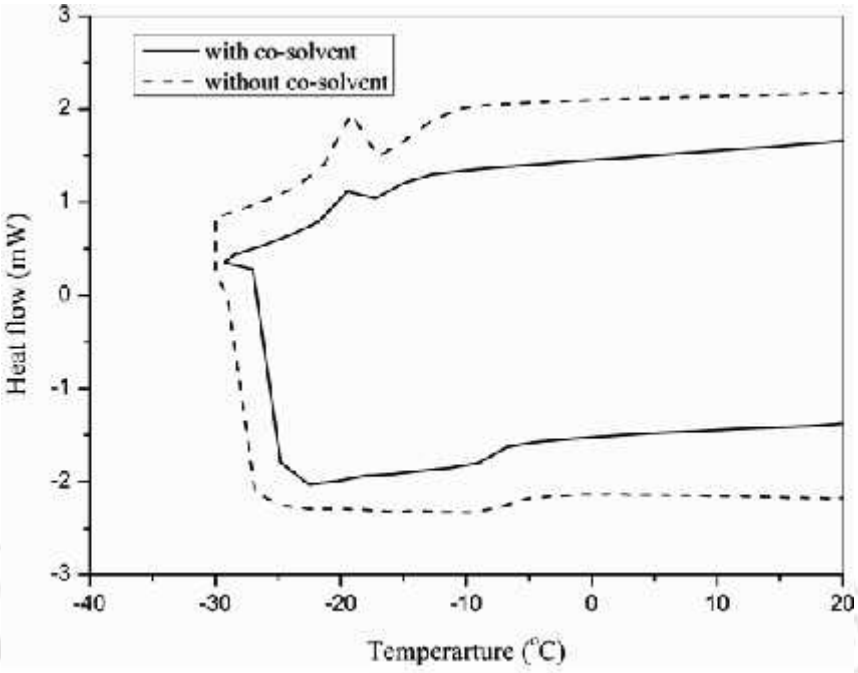


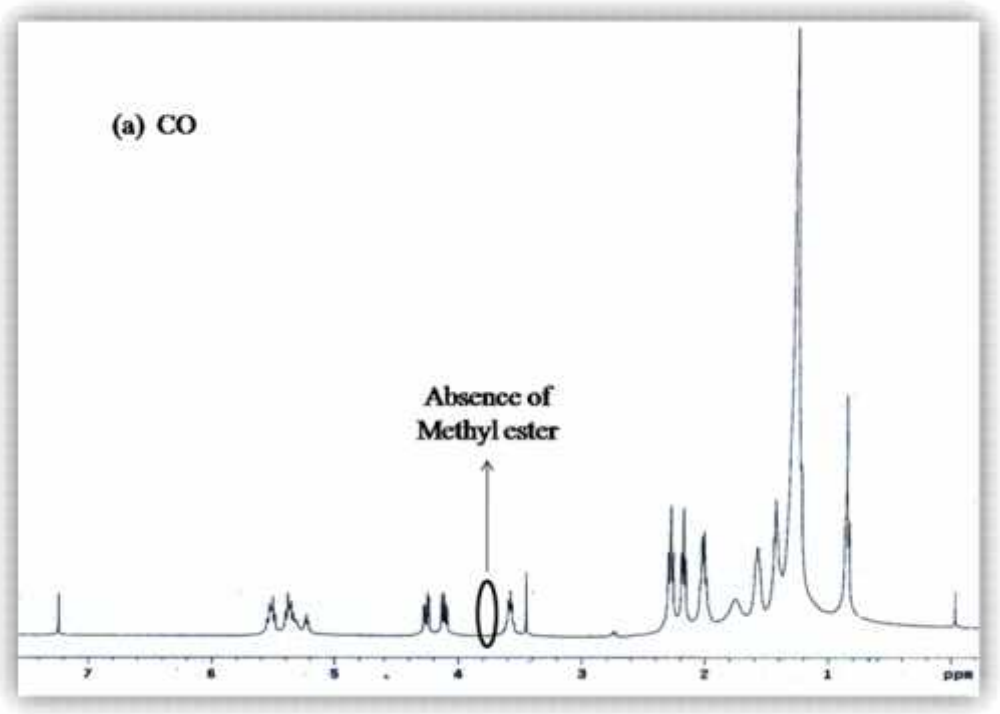
Figure 4.8: Pour point (by DSC) of castor oil methyl ester using KOH with co-solvent and without co-solvent

The pour point of castor oil methyl ester samples were found to be -19 °C which are within the ASTM biodiesel standards (Table 4.4). COME with a higher percentage of total unsaturated fatty acids showed lower pour point and qualifying COME as a perfect substitute for diesel fuel for its use in cold countries. Edith et al., (2012) reported that the fuel with high unsaturated fatty acids show better cold flow properties [166]. The results of the study revealed that DSC provides accurate means of monitoring the crystallization of biodiesel.

4.1.1.10. ^{1}H NMR analysis of oil and its methyl ester

^{1}H-NMR spectroscopy analysis of castor oil methyl ester samples have been carried out to estimate the gross conversion of triglycerides. Figure 4.9 shows ^{1}H-NMR

spectra of castor oil and methyl esters prepared with and without the use of co-solvent using KOH as a catalyst. The ^{1}H-NMR spectrum of castor oil shows the presence of glyceride protons at 4.2 ppm. Whereas, a strong singlet appeared in COME spectra at 3.7 ppm indicates the conversion of castor oil into methyl esters. From the figures it can be seen that the only significant change observed in the spectra is the appearance of a new singlet peak at 3.7 ppm when fatty acid methyl esters are formed. All other remaining multiple peaks in both oil and methyl ester spectra are common. Thus, the conversion of castor oil triglycerides into methyl ester was confirmed by comparing ^{1}H-NMR spectra of castor oil and its methyl ester.



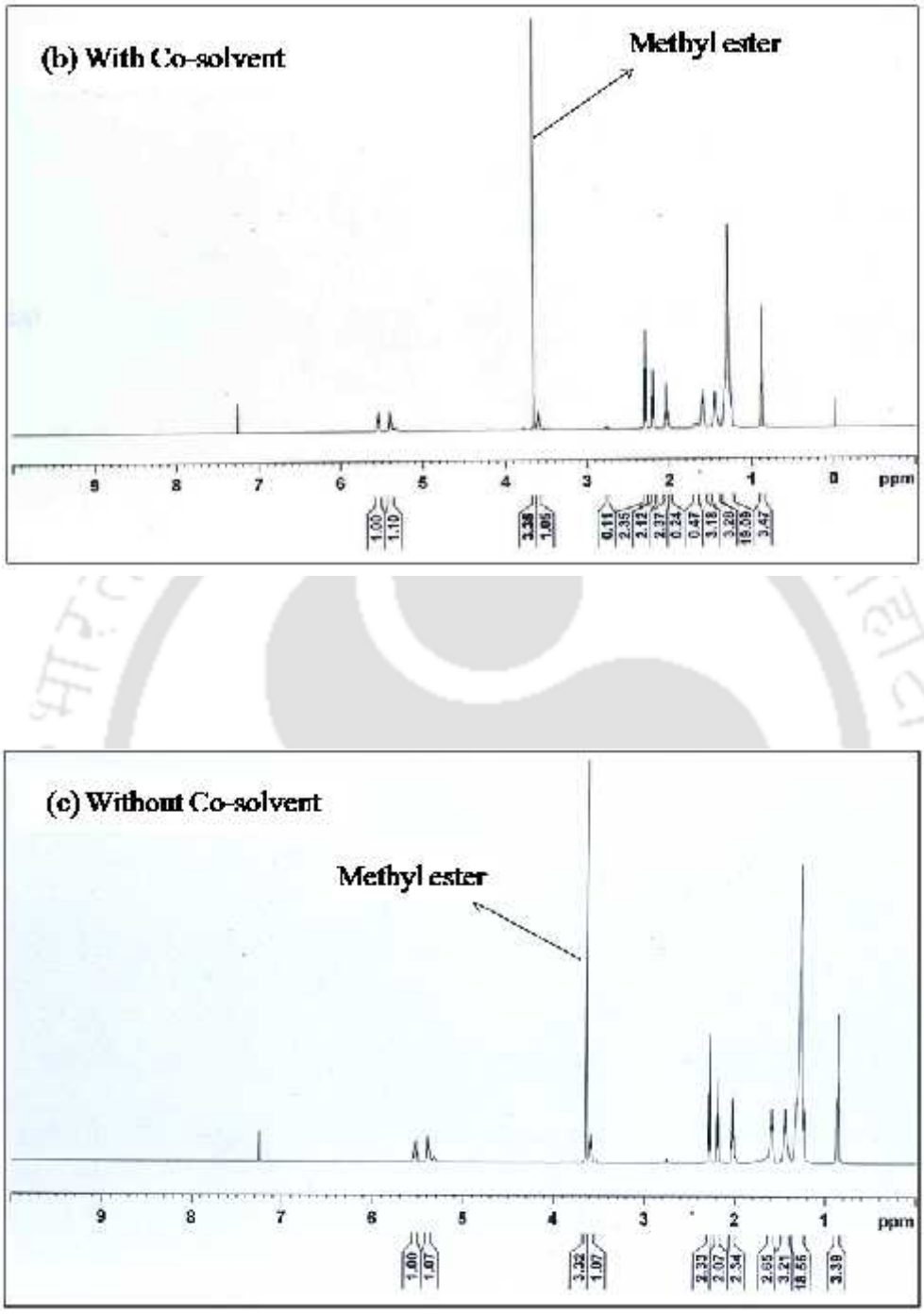


Figure 4.9: NMR spectrum of (a) castor oil; Methyl ester using KOH (b) with co-solvent (c) without co-solvent

4.1.2. Reactive extraction of castor seeds by non-integrated approach

4.1.2.1. Preliminary studies to optimize the reactive extraction of castor seeds

In order to optimize the reactive extraction process, a single parameter optimisation technique was followed. Madankar et al., (2013) reported preliminary study on optimization of castor seed using five different catalysts. The first highest COME yield (96%) was obtained with KOH as catalyst and second highest yield (86%) was with NaOH [86]. Therefore, in the present study NaOH was used as a catalyst for further enhancement of the COME yield. From the reported literature, it was observed that higher conversions are possible with higher molar ratios. Therefore, higher molar ratios (1:150-1:300 oil/methanol) are used in the present study. As the transesterification with acid catalyst is slower than alkali catalyst, hence reactions were performed with alkali catalyst. The range of variables used in this study such as reaction time, oil to methanol molar ratio, catalyst concentration, temperature, mixing speeds are selected based on the earlier reported literature [86]. The influence of eight parameters on the reactive extraction of castor seeds was studied and corresponding yields and conversions of COME are shown in Table 4.5.

4.1.2.1.1. Effect of reaction time on COME conversion

The effect of reaction time on reactive extraction of castor seed was investigated by varying time between 2, 3, 4 and 5 h. Other fixed parameters are 20 g grinded castor seed, temperature, 60 °C; oil to methanol molar ratio, 1:250; NaOH concentration, 1 wt %; and stirring speed, 600 rpm. The obtained yield and conversion of COME are shown in Table 4.5. The COME conversion was found to be increased with an increase in reaction time

up to 4 h and the optimum conversion recorded at this condition was 84.82%. Further increase in reaction time to 5 h has an insignificant effect on conversion. Madankar et al., (2013) studied the reactive extraction of castor seeds with five different catalysts using almost similar reaction conditions (65 °C, 3 h, 1:250 oil/methanol molar ratio and 600 rpm). The COME yield obtained in their study was around 85.9% in reaction time of 3 h with NaOH as a catalyst, which was close to the COME conversion (82.3%) obtained in the present study. The maximum COME conversion recorded in the present study was around 84.82% (70.75% yield) at 4 h reaction time and considered as the optimum reaction time for further experimentation.

Table 4.5: COME yields and conversions obtained for the list of experiments conducted with respective parameters setting

Reaction time (h)	Oil to methanol molar ratio	Catalyst concentration (wt % of oil content of seed)	Reaction temperature (°C)	Mixing speed (rpm)	Seed quantity (g)	Particle size (mm)	Co-solvent (vol %)	COME Yield (%)	COME Conversion (%)
2	1:250	1	60	600	20	1	-	66.75	80.47
3	1:250	1	60	600	20	1	-	67.11	82.3
4	1:250	1	60	600	20	1	-	70.75	84.82
5	1:250	1	60	600	20	1	-	72.51	76.62
4	1:150	1	60	600	20	1	-	63.11	62.86
4	1:200	1	60	600	20	1	-	71.11	68.26
4	1:250	1	60	600	20	1	-	70.75	84.82
4	1:300	1	60	600	20	1	-	71.2	66.88
4	1:250	0.5	60	600	20	1	-	52.71	62.77
4	1:250	1	60	600	20	1	-	70.75	84.82
4	1:250	1.5	60	600	20	1	-	68.71	72.46
4	1:250	2	60	600	20	1	-	Soap	-
4	1:250	1	30	600	20	1	-	68	71.19
4	1:250	1	40	600	20	1	-	73.15	89.85
4	1:250	1	50	600	20	1	-	73.68	62.77
4	1:250	1	60	600	20	1	-	70.75	84.82
4	1:250	1	40	200	20	1	-	71.91	93.45
4	1:250	1	40	400	20	1	-	71.89	92.85

4	1:250	1	40	600	20	1	-	73.15	92.54
4	1:250	1	40	600	10	1	-	66.72	93.27
4	1:250	1	40	600	15	1	-	78.05	92.02
4	1:250	1	40	600	20	1	-	71.89	92.85
4	1:250	1	40	600	20	0.75	-	71.73	92.43
4	1:250	1	40	600	20	1	-	71.28	89.44
4	1:250	1	40	600	20	2	-	71.36	84.22
4	1:250	1	40	600	20	1	10	72.66	92.67
4	1:250	1	40	600	20	1	15	72.16	92.35
4	1:250	1	40	600	20	1	20	70.89	91.62

4.1.2.1.2. Effect of oil to methanol molar ratio

The amount of methanol required in the reactive extraction is quite high compared that of conventional method [7]. The concentration gradient between the seed and bulk liquid plays an important role in the reactive extraction. Higher the concentration gradient, higher will be the oil yield [5]. Therefore in the present study, oil to methanol molar ratio was varied in the range of 1:150 to 1:300. The excess methanol in the reaction mixture not only helps in simultaneous extraction and transesterification of oil, but also to shift the reaction in the forward direction [162]. The conversion of 62.86% was obtained at 1:150 molar ratios and then gradually increased with an increase in the molar ratio (Table 4.5). The highest conversion of 84.82% was obtained at 1:250 molar ratio, while at other molar ratios, i.e. 1:200 and 1: 300 conversions were found to be 68.26% and 66.88%, respectively. Increase in the molar ratio from 250 to 300, decreased the COME conversion from 84.82% to 66.88%. Similar kind of behaviour was noticed by Zakaria et al., (2012) in their study on reactive extraction of rape seed [5]. However, higher oil to methanol molar ratio leads to the requirement of higher energy for recovery of methanol, which increases the production cost of biodiesel by this method compared to a conventional method.

4.1.2.1.3. Effect of catalyst concentration

Catalyst concentration is an important parameter in the reactive extraction technique. The transesterification process is incomplete without a catalyst [7]. In the present study, NaOH was used as a catalyst because it is cheap compared to KOH [167]. In the conventional method on the basis of oil weight, 0.5-1 wt % of NaOH is used as a catalyst. Lower catalyst concentration gives lower conversion while higher concentration

leads to saponification reaction. Hence, loading a specific amount of catalysts to the reaction mixture is important. Moreover, the catalyst concentration range used in the conventional method may not be sufficient enough to complete the reactive transesterification of extracted oil due to the direct usage of seed material and excess solvent [5]. Therefore, a systematic study on reactive extraction of castor seed was carried out by varying NaOH concentration from 0.5-2 wt % and the corresponding results obtained are shown in Table 4.5. The data shows that with an increase in NaOH concentration from 0.5 to 1 wt %, COME conversion increased from 62.77% to 84.82%. Further increase in the catalyst concentration from 1 to 1.5 wt %, decreased the COME conversion from to 72.46% (1.5 wt %). Beyond this concentration range (i.e. at 2 wt %), emulsion formation was noticed in the reaction mixture. Similar behaviour was noticed by Kasim and Harvey, (2011) in their study on reactive extraction of jatropha seeds with NaOH as a catalyst [7]. The formation of a emulsion in the reaction mixture was mainly due to increase in catalyst concentration which resulted in the side reaction called saponification.

4.1.2.1.4. Effect of reaction temperature

The effect of temperature on reactive extraction of castor seeds was studied at four different temperatures such as 30, 40, 50 and 60 °C under otherwise identical reaction conditions. Increasing temperature showed an uneven trend of COME conversion. At lower temperatures (30 and 40 °C), COME conversion continuously increased (71.19% and 89.85%) within the experimental time limit (Table 4.5). However, at 50 °C COME conversions gradually decreased to 62.77% and thereafter again increased to 84.42% with further increase in temperature to 60 °C. Temperature beyond

60 °C was avoided to prevent the loss of methanol during the reactive extraction [86]. A careful analysis of the results revealed that the maximum conversion of 89.85% was obtained at 40 °C, which shows that reactive extraction can be performed efficiently at lower temperatures which are favourable for process economics [5].

4.1.2.1.5. Effect of mixing speed

To investigate the effect of stirring speed, 20 g castor seed material was treated with oil to methanol molar ratio, 1:250; NaOH concentration, 1 wt %; and temperature, 60 °C. The experiments were performed in the range of stirring speeds 200 to 600 rpm. From Table 4.5, it can be seen that the conversion of COME was not substantially affected by stirring speed. This represents that mixing speed is not the limiting factor of mass transfer during reactive extraction in the present study. Similar kinds of results were noticed by other researchers during their study of reactive extraction with jatropha and castor seeds [7, 86]. However, all subsequent experiments were performed at a higher stirring speed of 600 rpm to ensure uniform distribution of seed material in the reaction mixture.

4.1.2.1.6. Effect of seed quantity

Effect of the seed quantity on reactive extraction was studied by varying seed quantity in the range of 10-20 g. The increase of seed quantity showed insignificant effect on COME conversion (Table 4.5). However, the seed quantity of 20 g was maintained constant throughout the study. The purpose of using excess seed quantity during the reaction was to have sufficient oil in the bulk phase for transesterification.

4.1.2.1.7. Effect of seed particle size

In order to study the effect of seed particle size on COME conversion, reactive extraction was studied for different seed particle sizes varying in the range from 0.75 to 2 mm. The obtained results are shown in Table 4.5. The other operating parameters used in the study were maintained constant, viz., oil to methanol molar ratio, 1: 250; catalyst concentration, 1 wt %; and temperature, 60 °C. From the table, it can be seen that the conversion of COME decreased from 92.43 to 84.22% with an increase in particle size from 0.75 to 2 mm. The maximum COME conversion of 92.43% was obtained with the lower particle size of 0.75 mm. Kasim et al., (2011) and Porwal et al., (2012) obtained almost similar results during their study with reactive extraction of jatropha and pongamia seeds, respectively [7, 162]. However, all the further experiments and previous experiments (other than the experiments related to effect of particle size) were carried at the average particle size of 1 mm which was nearer to the optimized particle size.

4.1.2.1.8. Effect of co-solvent (Hexane)

From the literature, it was observed that hexane plays an important role as a co-solvent in the reactive extraction of jatropha seeds [158]. Hence in the present study, to increase the extraction capacity, hexane was considered as a co-solvent. To explore the co-solvent effect on the reactive extraction of castor seeds, three different ratios were examined, namely, 10, 15 and 20 vol % (on a methanol volume basis). In the reactive extraction, hexane participates only in the extraction and not in the reaction. The results obtained during the study revealed that, hexane has an insignificant effect on the extraction as well as COME conversion. Hincapié et al., (2011) have reported similar observation during their study on *In situ* transesterification of castor seeds [168]. The

COME product produced in the present work are shown in Figure 4.10. Hence for subsequent experimentation, a co-solvent amount was fixed at 10 vol % with corresponding conversion of 92.67% (Table 4.5).

Figure 4.10: Purified COME obtained directly from castor seeds

From preliminary studies, an optimum COME conversion of ~93% was achieved under following conditions: 4 h, 1:250 oil to methanol molar ratio, 1 wt % NaOH, 40 °C, 0.75 mm particle size, 20 g seed, 600 rpm and 10 (vol %) co-solvent. 20% of higher COME conversion was obtained with NaOH as a catalyst compared to that of KOH at optimum condition. Therefore, based on the preliminary results, further investigation on optimization of reactive extraction by RSM (Response Surface Methodology) design technique was carried out using NaOH as a catalyst.

4.1.2.2. Model fitting and ANOVA

Central composite design (CCD) has been used to formulate the transesterification experiments, total 30 experiments were performed to find out the optimum combination and study the effect of process parameters on FAME conversion. The results of experiment are shown in Table 4.6 and summary of ANOVA is provided in Table 4.7. The associated probability (p) value for the model is lower than 0.05 implies that lack of fit is insignificant as compared to the pure error or in other words the model was significant. The value of regression coefficient R^2 (0.974) for the present study model was not only signify the excellent fit of the model to the experimental data but also explained about 97.4% of the effect on the conversion for reactive extraction by variation of the process parameters. The more the value of R^2 approaches 1, better the model fits the experimental data. The value of the adjusted coefficient of determination (R^2 adj = 0.95) is also high, thus representing the significance of the model. The value of coefficient of variation (CV) is lower (6.6%) indicating the reliability of the results of the fitted model [157]. p-values of all linear coefficients <0.05 shows that the model terms are significant. In this case, A (reaction time), B (oil to methanol molar ratio), C (catalyst concentration), interaction effects of AC (reaction time with catalyst concentration), BC (oil to methanol molar ratio with catalyst concentration) and quadratic effects of A^2 (time), B^2 (oil to methanol molar ratio), C^2 (catalyst concentration) have significant effect on the COME conversion.

Table 4.6: Experimental design matrix and responses for COME conversion

Run	Time (A, hr)	Oil/methanol mol ratio (B)	Catalyst conc. (C, wt %)	Temperature (D, °C)	COME Conversion (%)
1	4	250	1	40	90
2	4	250	0	40	0
3	3	200	0.5	30	68
4	4	250	1	20	91
5	3	200	1.5	50	92
6	4	250	1	60	90
7	4	150	1	40	88
8	3	300	1.5	30	67
9	3	300	0.5	30	60
10	4	250	1	40	90
11	5	200	0.5	50	56
12	5	300	0.5	30	67
13	3	300	0.5	50	70
14	5	200	1.5	30	65
15	6	250	1	40	60
16	3	200	1.5	30	91
17	4	250	2	40	32
18	5	200	0.5	30	50
19	3	200	0.5	50	59
20	3	300	1.5	50	70
21	5	300	0.5	50	60
22	5	300	1.5	30	50
23	5	300	1.5	50	57
24	2	250	1	40	85
25	5	200	1.5	50	68
26	4	350	1	40	60
27	4	250	1	40	90
28	4	250	1	40	90
29	4	250	1	40	90
30	4	250	1	40	90

Table 4.7: ANOVA for response surface quadratic model

Source	Sum of squares	Degrees of freedom (df)	Mean square	F value	p-value
Model	12470.13	14	890.72	41.06	< 0.0001
A-Time	988.16	1	988.16	45.56	< 0.0001
B-mol ratio	450.66	1	450.66	20.77	0.0004
C-cat	748.16	1	748.16	34.49	<0.0001
D-Temp	6	1	6	0.27	0.6
AB	90.25	1	90.25	4.16	0.059
AC	196	1	196	9.036	0.0089
AD	1	1	1	0.046	0.83
BC	576	1	576	26.55	0.0001
BD	9	1	9	0.41	0.52
CD	12.25	1	12.25	0.564	0.46
A^2	434.29	1	434.2	20.02	0.0004
B^2	356.29	1	356.29	16.42	0.001
C^2	8990	1	8990	414.49	< 0.0001
D^2	7.44	1	7.44	0.34	0.56
Residual	325.33	15	21.68		

CV: 6%, R^2_{model}: 0.974, R^2_{adj} : 0.95, predicted R^2_{model}: 0.853

The regression equation for the determination of predicted values of output parameter (i.e., COME in this study) is given as follows:

$$\text{COME Conversion (\%)} = 90 - 6.41A - 4.3B + 5.58C + 0.5D + 2.37AB - 3.5AC + 0.25AD - 6BC + 0.75BD + 0.87CD - 3.97A^2 - 3.6B^2 - 18C^2 + 0.525D^2 \quad (4.2)$$

The graph between the predicted and actual COME conversion (%) in Figure 4.11 shows that the predicted values are quite close to the experimental values and there by confirming the persistence of the model developed for establishing a correlation between the process variables and COME conversion. It should be noted that the quadratic regression model valid only within the experimental range applied in this study.

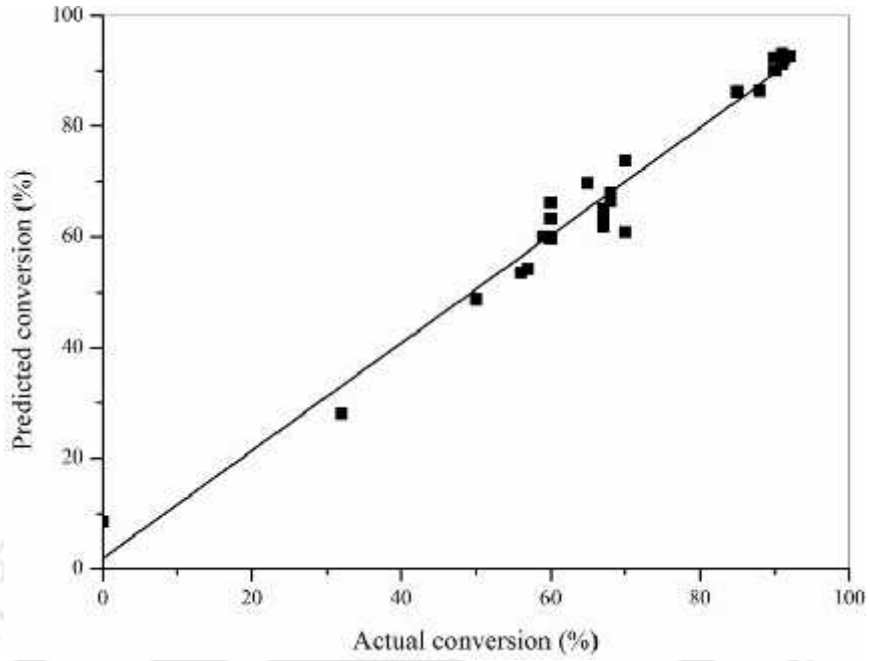


Figure 4.11: Predicted versus actual COME conversion (%)

4.1.2.3. Effect of process variables on COME conversion

3D response surfaces plots which are the illustration of the association between the responses and process parameters are shown in Figures 4.12 (a) to (f). The influence of reaction time and oil/methanol molar ratio on the COME conversion is shown in Figure 4.12 (a). The increase of molar ratio and reaction time has insignificant effect on the COME conversion. The optimum COME conversion was attained at the lower levels i.e. 1:200 oil/methanol molar ratio and 3 h reaction time. This shows that reactive extraction can reduce the time required for biodiesel production from various oil seeds compared to the conventional method and eventually will reduce the cost of biodiesel production [158].

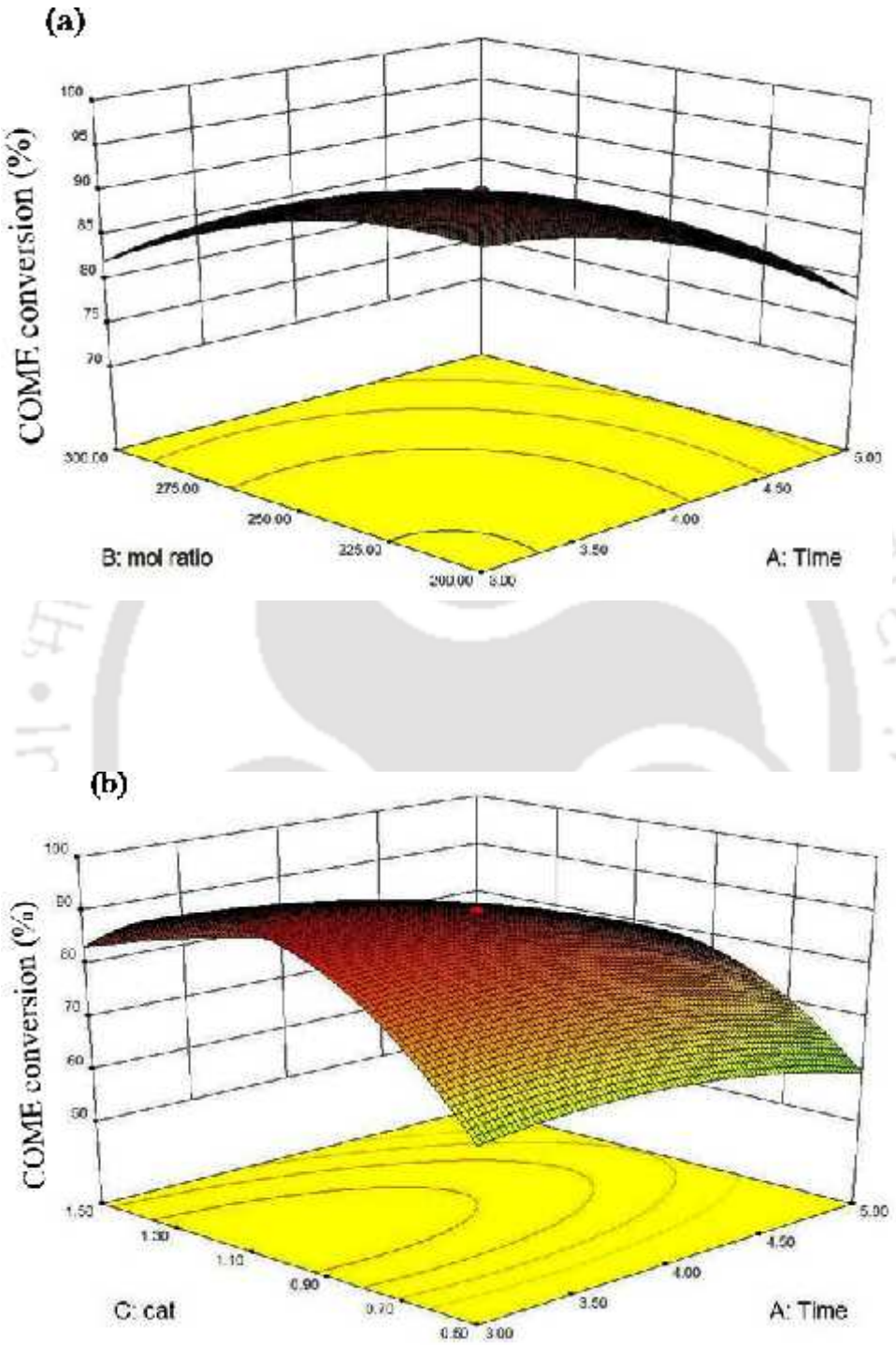
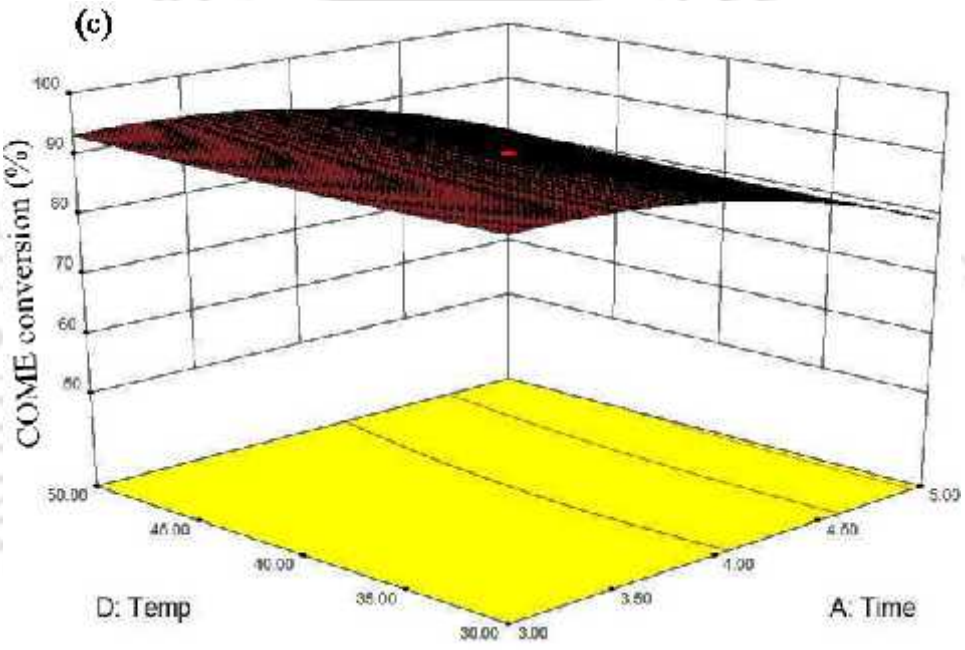


Figure 4.12: (a) Response surface of COME: effect of reaction time and oil/methanol molar ratio. (b) Response surface of COME: effect of reaction time and catalyst concentration

The influence of reaction time and catalyst concentration on the COME conversion is shown in Figure 4.12 (b). From the figure, it can be notice that COME conversion increased with an increase in the catalyst concentration up to certain level and decreased thereafter. However, an increase of reaction time did not show any considerable effect on the conversion.



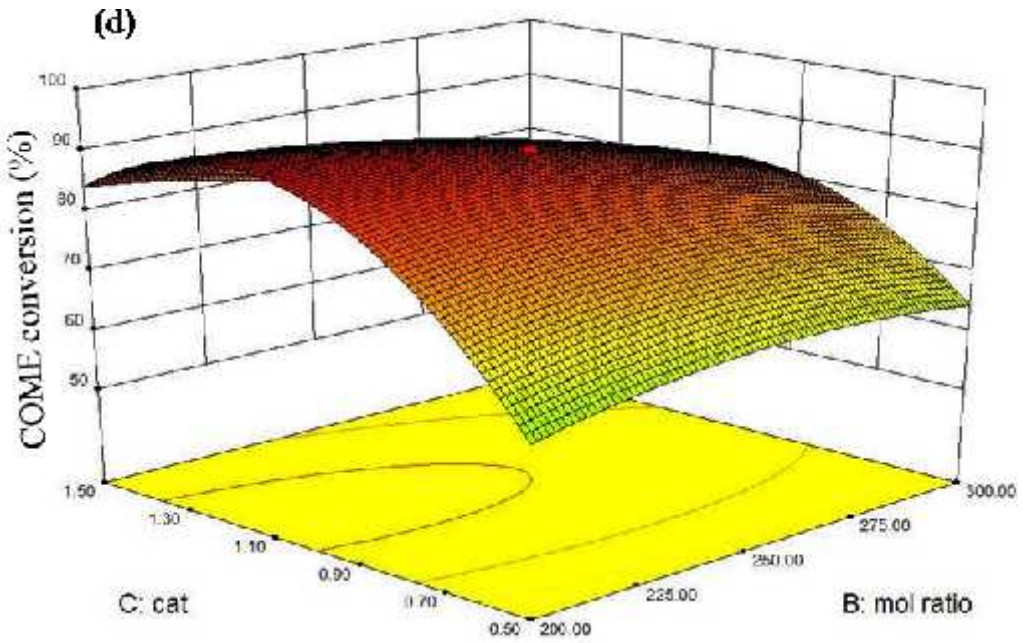


Figure 4.12: (c) Response surface of COME: effect of reaction time and temperature. (d) Response surface of COME: Effect of oil/methanol molar ratio and catalyst concentration

Figure 4.12 (c) gives the effect of reaction time and reaction temperature on COME conversion. It could be seen from the results that, both the response surfaces have an insignificant effect on the COME conversion. Figure 4.12 (d) establishes the interaction of oil/methanol molar ratio and catalyst concentration on COME conversion. From the plot, it can be observed that COME conversion increased with an increase in the catalyst concentration up to certain level and thereafter no substantial increase was observed in the conversion with increasing catalyst concentration, rather it decreased. And the oil/methanol molar ratio was relatively insensitive to COME conversion. These results are analogous to the result reported by Goyal et al., (2012), which effectively means that the rate of the reactive extraction may not be enhanced by oil/methanol molar ratio with the same interaction combination [157].

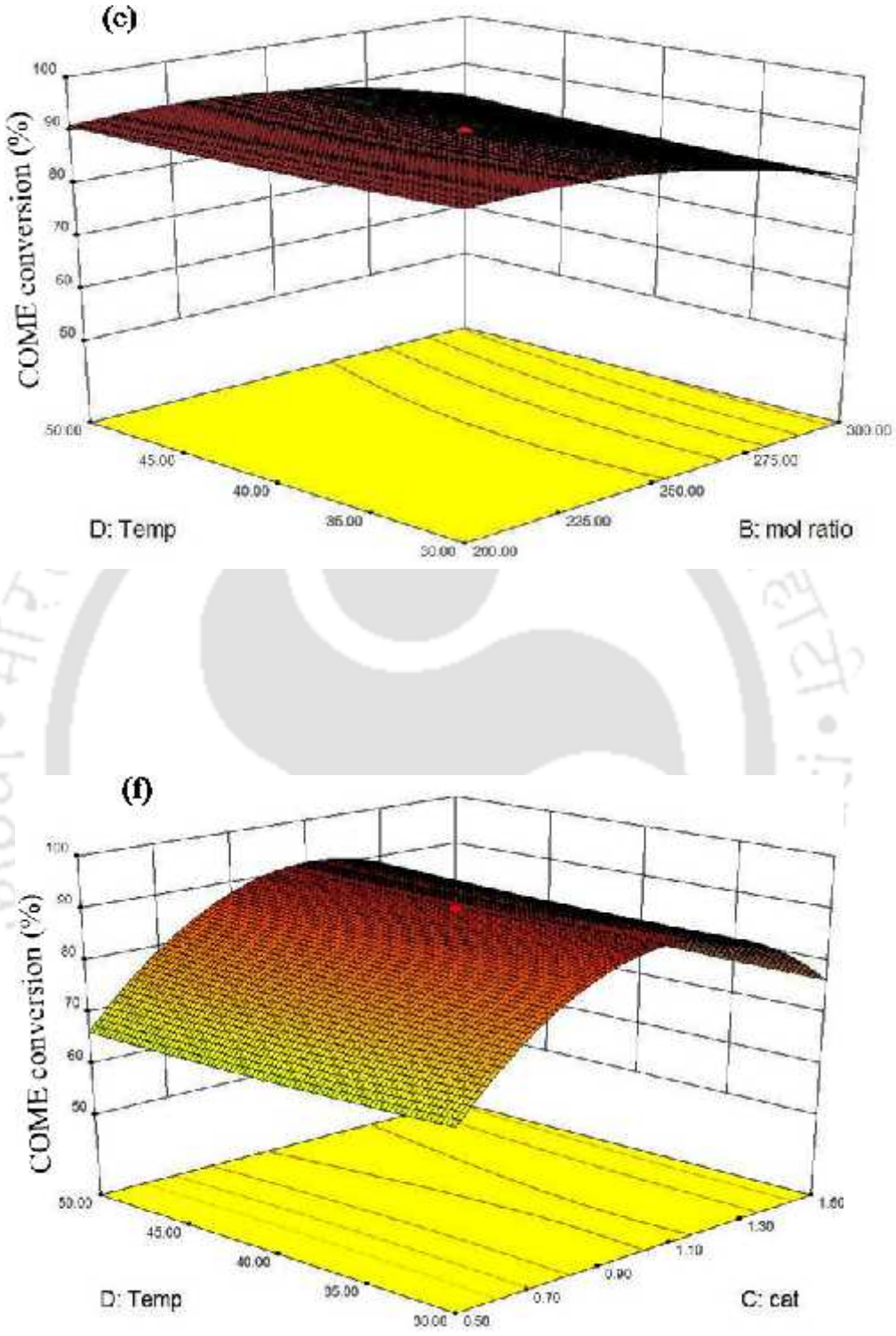


Figure 4.12: (e) Response surface of COME: effect of methanol/oil ratio and temperature. (f) Response surface of COME: effect of catalyst concentration and temperature

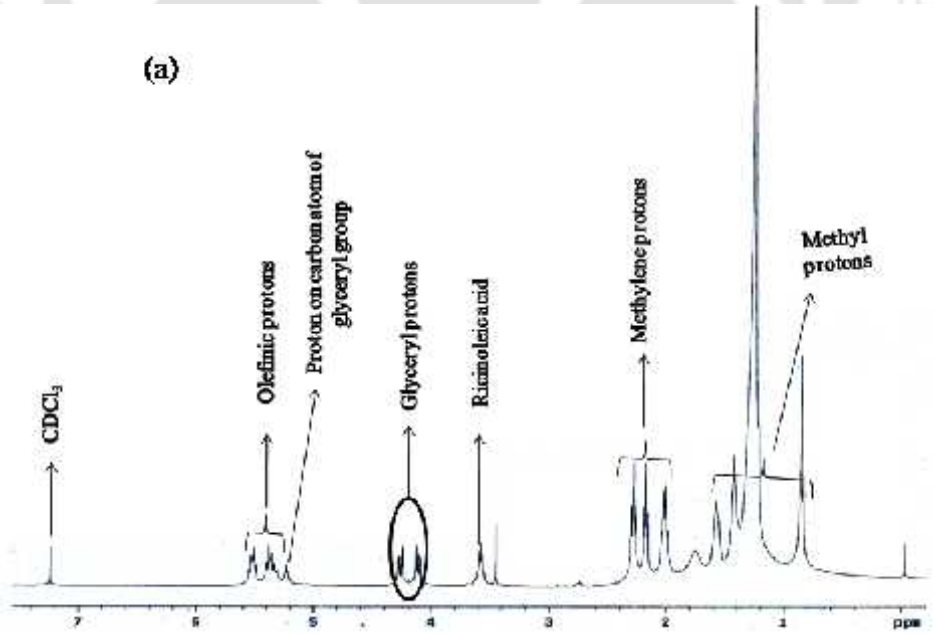
On the basis of this study, it was decided to carry out reactive extraction step by using lower level of oil/methanol ratio. The effect of oil/methanol molar ratio and reaction temperature on conversion (Figure 4.12 (e)) revealed that both the parameters had practically no effect on the conversion. The maximum conversion obtained was at lower levels i.e. 1:200 oil/methanol molar ratio and 30 °C and is comparable with the results obtained by other researchers [7, 95]. However in the present study, the higher COME conversion was obtained at 30 °C which shows that reactive extraction can be performed efficiently at a lower temperature which is favourable for process economics [5]. Moreover, transesterification reaction occurs in the liquid phase, hence it is essential that both methanol and oil remain in the liquid phase at the reaction temperature. The optimum temperature obtained in the present study was 30 °C, for which methanol exists in the liquid phase. Figure 4.12 (f) shows the influence of catalyst concentration and reaction temperature on the COME conversion. An increasing catalyst concentration has a significant effect on the conversion up to certain level, but later it has decreased, while an increasing reaction temperature had not shown any significant effect on the conversion. The decrease in the conversion beyond certain level mainly attributed to increase catalyst concentration which resulted in the side reaction called saponification [7].

4.1.2.4. Optimization of response parameters

Optimization of responses has been performed individually to attain the desired maximization of COME conversion based on the developed mathematical model. The Design Expert software has been used to optimize the response and value of the response (COME conversion) was set as maximum. The optimal value obtained was 3 h, 1: 200 oil/methanol molar ratio, 1.19 wt % catalyst concentration and 30 °C. A trial experiment

was carried out at the optimal parametric settings for COME conversion to get the targeted value of response. The predicted response (99%) was found to be in good agreement with the experimental results (97.15%) with an error of ~2%. The higher desirability of 0.99 was attained at the optimal conditions.

The conversion of COME samples was obtained from ^{1}H-NMR spectroscopy. The NMR spectra of CO and its biodiesel with NaOH are shown in Figure 4.13 (a) and (b). The ^{1}H-NMR spectrum of CO shows the presence of glyceride protons at 4.2 ppm. Whereas, a strong singlet peak appeared at 3.7 ppm indicates the conversion of CO into COME. The most important distinction between the ^{1}H-NMR spectrum of CO and its biodiesel can be observed from the spectrum of COME in terms of vanished glyceride protons at 4.2 ppm and the appearance of methyl ester protons at 3.7 ppm.



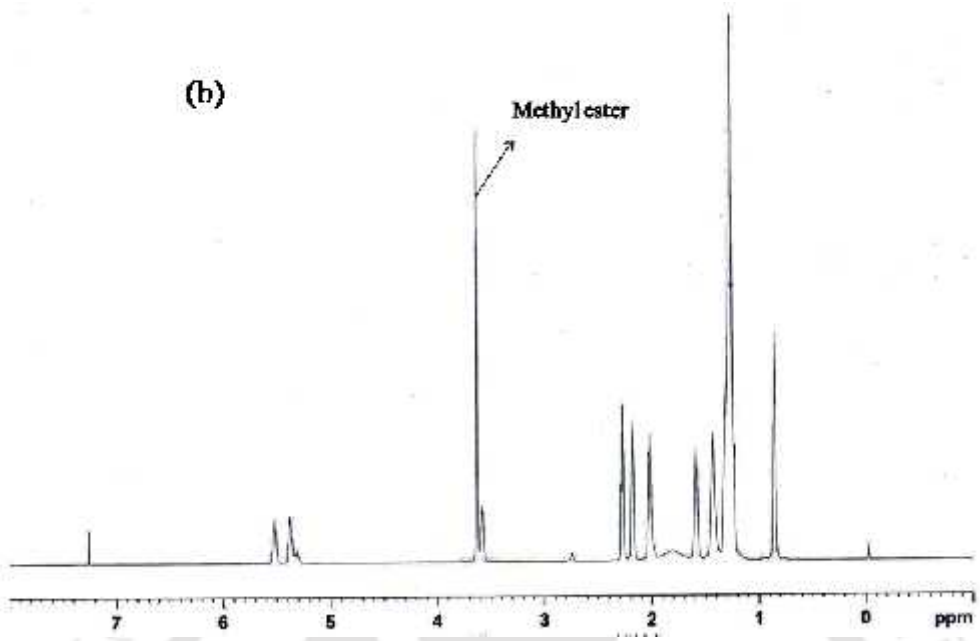


Figure 4.13: (a) ^{1}H NMR spectrum of CO; (b) COME with NaOH

All other common multiple peaks in both oil and biodiesel spectra at 0.82-1.03 ppm, 1.2-2.87 ppm and 5.29-5.4 ppm were terminal methyl protons (-CH_3), a mixture of various methylene protons (saturated, β, carbonyl, allyl, α and divinyl) and olefinic protons (-CH=CH-), respectively [169]. The singlet peak at 3.7 ppm in ^{1}H-NMR of COME confirms the complete conversion of CO into COME. The COME was also confirmed by FTIR spectrum and is shown in Figure 4.14.

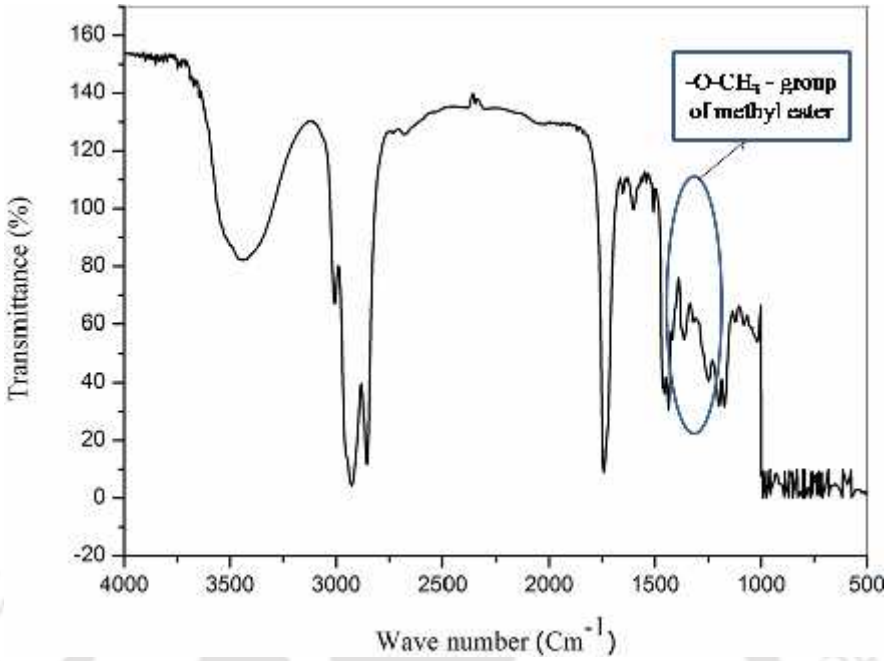


Figure 4.14: FTIR spectrum of COME

4.1.2.5. Characterization of diesel, COME and its blends

The physico-chemical characteristics of COME, COME-diesel blends and neat diesel estimated as per the standard methods are shown in Table 4.8. Some of the properties of COME such as acid value, FFA content, refractive index, oxidative stability, thermal stability, iodine value, saponification value, yield and COME conversion are not shown in the Table 4.8. The highest COME conversion of 97.15% (72.2 % yield) was obtained at optimum condition with NaOH as a catalyst. The obtained conversion was close to the castor biodiesel yield (96%) obtained with KOH by previous researchers. Density of castor oil methyl ester sample (868 kg/m^3) was found to be within the acceptable range of ASTM standard specifications. The kinematic viscosity of methyl esters was found to be 10.59 cSt and was beyond the standard limits. The biodiesel with higher viscosity leads to the incomplete combustion of fuel and causes formation of

deposits in the fuel injector of the diesel engine. Therefore viscosity of biodiesel ought to be low [161].

Table 4.8: Comparison of physico-chemical properties of castor oil methyl ester and its blends with diesel

Properties	**Diesel**	**COME**	**COME5**	**COME10**	**COME15**	**ASTM Biodiesel standards**	**Standard method**
Density (kg/m^3)	831	896	838	841	844	860-900	ASTM D 4052-91
Kinematic viscosity (mm^2/s) at 40°C	1.37	10.59	1.88	2.43	2.52	1.9-6	ASTM D-445
Kinematic viscosity (mm^2/s) at 25°C	2.31	19.12	2.74	2.97	3.13	-	ASTM D-445
Cloud point (°C)	3.0	-1.3	3.0	2.5	2.2	-	-
Pour point (°C)	0.7	-9.0	0.21	-0.7	-1.3	-15	-
Flash point (°C)	68	202	76	79	82	130-170	ASTM D92
Fire point (°C)	74	212	78	84	89	-	ASTM D92
Calorific Value (MJ/kg)	45.27	38.3	44.5	44.3	43.7	37.27	-

The acid value of COME sample was within the range of standard limits (0.8 mg KOH/g max) indicating that there will not be any operational problems like corrosion or pump plugging due to FFA (Free Fatty Acid) content [162]. The refractive index of oil was found to be 1.459. The iodine value of the methyl ester gives the number of double bond present in the sample. Iodine value is directly correlated with the viscosity, cetane number and cold flow properties [163]. The iodine value of COME (80.37 gI_2/100g oil) was far lower than the maximum limit of 120 prescribed in EN 14214 standards. The saponification value of COME was found to be 105.5 mg KOH/g. The pour point and cloud point of COME were -17.23 °C and -21.73 °C, respectively. Pour point is a cold flow property which is a good indicator for diesel fuel during extensive storage and pipe line fuel supply [166]. The estimated calorific value (39.07 MJ/Kg) was close to that of biodiesel standards. The oxidative stability (DSC) and TGA profiles of COME are shown in Figure 4.15 and Figure 4.16. The onset temperature of oxidation was found to be 191 °C, while the thermal decomposition temperature was found to be 220 °C. The onset temperatures were determined by extrapolation of the base lines. An oxidative stability of COME obtained in the present study indicates that the further addition of any synthetic antioxidants or antioxidant additives is not required to improve the oxidative stability. The TGA curve of COME showed decomposition in three stages at 30-220 °C, 220-300 °C and 300-700 °C, respectively. The flash and fire points of COME are higher than that of conventional diesel. The higher flash point of COME than petro-diesel indicates that COME is safe to handle than conventional diesel [170]. Pour point estimated by DSC is shown in Figure 4.17. The estimated properties of diesel such as density, pour point and cloud point are in well agreement with the values reported in the literature [170]. Density, viscosity and specific gravity are the important parameters of fuel, because the higher

values of these properties can affect the spray characteristics of the engine [170]. In this study, estimated values of density, viscosity and specific gravity of COME are higher than that of diesel. The flash point and fire point of diesel are found to be higher than the values reported in literature [170]. From the Table 4.7, it can be observed that other properties i.e. cloud point, pour point, flash point, fire point and calorific value were not affected significantly by the blending of COME with diesel. The comparative analysis of COME blend properties in the present study with that of the earlier published literature for various methyl ester blends showed that all the properties followed more or less similar trend [105-108, 110].

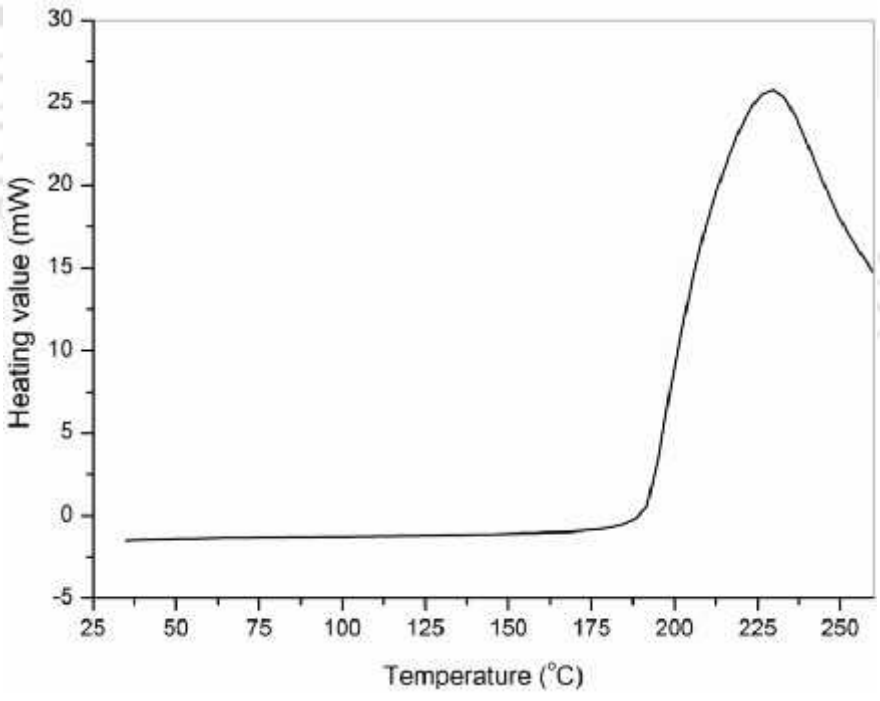


Figure 4.15: Oxidative stability of COME under air atmosphere

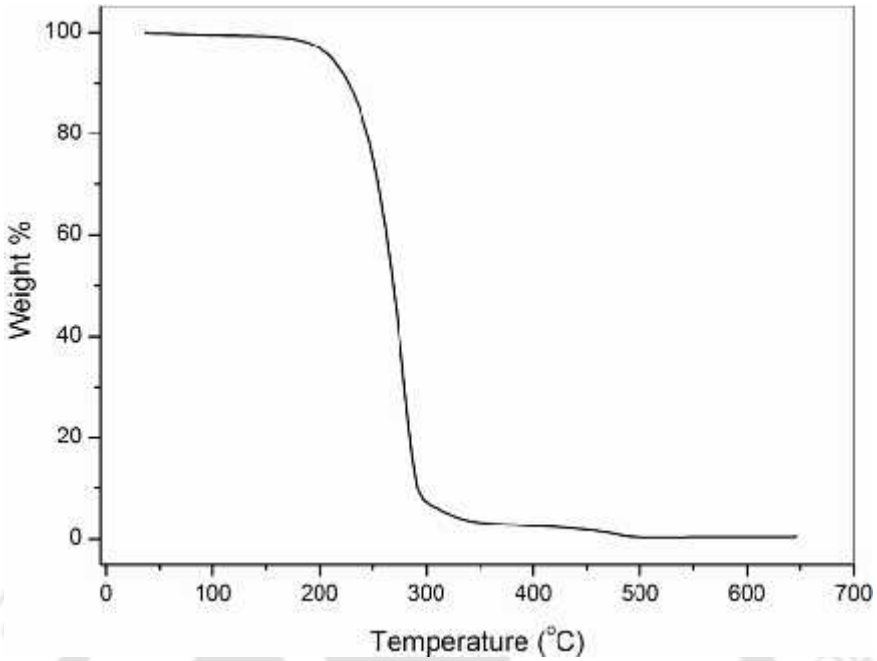


Figure 4.16: TGA profile of COME under inert gas atmosphere

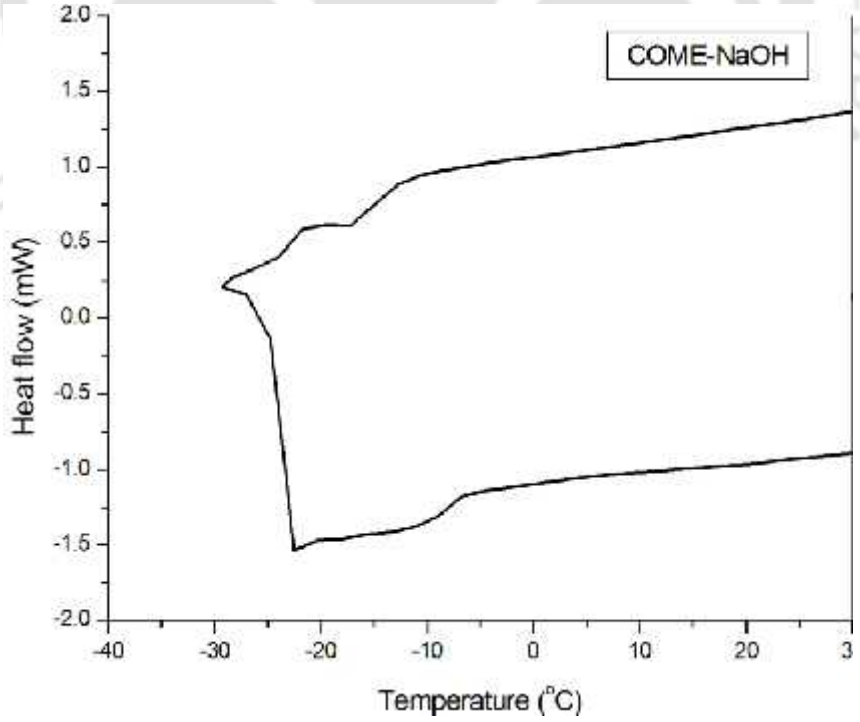


Figure 4.17: Pour point of COME by DSC

Density and viscosity of all the methyl ester blends (present study and reported) were slightly increased with increase in the methyl ester blending percentage from 5 to 15% [110]. Whereas cold flow properties (cloud point and pour point), flash point, fire point and calorific value did not show any significant change with increased blend percentage. Similar kind of trend has been reported by other researchers in their study with palm (cloud point, calorific value) and jatropha blends (cold flow properties). In the present study, calorific values were found to be decreased slightly with an increase in the blend percentage from 5 to 15%, which agreed well with the reported data for mahua, jatropha and rubber blends [107-108, 110]. However, flash point does not reveal any significant change with increase COME blend ratio, whereas by comparing our results with that of reported in literature using blends of palm and mahua showed slight increasing trend of flash point with blending percentage, while the trend for jatropha blends was uneven. The comparative analysis of COME properties obtained in the present study with that of reported in literature reveals that the density of COME in the current work is similar to that of obtained with other three methyl esters (i.e. mahua, jatropha, palm), but 50% lower than that of other COME which are reported in literature [105]. The calorific value for all the methyl esters was comparatively similar. The viscosity of COME in the present study was found to be two times higher than other three methyl esters. The higher viscosity of COME was mainly due to the presence of hydroxyl groups in the oil composition. The values of cold flow properties were 10-18% lower to other three methyl esters. The good cold flow properties of COME are due to the higher unsaturated fatty acid content of COME [156]. Flash point of COME in the present study was ~20% higher than that of other methyl esters. Nevertheless, all the estimated blends

properties are in the range of reported ASTM standards except few, which indicate that COME can act as a potential candidate to replace the conventional diesel.

4.2. Storage stability and biodegradability of COME

4.2.1. Storage stability of COME

The storage stability of COME samples (produced with NaOH via reactive extraction) was evaluated to understand the degradation level of COME over the long storage period (six months) under different conditions. The level of degradation was accessed by monitoring the changes in their physico-chemical properties such as density, kinematic viscosity, acid value and iodine value with respect to their initial values (Figure 4.18). Among all the storage conditions studied in this work, dark condition showed better stability of COME than the other two conditions such as open air and air tight in terms of increased trend of density, kinematic viscosity and acid value, while the decreasing trend of iodine value. Similar trend was noticed by several other researchers during the storage stability study of their methyl ester samples [52, 140]. The rate of degradation was significantly higher for the sample stored in an open air compared to that of other two conditions. The variation of density for all the three COME samples stored at three different conditions over six months of a timer period are shown in Figure 4.18. The density of COME was found to be increased from 0.888 to 0.984 g/cm^3 in the open air, 0.888 to 0.945 g/cm^3 in the air tight and 0.888 to 0.928 g/cm^3 in the dark conditions, respectively. Increase in the density of samples with storage duration resulted mainly due to the formation of degraded products or due to increase in the molecular weight of fuel molecules over the storage period [171]. Figure 4.18 represents the variation in kinematic viscosity of COME samples stored over the period of six months. The kinematic viscosity

of samples stored under different conditions such as open air, air tight and dark was found to be increased to maximum 16.18, 14.5 and 13.4 cSt, respectively. The increased kinematic viscosity of the samples resulted due to the polymerization and sedimentation of biodiesel over a long storage period [52]. The higher viscosity of fuel leads to lower atomization in the fuel injector which severely affects the engine performance [100]. Air exposure enhances the degradation of biodiesel samples. That is because a biodiesel oxidation process usually forms radical next to the double bonds which quickly bind with the oxygen in air.

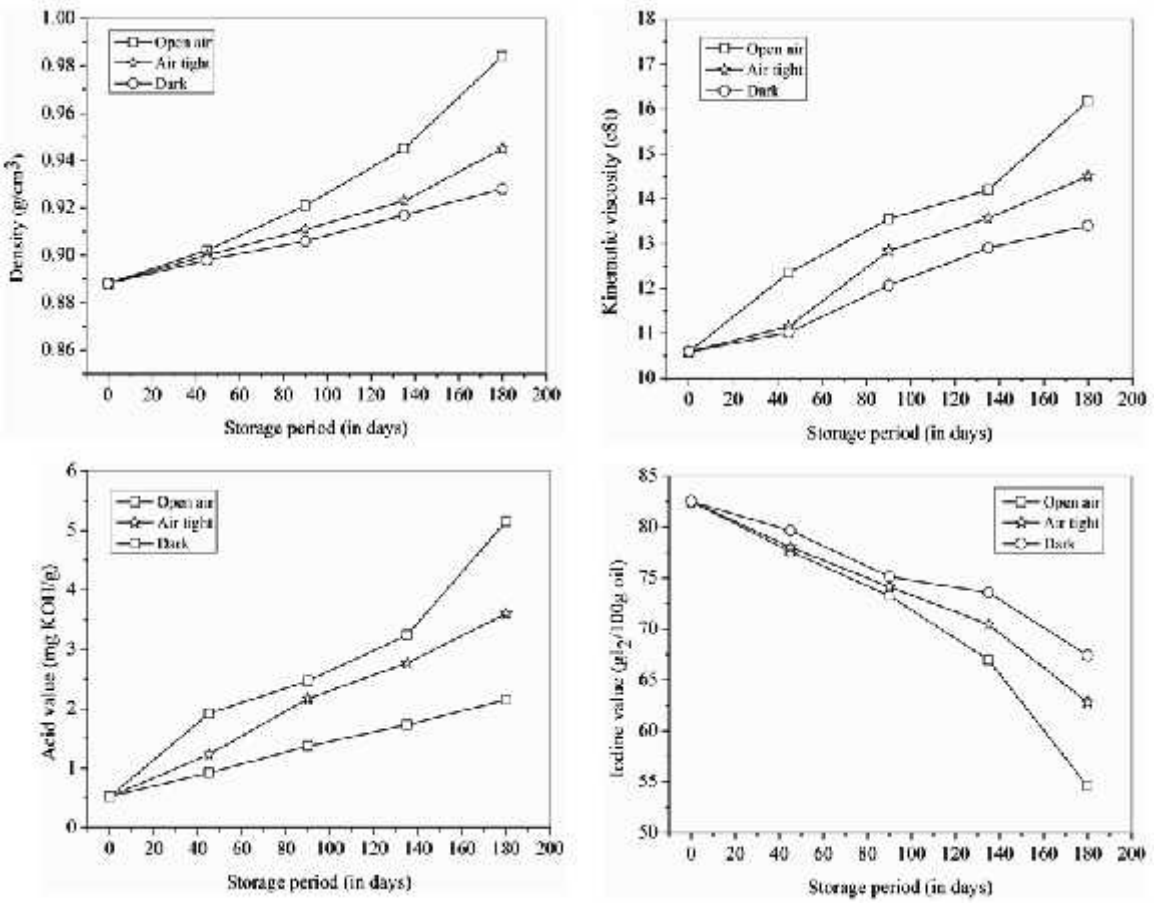


Figure 4.18: Effect of storage period on different parameters of COME under open air (exposed to light), air tight (exposed to light) and dark condition

This results in the formation of peroxide, which instantly forms new radical, and thus, the cycle of the radical auto-oxidation process starts, which exponentially increases the biodiesel degradation. The initial acid value of COME was around 0.52 mg KOH/g and over six months of a storage period increased to 5.15 (open air), 3.6 (air tight) and 2.15 (dark), respectively. Acid value was found to be higher for the sample stored in open air and air tight conditions compared to dark condition. Mazumdar et al., (2013) observed a similar trend of acid value during their storage stability study on jatropha derived biodiesel. Further, their study reveals that an increase in acid value is mainly due to the prolonged exposure of samples to the light which fastens the degradation rate compared to dark conditions. According to the reported literature, another reason for the increase in acid value over the storage period is due to breakage of long fatty acid chains into short-chain acids during oxidation or hydrolysis of biodiesel by the reaction of biodiesel with the moisture content in the ambient air or an increase of peroxides during the storage also leads to further oxidation into acids [52, 100, 171]. The iodine value of all COME samples was decreased from 82.5 (the initial value for all three conditions) to 54.57 (gI_2/100g oil) in an open air, 62.8 (gI_2/100g oil) in the air tight and 67.4 (gI_2/100g oil) in dark conditions respectively. The COME samples under the open air and air tight conditions showed a lower iodine value at the end of storage study compared to the sample kept in dark condition. Similar finding was observed by Bouaid et al., (2009) in their study on long-term storage stability of various vegetable oils under daylight and dark conditions [144]. The decrease in the iodine value of a COME sample over a storage period is due to the elimination of hydrogen which is closest to a double bond and the development of free radicals. However, the least degradation rate was found at the end of a storage period for dark condition sample implies that COME is more stable in dark

condition than other storage conditions used in this study (open air and air tight). The obtained over-all order of the degradation rate for three storage conditions was: Open air > Air tight > Dark. Thus, storage stability study revealed that dark condition is the safer condition for long-term storage of biodiesel.

4.2.2. Biodegradability of COME

The biodegradability of COME has been studied using bio-kinetic model. According to biodegradability screening tests, any substance which meets the OECD ready biodegradability pass levels (either 60% CO_2 evolution, 60% BOD/ThOD or 70% dissolved organic carbon (DOC) removal within twenty eight days test period) are considered as 'readily biodegradable [172]. The biodegradability of COME was 51% within 28 days. Corseuil et al., (2011) have reported similarly about 40% biodegradability of castor oil biodiesel within 90 days. The lower biodegradability was attributed to the higher viscosity and lower bioavailability [115]. Al-Darbi et al., (2005) have reported that various oils respond in different rates and extents to biodegradation which mainly depends on their viscosity, structure and composition [112]. Lisiecki et al., (2014) observed that blending of biodiesel with diesel has not shown impact on the long-term biodegradation [116]. However, fuels with established biodegradability in the range of 70-100% are not expected to cause environmental concern because its high biodegradability will leave very little residue and therefore it is not toxic to aquatic organisms [54]. Though the biodegradability of natural and vegetable oils are not in doubt, the lower COME biodegradability in the present study may be due to the higher viscosity (10.39 cSt) or other reasons as discussed. With this, it can be concluded that COME is biodegradable and eco-friendly.

4.3. Engine performance test of COME

4.3.1. Engine performance parameters

The effect of various engine performance characteristics were evaluated in the test using various COME blends prepared (5, 10 and 15 vol %) with diesel. The results of the tests are discussed below in detailed.

4.3.1.1. Brake power variation with BMEP

The brake power variation with Brake Mean Effective Pressure (BMEP) is shown in Figure 4.19. Similarly, variation of BMEP with load is given in Figure 4.20. The linear increase was observed with increasing power with increase in BMEP. And similar linear trend was also observed between BMPE and load. As the engine is a constant speed engine with respect to load, the speed remains constant in ±50 rpm.

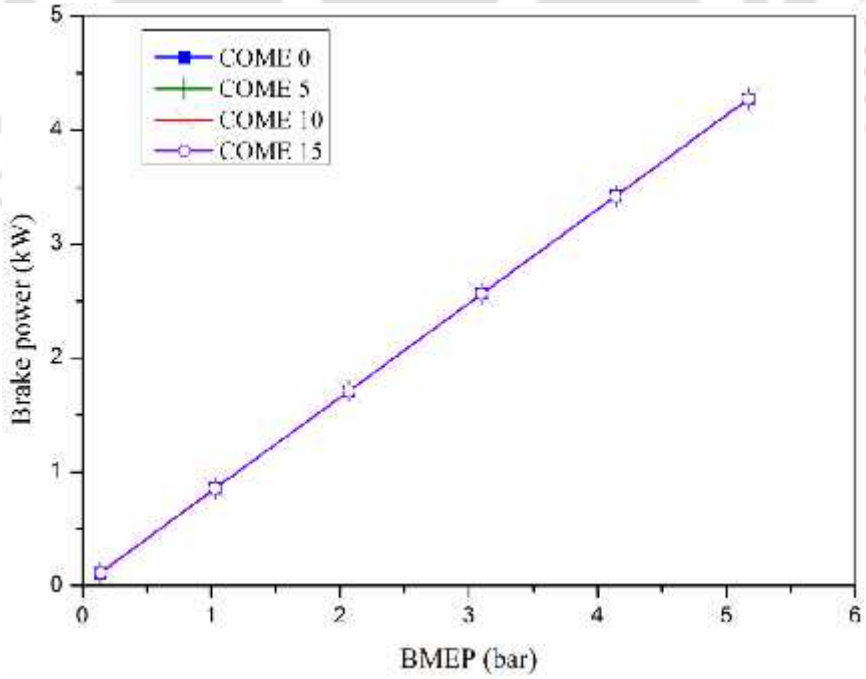


Figure 4.19: Brake power variation with BMEP

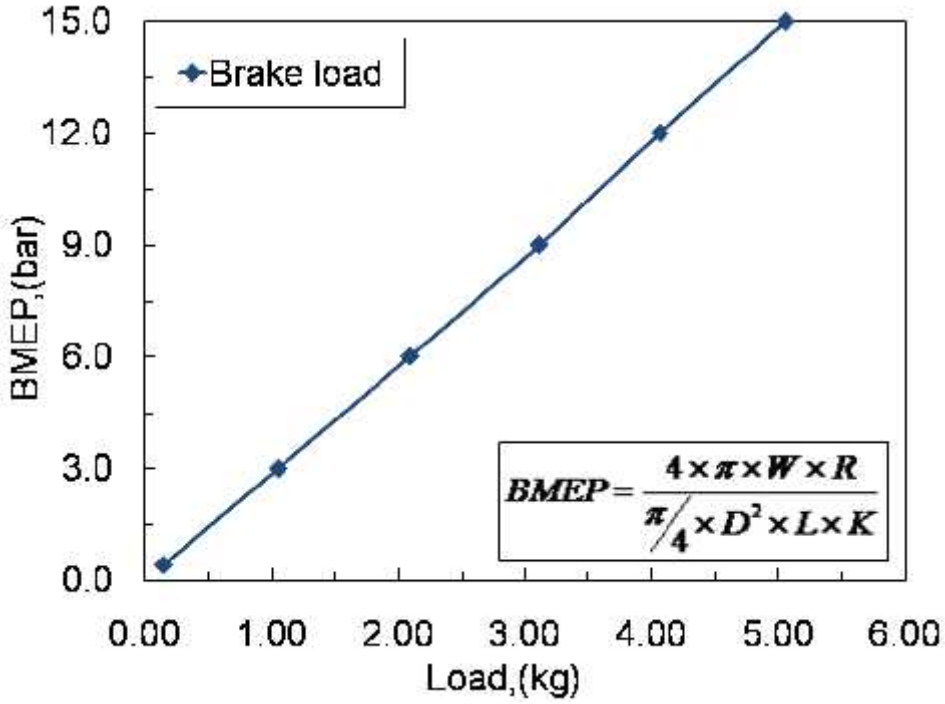


Figure 4.20: Variation of BMEP with load for all blends

Therefore, brake power is a function of brake load only which keeps on increasing with constant increment in load for every set of data [173]. Thus, it is the remark of validation of experimental procedure as the brake power remains constant throughout the BMEP. Moreover same trend and magnitude of brake power is noticed for all tested blends.

4.3.1.2. BSFC variation with BMEP

The Figure 4.21 shows the rate of fuel consumption in order to keep the brake power constant in terms of BSFC. The BSFC variation was found from 0.864 to 0.350 kg/kWh for diesel as well as 0.932 to 0.380 kg/kWh, 0.969 to 0.340 kg/kWh and 0.959 to 0.410 kg/kWh for COME5, COME10 and COME15, respectively with increase in BMEP over a wide range i.e. low to maximum. At mean effective pressure of 1.03 bar, BSFC reported

the increment of 8.13%, 12.79% and 11.62% for all tested fuels with respect to diesel. This increment in BSFC reduces with increase in BMEP at maximum load, the BSFC found to be increased by 8% and 18% for COME5 and COME15 respectively.

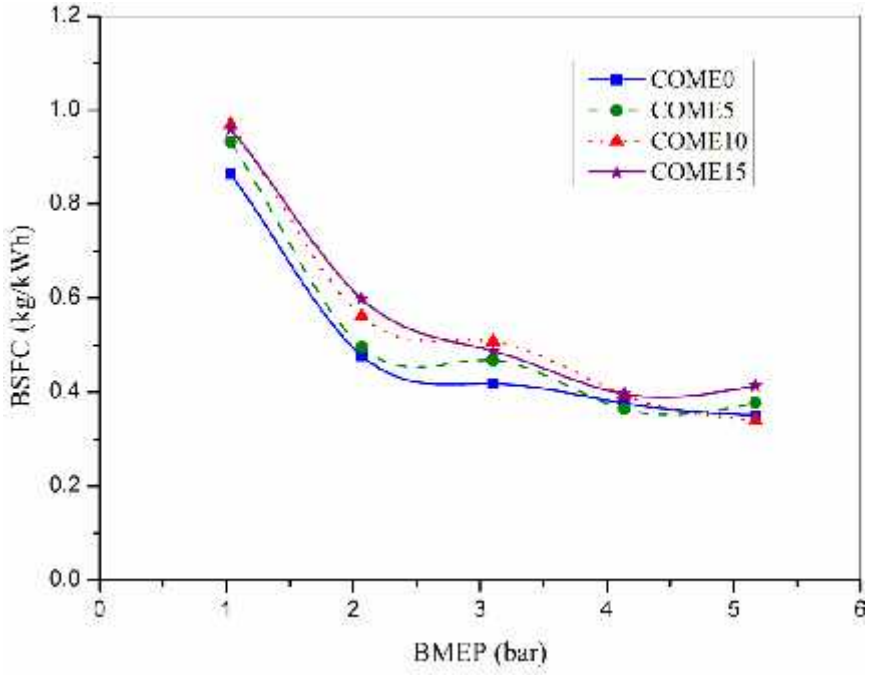


Figure 4.21: BSFC variation with BMEP

But, the decrease of 3% was obtained for COME10 with respect to diesel. Thus the important fuel properties such as blend density and lower heating value strongly dominate the fuel consumption in terms of BSFC. The lower heating value and higher density of biodiesel blended fuel reduce the flame speed for combustion which in turn affects the pressure and acting on the piston [174].

4.3.1.3. BTE variation with BMEP

The fuel consumption in terms of BSFC directly affects the brake thermal efficiency (BTE) of the engine cycle. As shown in Figure 4.22, BTE found to be increased with an increase in the BMEP for diesel as well as for all tested fuels.

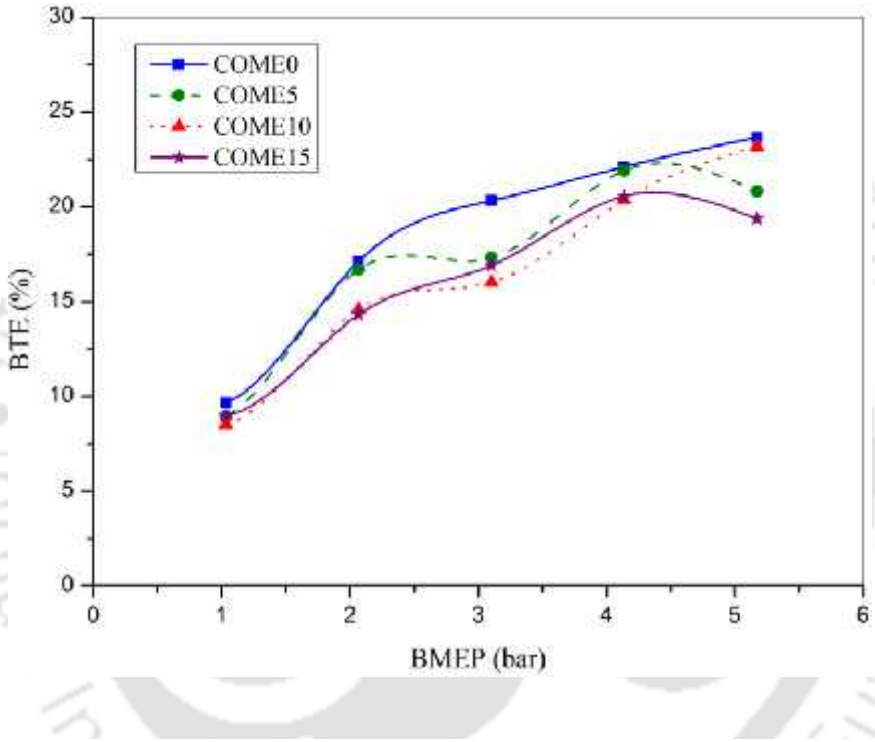


Figure 4.22: BTE variation with BMEP

The increment from 9.65% to 23.65%, 8.93% to 20.82%, 8.49% to 23.14% and 8.99% to 19.38% have been recorded for diesel, and all other tested fuels, respectively from lower to maximum BMEP [175]. At 1.03 bar and low load condition, the decrement of 8%, 12% and 7%, while at maximum load, decrement of 12%, 2% and 18% were found for all tested fuels respectively in comparison with that of diesel. Higher fuel consumption for blended fuels decreases the thermal efficiency of the engine.

4.3.1.4. Volumetric efficiency variation with BMEP

The increment or decrement in the Brake thermal efficiency was greatly influenced by the actual mass of air supplied for complete combustion of the fuel charged inside the engine. Figure 4.23 shows the mass of air actually supplied to the theoretical mass of air required for complete combustion in terms of volumetric efficiency.

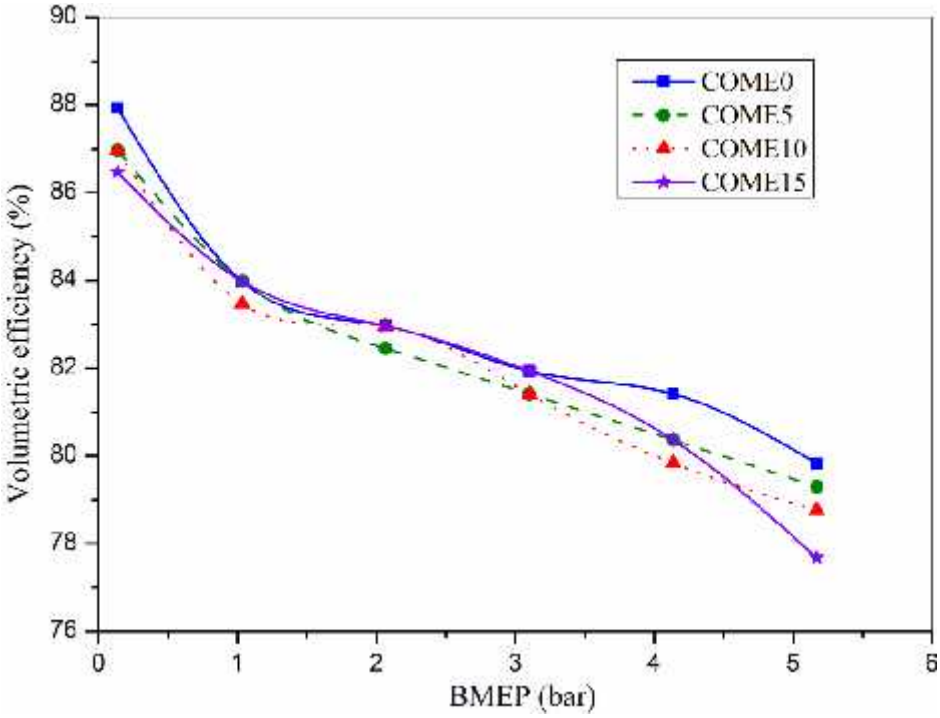


Figure 4.23: Volumetric efficiency variation with BMEP

The volumetric efficiency found decreasing with increasing load on the engine. The decrements of 9%, 10% and 11% have been attained by diesel along with all tested fuels, respectively which were tested for the range of BMEP from minimum to maximum position. At 1.03 bar, there is decrement of 1.11%, 1.11% and 1.62% while at 5.17 bar shows decrement of 0.65%, 1.34% and 2.70% in volumetric efficiency for all tested fuels, respectively with an increase in the blend percentage with diesel fuel. With an increase in

load, the fuel consumption increases which affect the volumetric efficiency for blended fuels. Results from presently conducted experiments are seen to have encouraging agreement with the literature reported results for performance analysis [173-177].

4.3.2. Emission analysis

4.3.2.1. Exhaust Gas temperature variation with BMEP

The exhaust gas temperature (EGT) variation with BMEP in Figure 4.24 shows that the temperature increases with an increase in the BMEP for all the tested fuels.

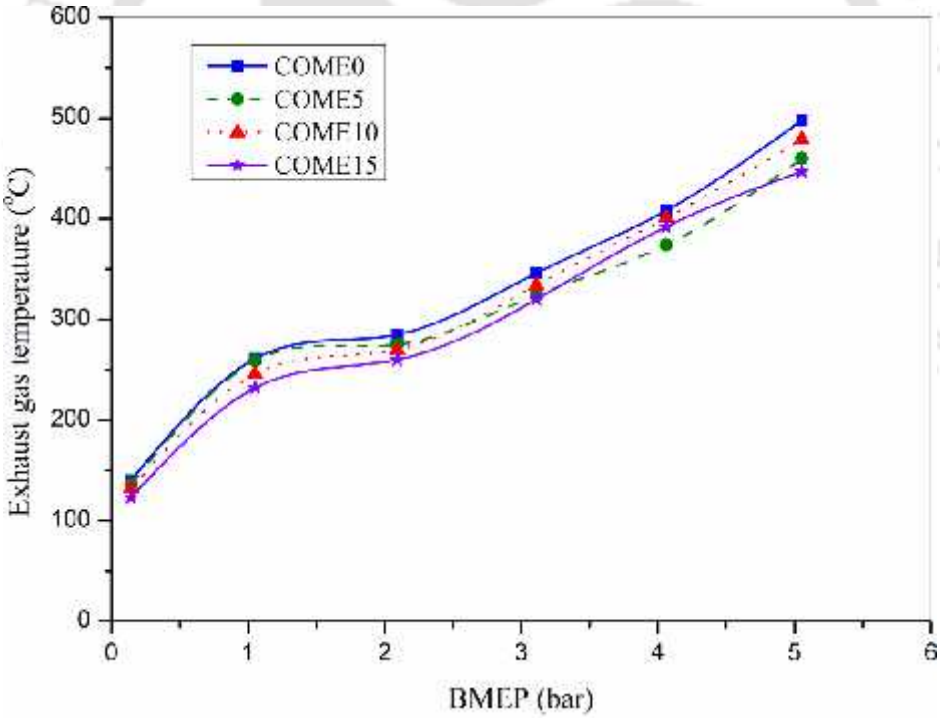


Figure 4.24: Exhaust gas temperature variation with BMEP

The EGT rise depends upon the increment in the load on the engine. But engine load increases fuel consumption with rise in cylinder pressure inside combustion

chamber. The increase from 140 to 498 °C, 136 to 460 °C, 132 to 479 °C and 123 to 447 °C have been found with the range of BMEP from low to maximum. The influence of blend percentage on EGT also shows decrement with respect to diesel by an amount of 1%, 6% and 11% at 1.03 bar and 8%, 4%, 10% at 5.17 bar for all tested fuels, respectively. The heating value and specific gravity of the fuel are responsible for the decrease in EGT for biodiesel blended fuel with respect to diesel fuel [176].

4.3.2.2. CO variation with BMEP

The variation in carbon monoxide (CO) emission with BMEP for different fuels is shown in Figure 4.25.

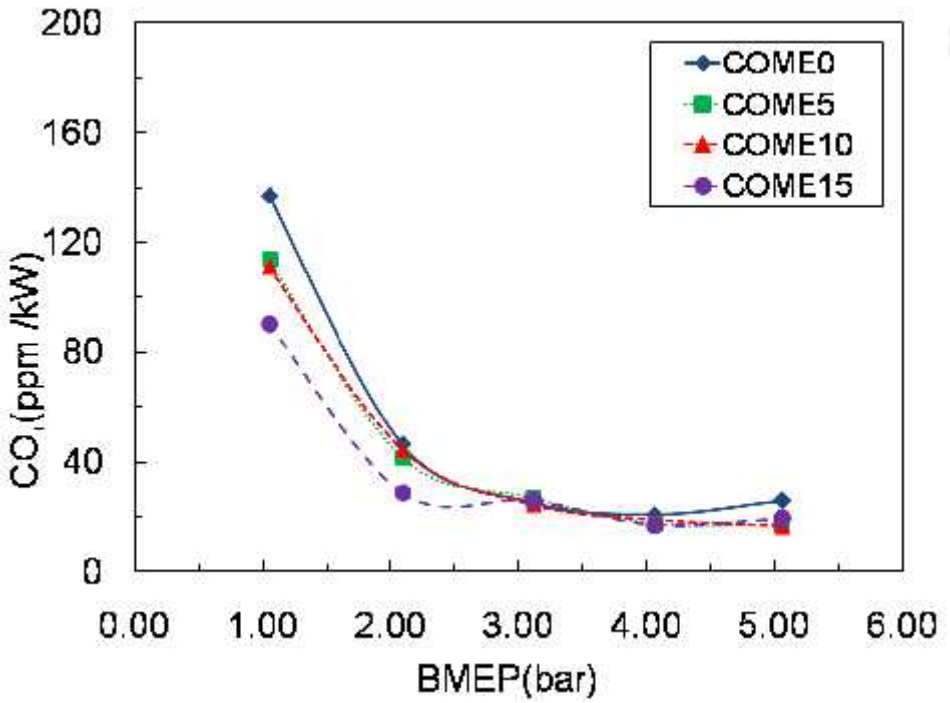


Figure 4.25: CO variation with BMEP

The CO emission is more during the low BMEP and decreases with increase in pressure. However, as per figure emission per unit power output is higher for low BMEP condition and decreases with further increase in BMEP. The variation of 111-150 ppm, 75-146 ppm, 71-120 ppm, 83-101 ppm from maximum to minimum load over a wide range of BMEP has been recorded. The maximum CO has been recorded for diesel test and reduces further with the increment of COME in blend throughout the load range from minimum to maximum. During cold staring of the engine, more fuel is required as well as during high load conditions also the fuel supply increases which affect the CO emission in exhaust gas, especially during minimum and maximum load. The extra oxygen in biodiesel fuel causes the complete combustion of fuel air mixture reducing CO with increase in the blend percentage and converting it to the green house gas [175-176].

4.3.2.3. CO_2 variation with BMEP

The green house gas carbon dioxide (CO_2) emission from the engine exhaust for different fuel blends are plotted in Figure 4.26. Actually, the absolute value of CO_2 emission for diesel and biodiesel blends was to be found increased with an increase in the BMEP. Moreover as per the figure, emission per unit power output decreases with increase in BMEP. The absolute value of percentage emission of CO_2 ranges from 0.78-3.12%, 0.99-4.68%, 0.8-4.02% and 0.98-3.91% for diesel and all tested fuels, respectively for minimum to maximum BMEP. However, these emissions are in the range of 0.73-8.68 percentage per unit power output. At 1.03 bar, the CO_2 shows 3%, 4%, 35% increment in absolute percentage emission, while the same at 5.17 bar was 50%, 28.85% and 25.32% for all tested fuels, respectively in comparison with that of diesel.

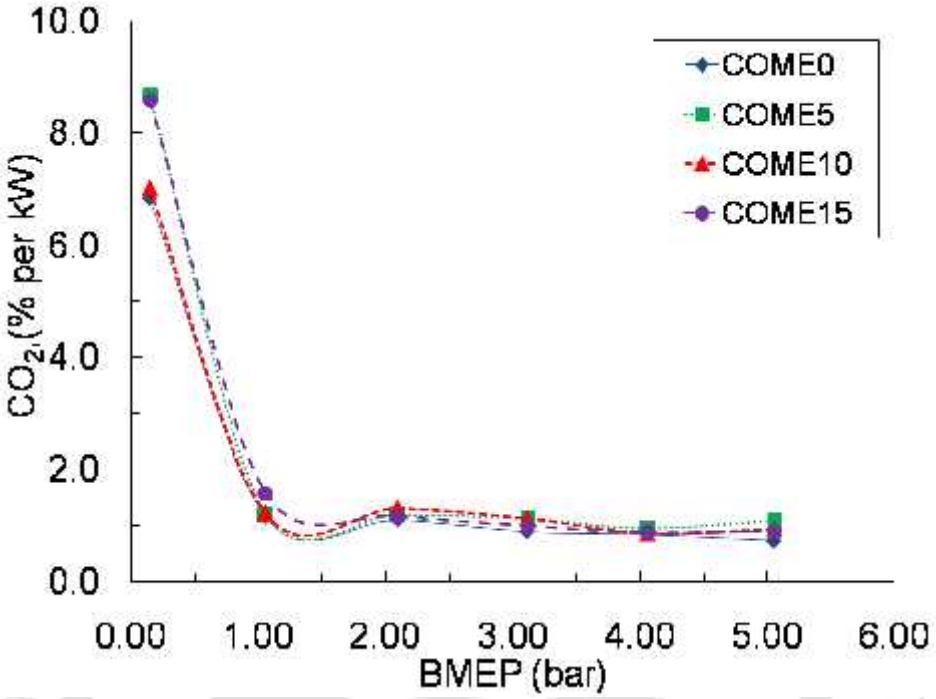


Figure 4.26: CO_2 variation with BMEP

Thus, higher the percentage of biodiesel, higher is the CO_2 level. Increased CO_2 in the exhaust with increase biodiesel blend percentage in diesel may be due to the excess oxygen present in the biodiesel which reacts with CO to form CO_2. This reasoning can be well justified with the variation of CO with BMEP given in Figure 4.25. Moreover, it has also been reported that the formation of particulate matter is higher in case of biodiesel [176]. Thus formed particulate matters react with the oxygen in fuel to form the CO_2.

4.3.2.4. Variation of oxides of nitrogen with BMEP

The emission of the oxides of nitrogen for diesel and all tested fuels are plotted in Figure 4.27. For the absolute value of emission, NOx emission was found to be increased with an increase in the BMEP for diesel and all the blends. But the figure depicts that the

emission per unit power output decreases for all the fuels, except for 15% blend it increases with increase in BMEP. The increment in absolute NOx from minimum to maximum load was 29-162 ppm, 13-140 ppm, 8-140 ppm and 3-129 ppm for diesel and all tested fuels, respectively. At 1.03 bar, the NOx decrement for absolute value was 9%, 42% and 79% while at 5.17 bar, the decrement noticed was 14%, 6%, 20%. For the higher blending ratio there was increment in NOx per unit power output which may be attributed to the higher oxygen content of the fuel. However, NOx variation for any fuel depends on the maximum temperature achieved during combustion. That means higher the load on the engine, higher will be the temperature which results in higher NOx [58].

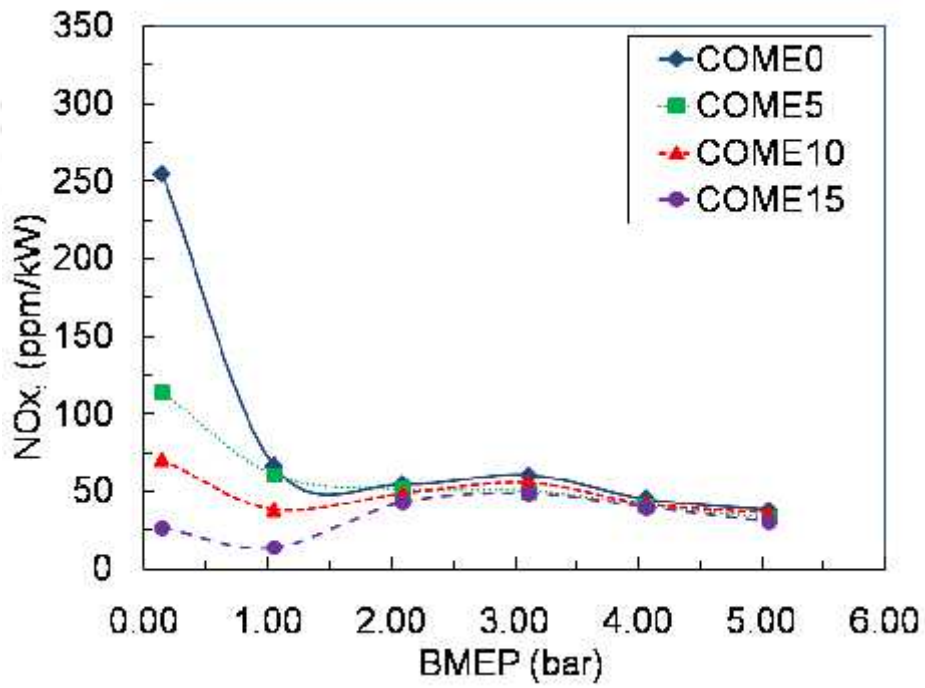


Figure 4.27: Oxides of nitrogen variation with BMEP

4.3.2.5. HC variation with BMEP

The unburnt hydrocarbon (HC) emission from the engine exhaust is shown in Figure 4.28. The emission of hydrocarbon for diesel fuel as well as for blended fuels was much higher initially when no load was applied. However with increase in load on the engine, HC emissions were found to be decreased till 60-80% load. But thereafter, slight increase in HC emissions was observed when engine was running at maximum BMEP. The HC emission shows variation from 74-221 ppm, 37-154 ppm, 60-134 ppm and 61-124 ppm from maximum to minimum BMEP.

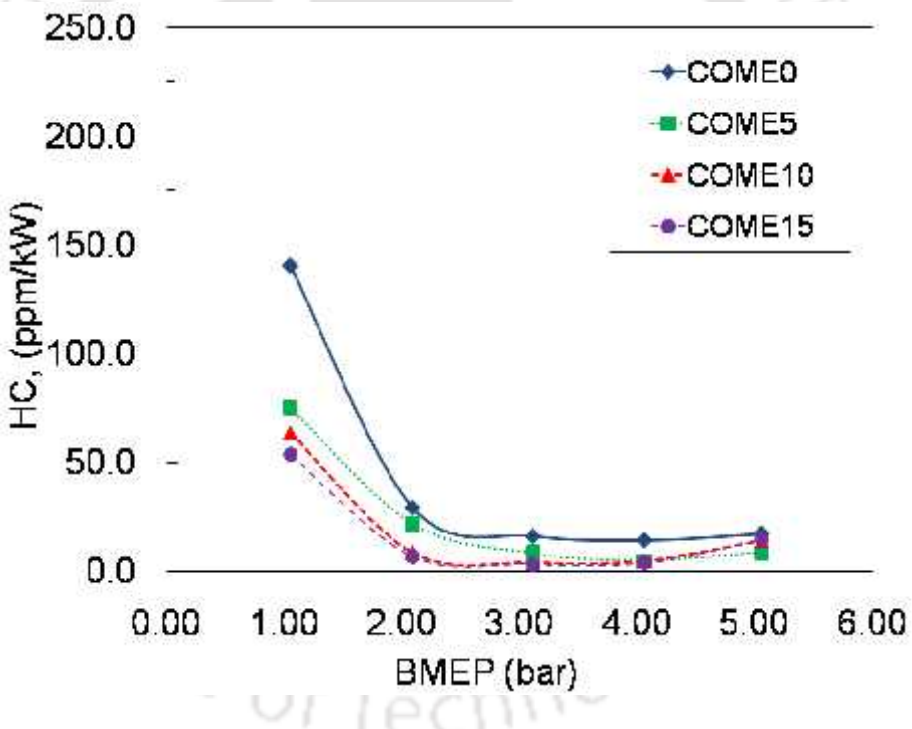


Figure 4.28: HC variation with BMEP

At 1.03 bar, the decrement in absolute value of HC was 46%, 55% and 61.6%, while at 5.17 bar decrement was 50%, 18.91% and 17.56% for all tested fuels, respectively in comparison with the diesel. Thus, HC emission decreases with an increase in biodiesel percentage in blend. Although the hydrogen to carbon ratio in both diesel and

COME are near to 2, extra hydrogen presents in COME carries away the hydrogen to form water. Due to which the HC for biodiesel blended fuel is lower [60].

4.3.3. Combustion parameters

4.3.3.1. Cylinder pressure variation with crank angle

The cylinder pressure as a function of crank angle has been plotted in Figure 4.29.

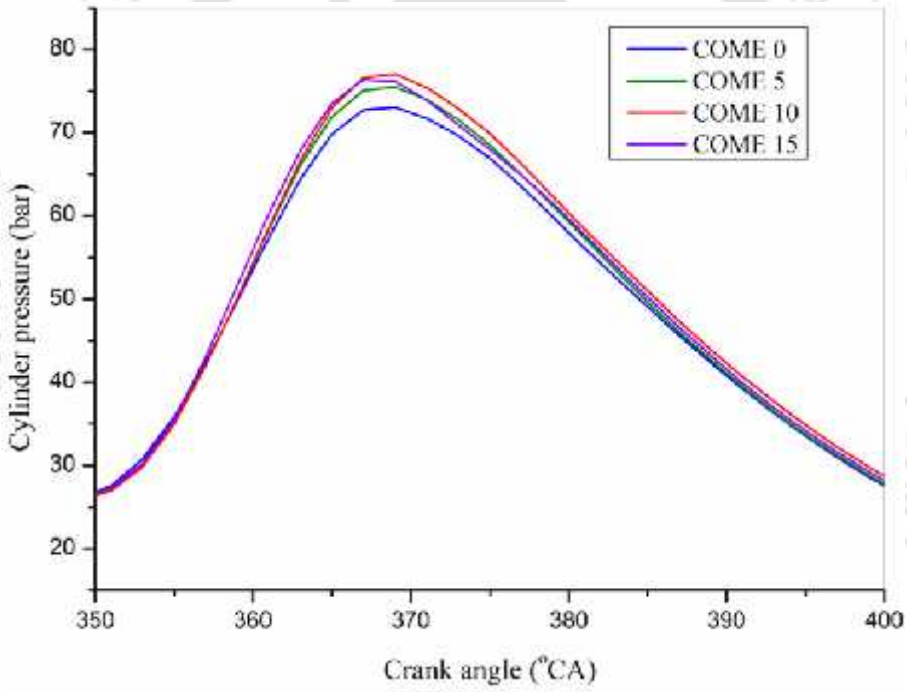


Figure 4.29: Cylinder pressure variation with crank angle

This figure for cylinder pressure corresponds to 100% load that is at maximum BMEP. Here, initial pressure increase is mainly due to compression of the air. Moreover, injection of the fuel at 23 °bTDC leads to combustion and onwards increases in pressure. The attainment of peak pressure is expected close to TDC. Similar, observation is evident

from Figure 4.29 for all blends. However, peak pressure is higher for blended fuel than diesel fuel. At the conditions stated here, the maximum cylinder pressure of 73.22 bar, 75.56 bar, 76.86 bar and 76.41 bar was achieved (Table 4.9) for diesel and all tested fuels, respectively. The rise in pressure at constant operating conditions reflects the more homogeneous combustion of the fuel air mixture inside cylinder [178]. The pressure-crank angle diagram clearly suggests a knock free operation of the engine since there exists no pressure pulsations.

Table 4.9: Combustion parameters of tested fuels on diesel engine at 100% load

Fuel mode	Max. cylinder pressure(bar)	Start of fuel injection (° bTDC)	Start of combustion (° bTDC)	Ignition delay (° CA)	Net heat release rate (J/° CA)
Pure diesel	73.22	23	21	16	68.792
COME5	75.56	23	19	14	70.265
COME10	76.86	23	19	14	73.717
COME15	76.41	23	19	14	77.049

4.3.3.2. Peak cylinder pressure variation with BMEP

The peak cylinder pressure as shown in Figure 4.30 does not remain higher always for biodiesel blended fuels. For the complete range of BMEP studied, the peak cylinder pressure was found to be increased with an increase in load on the engine. At BMEP 1.03 bar, the peak pressures for biodiesel blends were lower than that of diesel fuel. But, the opposite trend was observed at 2.1 bars, 3.1 bars and 5.17 bars. The peak cylinder

pressure was influenced by two major factors one of which is cetane number of the fuel. The cetane number of biodiesel blended fuel increases with an increase in blend percentage with respect to diesel. The other factor is the lower ignition delay of biodiesel blended fuels. These factors are expected to have their influence on peak cylinder pressure.

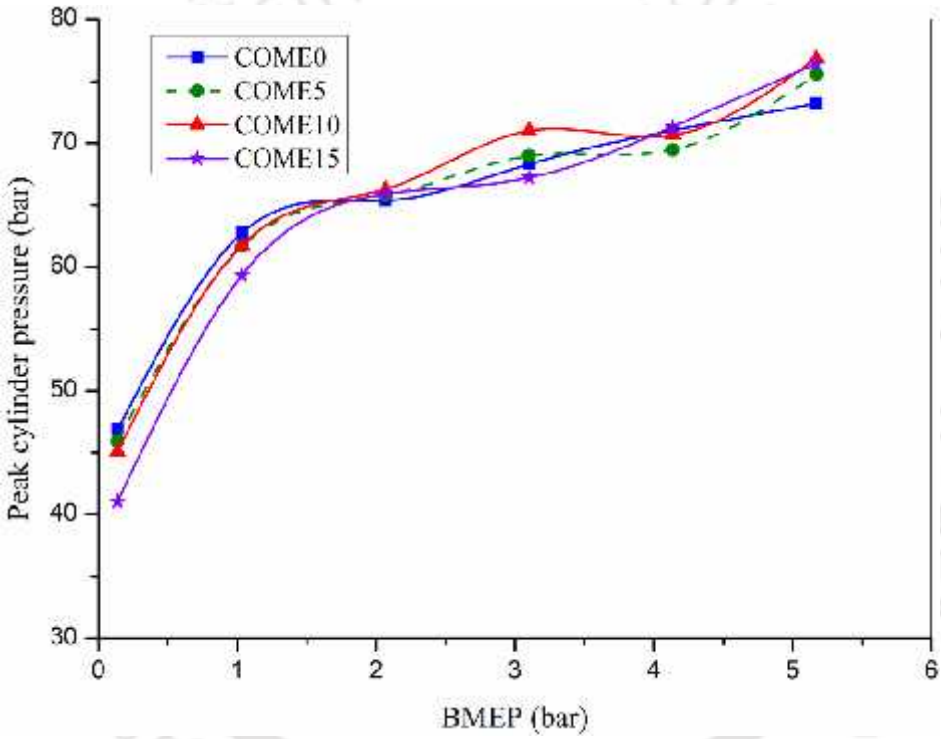


Figure 4.30: Peak cylinder pressure variation with BMEP

4.3.3.3. Net Heat Release Rate variation with crank angle

Net heat release rate can be evaluated from the pressure-crank angle diagram using Equation A.9 of Appendix. (Figure 4.29) [131]. This calculation is very much required for understanding the combustion initiation and combustion duration of the charge. Therefore, the net heat release rate (NHRR) as a function of the crank angle (CA) for diesel and different blended fuels are plotted and shown in Figure 4.31. Here, the rise of

NHRR corresponds to the crank angle where combustion initiates. In the further progress, NHRR attains the maximum at a particular crank angle. Thus, combustion duration can be evaluated from the difference between this crank angle and the crank angle corresponding to combustion initiation. In the Figure 4.31, combustion initiation and combustion duration was found to be almost same for all the blends. The maximum NHRR has been observed at 359 ° CA bTDC for all the tested fuels.

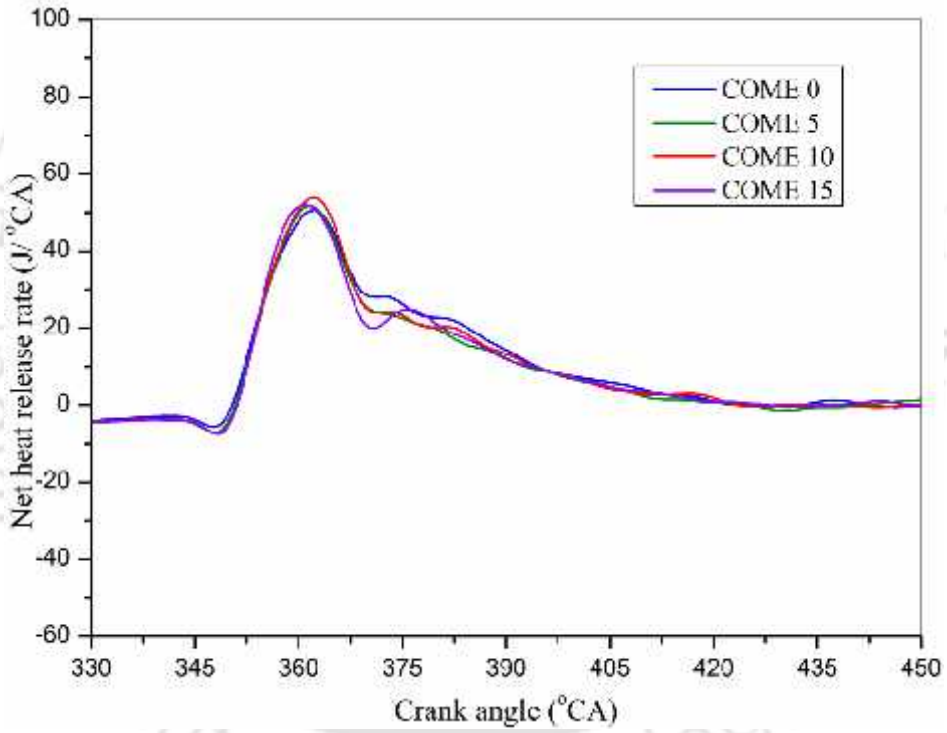


Figure 4.31: Net heat release rate variation with crank angle

4.3.3.4. Ignition delay with BMEP

It is possible to measure the ignition delay (ID) for a given fuel in an engine from the pressure-crank angle diagram (Figure 4.29) using Equation A.10 of Appendix. This quantity necessarily corresponds to the time duration between injection and combustion

initiation. the ignition delay obtained from present experiments in relation to the BMEP for different COME blends are depicted in Figure 4.32.

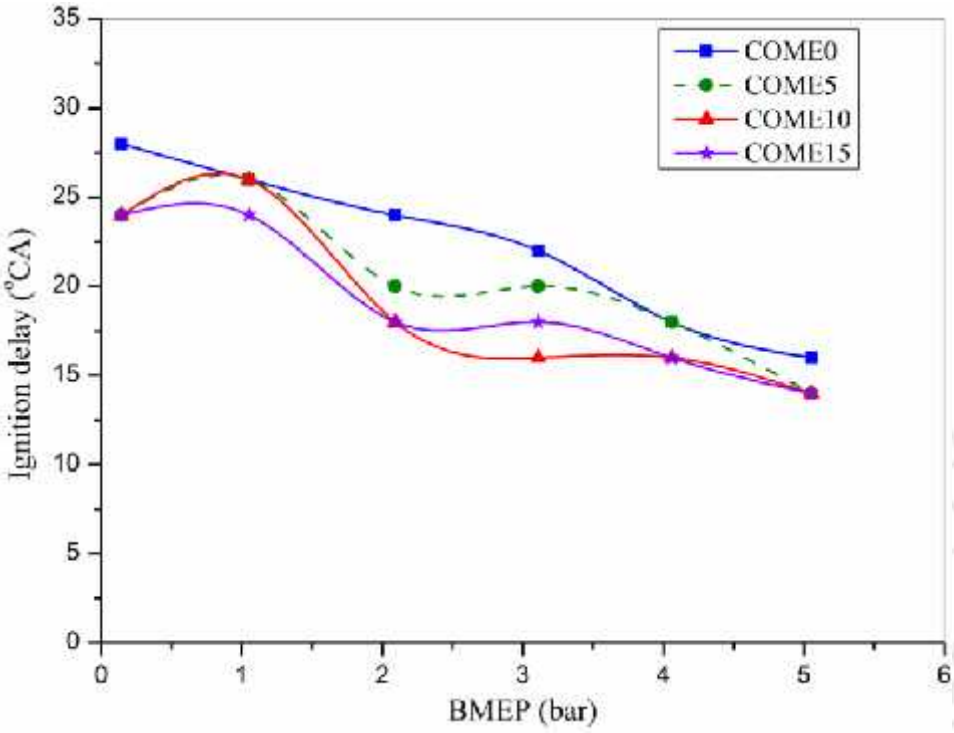


Figure 4.32: Ignition delay variation with BMEP

As seen in the figure, the ID was found to be reduced with an increase in BMEP for all the blends. Also, the ID for diesel fuel is higher than the biodiesel blended fuel. And with increase in blending percentage, the ID found to be decreased further. The ignition quality of the fuel called as cetane number, which is more for biodiesel as it contains straight chain paraffinic compounds which have highest ignition quality. That is the reason for which ID reduces with higher percentage of biodiesel in blend [177].

4.3.4. Uncertainty analysis

The real errors in experimental data needs the consistent way of specifying the uncertainty in analytical form. The more precise method of estimating uncertainty in experimental results has been presented in literature by using sequential perturbation technique [179-181]. Some of the observed parameter uncertainties are engine speed (0.5%), brake load (0.5%), mass flow rate of liquid fuel (1%), mass flow rate of air (1%), LHV of diesel (1%), LHV of biodiesel (1%), cylinder pressure (0.1%), cylinder volume (0.1%), temperature (3 °C), specific heat of exhaust gas (0.5%), ratio of specific heat (0.5%), CO, CO_2, NOx, HC emissions (3%). Based on these, the computed performance parameter uncertainties found are listed in Table 4.10.

Table 4.10: Uncertainty associated with computed parameters

Computed parameters	**Uncertainty**
Brake power	± 1.2%
Brake thermal efficiency	± 1.52%
Brake specific fuel consumption	± 1.04%
Net heat release rate	± 1.6%
Ignition delay	± 0.2%
Emissions	± 5%

4.4. Summary

This chapter has demonstrated the direct production of biodiesel from castor seeds via integrated and non-integrated approach. Optimization of these reactive extraction techniques have investigated by RSM design method. At the optimum condition maximum COME conversion in both approaches was found to be 95-96%. Thus, the

model can be effectively employed in the biodiesel industry to maximize the conversion of methyl esters. The results showed insignificant effect of co-solvent on the COME conversion. Nevertheless, all the estimated COME properties were in the range of reported ASTM standards except few, which indicate that COME can act as a potential candidate to replace the conventional diesel. The storage stability study of COME suggests that COME stored in a dark condition was more stable than other two conditions. The biodegradability of COME was found lower about 51% within 28 days, which may be due to its higher viscosity and lower bioavailability. The engine performance tests were conducted for castor oil methyl ester and its blends at 5%, 10% and 15% blends with diesel fuel. Among three blends, B10 blend gave the best brake thermal efficiency of engine at maximum load compared to other blends. The exhaust gas emission showed reduction in CO (26-36%), NOx (14-20%) and HC (17.5-50%) gases with increase of COME blending percentage compared to conventional diesel.

CHAPTER 5

An investigation on emulsion characteristics of two phase castor oil methyl ester-water emulsions by ultrasonic method

This section discusses the results obtained from the work done on emulsion characteristics of two phase castor oil methyl ester-water emulsions (W/ME and ME/W) by ultrasonic method, physico-chemical properties properties of emulsions and summary.

5.1. Effect of various variables on stability of W/ME and ME/W emulsions

In order to prepare the stable W/ME and ME/W two-phase emulsions, the effect of different variables on emulsion stability was studied. Based on the phase separation behaviour stability of emulsions was observed for more than two weeks. Though the initial stability of the samples was noted, optimization of the variables was carried out based on the long term observation of the phase separation for W/ME emulsion. The stability of ME/W emulsion was optimized based on the initial stability of the samples. The detailed discussion on the effect of various process variables in both emulsions is as follows.

5.1.1. Effect of HLB on emulsion stability

HLB can be defined as the measure of the degree to which a liquid molecule is hydrophilic or lipophilic. Hydrophilic molecules are those which interact with water or

polar substances while lipophilic molecules dissolve in fats, oils, lipids and non-polar solvents [60]. The effect of HLB on phase separation for both emulsions is shown in Figure 5.1 and Figure 5.2. With increasing the HLB values from 4.3 to 15 lead to increase the quantity of hydrophilic surfactant (Tween 80) in W/ME emulsion and lipophilic surfactant in ME/W emulsion.

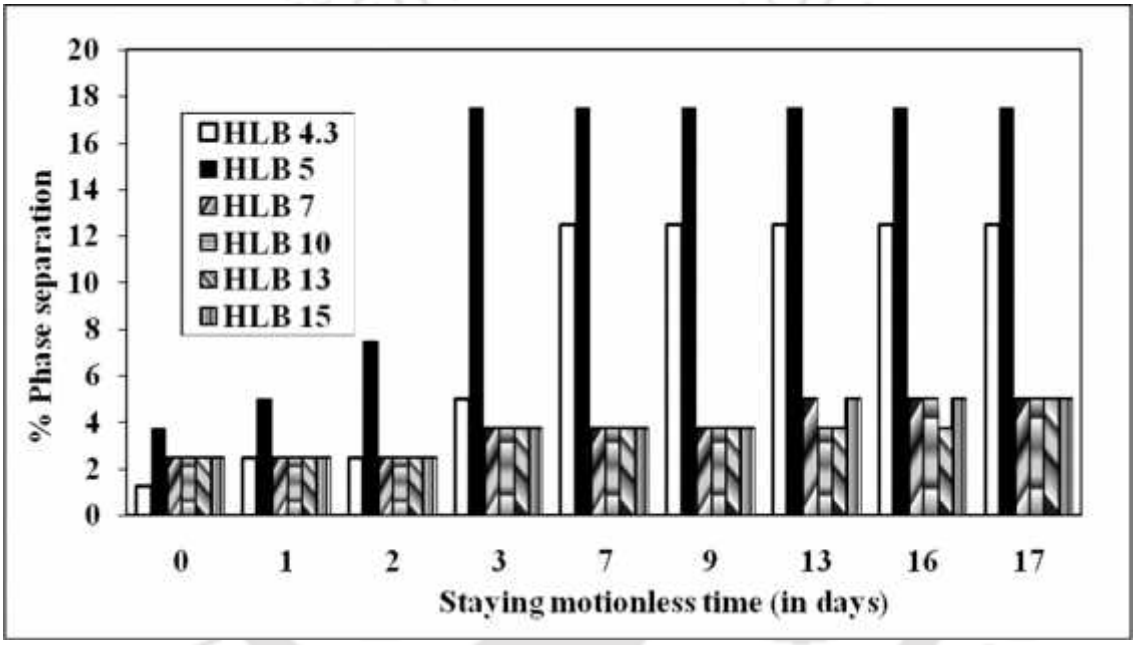


Figure 5.1: Effect of HLB on W/ME emulsion stability

Colour of the prepared W/ME and ME/W emulsions were found to be yellow and milky-white, respectively. It was found that the W/ME sediment layer separated from the W/ME emulsion and appeared at the bottom of the measuring cylinder after the emulsion had been kept motionless for 5 min. The white sediment layer was observed at the top of the ME/W emulsion. For both (W/ME and ME/W) emulsions, the volume fraction of the sediment layer was kept increasing when it was kept motionless. The sediment layer forms mainly due to the phenomenon of the coalescence process where formation of

larger droplets occurs and then lead to the sedimentation [182]. In case of both the emulsions, throughout motionless time of two weeks, phase separation of the emulsified layer was found to be increased with an increase in the HLB from 4.3 to 15 for all the samples.

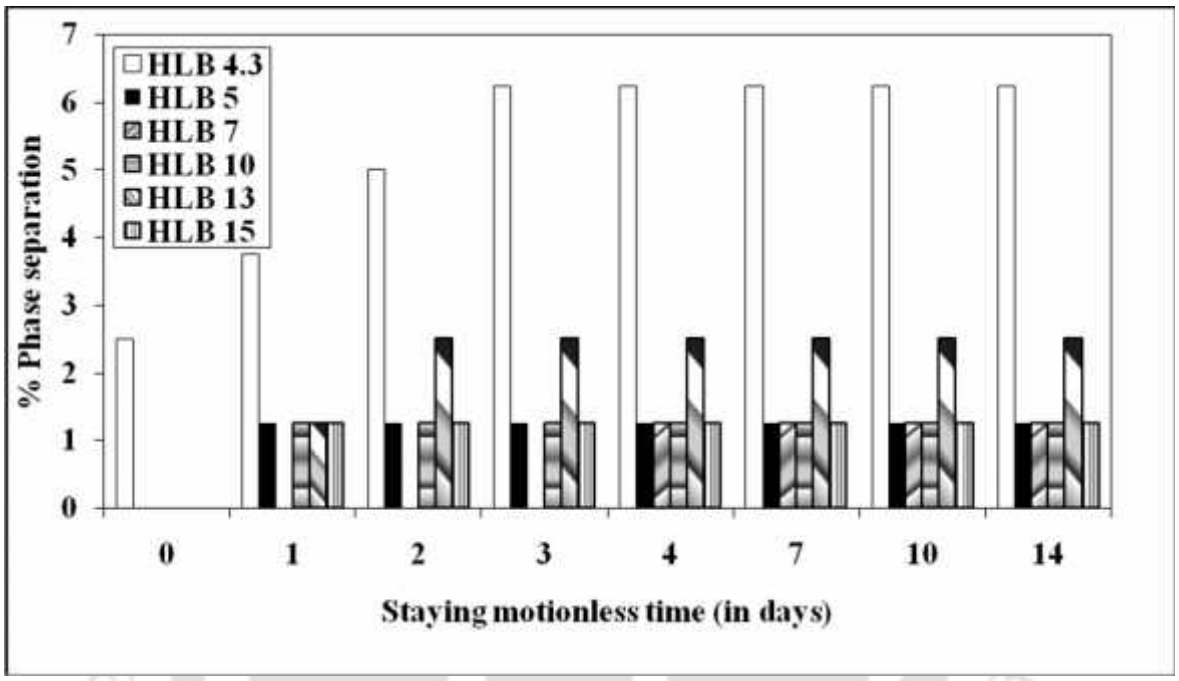


Figure 5.2: Effect of HLB on ME/W emulsion

The initial stability of W/ME emulsion observed was longer about 3 h for HLB 15 compared to other HLB followed 4.3 (15 min), 5 (seconds), 7 (15 min), 10 (30 min) and 13 (30 min), respectively. However, for prolonged motionless time, higher phase separation was observed for lower HLB samples such as 4.3 (1.25 to 12.5%) and 5 (3.75 to 17.5%). On the other hand, HLB from 7 to 15 showed lower phase separation during the motionless time. Among these HLB values (i.e. 7 to 15), HLB 13 showed the highest stability for the prolonged motionless time. The HLB values of the surfactants i.e. Span 80 and Tween 80 are 4.3 and 15, respectively. This implies that with an increase in HLB value of surfactant in the emulsion results in large Tween 80 content in the mixture than

Span 80. This is because surfactant Tween 80 is a hydrophilic emulsifier that adheres to both dispersed water phase and the biodiesel phase of the emulsion. Thus, the increase of Tween 80 in the mixture promotes coverage capability of the dispersed phase with the biodiesel phase [59]. These results are analogous with those of Lin et al., (2007), who reported that surfactant mixture of HLB 13 and HLB 6 was able to produce the highest and lowest emulsification stability, respectively for two-phase soybean oil biodiesel emulsions [59]. Therefore, in the present study HLB 13 was considered as the optimum HLB value for W/ME emulsion.

For ME/W emulsion, the initial stability was found to be longer up to 3 days for HLB 7 compared to other HLB values which followed 4.3 (3 h) and remaining all HLB samples were stable up to one day. Therefore, HLB 7 was considered as the optimum HLB value for ME/W emulsion. The optimum HLB value obtained for the ME/W emulsion in the present study agrees well with the values reported in literature for castor oil methyl ester-water emulsion [63].

5.1.2. Effect of water content on W/ME emulsion

The effect of water content on W/ME emulsion w. r. t percentage phase separation is presented in Figure 5.3. Instantly after the emulsions were ready, after having remained motionless in a cylinder for various periods, fractions of water separation (vol %) from these W/ME emulsions were observed. Initially, the emulsion was stable for the first hour of having remained motionless for emulsions with the initial 10% and 20% water content. The sample with 15 vol % water content was less stable about 30 min. After having remained motionless for longer period, rapid deterioration of the emulsion was observed for the sample prepared with 20% water content. Higher emulsion stability (with lower

phase separation) was observed for the sample with 15% water content during the motionless period. The trend of this result is similar to those reported by earlier researchers [183, 184].

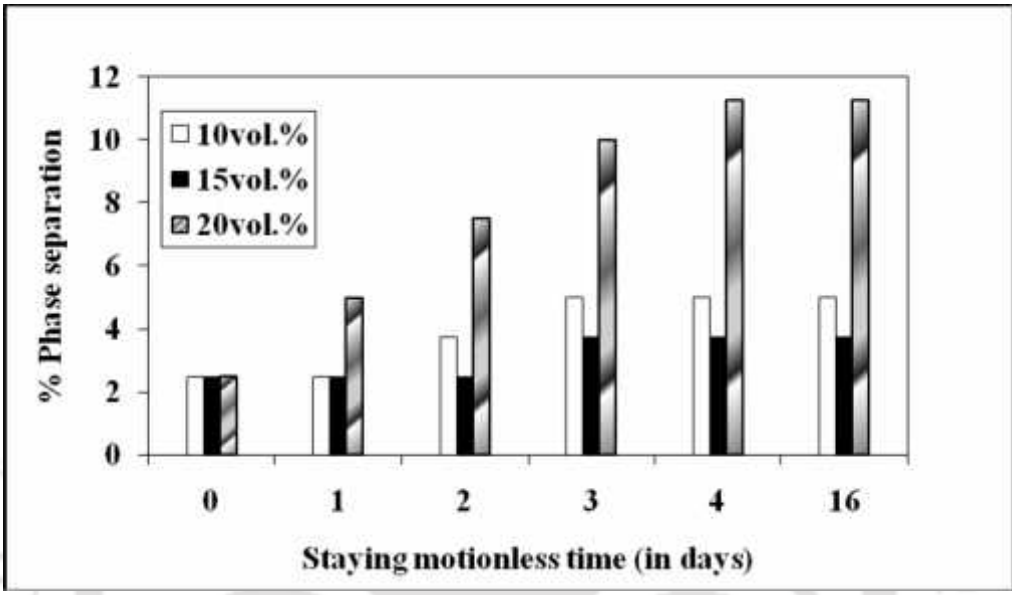


Figure 5.3: Effect of water content on W/ME emulsion

Apart from those Lin et al., (2008) investigated the engine performance and emission characteristics of biodiesel emulsion and reported that W/ME emulsion with 15 vol % water prepared by mechanical homogenizer had shown lower basic specific fuel consumption (bsfc) and higher thermal efficiency than those of neat diesel [61]. Based on this initial study, water content of 15% was considered as the optimum percentage for further experimentation.

5.1.3. Effect of COME content on ME/W emulsion

In the preparation of two phase ME/W emulsion, most of the un-emulsified methyl ester still occur in the top layer and the bottom layer of the emulsion has become a

milky-white coloured liquid. This indicates a slow rate of emulsification by means of the ultrasonic vibration process. Hence, to understand the effect of oil-in-water content, vol % of COME content on emulsion stability was studied and shown in Figure 5.4.

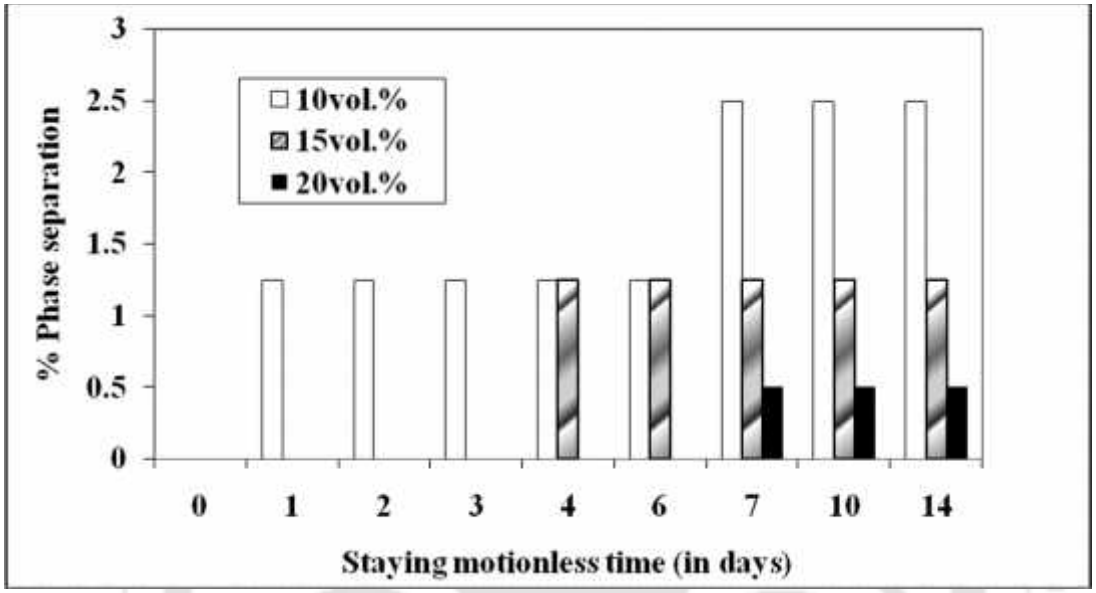


Figure 5.4: Effect of COME content on ME/W emulsion

With the increase of COME content from 10 to 20%, the stability of emulsion increases. There was no separation of either biodiesel or water, and the highest emulsification stability was observed for 20% COME content sample (6 days) compare to that of 10% (within a day) and 15% (3 days). Thus, for further study the emulsions were prepared considering 20 % as the optimum value.

5.1.4. Effect of surfactant quantity on W/ME and ME/W emulsions

The emulsification process is difficult to manage due to immiscibility of water and fuel. This problem can be overcome by adding surfactants [62]. Surfactants reduce the surface tension between water and oil thus maximizes their superficial contact area and activates their surfaces [60]. An effect of surfactant variation on stability of W/ME and

ME/W emulsions is shown in Figure 5.5 and Figure 5.6. The surfactant quantity selected and was varied in the range of 1-3 vol % based on the results of earlier published literature [182, 185]. In order to maintain stability, two surfactants were used in the present study and the quantity of each surfactant was calculated according to the formula given by Debnath et al., (2013) and Raheman and Kumari (2014) [60, 62].

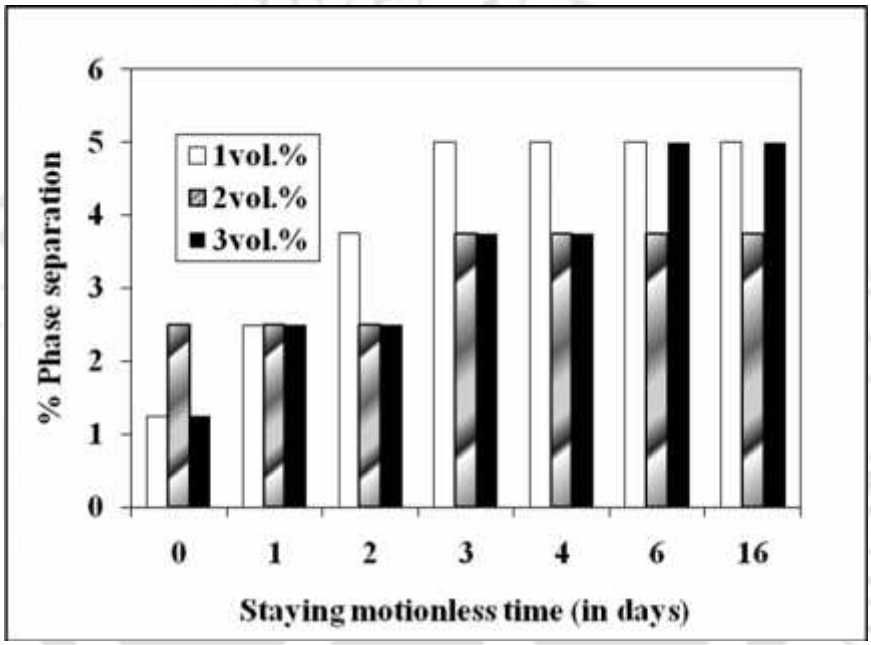


Figure 5.5: Effect of surfactant on W/ME emulsion

A surfactant with a larger HLB value represents the more hydrophilic characteristics and lower HLB value represents the more lipophilic characteristics [182]. The initial stability of W/ME emulsion was found to be highest about 5 h for the samples containing 1% and 3% surfactant and lower stability (30 min) was observed for 2% surfactant. In contrast, the sample kept motionless for longer duration, the phase separation increased gradually for the sample prepared with 1 and 3% surfactant compared to 2%. Almost similar kind of trend was reported by other researchers during their study with biodiesel emulsions [62, 182].

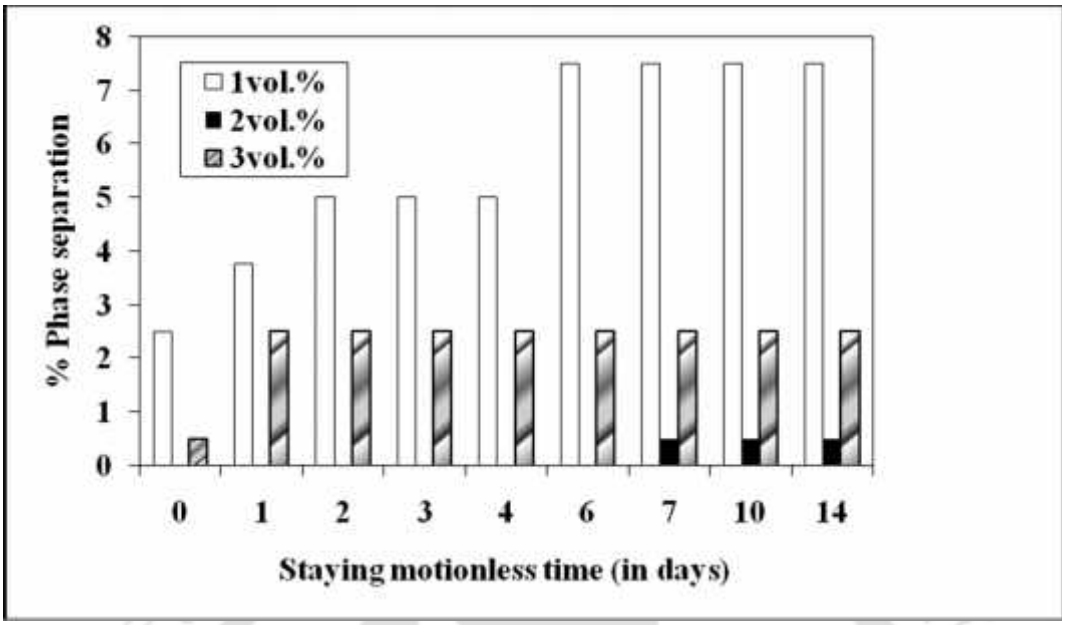


Figure 5.6: Effect of surfactant on ME/W emulsion

However, it was also reported that excess surfactant reduces the stability by disturbing the oscillatory structural forces [185]. Therefore, 2 vol % surfactant was fixed as the optimum for further experimentation. Similar trend was noticed with ME/W emulsion in which higher stability was observed for the sample prepared with 2 vol % surfactant (6 days). Therefore, 2 vol % was measured as the optimum quantity for further ME/W emulsion as well.

5.1.5. Effect of ultra-sonication time interval on W/ME and ME/W emulsions

A high frequency ultrasonic emulsification method was applied to prepare two-phase emulsions. The reason for using an ultrasonic technique for emulsification is that the liquids which are immiscible with each other thus may become highly homogeneous solution resulting in a stable emulsion. In this study, high frequency ultra-sonic waves were applied using sonication bath and varied over the time interval of 10, 30, 60, 120

and 180 min for both W/ME and ME/W emulsions. The effect of sonication time interval on stability of W/ME and ME/W emulsions are shown in Figure 5.7 and Figure 5.8.

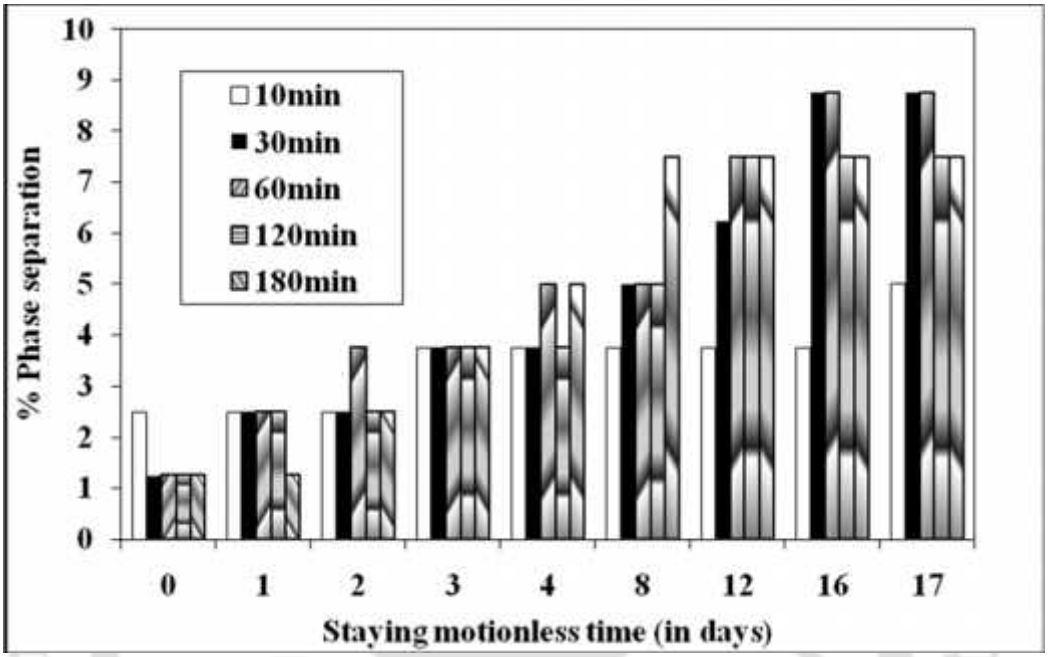


Figure 5.7: Effect of ultra-sonication time interval on W/ME emulsion

If we compare the initial stability of the samples prepared by varying ultrasonic time period, it has been observed that the samples sonicated for 2 h and 3 h showed highest and almost the same stability about 5 h while other samples followed by 3 h (stability) for 30 min and 1 h sonicated samples, while 30 min (stability) for 10 min sonicated sample, respectively. However, the tendencies of separation for the emulsion being kept motionless for a longer duration, showed higher stability for 10 min sonicated sample with lower phase separation compared to other samples. And the higher phase separation was observed for 30 min and 60 min sonicated samples. Wei et al., (2013) reported that the sample prepared with 6 to 8 min processing time gave highest and best

stability for 8 min sample [186]. Further, increase in the processing time leads to the deterioration of emulsion stability.

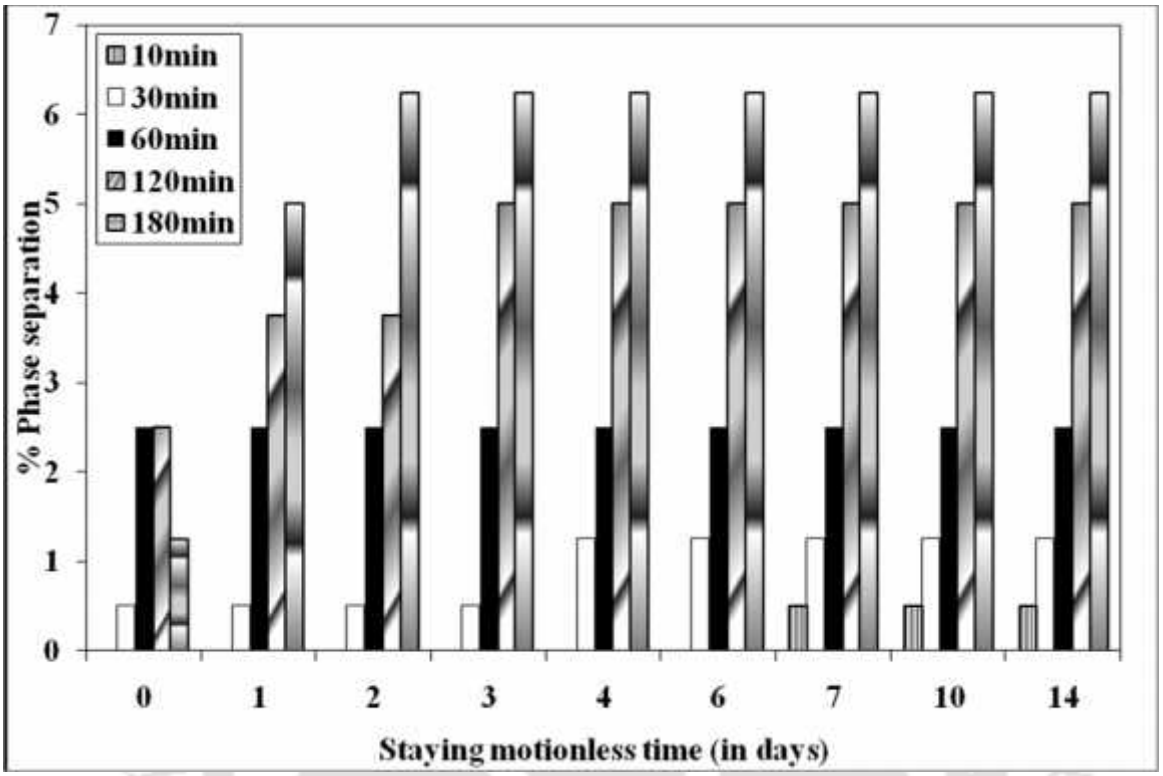


Figure 5.8: Effect of ultra-sonication time interval on ME/W emulsion

They also observed that an optimal processing time was not consistent and varies with conditions of different ultrasonic frequencies, powers and wave forms [186]. In the present study comparative analysis of different sonication time intervals of 10 min, 30 min, 1 h, 2 h, and 3 h revealed that the sample sonicated for 10 min achieved better stability for ME/W emulsion. The stability of other samples sonicated for 30 min, 1 h and 3 h was found to be 3 h; while for 2 h, the stability was 5 h. Although better stability was observed for the sample sonicated for 2 h compared to 10 min, but based on the sonication time period, 10 min was considered as optimum. This indicates that ultrasonification can be used to form ME/W emulsions in a very short time.

5.1.6. Effect of agitation time on W/ME emulsion

The effect of agitation time on emulsion stability is presented in Figure 5.9. The agitation time was varied from 10-30 min with an interval of 10 min. Results of the study revealed almost identical stability (24 h) for the sample stirred for 20 and 30 min. But the sample stirred for 10 min showed lowest stability of 30 min. However, under prolonged motionless time higher phase separation was observed for 20 min and 30 min agitated samples compared to 10 min. From published literature, it was observed that lower agitation time of 10 min and 15 min showed highest emulsions stability up to 7 days [118, 187]. Hence the emulsion prepared with 10 min stirring time has sufficient stability and can be considered as the optimum for W/ME emulsion.

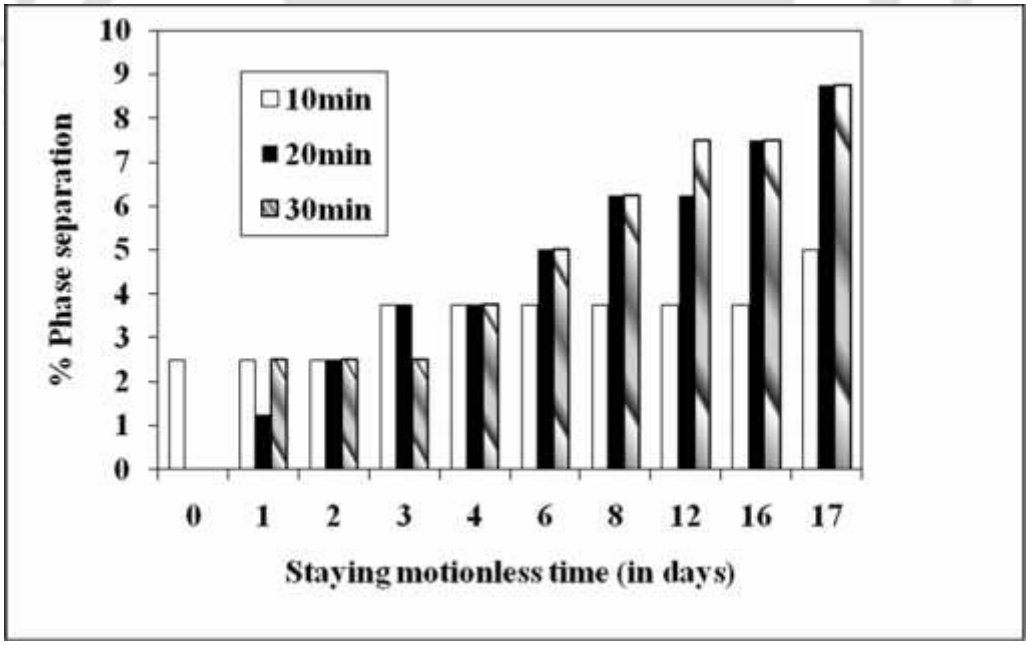


Figure 5.9: Effect of agitation time on W/ME emulsion

5.1.7. Effect of agitation speed on W/ME emulsion

The effect of agitation speed on emulsion stability is shown in Figure 5.10. To study the effect of agitation on emulsification, the experiment was performed at different agitation speeds ranging from 2500 to 3500 rpm [188, 119].

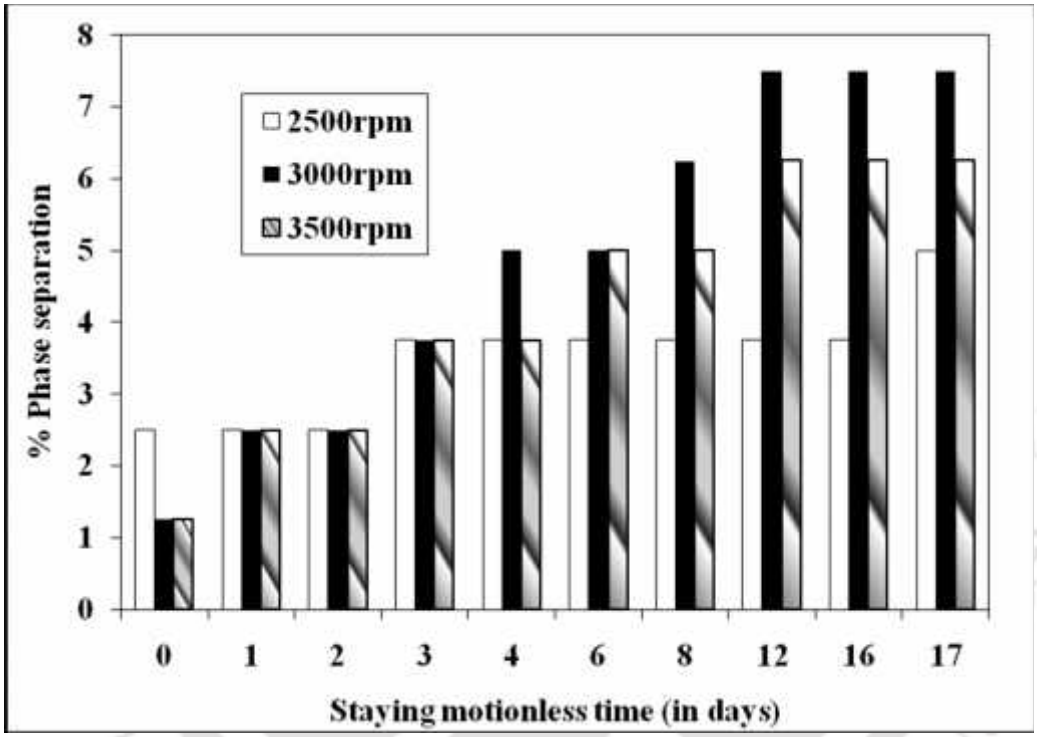


Figure 5.10: Effect of agitation speed on W/ME emulsion

From the figure it can be seen that no separation of the layer was observed at the beginning for all the emulsified samples and after that, there were some variations in separated layer of water. No significant change was observed in the initial stability (3 h) for the sample agitated at 3000 and 3500 rpm. But, the lower stability of 30 min was recorded for the sample agitated at 2500 rpm. While, the samples kept under prolonged motion less condition were showed higher phase separation at 3000 and 3500 rpm compared to 2500 rpm. Raheman et al., (2014) have observed similar results for jatropha

emulsion when agitation speed varied in the range of 2000-3000 rpm [188]. Therefore, 2500 rpm was considered as optimum for further experimentation.

5.2. Emulsions at optimum conditions

The optimum conditions for preparing the two-phase emulsion (W/ME) are: HLB 13, 15 vol % water content, 2 vol % surfactant, 10 min sonication time, 10 min agitation time, 2500 rpm agitation speed. For the ME/W two-phase emulsion preparation,conditions are: HLB 7, 20 vol % oil content, 2 vol % surfactant and 10 min of sonication, respectively.

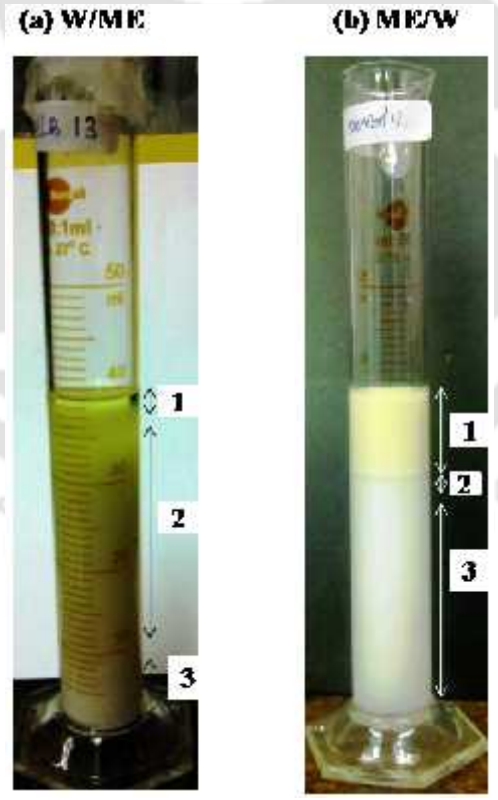


Figure 5.11: Emulsion samples at optimum conditions (a) W/ME: 1-Unemulsified layer, 2-Emulsified layer, 3-Sediment layer; (b) ME/W: 1-Sedimentlayer, 2-Unemulsified layer; 3-Emulsified layer

The comparative evaluation of the percentage of emulsion separation among the two-phase W/ME and ME/W emulsions at optimum condition are shown in Figure 5.11. From the figure (a) W/ME emulsion, numbers 1, 2, and 3 specify an unemulsified layer, emulsion layer and white sediment layer, respectively. While, in the figure (b) ME/W emulsion, 1, 2 and 3 denotes white sediment layer, unemulsified layer and emulsified layer, correspondingly. For W/ME emulsion, sediment layer was observed at the bottom of emulsified layer and for ME/W emulsion, sediment layer was observed at the top of emulsion layer. Sediment layer consists of the larger particles which separate from the emulsion due to the coalescence phenomenon. When the speed of coalescence of the dispersed phase slows down, then a better stability of the emulsion is achieved. The separation of the sediment layer depends on the density of the continuous phase [189]. If the density of the continuous phase is higher, then the sediment layer appears at the top. These observations have found the similarity with the reported literature [182]. Among these optimized two phase emulsions, W/ME showed stability superior to ME/W emulsion.

5.3. Droplet size of dispersed phase

An optical electron microscope was used to observe the distribution of the dispersed phase of the water or oil in the emulsion and droplet-size variations. An image analyser was used to calculate the mean droplet diameter of the emulsion (Figure 5.12). The droplet size of the dispersed phase was measured by varying the ultrasonication processing time from 10 min to 3 h for both W/ME and ME/W emulsions and represented in Table 5.1. From the table, it can be observed that with the increase in sonication time, the droplet size of the dispersed phase reduced for both the emulsions. For the W/ME

emulsion, the average droplet size was reduced from 4.5 to 1.73 µm. This is because the dispersed water phase has to envelop the inner oil phase completely as a result it creates smaller water droplets in its inner phase which helps for the creation of micro-explosions and the burning process [182, 189]. The droplet size of the dispersed phase in ME/W emulsion reduced from 14 to 7 µm and found to be higher compared to W/ME emulsion.

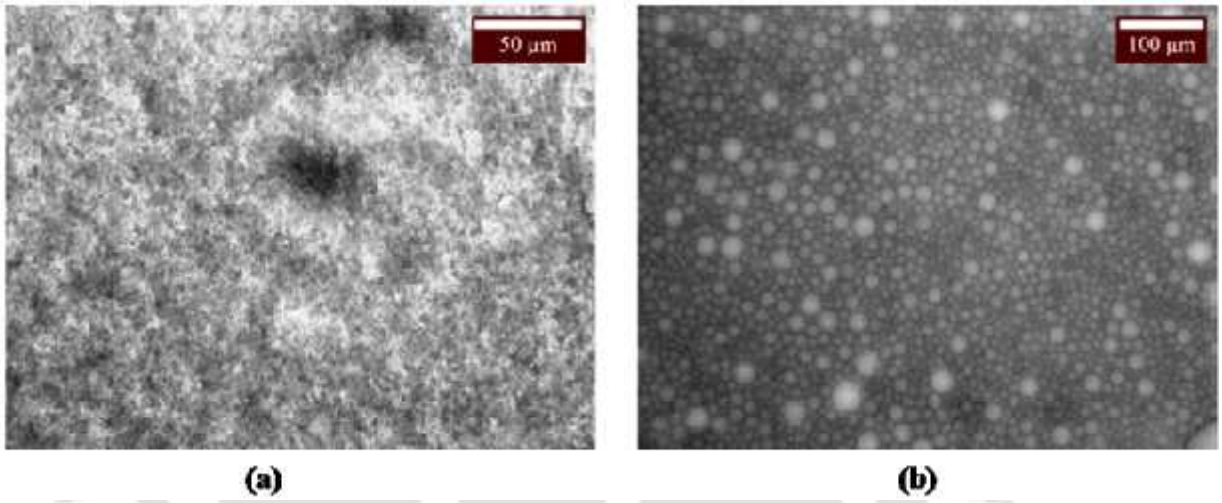


Figure 5.12: Photographs (by optical microscope) of dispersed phase droplet size of emulsions (a) W/ME (b) ME/W

Table 5.1: Droplet size measurements

Sonication time	Droplet size	
	W/ME (in µm)	ME/W (in µm)
10 min	4.5	14
30 min	3.95	9
1 h	3	8
2 h	2.6	7
3 h	1.73	7

On other hand, large droplets of various size of the dispersed phase of the emulsions will move, collide and merge into each other, after which result in to the phenomenon of coalescence, which lead to the destabilization of the emulsion [189].

5.4. Properties of emulsions

The physico-chemical properties of COME, W/ME and ME/W emulsions such as density, specific gravity, viscosity, pour point, flash point, fire point, thermal stability and calorific value are estimated and presented in Table 5.2.

Table 5.2: Properties of two phase emulsions

Property	COME	W/ME emulsion	ME/W emulsion
Density (kg/m^3)	878	900	979
Specific gravity	0.878	0.9	0.979
Kinematic viscosity (cSt) at 25 °C	19.13	27.96	5.86
Kinematic viscosity (cSt) at 40 °C	10.59	15.22	4.03
Flash point (°C)	202	200	-
Fire point (°C)	212	210	-
Pour point (°C)	-21.2	-19	-11
Thermal onset temperature (°C)	260	197	65
Calorific value (MJ/Kg)	37.74	33.57	-

The density of both emulsions was found to be higher compared to neat methyl ester (COME) and among these, ME/W emulsion density was highest compared to COME and W/ME emulsion. This increase in density may be related to the amount of water and biodiesel present in the system, which has a higher density than the COME [62]. There was significant increment in the viscosity for W/ME emulsion and drastic decrease in the ME/W emulsion showed a direct relationship with the amount of water and biodiesel

added to the system. Increase in the viscosity of W/ME emulsion was due to the existence of both the water [62] and surfactant [120]. Similarly, reduction in water droplet size also leads to increase the viscosity of emulsion [190]. The flash point and fire point were not changed significantly for W/ME emulsion compared to pure COME, but found to increase as the water concentration in the emulsified fuel increased [62]. The pour point was increased for both emulsions compared to COME. Noteworthy, decrease in the thermal stability and slight decrease in the calorific values were noticed for the W/ME emulsion compared to its COME. The results found for W/ME emulsion w. r. t calorific value agrees well with the reported literature [62]. The decreased in calorific value was mainly due to water present in the fuel, which was transformed to vapour by the heat generated during the combustion of fuel and the vapour obtained was not condensed resulting in a lower calorific value [62]. The measurement of flash point, fire point and calorific value for the ME/W emulsion are found to be difficult due to larger amount of water present in ME/W emulsion.

5.5. Summary

In this chapter an attempt has been made to used an ultra sonification method to investigate the emulsion characteristics of two phase emulsion systems i.e. water-in-methyl ester (W/ME) and methyl ester-in-water (ME/W). The optimum conditions in terms of higher emulsion stability for both emulsions were found to be HLB 13, 15 vol % water content, 2 vol % surfactant, 10 min sonication time interval, 10 min agitation time, and 2500 rpm agitation speed for W/ME, and HLB 7, 20 vol % oil content, 2 vol % surfactant and 10 min sonication time for ME/W emulsions, respectively. W/ME emulsion showed superior results than ME/W emulsion w.r.t dispersed phase droplet size

and properties. The effect of sonication time showed positive effect on the droplet size reduction in both emulsions. The findings of the study have demonstrated the feasibility to produce stable W/ME emusified fuel with castor oil methylester as an alternate fuel in a diesel engine to reduce NOx emissions.

CHAPTER 6

Conversion of glycerol to glycerol acetal using heterogeneous catalyst

This section discusses the results obtained from the preliminary studies for the optimization of production of solketal from glycerol using purolite as a catalyst. The effect of different process variables on solketal yield was also discussed.

6.1. Effect of various variables on acetalization of glycerol

In order to optimize glycerol acetalization, an effect of various variables on solketal yield was studied. The range of the variables was fixed on the basis of our trial runs. The yield and conversion values were estimated using GC-MS analysis. GC-MS peaks areas were identified by authentic standards based on specific retention time of each compounds. The detailed discussion on results is given below.

6.1.1. Effect of reaction time

The influence of reaction time on solketal yield is shown in Figure 6.1. The reaction was studied by varying the reaction time from 1-4 h, at room temperature, 500 rpm and 1 wt % catalyst loading. From the figure, it can be observed that solketal yield increases from 19.76% to 74.68% with increase in the reaction time up to 3 h. Further increase in reaction time to 4 h, decreased the solketal yield to 29.98%. A similar type of observation was made by Nanda et al., (2014) on conversion of glycerol to solketal using different catalysts. The reason for such decrease in yield is because for reaction not being at equilibrium a shorter residence time (or longer time) would lead to lower conversion

[124]. This is also may be due to the formation of by-product water during the reaction. Thus, for the present study the optimum reaction time was considered as 3 h.

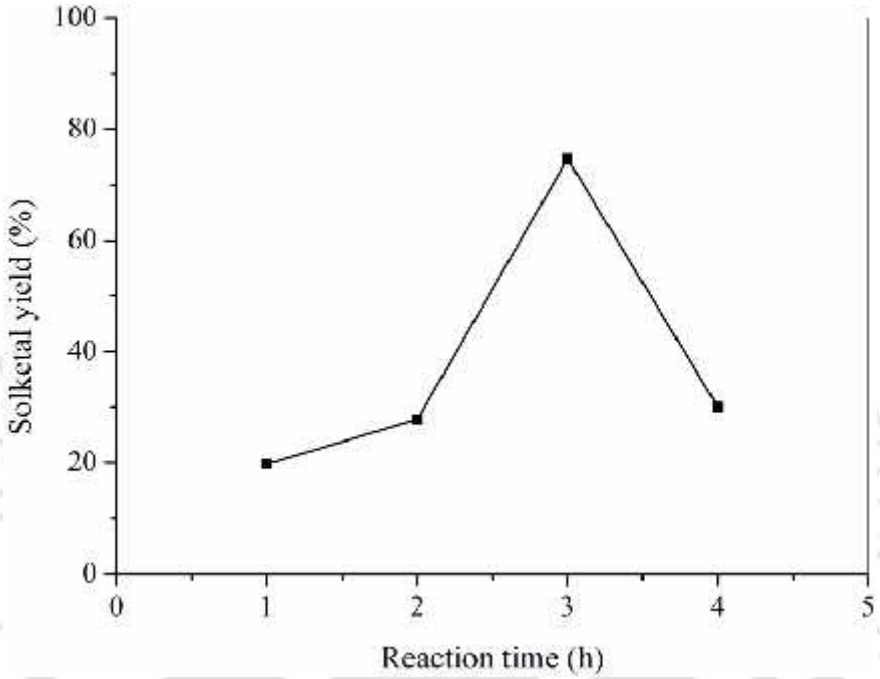


Figure 6.1: Effect of reaction time on solketal yield

6.1.2. Effect of catalyst concentration

The effect of catalyst concentration on solketal yield was studied using purolite as a catalyst. From the previous literature reports, it was observed that the purolite catalyst exhibit promising catalytic activity in a continuous reactor [126]. But its performance has remained largely unexplored in the batch reactor. In this study, we have addressed this issue with approach of performing the experiments in a batch reactor using the same catalyst. From the Figure 6.2, it can be seen that with an increase in catalyst concentration from 0.5 to 1 wt % at fixed room temperature, 500 rpm and 3 h, solketal yield was found to increase from 35.49% to 74.68%, respectively and thereafter decreased to 27.99% with a further increase in the catalyst concentration to 1.5 wt %. Menezes et al., (2013)

reported that increase in catalyst concentration did not significantly favour the conversion of glycerol to solketal [136].

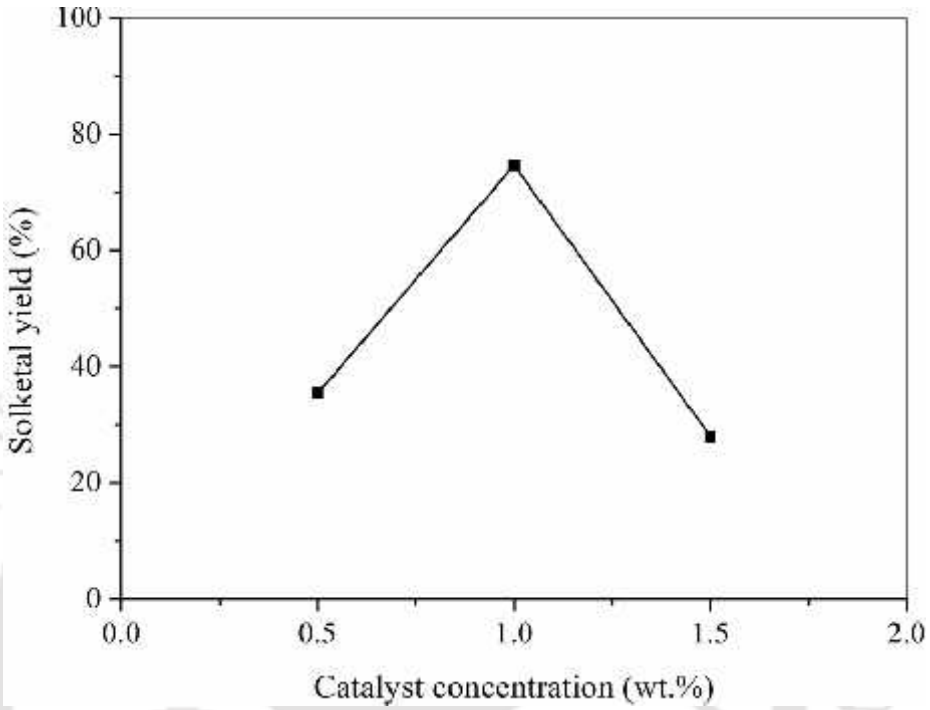


Figure 6.2: Effect of catalyst concentration on solketal yield

This mainly attributed to decrease in the acidic strength of the catalyst due to the formation of by-product water in the medium as acetalization is a reversible reaction [191]. This indicated that an optimum solketal yield existed at about 1 wt % catalyst concentration.

6.1.3. Effect of glycerol/acetone molar ratio

In order to check the effect of glycerol/acetone molar ratio on solketal yield, experiments were carried out with 1 wt % catalyst concentration at room temperature, 500 rpm and 3 h. The range of glycerol/acetone molar ratio (i.e. 1:2-1:8) was fixed on the basis of our preliminary experiments and reported literature [124, 125]. The effect of glycerol/acetone on solketal yield is shown in Figure 6.3. From the figure, it can be seen

that with increase in the molar ratio from 1:2 to 1:4, solketal yield was increased from 35.57% to 74.68%, respectively. Further increase in the molar ratio to 1:6 (35.36% yield) and 1:8 (35.38%) drastically decreased the solketal yield. The yield obtained in the present work does not follow the trend as reported in literature [124]. The decrease in the solketal yield with increase in the molar ratio could be due to the formation of glycerol oligomers and water in the reaction medium which has an adverse effect on the solketal yield [125]. Suriyaprapadilok et al., (2011) reported that even though decrease in the area under glycerol GC peak occurred, but no product was detected. Possibly, these products are glycerol oligomers, which are not detectable via GC analysis [127]. The conversion of glycerol was not changed significantly with varying the molar ratio. Therefore, 1:4 molar ratio was considered as an optimum and was used for further experimentation.

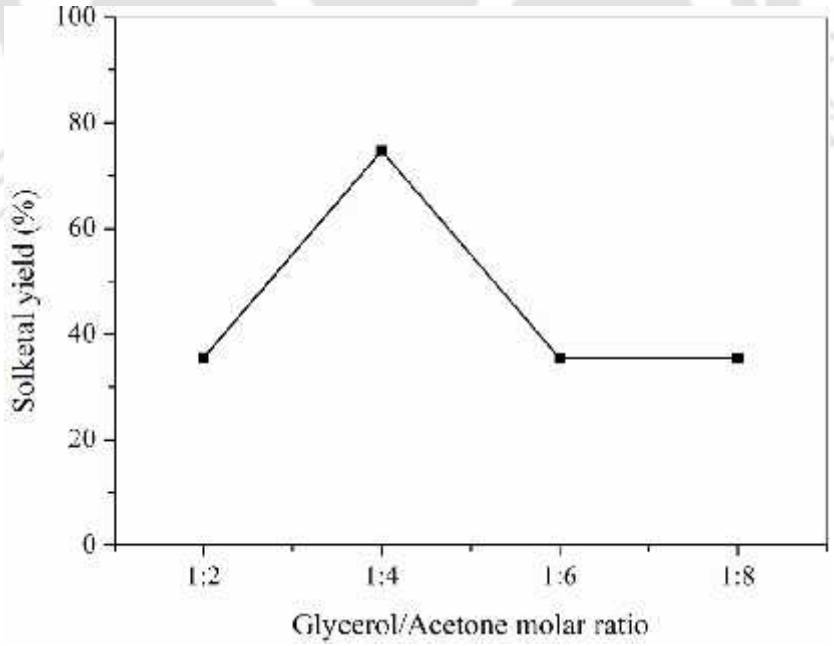


Figure 6.3: Effect of glycerol/acetone on solketal yield

6.1.4. Effect of catalyst type

The effect of catalyst type on solketal yield was investigated by using three different catalysts viz. Amberlyst-15, Purolite and H_2SO_4 and their results are shown in Figure 6.4.

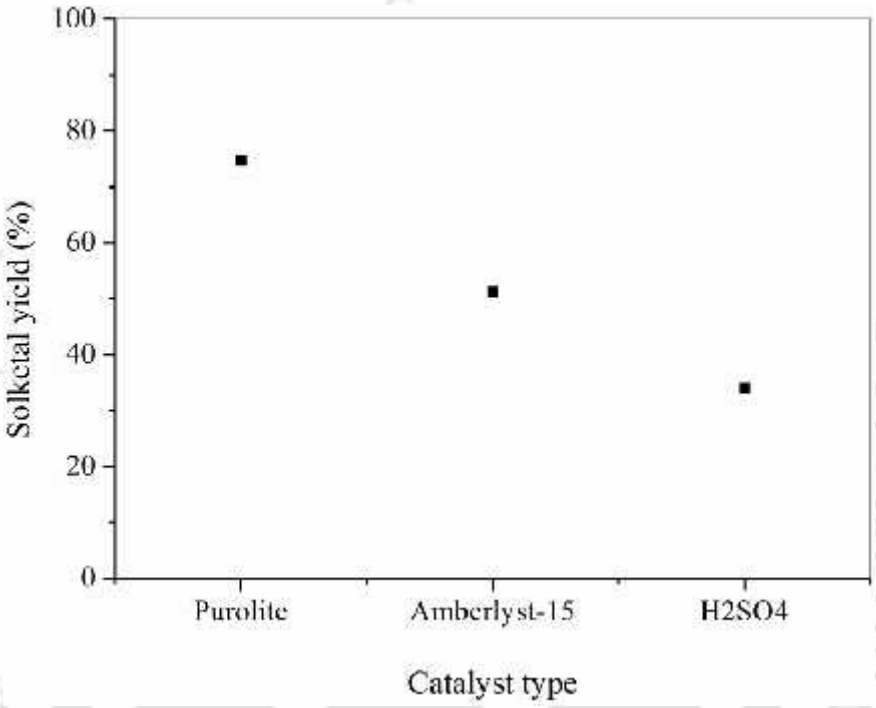


Figure 6.4: Effect of catalyst type on solketal yield

Among the studied catalysts, highest solketal yield of 74.68% is obtained with purolite as catalyst at 1:4 molar ratio; other catalysts such as Amberlyst-15 and H_2SO_4 gave the yield as 51.18% and 33.99%, respectively. Nanda et al., (2014) have reported that catalyst with a stronger acidity showed better performance and higher solketal yield [124]. In another study by Shirani et al., (2014) have shown that higher solketal yield of 95% can be obtained in continuous reactor using purolite as catalyst [126]. Therefore, it could be suggest that purolite can be act as a potential catalyst for synthesis of solketal. However, in the present investigation, solketal yield was found to be lower than the expected value

which could be due to the formation of water during the reaction which hinders the solketal yield. Some authors have reported that water needs to be removed during the process, otherwise it is detrimental to the process to produce good amount of solketal [125].

6.2. Summary

In this chapter, an attempt has been made to optimize the glycerol acetalization at room temperature using purolite resin as catalyst. From the preliminary study, the combination of optimum process parameters obtained for the highest solketal yield (74.68%) were 3 h reaction time, 1 wt % catalyst concentration, 1:4 glycerol/acetone molar ratio, at which the glycerol conversion was 96.57%. Comparison of solketal yield obtained for the present system with the reporetd in literature (continuous reactor) usingpurolite catalyst reveals that the yield of solketal in the present study found to be lower (74.68%) due to the formation of by-product water during the reaction. Therefore, results of the study seggested that irrespective of the catalyst used, removal of water is necessary to achieve higher solketal yield.

CHAPTER 7

Over all conclusions and future prospects

This chapter summarizes the major conclusions drawn from the research work presented inthis dissertation. Other portion of this chapter focuses towards the scope for future research area that can be carried out.

7.1. Significance and salient features of the study

This work dealt with castor oil extraction, production, characterization and applications of the prepared biodiesel from castor seeds via reactive extraction and to seek the possibility of using crude glycerol to produce value added acetal. The produced castor oil methyl ester properties showed that it can act as an alternative to conventional diesel. From the perspective of thesis novelty, the major conclusions obtained from this study are summarized below.

- This is a first comprehensive report on extraction of oil from castor seeds using polar and non-polar solvents and subsequent biodiesel production from castor seeds using integrated system [i.e. Soxhlet method]
- Effect of heat treatment on castor seeds showed positive result in terms ofincreased oil yield and decreased acid value.
- The acid value of an oil extracted using methanol as solvent was found to be 0.92 mg KOH/g oil.
- Polar solvents such as ethyl acetate and methanol gave higher castor oil yield about 55-56% by Soxhlet method. Since methanol showed higher oil yield with low FFA

content, this can be act as a highly desirable solvent for reactive extraction and transesterification of castor seed in a single step.

- Optimization of reactive extraction was investigated by RSM design technique to maximize the desired product in reactive extraction via integrated and non-integrated approaches. About 95-97% conversion of castor oil methyl ester was achieved by both techniques (integrated and non-integrated).
- The estimated fuel properties of COME indicates its potential use as a transport fuel due to its high thermo-oxidative stability, flash pointand significant cold flow properties
- The storage stability study of COME suggests that COME stored in a dark condition was more stable than other two conditions i.e. open air or air tight conditions
- The biodegradability of COME carried out using bio-kinetics model showed lower biodegradability (about 51% within 28 days) which may be due to the higher viscosity of COME
- Engine performance tests conducted using castor oil methyl ester and its blends of 5%, 10% and 15% with diesel fuel significantly reduced the percentage of CO, NOx and HC gases compared to that of conventional diesel
- Among the studied blends, B10 has given the best brake thermal efficiency of engine at maximum load compared to other blends. The exhaust gas emission showed reduction in CO (26-36%), NOx (14-20%) and HC (17.5-50%) gases with increase of COME blending percentage compared to conventional diesel.
- The findings of the emulsion study have demonstrated the feasibility to produce stable emusified fuel with castor oil methylester and can be used as an alternate fuel in diesel engine to minimize the NOx emissions

- The preliminary studies carried out to convert glycerol to solketal showed good performance by using puroliteas a catalyst. The by-product water needs to be removed otherwise it will be detrimental to the yield of solketal

To summarize the thesis outlines, the use of low cost non edible oil feed stock thought to lower the production cost of biodiesel fuel in order to substitute the conventional diesel. The obtained data expected to affordas a reference data for further research in the field of low cost non-edible based biodiesel synthesis and further seek the possibilities in order to use the by-product glycerol to intensify the process of reactive extraction.

7.2. Future prospects

Research findings in this work provided a good number of insights with respect to preparation, characterization and application of biodiesel synthesis from renewable feedstock such as castor seeds via reactive extraction and further utilization of crude glycerol. There are certainly several areas which merit further research attention. Few research areas for future work are presented as follows:

- Pre-treatment of oil seeds before extraction could be an innovative step to increase oil yield and reduce the acid value of feedstock and can be implemented for other oil bearing seeds as well.
- Studies on long term storage stability of prepared methyl esters and its blend.
- Studies onthe utilization of emulsified methyl esters and its blends with diesel in a CI engine.
- Glycerol acetalization using purolite shown good performance and can be studied for further optimization by design techniques.

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Appendix

Combustion Parameters

The basic equations used for performance analysis are as follows:

- Brake power (BP)

$$BP = \frac{2 \times ® \times N \times W \times R}{60000} kW \text{.....(A.1)}$$

Where, N is speed in rpm, W is the brake load in N and R is brake dynamometer arm length in m.

- Brake specific fuel consumption (BSFC)

$$BSFC = \frac{m_F}{BP}, \quad kg / kWh \text{.....(A.2)}$$

Where, m_F is the mass of fuel supplied in kg/hr

- Brake thermal efficiency (BTE)

$$BTE = \frac{BP \times 3600}{(m_F \times LHV)}, \quad \% \text{.....(A.3)}$$

Where, LHV is the lower heating value of the fuel, kJ/kg

- Lower heating value of the fuel bend

$$LCV = (1.8 \times GCV) - (91.23 \times H), \quad kJ / kg \text{.....(A.4)}$$

Where, GCV is the gross calorific value of the fuel blends in different percentages evaluated experimentally using Bomb calorimeter in kJ/kg, H is the Hydrogen percentage in hydrocarbon fuel blend obtained experimentally using CHNS study in %.

- Volumetric efficiency

$$\eta_{vol} = \frac{m_A}{\left(\frac{\pi}{4} \times D^2 \times L \times \frac{N}{n} \times no.\ of\ \ cylin \times \rho_A \times 60\right)} \quad \text{.....(A.5)}$$

Where, m_A is mass of air consumed in kg/hr, D is the cylinder bore diameter in m, L is the stroke length in m, n is number of cycles for two stroke 1 and for four stroke 2, ρ_A is density of air in kg/m^3 [133].

- The combustion study has been performed based on cylinder pressure variation with each degree of crank angle change. Differentiating the raw pressure data shows a noisy trend between successive values. Therefore, after treatment of these pressure data in the form of smoothing becomes necessary. The smoothing algorithm for (2b+1) value is used as follows:

$$P_n = \frac{1}{b^2}\left[P_{n-(b-1)} + 2P_{n-(b-2)} + 3P_{n-(b-3)} + \ldots + bP_n + \ldots + 3P_{n+(b-3)} + 2P_{n+(b-2)} + P_{n+(b-1)}\right] \quad \text{.....(A.6)}$$

The terms in Eq. (A.6) are only evaluated when the part of the subscript in bracket is not negative. This is illustrated by simplest case when *b = 2*

$$P_n = \frac{(P_{n-1}) + 2(P_n) + (P_{n+1})}{4} \quad \text{.....(A.7)}$$

The rate of pressure rise calculated from the smoothened pressure data by using first order finite difference equation with fourth order accuracy.

$$\frac{dP}{d\theta} = \frac{(P_{n-2}) - 8(P_{n-1}) + 8(P_{n+1}) - (P_{n+2})}{12(\Delta\theta)} \quad \text{.....(A.8)}$$

The net heat release rate is obtained from the first law analysis by implementing rate of pressure rise and rate of volume change which is given below.

$$\frac{dQ_n}{d\theta} = \left(\frac{¥}{¥-1}\times P\times\frac{dV}{d\theta}\right)+\left(\frac{1}{¥-1}\times V\times\frac{dP}{d\theta}\right) \quad \text{.....(A.9)}$$

The ranges of ¥ varies from 1.3 to 1.35.

- Ignition delay

$$\theta_R = \theta_{IG} - \theta_{IN}, \quad {}^{o}CA \text{.....(A.10)}$$

Where, θ_{IN} is fuel injection angle in degree CA, θ_{IG} is the angle at which combustion starts in degree [131, 134].

List of Publications

Journal Publications:

1. **S. R. Dasari**, V. V. Goud, (2013). Comparative extraction of castor seed oil using polar and non polar solvents. International Journal of Current Engineering and Technology, 121-123. [Published in conference Proceeding]
2. **S. R. Dasari**, V. V. Goud, (2014). Effect of pre-treatment on solvents extraction and physico-chemical properties of castor seed oil, Journal of Renewable and Sustainable energy 6: 063108.
3. **S. R. Dasari**, V. Borugadda, V.V. Goud (2016), Reactive extraction of castor seeds and storage stability characteristics of produced biodiesel, Process Safety and Environmental Protection, 100, 252-263.
4. **S. R. Dasari**, V. V. Goud (2017), Simultaneous extraction and transesterification of castor seeds for biodiesel production: Assessment of biodegradability, Process Safety and Environmental Protection, 107, 373-387.
5. **S. R. Dasari**, A. Chaudhary, V.V. Goud, N. Sahoo, V.N. Kulkarni (2017), In-situ alkaline transesterification of castor seeds: Optimization and engine performance, combustion and emission characteristics of blends, Energy Conversion Management, 142, 200-214.
6. P. Mazumdar, **S. R. Dasari**, V.B. Borugadda, G. Srivasatava, L Sahoo, V. V. Goud, (2013). Biodiesel production from high free fatty acids content jatropha curcas L. oil using dual step process, Biomass Conversion and Biorefinery, 3, 361-369.

7. S. K. Achar, **S. R. Dasari**, R. Saha, V. V. Goud (2014), Studies on thermal, oxidative and cold flow properties of ethyl esters prepared from high FFA karanja oil, International Energy Journal, 14.
8. A.K. Paul, S. K. Achar, **S. R. Dasari**, V.B. Borugadda, V.V. Goud, (2017), Analysis of thermal, oxidative and cold flow properties of methyl and ethyl esters prepared from soybean and mustard oils, Journal of Thermal Analysis Calorimetry, doi:10.1007/s10973-017-6424-z.

Manuscripts to be communicated:

1. **S. R. Dasari**, V. V. Goud, An investigation on emulsion characteristics of two phase castor oil methyl ester-water emulsions by ultrasonic method.

Conference Presentations [National/International]:

1. **S. R. Dasari**, V. V. Goud, Optimization of biodiesel production from castor oil using reactive extraction technique, International Conference on "Membranes and Applications" (ICMA 2013), November 22-23, 2013, CSIR-Central Glass and Ceramic Research Institute (CSIR-CGCRI) Kolkata, West Bengal, India.
2. **S. R. Dasari**, V. V. Goud, Comparative extraction of castor seed oil using polar and non polar solvents, “Women in Science and Engineering (NCWSE2013), Sri Dharmasthala Manjunatheshwara College of Engineering & Technology, Dhavalagiri, Dharwad, Karnataka.

3. **S. R. Dasari**, Ashish Jagannath Chaudhary, V.N. Kulkarni, N.Sahoo,Vaibhav V. Goud, Alkaline *insitu* transesterification of castor seed by RSM design technique and an engine study, Reflux 2015, IIT Guwahati. **[Best paper award]**
4. **S. R. Dasari**, V. V. Goud (2015), An investigation on emulsion characteristics of two phase castor oil methyl ester-water emulsions by ultrasonic method, Workshop, Feriap 2015, IIT Guwahati. **[Poster]**

Chapter 1:

Introduction and Literature Review

Background;

State- of -the- art;

Objectives;

Organization of thesis;

Chapter 2:

Experimental and Characterization

Experimental procedures;

Physico-chemical characterization methods;

Chapter 3:

Oil extraction and Characterization

Optimization of castor oil extraction using different solvents;

Evaluation of estimated oil properties;

Dasari SR and Goud VV (2014) Journal Renew Sustain Energy 6: 1-16

Chapter 4:

Reactive extraction and Characterization

Optimization of reactive extraction by two approaches;

Evaluation of estimated methyl ester properties;

Stability and biodegradability of methyl ester;

Engine performance test;

Dasari SR and Goud VV (2016) Process Safety and Environmental Protection 100: 252–263

Dasari SR and Goud VV (2017) Process Safety and Environmental Protection 107: 373-387

Dasari SR, Chaudhary A, Goud VV, Sahoo N and V.N. Kulkarni (2017) Energy Conversion Management 142: 200-214

Chapter 5:

Emulsion and Characterization

Optimization of two-phase emulsions parameters;

Evaluation of emulsion properties;

Chapter 6:

Glycerol Acetalization

Preliminary studies in acetalization;

Chapter 7:

Over all conclusions and future scope

Concluding remarks;

References

Appendix

List of Publications