IMPROVEMENT OF STORAGE BEHAVIOR OF BIODIESELS AND THEIR DIESEL BLENDS WITH THE USE OF ANTIOXIDANTS

By

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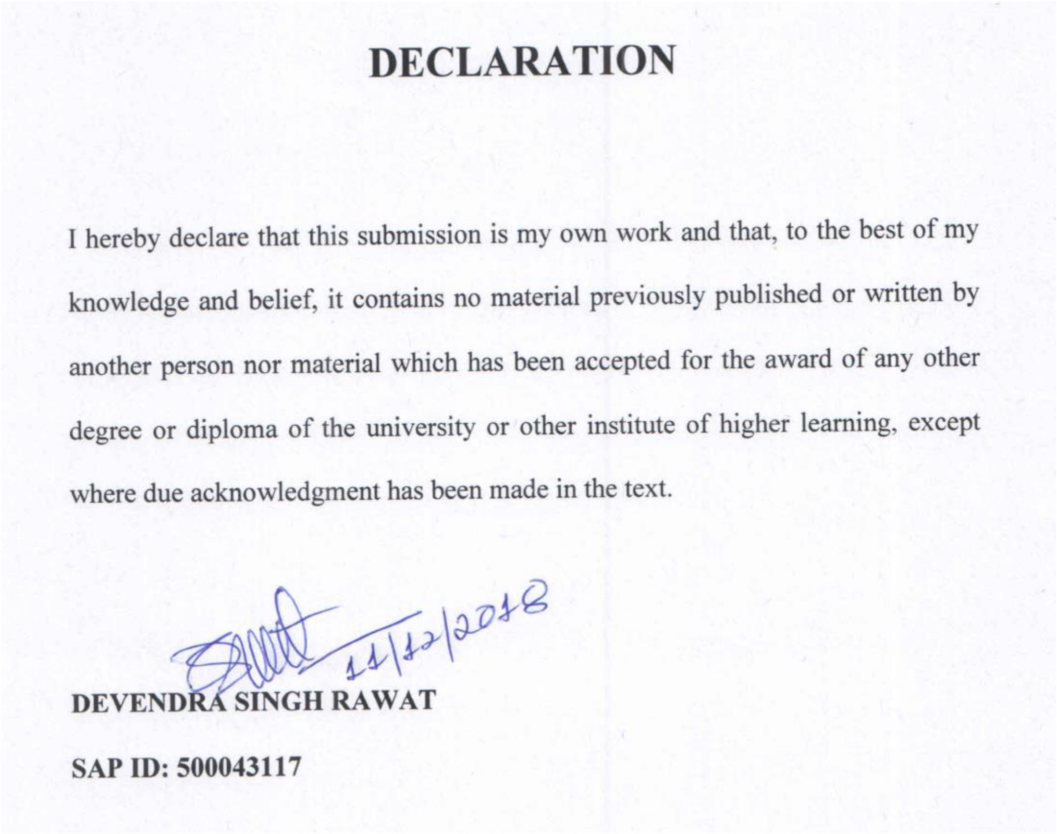

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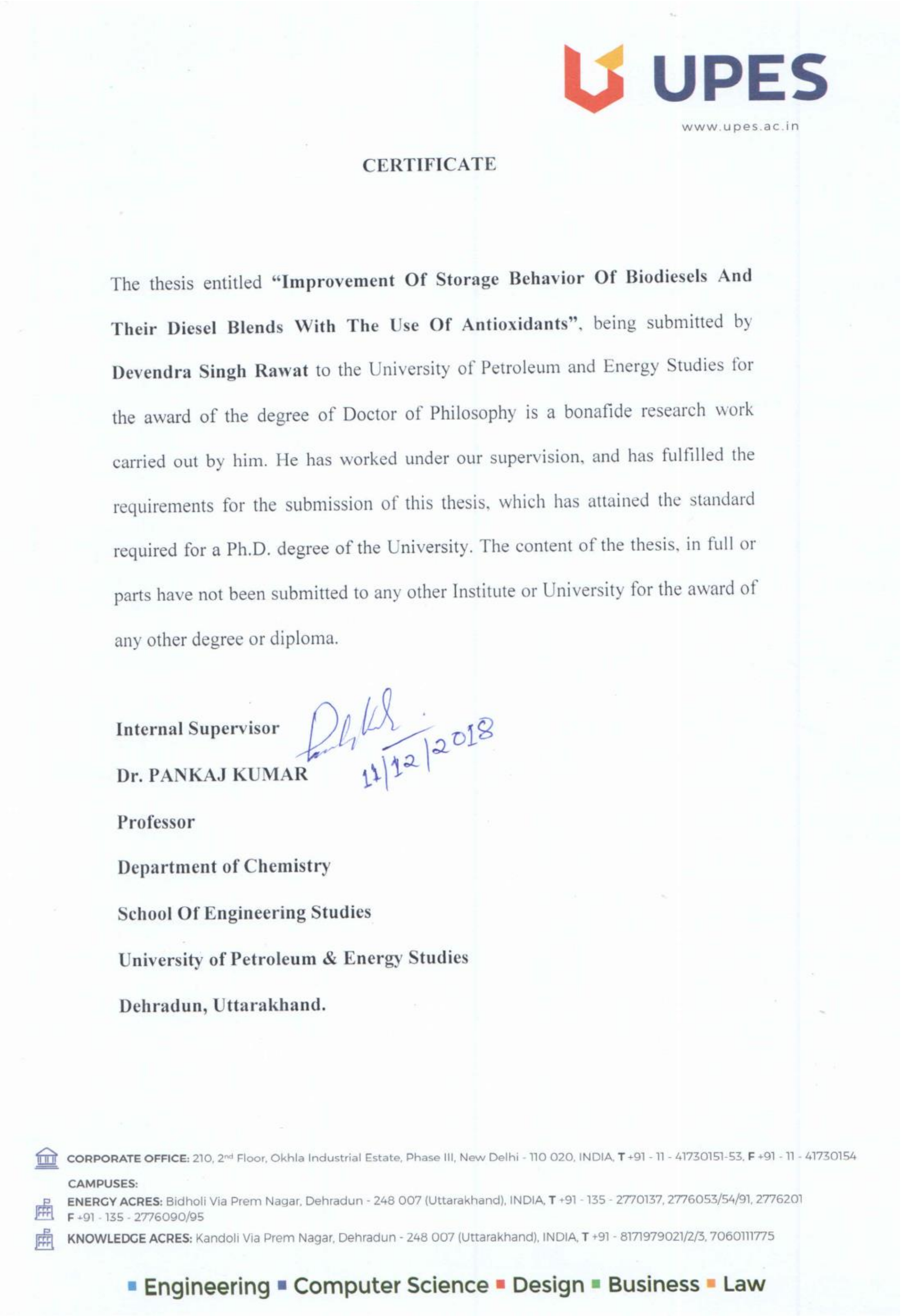

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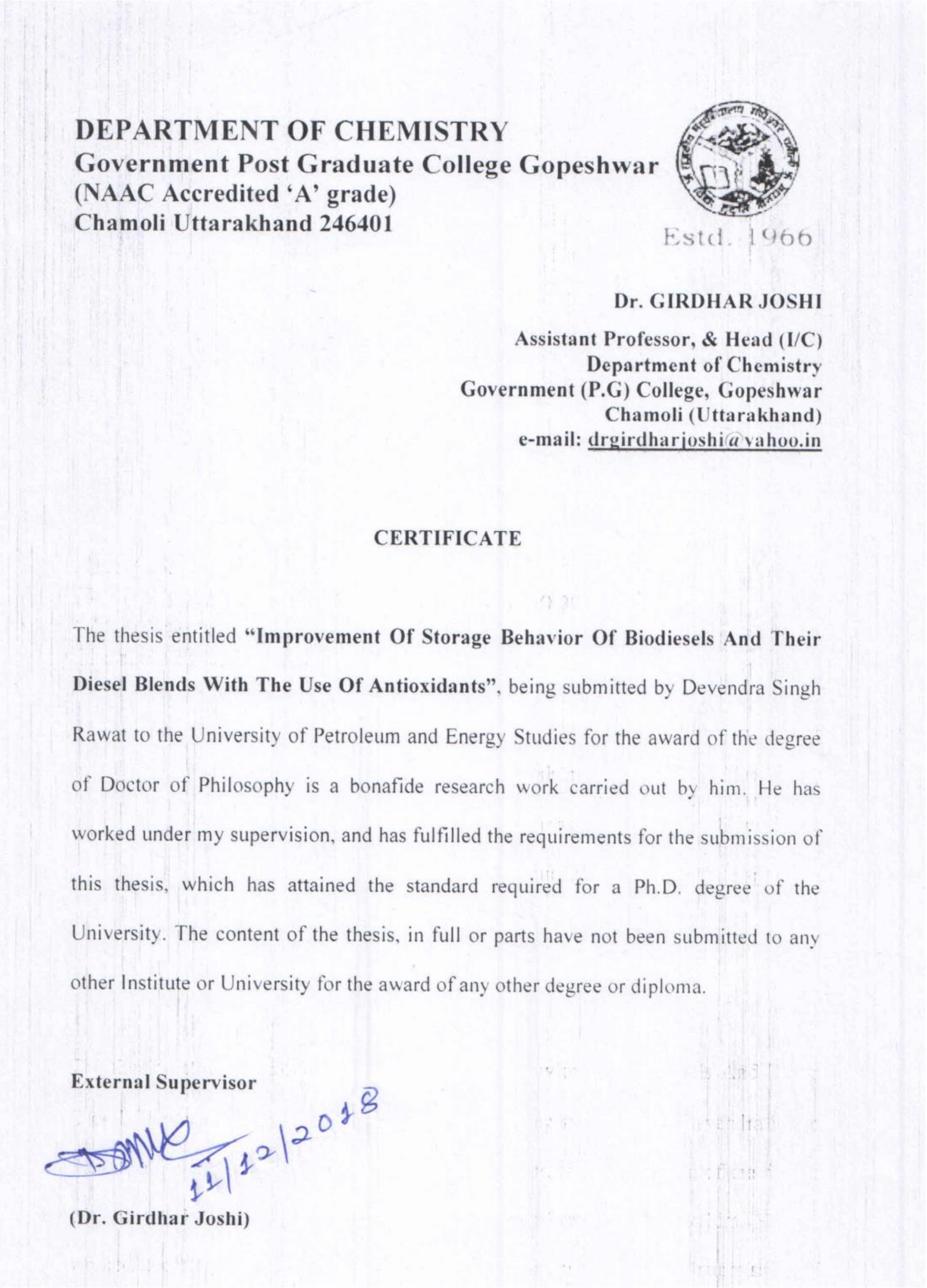

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Executive Summary

Biodiesel is a green alternative fuel produced from renewable resources, and it is a much cleaner burning alternative fuel which drawn a wide attention of the energy researchers for last couple of decades. In the present thesis the Jatropha and Karanja biodiesel is prepared by transesterification method using both homogenous and heterogeneous catalyst. The yield percentage of Jatriopha and Karanja biodiesel prepared from homogenous (KOH) catalyst is about 75-80 %. In addition, different transition metal mediated CaO (derived from waste egg shell) based solid catalyst is also studied for the preparation of biodiesels, the catalyst has shown good catalytic activity due to its high basicity. The maximum conversion (95-98%) for the transesterification of Jatropha and Karanja oils were achieved using 5 wt% of the as synthesized catalyst at 65°C temperature with 12:1 methanol/oil ratio. The catalyst could be reused effectively during four cycles. Use of the $CaO_{(cesp)}$ based mixed oxides made the process more environmental benign and economical. The biodiesel prepared has shown good fuel characteristics as per EN, ASTM and IS standards.

Poor oxidation stability of biodiesel is considered a major problem for its commercialization. The fuel characteristics of biodiesel are adversely affected by its auto oxidation, which takes place when biodiesel is exposed to air, heat, light and metallic contaminants. This study also investigated the effect of commercial antioxidant additives on oxidation stability of neat biodiesel and its diesel blends. Various diesel-biodiesel blends (B5, B10, B15, B20, B25 & B40) were prepared with conventional diesel sold at retail outlets of Northern India. Butylated Hydroxy Anisole (BHA), Butylated Hydroxy Toluene (BHT), Pyrogallol (PL), Propyl-gallate (PG), *tert*-Butylhydroxyquinone (TBHQ) and Diphenylamine (DPA) additives were selected for this study of oxidation stability of biodiesels and their diesel blends. Significant improvement in oxidation stability as well as in density and kinematic viscosity of diesel-biodiesel blends was observed with all antioxidants studied. TBHQ, PrG and PY were found most effective among all antioxidants tested, also their use in diesel/jatropha biodiesel blends showed a greater stabilizing potential; however PY, PrG and BHA were found most effective among all antioxidants tested, and their use in diesel/karanja biodiesel blends showed a greater stabilizing potential. In addition to individual antioxidants, the use of binary combinations of optimized concentrations antioxidants was also studied for the improvement in oxidation stabilities of biodiesels and their diesel blends. The binary antioxidants system was found to be more effective than the individual. The binary antioxidant combinations not only enhance the stabilities of biodiesel and their blends by manifold but it also observed that such combinations were more economical in comparison to individual antioxidants. 500, 600 and 700 ppm of antioxidant combinations *i.e.* (PY:PrG), (PY:TBHQ) and (PY:BHA) at weight ratios of 9:1, 3:1, 2:1, 1:1, 1:2, 1:3 and 1:9 were studied. Based on the observations it was found that the 1:3 weight ratios of binary antioxidants have shown best effectiveness among all. Study of the synergistic behavior of various binary antioxidants were also calculated and it was concluded that the best synergy may achieved at the lower concentration of the antioxidants.

CONTENTS

S.No **List of Tables** **Page No.**

List of Symbols

%	per cent
η	kinematic viscosity
ρ	Density
µ	Specific growth rate
₹	Rupees
°C	degree Celsius
°F	degree Fahrenheit
Cal	calorie
cm	centimeter
cSt	centistokes
g	gram
h	hour
j	joule
kCal	kilocalorie
kg	kilogram
KW	kilowatt
Kpa	kilopascal
L	liters
m	meter
min	minutes
MJ	mega joule
ml	milliliters
ppm	Part Per Million
rpm	revolutions per minute

List of Abbreviations

AD	Anaerobic Digestion
ASTM	American Society for Testing
B5	Biodiesel-Diesel Blend (5:95)
B10	Biodiesel-Diesel Blend (10:90)
B15	Biodiesel-Diesel Blend (15:85)
B20	Biodiesel-Diesel Blend (20:80)
B25	Biodiesel-Diesel Blend (25:75)
B40	Biodiesel-Diesel Blend (40:60)
BD	Biodiesel
BIS	Bureau of Indian Standards
BTL	Biomass to Liquid
BtO	Butanol
CAGR	Compound Annual Growth Rate
CCR	Conradson Carbon Residue
CDM	Clean Development Mission
H_2S	Hdrogen Sulphide Gas
H-Bio	Biohydrogen
HCs	Hydrocarbons
HSD	High Speed Diesel
HT Oil	Heat Transfer Oil
IEA	International Energy Agency
IP	Induction Period
IOC	Indian Oil Corporation
IRENA	International Renewable Energy Agency
LC Ethanol	Ligno-Cellulosic Ethanol
LFG	Land Fill Gas
Lge	Liters of Gasoline Equivalent
LPG	Liquid Petroleum Gas
Mag	Ministry of Agriculture
MNRE	Ministry of New & Renewable Energy

CFPP	Cold Filter Plugging Point	MPNG	Ministry of Petroleum & Natural Gas
CH_4	Methane Gas	MST	Ministry of Science & Technology
CO	Carbon Mono-Oxide	N_2	Nitrogen Gas
CO_2	Carbon Dioxide	NBM	National Biofuel Mission
CSIR	Council of Scientific & Industrial Research	NBDB	National Biofuel Development Board
DIN	Deutsches Institut für Normung	NOx	Mono-Nitrogen Oxides NO & NO_2
DME	Dimethyl Ether	O_2	Oxygen
CSMCRI	Central Salt & Marine Chemicals Research Institute	OECD	Organization for Economic Co-Operation and Development
DST	Department of Science & Technology	SNG	Substitute Natural Gas
DBT	Department of Bio Technology	SYN	Synthesis Gas
EIA	Energy Information Administration	WEO	World Economic Outlook
EBPP	Ethanol Blended Petrol Program	EJ	Exa Joules
EN	European	EtO	Ethanol
FAAE	Fatty Acid Alkyl Ester	FFA	Free Fatty Acid
FAME	Fatty Acid Methyl Ester	FT	Fisher Tropsch
GC	Gas Chromatograph	GHGs	Green House Gasses
H_2	Hydrogen Gas	GOI	Government of India

Chapter 1: Introduction

The remarkable progress of industrialization, modernization in life style and vehicular population of the world has led to significant increase in petroleum based fuel demand [1-2].Presently, more than 80% of primary energy demand of entire world is met by the petroleum based fuel, out of which ~60% of share is consumed by transportation sector [3]. Continuous over exploitation of petroleum fuel reserves to fulfill current energy demand have led to the rapid depletion of these energy sources. Continuous growth and fluctuation in crude oil prices along with major contribution in greenhouse gases (GHGs) emissions by their consumption [4-7], causing several negative impacts on human health along with earth's ecology. Therefore, it is essential to find out new alternative energy sources those must be renewable, sustainable, environmental friendly, efficient and economically viable [8-9]. Among many alternative energy sources, biofuel have gained greater attention across the globe because the biofuel are considered the most sustainable and environment friendly energy source. Generally biomass derived liquid, solid and gas fuel are broadly known as biofuel (e.g. methanol, ethanol, bio-diesel, bio-oil, FT (Fisher Tropsch) diesel, hydrogen and methane [10-11]. The purpose of this study is to review the status of global liquid biofuel production (biodiesel and bio-ethanol), associated challenges and constraints for their effective commercialization to meet the global energy demand.

1.1.Biofuels – Overview

According to International Energy Report 2014, global energy demand is expected to grow by 37% by 2040. Owing to limited and depleting resources of traditional petroleum fuels researchers are making their best attempts to meet the energy demand and finding out alternatives from renewable raw materials. The renewable energy technologies may not only fulfill the world's energy demand, but are also important parameters to reduce the emission of greenhouse gases [12]. Although, there are several ways to produce fuel from renewable resources; however, their commercial productions still an unfinished task [13]. Sources of non-edible raw materials are of great potential to produce biofuel, mainly because of the limitation of direct food and parallel race associated with biofuel [13-16]

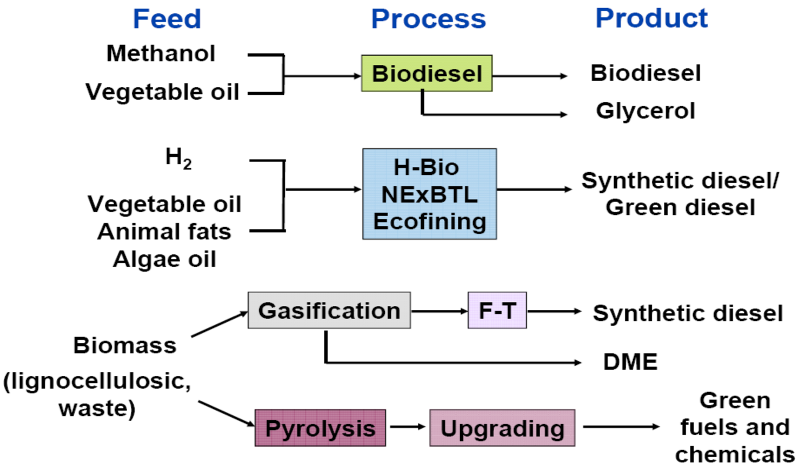


Figure 1.1: Process of using various feedstocks to extract the different biofuel

Selected social, economical, environmental and technical issues for biofuel generation have been discussed in the form of several articles and scientific journals [17-22]. The main parameters regarding biofuel production are carbon emission levels and nitric oxide (NO_2) emissions including energy consumption and environmental issues [15]. Developed countries are having their research targets to develop biofuel industry, in particular for transport sector. Growing concerns in many developing countries to upgrading of biomass for acceptable climate and employment creation has been focused, as this is a labor intensive area. Besides, the restoration of degraded land through biomass-energy production is also of interest in some areas.

The common process of development of biofuel may as shown in Figure 1.1. In general, bio-fuel can be classified as follows:

1.1.1. **First generation biofuel** is derived from starch, sugars, fats and vegetable oil that can be categorized as follows:

i. **Biodiesel:** European countries are using such type of bio-fuels mainly produced by transesterification process, similar to the mineral diesel and applicable with various engines with some additives [21,23].

ii. **Vegetable oil:** Cooking purpose oil may also be converted to biofuel; however, this is not considered as a feasible method as it is directly affecting the food security issues.

iii. **Biogas:** Anaerobic digestion of the organic materials generates the biogas by the process called biodegradation, where chain scission is mediated by microbes. After the conversion of bio-gas some non-harmful residue are also helpful for generating bio fertilizers [24]. Methane rich biogas is recovered using a sequential treatment. Bio-gas can also be generated from landfills; however, chamber controlling is very essential as methane can release to the atmosphere.

iv. **Alcohols:** Fermentation of long chain bio-polymers such as starch and cellulose may generate the different types of alcohols mainly ethanol with some butanol and propanol. Recently it has been experimentally shown that butanol can be use directly instead of gasoline [25-27].

v. **Syngas:** Indirectly, syngas can be produced through bio-fuel after converting it into carbon mono-oxide followed by pyrolysis [28].

Ethanol and biodiesel are commonly used biofuels in engines and the following section will emphasize on the technological development particularly in these areas of research.

1.1.2. Second generation bio-fuel:

As per the IEA (International Energy Agency) Bioenergy Task 39, 2009, Biofuel derived from cellulosic biomass (cellulose, hemicellulose and lignin) with more sustainable fashion are known as second generation biofuel. The second generation biofuel are generally called the carbon neutral or carbon negative in terms of their impact on carbon dioxide concentration [29]. Comparatively easier abundance of non-fodder feedstocks from plants makes it more economical in comparison to first generation biofuel [29-31]. The second generation biofuel, like bioethanol, biodiesel, Dimethyl-ether, bio-SNG FT diesel etc., can be produced through hydrolysis, fermentation (*i.e.* bioethanol) esterification and/or gasification [29,32]. Bioethanol has been considered as a substitute of gasoline; whereas, FT-diesel or

BTL (biomass to liquid) is used as a substitute for conventional diesel [21]. However, SYN gas can be converted in to liquid hydrocarbons mainly diesel, kerosene, methane and DME [28]. The conventional petroleum based fules when blended with 2nd-generation biofuel may be used either as an alternative for existing internal combustion engines or get distribute through existing infrastructure or dedicated as fuel for slightly adapted vehicles with internal combustion engines (e.g. vehicles for DME)" [33]. These second generation biofuel can be supplied or distributed through existing infrastructure without any significant modifications. Table 1.1 presents the generation of this class of bio-fuel by various processes.

Table 1.1: Processes of production of second generation bio-fuel [34]

Process	**Bio-fuel**
Fermentation / enzymatic hydrolysis	Ethanol from cellulose
Gasification	Fischer-Tropsch biodiesel, Butanol, Dimethyl ether
Methane	Natural gas from synthesis
Hydrogen	Gasification, product of biological processes

1.1.3. Third Generation bio-fuel:

The concept of third generation biofuel is mainly refers to algae based biofuel, because of much higher quality yield of biofuel (Holds up to 9000 liters of biofuel per hectare, which is to produce 10 times more than the best traditional feedstock) in comparison of other fuel generation feedstock along with a wider variety of fuels/other valuable chemical such as bio-methane, biodiesel, bio-ethanol, bio-butanol, vegetable oils gasoline, and jet fuel [29, 35].In addition, the main advantage of algae biomass is that, they can grow over a variety of carbon sources, *i.e.* they grow directly on the carbon emission sources (power plants, industry, etc.) to convert the emissions directly into usable fuel, [36] with zero emission of carbon dioxide.The prime challenges associated with 3rd generation biofuel are the cultivation of microalgae at very large scale in order to meet the demand of industry, as they require plenty of water, nitrogen and phosphorus [37]. Thus, theproduction of fertilizers requires for the growth of algae, required much more energy and generate greenhouse gases than the product can contribute in green climate [36, 37].

According to the joint nature conservation committee (Gov of UK) report on biodiesel and bioethanol in 2009; the global market for biofuel is expected to grow by 247 million USD by ~ 2020. There is a clear demand for new technologies and value chains for the commercial use of second and third generation biofuel. These advanced biofuel have more advantages compared to first-generation biofuel (*e.g.* corn-based bioethanol, oil seed residue based biodiesel) and found to have better sustainability criteria [3]. Second generation biofuel can be generated from non-food crops and third generation biofuel do not require even land for their production [15, 29].

Worldwide status of biofuel technologies development *(2012 data from www.europabio.org fact sheet for advance biofuel)*

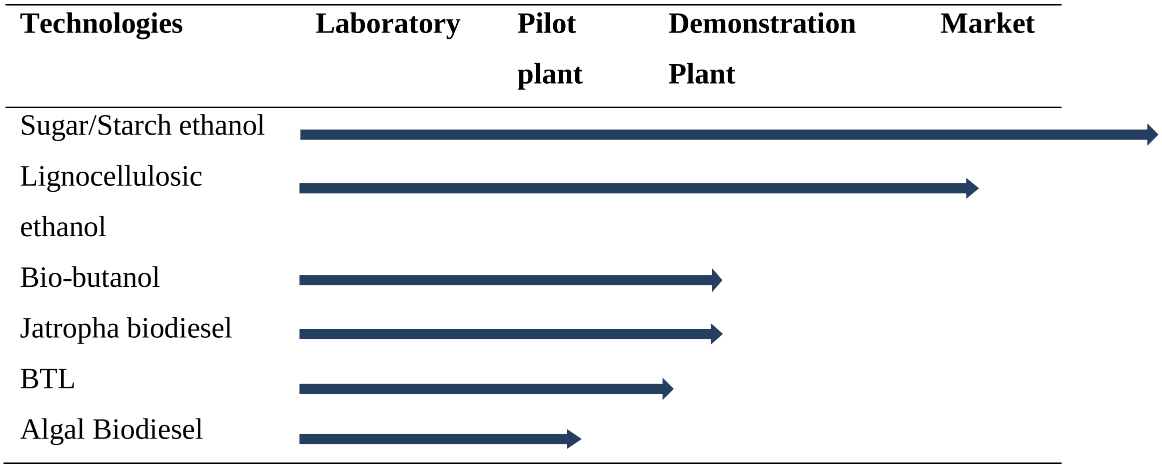


Figure1.**2**: World biofuel technology status

Countries like US, Brazil etc. where 1st and 2nd generation biofuel are being used as vehicle engine fuel and these trends may continue for coming years mainly because of sufficient availability of edible oils (soya oil, sunflower oil, rapeseed oil, starch and maize). However, in developing countries, like India and China, where the above mentioned biofuel technologies are yet to commercialize. As these kinds of resources in India are scarce as the demand and supply ratio is poorly matching and production of edible oil is much lower than the actual requirement. Therefore, from Indian perspectives using non-edible oil resources like *Jatropha*, *Pongamia, Mahua*, algae and *Sal* etc.for the production of bio-fuel seems the comparatively better available options [15,38]. Therefore, the use of agriculture crop waste or waste biomass material (*like agro waste, forestry waste, Pulp/Paper, Wood, etc.*) is advisable for 1st generation biofuel (Figure 1.2). Although continuous efforts on biofuel technology development have started in India, still some gap areas are there which includes development of industrially viable technologies along with expertise. The global biofuel technology status is presented in Figure 1.2.

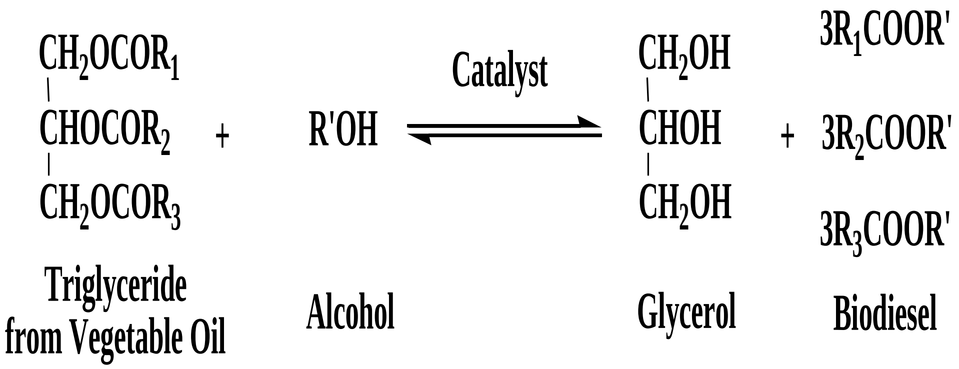
1.1.4. Fourth Generation bio-fuel:

The Fourth Generation bio-fuelsare meant at not only producing sustainable energy but also a way of taking and storing CO_2. Biomass materials, which have absorbed CO_2 while upward, are converted into fuel using the same processes as second generation biofuels. This process differs from second and third generation production as at all phases of production the carbon dioxide is taken using processes such as oxy-fuel combustion. The carbon dioxide can then be geosequestered by storing it in old oil and gas fields or saline aquifers. This carbon detention makes fourth generation biofuel production carbon adverse rather than simply carbon neutral, as it is 'locks' away more carbon than it produces. This system not only detentions and supplies carbon dioxide from the atmosphere but it also decreases CO_2 emissions by substituting fossil fuels.

1.2.Biofuel conversion technologies:

1.2.1. Conversion technologies for first generation biofuel

1.2.1.1.**Biodiesel production by transesterification processes:**The vegetable oil derived fatty acid methyl ester (FAME) generally known as Biodiesel, has been considered a potential substitute of conventional diesel, obtained from renewable biological resources such as edible and non-edible oils, animal fats *via* acid or base catalyzed chemical reactions of these oils with alcohols (methanol/ethanol) [16, 39-42].The resultant product of such reaction is a combination of fatty acid alkyl ester (FAAE), and high value co-product glycerol. The catalysts used for biodiesel production are either may be acidic or basic, homogenous or heterogeneous. Homogeneous transesterification is a reversible chemical process in which reactants (vegetable oil + alcohol) are being mixed together with the catalyst which is also a liquid acid or liquid base (Scheme 1.1).



Scheme 1.1: Transesterification of vegetable oils

Due to corrosive nature of liquid acids, liquid bases are generally preferred for homogenous transesterification of vegetable oils [16]. Although, homogeneous catalysis provides high reaction rate under mild reaction conditions, yet these catalysts have several drawbacks such as corrosive nature, non-recyclable, non-eco-friendly and formation of sodium or potassium ion contaminated biodiesel and glycerol [43]. Homogeneous catalysts also produce large amount of waste water that reduces their attractiveness. Heterogeneous transesterification is a process where solid acid or solid base catalysts are used to convert the vegetable oils to corresponding alkyl esters (Biodiesel), and provides better yield in comparison of homogeneous catalysts, specially used for transesterification of triglycerides to produce biodiesel. Heterogeneous catalysts provide easier separation, catalyst free product formation and no requirement of product neutralization and purification steps. Moreover, less consumption, and reusability of heterogeneous catalysts makes the biodiesel production much economical in comparison to homogeneous catalyzed processes [43].Theoretically, both solid acid and solid base can be used for transesterification processes to produce the biodiesel; however, the solid acid catalysts are found practically more suitable for transesterification of concentrated fatty acid content vegetable oils in comparison to solid base catalysts, [43, 44] which might be due to saponification process lead by solid base catalysts while used with high free fatty acid containing oils.

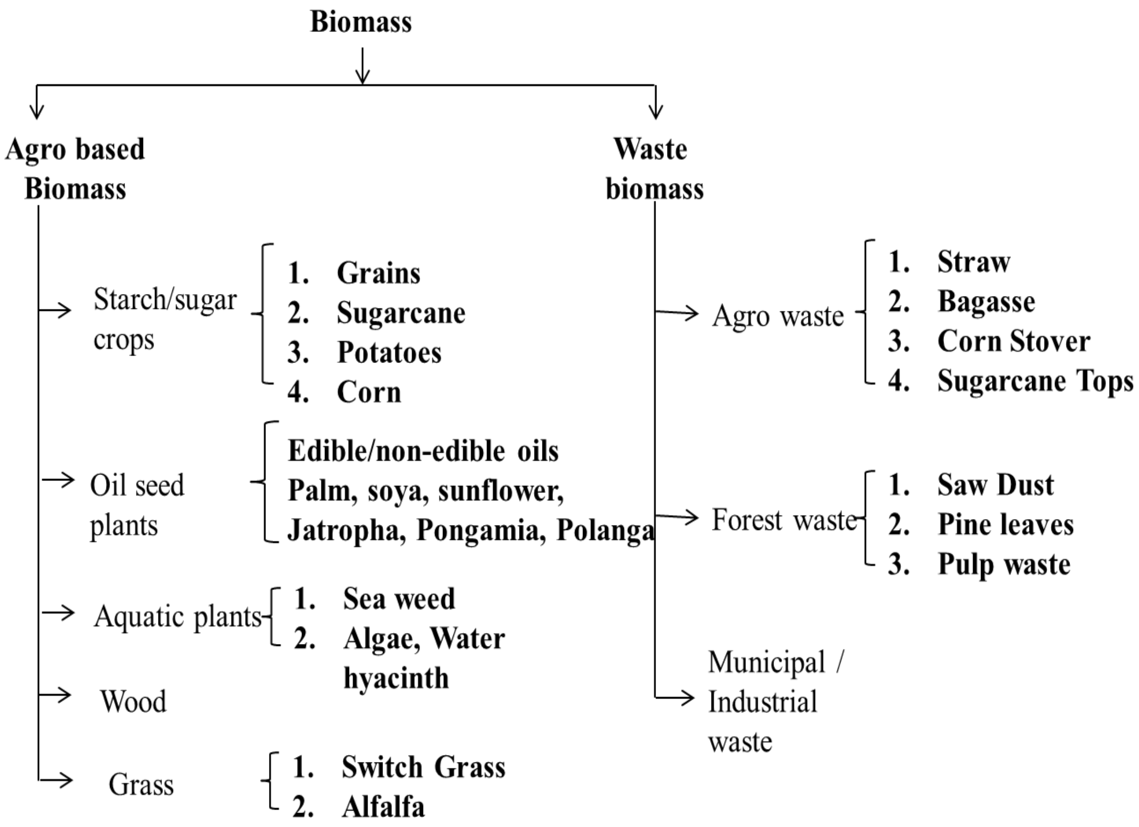


Figure 1.3: Sources of biomass feedstocks for biofuel production [29]

Acid catalysts, solid in nature, are able to produce the biodiesel by transesterification of triglyceride. This can also be additionally produced by esterification reaction of free fatty acid present in parent oil. However, in case of solid base catalyzed processes the degumming of parent oil to reduce the free fatty acid content is recommended, which is additional to transesterification and also enhance the overall cost of production.

1.2.1.2. **Ethanol conversion processes:** Globally the carbohydrate containing feedstocks (crops with sugar content: sugarcane, fruits, beetroot, wheat etc.; crops containing starch: all kind of carbohydrates rich grains etc.; cellulosic biomass: wood, wood waste, agricultural residue, non-fodder biomass etc.) have been extensively used for the production of ethanol via fermentation or biochemical processes [45]. Food crops based ethanol generally called grain-ethanol; whereas, biomass based ethanol (bioethanol) is produced from lingo-cellulosic biomass like agro waste. Carbohydrates are long chain polymers of glucose etc. therefore, the process of conventional fermentation and biochemical methods cannot convert these macromolecules to ethanol directly. These polymeric structures first broke down to smaller units of glucose, and the glucose finally converted to ethanol and other valuable chemicals [46].

1.2.1.3. **Biogas production processes:** Biogas is a composition of different gasses (CH_4,CO, CO_2, H_2S and H_2O) and consist methane (CH_4) as the major constituent. It is produced from the biodegradation of organic materials in absence of oxygen. The process for biogas production is known as Anaerobic Digestion (AD). It is a natural process in which microorganisms decomposes biomass or organic matter (also known as feedstock) in airtight digester tanks to produce biogas as well as digestate. The biogas conversion through anaerobic digestion of biodegradable organic materials consists of four different stages such as hydrolysis, acidogenesis, acetogenesis and methanogenesis which leads with the formation of methane and carbon dioxide are the primary gaseous end products [47, 48]. The usual mixture of gas mixture is methane (60-70%) and carbon di-oxide (30-40%) [48]. The production of fuels and bio fertilizers via the process of AD of biomass is an environment friendly and attractive process at present in an era of increasing energy demand and increasing per capita cost of energy. AD in landfills for solid waste management is one of the potential sources of bio-methane productions. This process produces the landfill gas (LFG), also known as low quality natural gas is a mixture of methane, oxygen, nitrogen, carbon dioxide and traces of organic compounds. The removal of carbon dioxide and organic contaminants which are volatile in nature are necessary in order to improve the commercial value of LFG [49, 50].

Conventionally, the LFG is used to generate energy via the power generation in internal combustion engine, direct use in boilers, turbines, micro turbines, green house and co-generation [51,52]. Due to higher cost associated with the current technologies for the production, purification, separation and collection of methane, more emphasis is being laid on the conversion of LFG into liquid fuel instead of gaseous fuel from anaerobic digestion. Methane can be converted to methanol via various catalytic routes. Liquid fuel and bio-fertilizers for agro production can be generated using the waste lignocellulosic biomass obtained after anaerobic digestion.

1.2.2. **Conversion processes for second generation biofuel:** Currently, biochemical and thermochemical conversion processes for the production of second generation biofuel are being used extensively [2,29,53]. Gasification, direct combustion, liquefaction and pyrolysis fall under the category of thermochemical conversion process. Syn gas is produced when biomass is heated under limited supply of oxygen, which primarily consists of hydrogen and carbon mono oxide. Syn gas can be burnt directly or reformed in to other gaseous and liquid fuels. Combustion of biomass for energy harvesting is the most conventional route, where the biomass is burnt directly in presence of oxygen or air.

However, liquefaction of biomass can be achieved either directly or in the presence solution of alkalis, glycerine and alcohols like propanol and butanol [29]. This process mainly produces the highly viscous water insoluble oils and requires specific reducing gases (e.g. CO or H_2), solvents and/or some catalysts as well. Also, in presence of solid catalysts and SYN gas the lignocellulosic biomass can be converted effectively in to liquid fuel similar to the heavy oils [29] The highly viscous heavy oil sometimes very difficult to handle and hence needs some organic solvents to reduce their viscosity. Hydrolysis (alkaline) of lignocellulosic biomass leads to the degradation of cellulose and hemicellulose in to smaller fractions which are being used as precursor of various value-added products including gasoline and other fuel additives [54,55].Bio-oil is another class of product obtained from liquefaction of air dried biomass at very high pressure or by fast pyrolysis path [56]. It is a multifarious combination of volatile organic acids, hydroxy aldehydes and hydroxy ketones, ethers, alcohols, esters, sugars and phenolics[57, 58]. Organic distillate products which are rich in hydrocarbons and useful chemicals can be produced if the bio-oil is upgraded catalytically.

Gasification is a well-known process of converting the biomass to viable fuels, and has been investigated for past forty years. This process generally involves the reaction of biomass with air, oxygen or steam to produce the mixture of Hydrogen (H_2), Methane (CH_4), carbon monoxide (CO), carbon dioxide (CO_2) and nitrogen (N_2). Mixture of these gasses is either known as producer gas or synthesis gas. A range of fuels and chemical intermediates are produced using Syngas whereas the producer gas is mainly useful for the stationary power generation [59, 60].

The thermal degradation of biomass in the absence of oxygen in order to produce bio-oil, gaseous mixture of fuel and solid charcoal is known as pyrolysis, where conventional pyrolysis, fast pyrolysis, and flash pyrolysis are the three different categories of pyrolysis based on the various operating conditions [57]. Conventional pyrolysis is a slow pyrolysis process, it occurs with slow heating rate and high residence time. During the first stage of conventional pyrolysis, biomass decomposition takes place at a temperature between 550 and 950 K, called pre-pyrolysis. During pre-pyrolysis some initial molecular changes occur such as elimination of water, bond cleavage, free radical generations etc. During the second stage of conventional pyrolysis, solid decomposition of biomass takes place which results the formation of pyrolysis products. However, in the third stage of pyrolysis carbon rich solid formation occurs from the slow decomposition of char [61, 62].

Fast pyrolysis generally takes place at high temperature (850-1250 K) with short residence time and high heating rate with fine particle of biomass as feed, [58]and used mostly to produce liquid and/or gaseous products, where the decomposition of biomass generates vapours, aerosol and char. The product of fast pyrolysis generally contains 60-75% of bio-oil including condensable gasses/vapours, 10-20% of non-condensed gases and 15-25% of char [58].

Flash pyrolysis occurs at very high temperature (more than fast pyrolysis) 1100-1400 K, at an extremely quick heating speed (>1000K/s), with very short residence time (0.5s) and very fine particles of biomass (<0.2mm). Due to typical operating conditions this process is not used very often [63].

Catalytic hydro-treatment of vegetable oils helps to obtain green diesel, another form of diesel fuel [64]. The vegetable oils are renewable feedstocks and being used for the production of biofuel. The existing technology for the production of diesel like fuels from biomass is dependent on the transesterification process of edible and non-edible oils and termed biodiesel. Since biodiesel have some technical issues related to its physico-chemical properties [16], hence the future widespread utilization of biofuel depends on the development of newer and advanced technologies to produce high quality transportation fuel from biological sources [65].

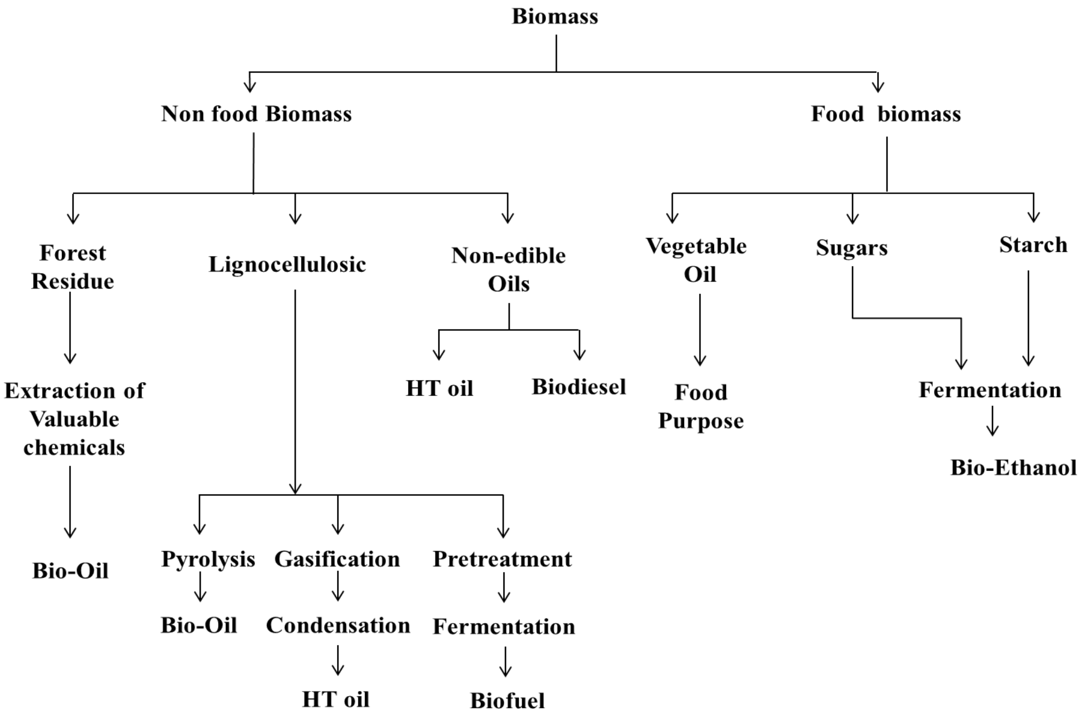


Figure 1.4: Second generation biofuel conversion Process [29]

Conversion of vegetable oils into a high quality diesel fuel or diesel blend including compatibility with petroleum derived diesel fuel is highly desirable. Using the process of hydrodeoxygenation, catalytic saturation, hydro-isomerization and decarboxylation the renewable feedstock containing triglycerides and fatty acids can be helpful in the production of isoparaffin-rich diesel known as ‘green diesel’, which is an aromatic and sulphur free diesel fuel having a very high cetane blending value [66, 67]. In contrast to fatty acid methyl esters, the properties of green diesel do not depend on feedstock, its origin and the process adapted for the conversion [66, 67]. The fully deoxygenated fuel product of this process is readily blended with petroleum derived diesel fuel. Chemical conversion of lignocellulosic biomass is a process of conversion of biomass to bioethanol along with other value added chemicals and fuel additives by chemical route. It can be done by chemical hydrolysis, solvent extraction and super critical water conversion of biomass. The cellulosic biomass first reduced to its lower members (starch, sugars etc.) and then chemically converted to other value added products like alcohols, other solvents of interest to fuel and chemicals [68]. Figure 1.4 shows the pathway for second generation biofuel.

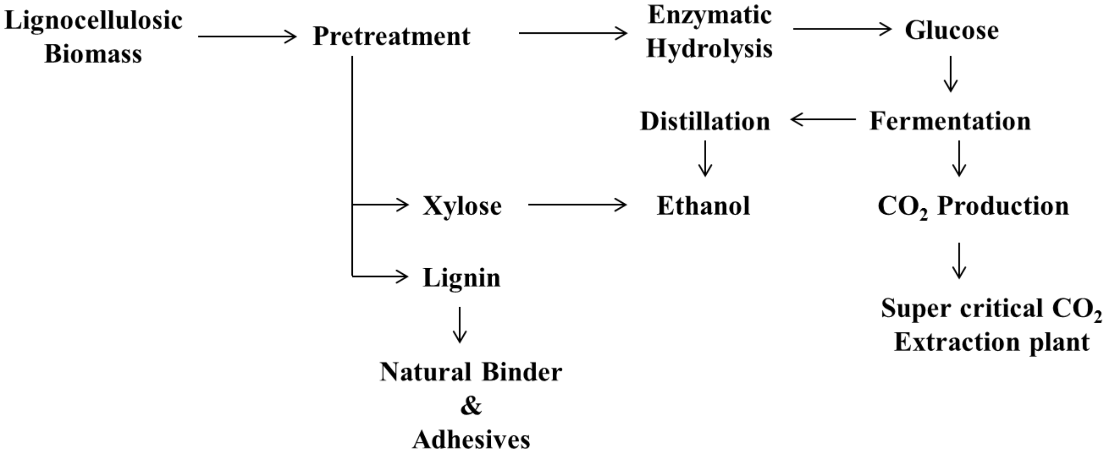


Figure 1.5: Lignocellulosic biofuel conversion process [29]

Ethanol production from corn, sugarcane by biochemical route has already been commercialized. The production of ethanol from bio origin requires the understanding of various operational techniques like pre-treatment, hydrolysis, fermentation, enzyme production and product recovery (Figure 1.5).

Presently, the ethanol production technologies are not much economical; more research emphases is on reduce the overall production cost which requires improved and much advance technique for conversion of cellulosic and hemi-cellulosic biomass to sugars, low pre-treatment energy consumption, more efficient separation technologies and finally the value-addition of lignin [69].

Besides the above mentioned biomass sources, agro waste residues, forestry waste and post-harvest processing of industrial crops produces enormous amount of lignocellulosic waste biomass. These lignocellulosic wastes can be the promising sources of bioethanol production along with other value added chemicals and fuel additives. The biomass derived oxygenated fuels and fuel additives can be easily blended with gasoline to produce a fuel with less GHG emissions. Ethanol is being blended with gasoline from 5% to 25% without any modification in engine system or setting [70, 71].

1.2.3. **Conversion processes for third generation biofuel:**Generally algal basedbiofuel are considered as third generation biofuel. The selection of conversion technology for the production of third generation biofuel are particularly depend on the type and quantity of feedstock, desired product, production cost and type of energy requirement, economic considerations and the desired form of energy [36, 72]. Like second generation biofuel, the conversion technologies for third generation biofuel production can also be categorized as Thermochemical and Biochemical conversion processes along with the biodiesel production [2,29,53]. Thermal decomposition of organic molecules present in biomass to give fuel or fuel precursor is known as Thermochemical conversion. It includes the various co-processes like gasification, thermochemical liquefaction, direct combustion and pyrolysis.

Energy harvesting from biomass using biological routes is known as biochemical conversion process. Most commonly utilized biochemical techniques include anaerobic digestion, fermentation and photo-catalytic production of hydrogen [2,73,74,75,76].

In anaerobic digestion process of algae mainly the bio-organic wastes is converted into biogas, consists of methane (CH_4), carbon-dioxide (CO_2) along with the traces of hydrogen sulphide (H_2S). The anaerobic digestion process is suitable for the conversion of high moisture content (>75%) bio-organic wastes [77]. The anaerobic digestion has generally three sequential stages: a) hydrolysis; b) fermentation; and c) methanogenesis[78]. The complex organic compounds present in waste are broken down in to soluble sugars during hydrolysis process, and these simpler organic molecules further get converted in to corresponding alcohols, acetic acid, volatile fatty acids and mixture of H_2 and CO_2 during fermentation process. Further the metabolites obtained from fermentative step then get converted in to CH_4 (~70%) and CO_2 (~30%) via methanogenesis[78].Also, the nutrient rich waste produced during anaerobic digestion process can be recycled for new algal growth medium [79].

In fermentation process, ethanol is produced via degradation of cellulosic biomass in to lower sugars and subsequent conversion of those sugars into ethanol. The biomass is crushed and then hydrolyzed to starch molecules then converted into respective sugars; finally these sugars are fermented using yeast which breaks down these sugars into ethanol. Selection of algae for ethanol production depends on the available starch content in algae. Higher the starch content higher will be the ethanol yield. Because of this, Chlorella *Vulgaris* (starch content ca. 37% dry wt.) is considered as an excellent algal feedstock for ethanol production [80, 81].

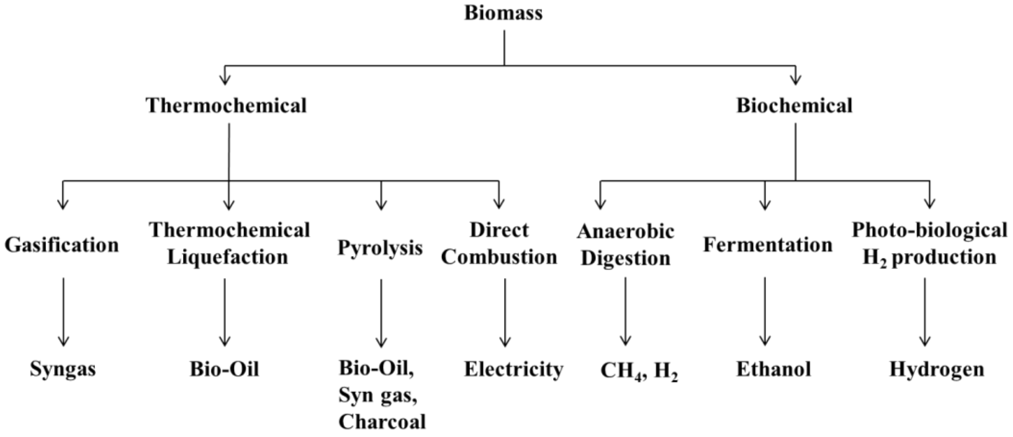


Figure 1.6: Algal biofuel conversion process [29]

Since, hydrogen is considered an ultraclean and efficient energy carrier and is naturally occurring molecule. Algae possess the required genetic metabolites and enzymatic characteristics to photo produced H_2 gas under anaerobic conditions either via electron donor path during CO_2 fixation or involve in both light and dark [82,83,84]. Microalgae during photosynthesis process converts H_2O in to H^+ ions and oxygen, these H^+ ions then get converted in to H_2 by hydrogenase enzyme under anaerobic conditions [84]. Since, this process is reversible, hence during simple conversion of proton to hydrogen the H_2 is either produces or consumed. Mainly two approaches are being used for H_2 production from H_2O via photosynthetic route [85, 86].

a) A two stage H_2 production along with O_2, but the production of both (H_2 and O_2) takes place separately.

b) Photosynthetic production of both H_2 and O_2 occurs simultaneously.

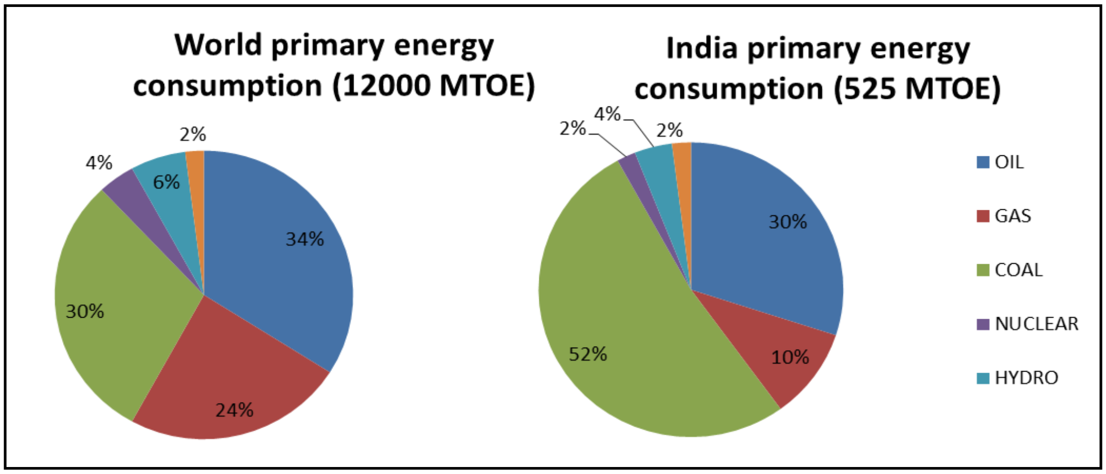
Out of these two processes the second process is preferred theoretically however; first process has an advantage of being green and environmental friendly. Hence, the first process for hydrogen production is generally preferred by the researchers across the globe [87]. The overall biofuel production pathway from 3rd generation biofuel feedstock is shown in Figure 1.6.

1.2.4. Conversion process for fourth generation biofuel:

The atmospheric CO_2 is sponged by the bioengineered crops by photosynthetic pathway to make it a part of their foliage and hard material like stem, branches etc. These bioengineered plants possess a higher CO_2 utilization tendency due to which their biomass is usually higher than their conventional counterparts. This biomass is converted to clean fuels like hydrogen and methane on pyrolysis, gasification and digestion. The unessential CO_2 liberated by these methods is sequestered by the depleted oil and gas fields, saline aquifers and unmineable coal seams. The clean fuel obtained is eventually upgraded by gas cleaning and liquefaction methods to obtain ultra clean carbon negative fuels in the form of biohydrogen, biomethane termed as the fourth generation biofuels.

1.3. Energy demand of India and challenges:

The energy demand of India is mainly met through the conventional and non-renewable energy sources like coal, crude oil and natural gas. India, being a largely populated and rapid growing economy, is currently facing a considerable challenge to meet its energy demand in a sustainable and responsible manner (Figure 1.7). As per IEA 2007b, and IEA 2012 reports, India needs to generate approximately three-fold more energy than its present energy production, to meet the current energy demand and to sustain with its 8% average annual growth to support its growing population. Industrial and transportation sector are the two major areas having highest energy demand among all other sectors in India.



Source: BP statistical review 2011

Figure: 1.7 Global and India's primary energy consumption

This indicates that India will have a need of 1516 million tons of oil equivalent by 2030. As per GOI Energy Statistics 2013 (Ministry of Statistics and Program Implementation, GOI) there is a tremendous increase in consumption of major energy resources (like coal, crude oil and other petroleum products) in last decades. The estimated consumption of raw coal by industry has increased by a compound annual growth rate (CAGR) of 4.86% (72.95 million tons during 1970-71 to 535.88 million tons during 2011-12). Because of the dependency on foreign crude oil (India's 70% of total crude oil demand met through imports) the estimated consumption of crude oil has shown a steady increase with a CAGR of 5.99% (18.38 million ton during 1970-71 to 211.42 million tons during 2011-12). Among all types of petroleum products, the consumption of high speed diesel oil is estimated for 39.62% in 2011-12; however, a 28% of total consumption of petroleum products is equally shared by other sectors like refinery, LPG and gasoline in 2011-12. Within the transportation sector only, the consumption of HSD increased by 4.1% from 36.55 million tons in 2001-02 to 51.67 million tons in 2008-09, and that of gasoline by 6.64% from 7.0 million tons to 11.26 million tons. This growth rate will become more prominent in coming years because, it is estimated that India's vehicular population is expected to increase by 10-12% per annum.

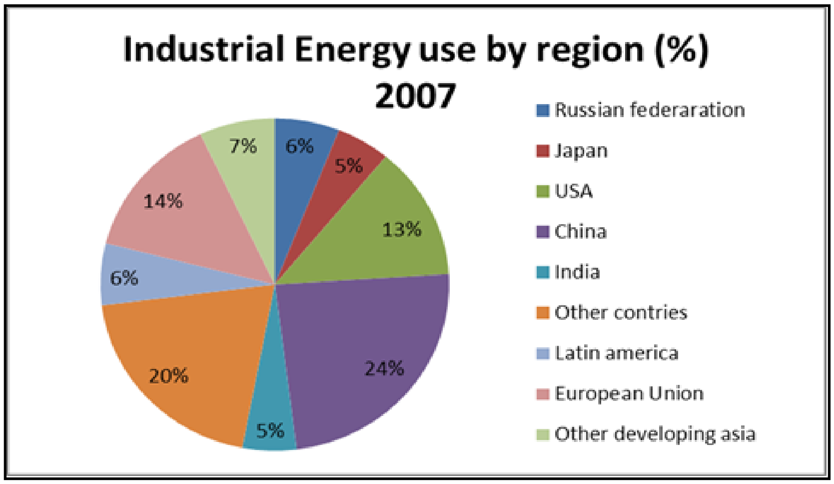


Figure:1.8 Global industrial energy consumption (region wise)

Note: This includes coke ovens, blast furnaces and petrochemical feedstock.

Sources: IEA, 2009b; IEA, 2009c.

Although the per-capita energy consumption in India is one of the lowest in in global prospects (Figure 1.8), *i.e.* India's per person energy consumption is 439 kg oil equivalent (kgoe) in comparison to 1090 kgoe energy consumption per person in China and 7835 kgoe of energy consumption per person in USA; however, India's per person energy consumption is expected to reach up to 1250 kgoe by

2032. Per-capita energy consumption (ratio of the total estimated energy consumption during the year to the estimated midyear population of the year) has increased by a CAGR of 4% (from 1204 KWh in 1970-71 to 6420 KWh in 2011-12). Hence, long term energy security and sustainable energy resource development is very critical to ensuring the India's future energy requirement. Therefore, exploration and exploitation of new energy resources, their capacity addition, clean and renewable energy development, energy conservation and more likely the energy sector reforms will be critical for India's energy security. However, energy conservation and it'sefficient utilization could be a key factor in tightening the gap between demand and supply of India's energy sector. Currently, India is putting more emphasis on development of Indigenous alternate energy resources from biofuel to meet the transportation sector demand. In this regard, Government of India approved mandatory blending requirement of gasoline and diesel with biofuel to promote biofuel as an alternate energy source. As per GOI biofuel policy mandate 2009; blending of 20% bio ethanol in petrol blending of biofuel (both biodiesel and bioethanol) with diesel and petrol by 2017 has been set as an indicative target.

1.4. Technical, Environmental and Economic Challenges and Constraints for Biofuel Production

1.4.1. Feedstock Availability, Food Security, Land use Changes and Water Source:

Biofuel technologies would only be successful and useful for society if there is sufficient availability of biomass feedstock for those technologies in a sustainable way by keeping in mind the environmental impacts and "food vs fuel" issues [17,22,23,88]. In one of the review by Groom et al. 2008, a sustainable and environmental friendly route for cultivation of oil crops has suggested. The authors have also recommended the promotion of carbon neutral, more sustainable and almost non-fodder feedstocks without affecting the biodiversity and maintenance of essential and native food crops. In another reports, [89,90,91], the challenges of sustainable availability of feedstocks for biofuel production were also addressed; where authors have particularly focused on the *food vs fuel* debate. The demand for food and water will continuously keep on growing with the world's growing population. It is one of the consequences that food prices have been increaseddramatically across the globe. Previously, there was no significant correlation between biofuel and food prices; however, as the food crops (sugarcane, maze, soybean and rapeseed etc.) based biofuel production increases, this correlation has strengthened. Continuously increasing demand and production of biofuel and competitiveness of the biofuel sector also causes the increase in the costs of source materials. These emerging trends suggest that food and biofuel markets are likely to be more strongly linked in future, which would certainly affect the food prices. Therefore, trend of the biofuel research is shifting towards the development of biofuel production from non fodder feedstock (like Jatropha, Karanja, Polanga oils etc. for biodiesel production and agro and forestry waste cellulosic biomass for bio-ethanol production). This is one of the reasons that, much of the literature on biofuel production focuses on the potential impacts on food security as well as land use changes and water source [17,22,23]. Farmers, particularly in developing country like India, started shifting their farming trends from producing food crops to producing biofuel crops in the agriculture land to boost their incomes and employment in agriculture sector, even if the new crops are not edible. As a result the food availability and food security will go down and price of the food will rise [22,23]. Besides, there are certain other barriers to sustainable development of existing biofuel technologies. The biomass derived fuels have low energy density and high cost of collection and transportation of biomass. Furthermore, growing more biofuel based crops to boost the biofuel production without considering the quality and availability of water by region could put a significant strain on water resources, especially in developing countries. Such agricultural shifts to growing biofuel crops could change the availability of clean and potable water and significantly increase pressure on water local resources [22,23]. Also, the intensive input requirement (land, water, crops, energy etc.) for the production of biofuel is mainly responsible for the poor economics associated with these biomass derived fuels, and hence, is observed as one of the major constraints in their sustainable development [3,11,22].

The major barriers for sustainable development of biofuel may be summarized as follows:

1. Expansion of biofuel production may require the extra land to maintain the sustainability as production of biomass is always depend on several factors.
2. Added pressure on water resources for growing biofuel feedstocks.
3. Preserving the biomass has been a big challenge and addition of storage cost decrease the cost competitiveness.
4. Advancement in the equipments for cleaner, continuous and smoother production.
5. Application of by-products should be clearly classified
6. Most of the processes may involve the application of organic chemical, harmful for the environment and thus green process of development with high yield has become a serious challenge.
7. Currently used engines are not fully compatible for bio-fuel and have shown the adverse effects on stability and durability of existing engines.

As per the International Energy Agency Report, Feb 2010; "In comparison to 2007, the residual biomass production may increase approximately ~28% from agricultural sector and ~50% from forestry sector by the year 2030'. According to this report:

a. 10% of global residues could then produce around 155 billion LGE (billion liters of gasoline equivalent) (5.2 EJ) BTL - diesel or lignocellulosic ethanol or approximately 4.1% of the projected transport fuel demand in 2030. The yield of conversion to organic - SNG could even produce 222 billion LGE (7.4 EJ), or approximately 5.8% of total transport fuel. This means that second-generation biofuel using 10% of global residues would be sufficient in meeting

45-63% of the total projected demand for biofuel (349 bnlge) in WEO 2009 450 scenario.

b. 25% of global residues can be converted either LC -ethanol, BTL - Diesel or Bio - SNG which could contribute 385-554 billion LGE (13.0 to 23.3 EJ) globally (Figure 2). These quantities of second generation biofuel are equal to a share of 10.3 to 14.8% of the total projected transport fuel demand by 2030 and could be able to fully meet the entire demand for biofuel as predicted in the WEO 2009 450 Scenario. Considering that, about two-thirds of the potential of such alternatives is located in developing countries in Asia, Latin America and Africa. Hence including these countries in the development of new technologies will be particularly important.

However, since the agricultural sector differs markedly from that in many developing countries in the OECD, a better understanding of the material flows is an important aspect to ensure the sustainability of biofuel production. More detailed country and residue- specific studies are still required to evaluate the economic feasibility of the acquisition and pre-processing agricultural and forestry residues.

1.4.2. Environmental constraints (*viz. Deforestation, Pollution etc.*)

Although the biofuel are considered environmentally benign; however, the extensive production of biofuel has also highlighted a number of environmental concerns associated with its use. Being a bio-derived product, biofuel have the potential to be “carbon–neutral” over their life cycles. Since, after their combustion the CO_2 returns to the atmosphere is utilized by the feedstock crops for photosynthesis process and hence contribute to mitigate the GHG emission. Based on the fact that the biofuel are "carbon-neutral" source that deliver greenhouse gas savings compared with petroleum fuels is a key component of many countries efforts to set standards worldwide for lowering emissions in the future. India has also set their GHG emission reduction target and development program of substitute energy in the future. This initiative has provided biofuel industry many opportunities of development. Apart from the various advantages of biofuel over petroleum fuel, the extensive development of biofuel industry may directly or indirectly cause other negative effects on environment. To meet the demand of biofuel and in order to grow the required oil crops to produce biofuel, additional land is needed. This has led to extensive deforestation to complete the additional requirement of land. Large scale deforestation has many adverse effects such as soil erosion, loss of ecological system loss of biodiversity etc. [22,23]. Moreover, the ethanol blended fuel has some serious emission related issues. Due to highly oxidizing in nature alcohols may produce various toxic aldehydes (e.g. formaldehyde, acetaldehyde etc.) Biodiesel on burning also emits some aldehydes and other potentially hazardous aromatic compounds which are not regulated in emissions laws [7].

1.4.3. Cost competitiveness of existing biofuel production technologies

Although the biomass derived fuels are advantageous over conventional fuels, particularly environment related advantages like emissions of GHG's etc; but, there are many other challenges to be resolved before they can be considered as environmental and economically viable alternate to the conventional fuels being currently used. Currently, intensive efforts and research are being focused towards improving the economics for sustainable development of biofuel. Since the conventional fuels driven transportation sector has already been considered the most polluting sector responsible for GHG emissions which have major impact on environment by causing global warming. Because of the geographical, societal, environmental and technical constraints, the high production cost of biofuel does not favor them to be used as alternative of conventional fuel in present. Many countries in the world are using the ethanol/bioethanol as an alternative fuel in transportation sector due to excellent compatibility with the existing gasoline, high octane value, and also provide vehicle power and performance. Though the ethanol-gasoline blends results less GHG emissions, but because of the less energy value of ethanol in comparison to gasoline makes it an alternate fuel with low fuel economy [21,71]. Moreover, fermentation route is still being used most frequently for the production of bioethanol which includes the initial pretreatment cost, high charge enzymes to get better yield makes the produced bioethanol much costlier than the conventional gasoline [1,21,69].

Besides, biodiesel has also gained much interest as an alternative of conventional diesel; though due of its good compatibility with conventional diesel, biodiesel is being used directly or as diesel blend in internal combustion engine, still its complete commercialization has yet to be attain. Presently, the vegetable oil is a prime source of biodiesel production globally, about >90% of biodiesel is produced from vegetable oils world-wide. According to the literature the worldwide biodiesel production is expected to reach 150 million tons by 2020 [92]. However, the economics of biofuel production is highly affected by the limitations of feedstock availability and good production technology. Based on the literature reports the biofuel production cost from different feedstock is summarized in table 1.2 [93,94].

Table 1.2: Production cost of Biofuel *(as reported in literature)*

Biofuel Production Cost				
	Biodiesel		Bio-ethanol	
S. No	Raw Material	Production Cost (Rs.)	Raw material	Production Cost (Rs.)
1	Jatropha	22.4	Sugarcane molasses	15.36
2	Karanja	23.52	Sugarcane juice	14.89
3	Soybean	~28	Corn	16.36
4	Rapeseed	55.44	Damaged food grain	6.27
5	Sunflower	34.72	Agro residue	23.64
6	Palm Oil	38.08	Corn Stover	31.03
7	Castor Oil	53.2	Sweet Sorgam	23.54
8	Algae	~146	Cassava	22.78

1.4.4. Limitations of bio-fuel e.g. biodiesel

Although the direct practical application of biofuel is still under trial and requires a significant amount of research for either engine modification or fuel modification. Bioethanol and biodiesel are the only primary bio-fuel at present that can be applied for engines. In ethanol is being partly used as a blending component for gasoline driven engine; however, biodiesel is been tested and recommended as fuel for heavy duty engine as an alternative of conventional diesel.

Table 1.3: Specifications of fuel properties for biodiesel and diesel

Applies to el Standards		**BIODIESEL**				**PETROLEUM DIESEL**
		EUROPE	**GERMANY**	**USA**	**INDIA**	
Specification	**Units**	**EN 14214:2003**	**DIN V 51606**	**ASTM D 6751-07b**	**BIS (P)**	**EN 590:1999**
Density 15°C	g/cm³	0.86-0.90	0.875-0.90	0.85-0.90	0.87-0.90	0.82-0.845
Viscosity 40°C	mm²/s	3.5-5.0	3.5-5.0	1.9-6.0	3.5-5.0	2.0-4.5
Distillation	% @ °C			90%,360°C	< 360	85%,350°C - 95%,360°C
Flashpoint	°C	120 min	110 min	93 min	> 100	55 min
CFPP	°C	* country specific	summer 0 spr/aut -10 winter -20		------	* country specific
Cloud point	°C			* report		
Sulphur	mg/kg	10 max	10 max	15 max	0.035	350 max
CCR 100%	%mass		0.05 max	0.05 max	0.05 max	
Carbon residue (10%dist.residue)	%mass	0.3 max	0.3 max			0.3 max
Sulphated ash	%mass	0.02 max	0.03 max	0.02 max	0.02 max.	
Oxid ash	%mass				------	0.1 max
Water	mg/kg	500 max	300 max	500 max	500 max	200 max
Total contamination	mg/kg	24 max	20 max		20	24 max
Cu corrosion max	3h/50°C	1	1	3	1	1
Oxidation stability	hrs;110°C	6 hours min		3 hours min		N/A (25 g/m3)
Cetane number		51 min	49 min	47 min	> 51	51 min

Acid value	mgKOH /g	0.5 max	0.5 max	0.5 max	< 0.8	N/A
Methanol	%mass	0.20 max	0.3 max	0.2 max or Fp<130°C	< 0.02	N/A
Ester content	%mass	96.5 min			> 96.5	N/A
Monoglyceride	%mass	0.8 max	0.8 max		< 0.8	N/A
Diglyceride	%mass	0.2 max	0.4 max		< 0.2	N/A
Triglyceride	%mass	0.2 max	0.4 max		< 0.2	N/A
Free glycerol	%mass	0.02 max	0.02 max	0.02 max	< 0.02	N/A
Total glycerol	%mass	0.25 max	0.25 max	0.24 max	< 0.25	N/A
Iodine value		120 max	115 max		< 115	N/A
Linolenic acid ME	%mass	12 max				N/A
C(x:4) & greater unsaturated esters	%mass	1 max				N/A
Phosphorus	mg/kg	10 max	10 max	10 max	< 10	N/A
Alkalinity	mg/kg		5 max			N/A
Gp I metals (Na,K)	mg/kg	5 max		5 max	< 10	N/A
GpII metals (Ca,Mg)	mg/kg	5 max		5 max		N/A
PAHs	%mass					11 max
Lubricity / wear	µm at 60°C					460 max

The fuel properties of biodiesel depend on the fatty acid composition of respective feedstock. The fuel characteristics of biodiesel must be comparable to diesel fuel in order to run the engine efficiently. The most important fuel properties includes flash point, viscosity, density, calorific value, moisture content, oxidation stability, acid value, cetane value and cold flow properties [95,96,97]. Depending on the diverse global geographical conditions, different agencies have formulized the specifications for diesel and bio-diesel (Table 1.3), which has to be met by diesel and biodiesel fuels prior to use in engines. Sustaining the above standard parameters is one of the important factors for bio-diesel application. It is believed that most diesel engines may adopt the bio-diesel for limited hours under mild weather conditions.

Table 1.4: Important fuel properties of biodiesel as per ASTM specifications [14,15,38]

Properties	**Non-edible feedstock based biodiesel**							
	Jatropha Curcas	**Pongamiapinnata**	**MadhucaIndica**	**AzadirachtaIndica (neem)**	**Moringa Oleifera**	**Rice barn**	**Rubber seed**	**Polanga seed**
Density @ 15°C, g.cm^3	0.8642	0.8690	0.875	0.8850	0.8591	-	-	0.878
Viscosity @40°C,mm^2/s	4.3	4.65	5.10	5.21	5.07	3.5	3.89	5.5
Oxidation stability (h, at 110°C)	2.8	2.5	-	-	-	1.7	-	-
CFPP (°C)		-7	6	11	18	0	0	11
Pour point (°C)	3	-1	4	14.4	21	-10	3.2	12
Cloud point (°C)	3	-6	-	2	19	-11	-2	13
Flash point (°C)	169	180	159	-	176	169	152	163
Calorific values (kJ/kg)	39698	38960	36914	37810	39560	38853	39700	39513

The restrictions on the use of biodiesel fuels are typically imposed through the variability of a non-standard fuel without a widely acceptable and enforced quality specification. Neat biodiesel was available at the pump in Germany; however, fuel compatibility issues have forced to cut down the percentage of blending at very low level and adoption of the ASTM D-7467 standards has opened the new possibilities of higher blending fuel. Since biodiesel is a mixture of saturated and unsaturated fatty acid esters, due to which biodiesel is highly susceptible for auto-oxidation [95,97]. The auto-oxidation of biodiesel results its degradation and formation of undesired by-products, results a poor fuel quality. Thus the oxidation stability is considered as one of the most important property of biodiesel [14,38,98]. Table 1.4 shows some of the main fuel characteristics of biodiesel produced from various non-edible feedstocks.

In general, the following factors related to fuel compatibility should be considered for any IC engine.

1. **Compatibility:** The effect of blended biodiesel on engine's performance is the most significant in terms of precipitation of fuels in soluble and filter plugging. Prolonged operation with low biodiesel blends also requires careful evaluation.
2. **Concentration:** Leaching of biofuel in engine's crankcase where it can dilute the lubricating oil with time and effect of oil/fuel mixture on engines can have an impact on engine durability and longevity.
3. **Equipment**: What is the effect on fuel injectors, filters and other fuel system components is not well known and can cause a significant deterioration in engine performance.

4. **Emission control:** Biodiesel can negatively affect the emission control system possibly by killing catalysis efficiency and finally increase in engine emissions and decrease durability of components.

Various reports in literatures are available to evaluate the engine performances and its emissions when using biodiesel, however, quantification is still lacking from such reports. In most of the reports available, more emphasis has been given on the effect of biodiesel on engine performance and emission only, whereas very less information is listed about engine durability and life time. Table 1.5 represents the summarized data of engine performance and emission tests fueled by biodiesel derived from non-edible feedstock.

Table 1.5: Engine performance and emission results of IC engine fueled with biodiesel (non-edible oil source) [14,15,38]

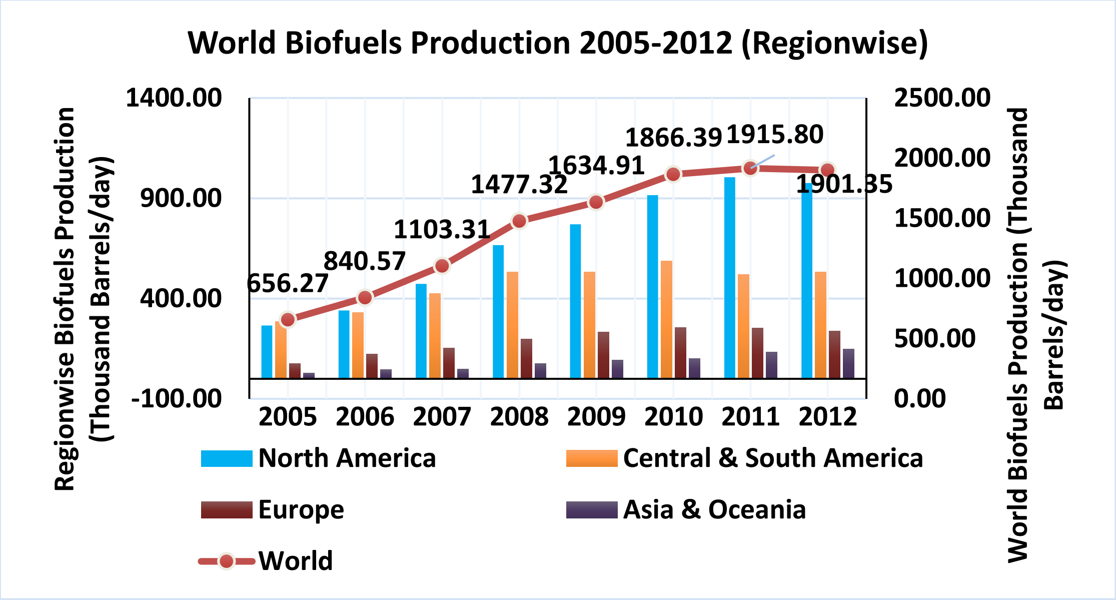
Biodiesel	**Engine Operating conditions**	**Emissions**	**Engine performance**	**Reference**
Jatropha Curcas	Full load, variable speed	All other Exhaust emissions get reduced except NOx than regular diesel	B10 was found the best among all and gave lesser fuel consumption and complete combustion compared to other blends	(Mofijur, Masjuki et al. 2013; Ong, Masjuki et al. 2014)
PongamiaPinnata	Gradually variable load, constant speed	Reduced unburnt HCs, CO, CO_2 with increase in NOx than diesel	Up to 5% lower break thermal efficiency that diesel for all blends was found	(Sureshkumar, Velraj et al. 2008; Chauhan, Kumar et al. 2013)
MadhucaIndica	Gradually variable load, constant speed	Reduced unburnt HCs, CO, CO_2 with increase in NOx than diesel	B20 has shown lesser break thermal efficiency than diesel	(Godiganur, Murthy et al. 2009; Saravanan, Nagarajan et al. 2010)
AzadirachtaIndica	variable load, constant speed	Reduced unburnt HCs, CO, CO_2 with increase in NOx than diesel	Higher break thermal efficiency and break specific fuel consumption was observed than convention diesel	(Dhar, Kevin et al. 2012)
MoringaOleifera	variable load, constant speed	Reduced unburnt HCs, CO, CO_2 with increase in NOx than diesel	For B10 and B20 blends lesser break power and higher fuel consumption	(Mofijur, Masjuki et al. 2014; Rahman, Hassan et al. 2014)

			was observed compared to diesel	
Rice barn	variable load, constant speed	Lower smoke and higher NOx were reported	For B20 blends slight difference in fuel consumption was observed compared to diesel	(Saravanan, Nagarajan et al. 2010)
Polanga seed	variable load, constant speed	CO and smoke were reduced but NOx increases	For B10 blend higher thermal efficiency and lower fuel consumption and lesser exhaust temperature was found in comparison to diesel	(Ong, Masjuki et al. 2014)
Castor oil	variable load, constant speed	At low load NOx were same as diesel but at full load slight increase in NOx was observed	For lower blends less fuel consumption and higher thermal efficiency was found	(Panwar, Shrirame et al. 2010; Kulkarni and Kore 2013)
Cotton oil	variable speed, full throttle condition	Lesser smoke was reported for all blends, NOx was also found less for all blends except B5	No significant change in engine performance of B5, and B20 blends was observed in comparison to diesel	(Aydin and Bayindir 2010)

1.5.Biofuel Scenario in India: Production, Consumption and Targets

1.5.1. Global bio-fuel production scenario

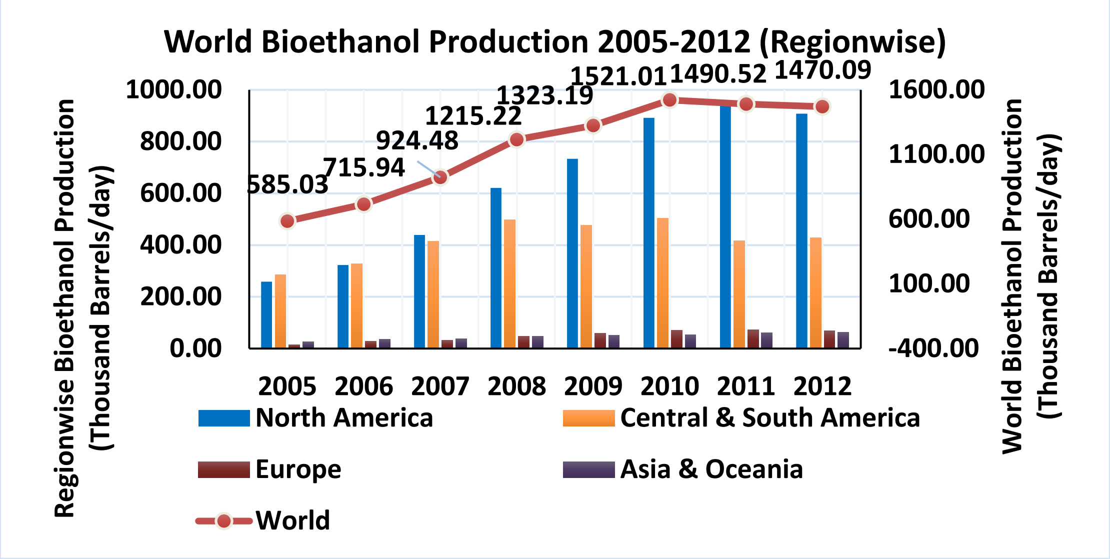
Global production of liquid biofuel in 2012 (Figure 1.9) was calculated about 1.9 million barrels/day which includes 1.47 million barrels/day of fuel ethanol and 0.43 million barrels/day of biodiesel, which was about 3% of total transportation fuel demand of the world (IRENA 2014; International Energy Statistics –EIA 2012) [99]. Currently, ethanol is the primary liquid biofuel produced world-wide, which is about 85% share of total liquid biofuel Figure 1.10. United States and Brazil are the largest fuel ethanol producing countries produced >85% of total world production of ethanol in 2012 (IRENA 2014) [100]. Existing global biodiesel production still is a smaller proportion of total liquid biofuel; however, global biodiesel production in 2013 (Figure 1.11) increased by 47-times in comparison to 2000 (IRENA 2014, IEA 2013b) [99,100].



Source: US EIA; IES; and Short Term Energy Outlook 2014

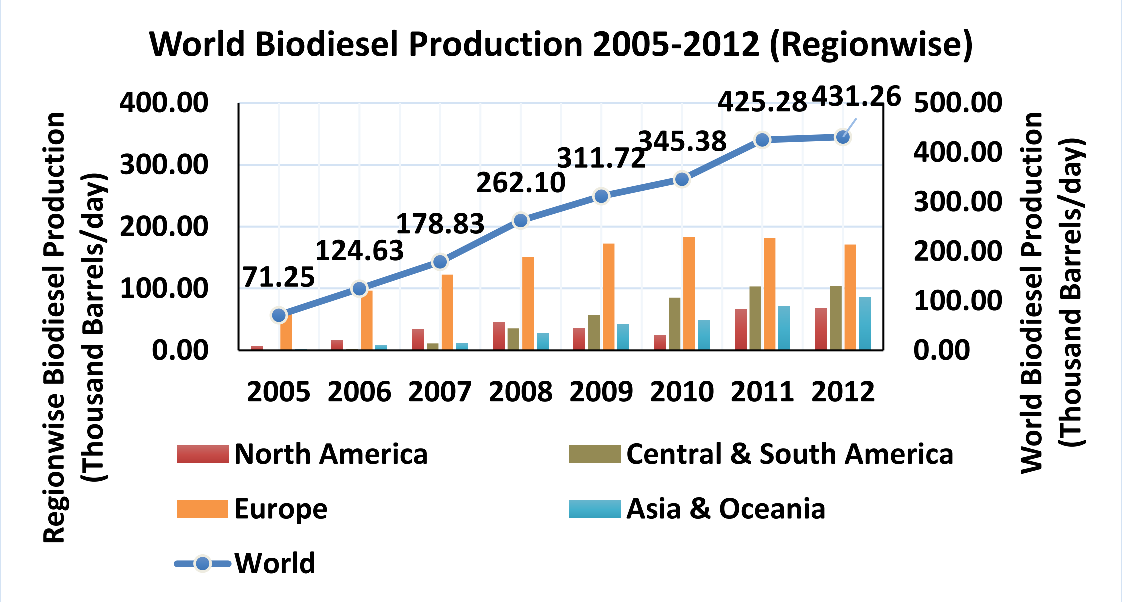
Figure: 1.9 Global biofuel production from 2005-2012 (Region wise)

As per the IEA report 2014, India's domestic crude oil production in 2011-12 was about 40.4 million tonnes with a marginal increase of 5% in comparison to 2010-11. This is only 1% share of world's total crude oil production.



Source: US EIA; IES; and Short Term Energy Outlook 2014

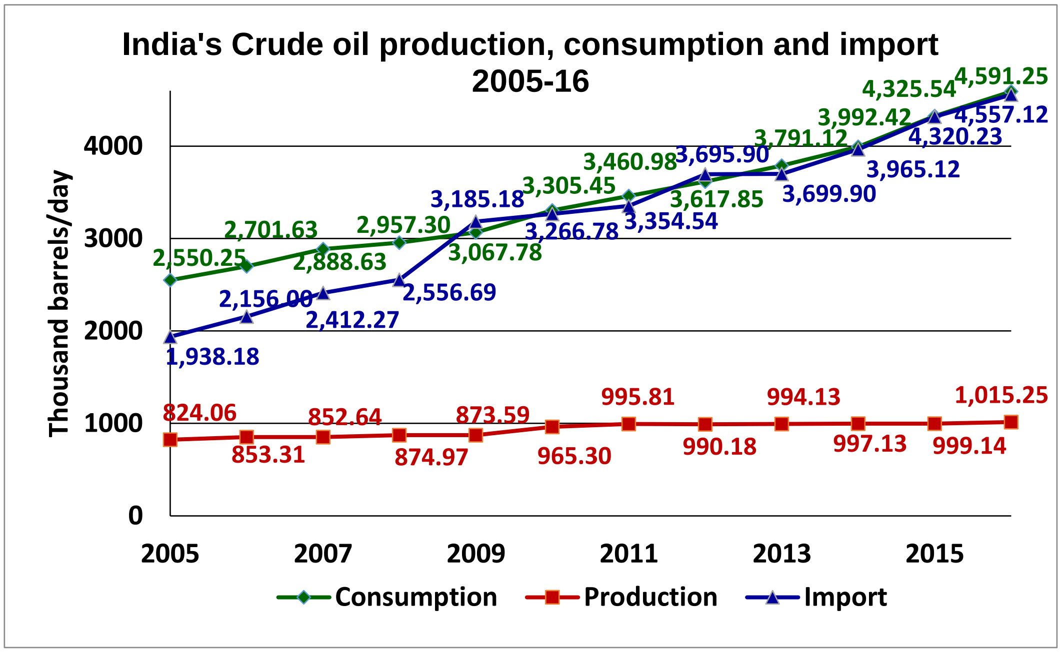
Figure: 1.10 Global bioethanol production from 2005-2012 (Region wise)



Source: US EIA; IES; and Short Term Energy Outlook 2014

Figure: 1.11 Global biodiesel production from 2005-2012 (Region wise)

However, India being the 4th largest consumer of crude oil with total consumption of 162.3 million tonnes of crude oil in 2011-12, which is about 4% share of world's total crude oil consumption.



Source: US EIA; IES; and Short Term Energy Outlook 2016

Figure: 1.12 India's crude oil production, consumption and import 2005-2016

The domestic crude oil production of India meets only 30% of actual demand, rest 70% demand is met with the imported crude oil (Figure 1.12), which has a major impact on country's foreign exchange reserves and policies. According to IEA 2009 report, with such huge gap in demand and supply India's crude oil import may rise to 92% by 2030. Therefore, the high dependency on imported crude oil for powering the transportation sector and other energy related demands are the major reasons for the country to look forward for developing the new and renewable biofuel sectors. India, due to tropical climatic conditions, has vast potential for generation of power from renewable energy sources like hydro, solar, wind and biomass [101]. After wind and solar energy sources, bioenergy has the 3rd largest potential for power generation in India. As per the projection of Govt. of India 12th five year plan, by 2016-17 the total domestic energy production will reached by 669.6 million tonnes of oil equivalent and it is expected to achieve the total domestic energy production of 844 million tonnes of oil equivalent by 2021–22; which could be able to meet 69% demands of expected energy consumption [101]. The domestic ethanol production of India is mainly dependent on the agro based residue like sugarcane molasses, sugarcane bagasse, sugarcane tops, sweet sorghum, rice husk, wheat straw etc.; whereas the biodiesel is mainly produced only by using non-edible oils like Jatropha, PongamiaPinnata, AzadirachtaIndica (Neem), MadhucaIndica (Mahua) etc. [99,102,103,104].

1.5.2. National Biofuel Policy of India

India, being one of the fastest growing economies, happens to be the world's 4th largest energy consumer after United States, China and Japan [105]. To sustain the pace of such economic growth, India needs to develop in-house technologies for alternative energy sources from renewable feedstock to substitute the petro based energy sources. Among the various energy alternatives available, biofuel form renewable feedstock has emerged as the preferred option, particularly for the transportation sector. A number of initiatives for the renewable energy production, improvement in energy efficiency and conservation are being promoted by Government of India during the past one decade [103]. In the year 2003, GOI has launched "National Policy on Biofuel" under the flagship of "National Biofuel Mission (NBM)" for accelerating development of the biofuel sector with a focus on research and development, capacity building, biofuel marketing and purchasing policy to support and promote the biofuel technologies in India. The policy consider the utilization of a wide range of energy crops (such as sugarcane, sweet sorghum, maize, cassava and tree born oil) and seeds (like Jatropha, Pongamia etc.) for biofuel production (Ministry of New and Renewable Energy, 2009; National Policy on Biofuel; http://www.mnre.gov.in) [104]. The policy also envisioned the setting up of a "National Biofuel Development Board (NBDB)" to develop a road map for the use of such biofuel in diesel and petrol engines in a time bound manner with all other policy measures. The targets of "National Biofuel Policy 2009" have not been met due various reasons; therefore on June 2015, the Govt of India has reviewed it and issued the updated biofuel policy. The recommendations are based on the current status of biofuel research and development, and its future prospects. The salient features of the "National Policy on Biofuel" are listed as:[106, 107, GAIN: India Biofuel Annual 2016].

a. Proposed target of 20% blending of biofuel (ethanol and biodiesel) in respective conventional fuels to be achievedby end of 12th Five-Year Plan.
b. Biodiesel must be produced from the non-edible oil seeds and the cultivation of such crops would be encouraged on waste, marginal and nonagricultural land. Government will promote the production of non-edible oilseeds by providing financial incentivization; and by fixing minimum support price for the feedstock.

c. Relaxation in marketing resolution No. 23015/1/20001 dated March 8, 2002 and a new clause give marketing rights for B-100 to the private bio-diesel manufacturers and authorized dealers.
d. The price of bio-diesel will be market determined
e. Ethanol produced from non-food feedstock besides molasses like cellulosic and ligno cellulosic materials and including petro-chemical route, may be allowed to be processed subject to meeting the relevant BIS standard.
f. Sugarcane or sugarcane juice may not be used for production of ethanol and it be only produced only from molasses.
g. Oil Marketing Companies propose to purchase bio ethanol at Minimum Purchase Price (MPP) based on the actual cost of production and import price of bio-ethanol. In the case of biodiesel, The MPP should be linked to the prevailing retail diesel price.
h. If necessary, GOI proposes to consider creating a National Biofuel Fund for providing financial incentives, including subsidies and grants, for new and second generation feed stocks, advanced technologies and conversion processes, and production units based on new and second generation feedstock.
i. Thrust for innovation, (multi-institutional, indigenous and time bound) research and development on biofuel feedstock (utilization of indigenous biomass feedstock included) production including second generation biofuel.
j. Meet the energy needs of India’s vast rural population by stimulating rural development and creating employment opportunities and addressing global

concerns about containment of carbon emissions through use of environment friendly biofuel.

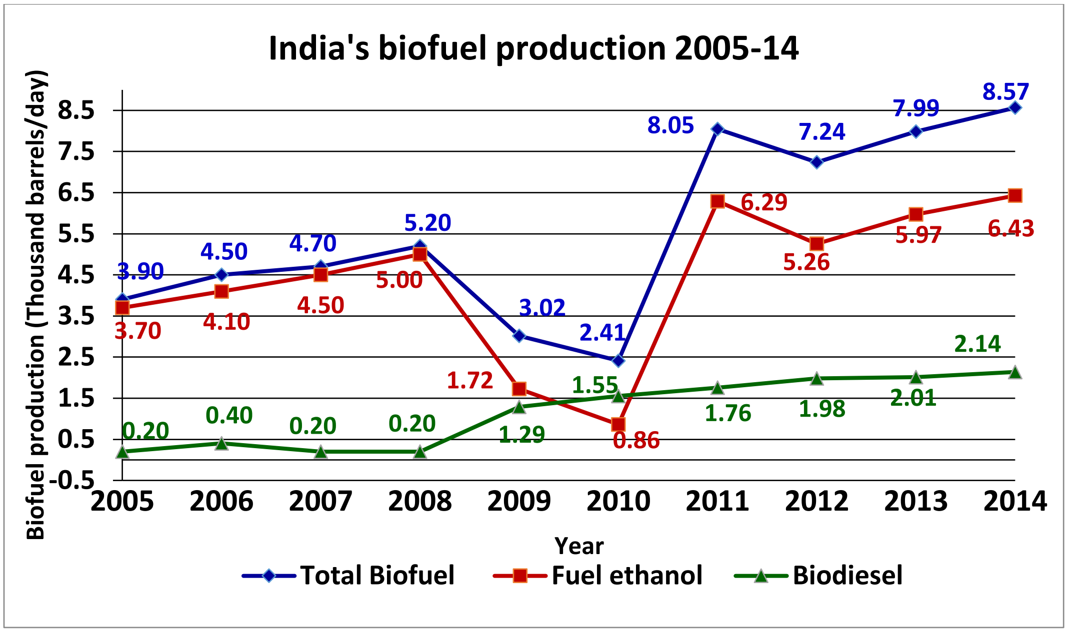
k. Policy will be made to ensure the uninterrupted supply of these biofuel within the country and these biofuel will be put under the domain of "declared good".
l. Biofuel technologies and projects would be allowed 100 percent foreign equity through automatic approval to attract foreign direct investment (FDI), provided the biofuel is for domestic use only, and not for export. Plantations of inedible oil bearing plants would not be open for FDI participation.
m. The objective of biofuel program is to support R&D, Pilot plant/Demonstration projects leading to commercial development of second generation biofuel.
n. Separate committees for a broader policy perspective and policy implementation will be made and named as "National Biofuel Coordination Committee" and "Biofuel screening committee", respectively.

To succeed the "National Biofuel Mission" of India several agencies are currently involved in the promotion, development, and policy making for the biofuel sector such as the Ministry of New and Renewable Energy (MNRE, GOI), overall policy maker and R&D promoter, Ministry of Petroleum and Natural Gas (MPNG, GOI),responsible for marketing of biofuel, and the Ministry of Agriculture (MAg, GOI), promotes the research and development for the production of feedstock crops, as well as the Ministry of Science and Technology (MST, GOI), supports research in biotechnology for biofuel crop production [106].

1.5.3. India’s Biofuel status: biofuel mandates, demand, supply and current usage

1.5.3.1. Bio-ethanol

Globally, India is one of the largest producers of sugarcane. However, because of the cyclical nature of sugarcane and sugar production in India, the fuel ethanol production is highly fluctuating [99,108]. Sugarcane molasses is the major source of fuel ethanol production in India. It is estimated that only 4% molasses can be recovered from 1 tonne of sugar cane; however, as per Indian standards, the recovery percentage of ethanol is only 25% of total molasses [99,101,108]. India’s domestic biofuel (bioethanol and biodiesel) production from 2005 to 2012 is shown in Figure 1.13. Currently, the domestic fuel ethanol production of India is about 1.3 million liters against the installed capacity of 3.2 billion liters [109]. As per the planning commission of India (Government of India) report on the development of biofuel; fuel ethanol has been identified a major fuel and fuel blending source to be developed [109,110,111]. The phase wise bioethanol blending with transportation fuel in India was commenced in 2001 starting with 5% blending of ethanol in Petrol. In first phase three pilot projects were started for required ethanol production to confirm the smooth functioning of the task; besides, research and development activities were also undertaken simultaneously to evaluate the techno-economic feasibility and identify the engine modifications if required.



Source: US EIA; IES; and Short Term Energy Outlook 2014, GAIN India Biofuel Annual 2015.

Figure: 1.13 India's Biofuel production from 2005-2014

Based on the expert studies the 5% blending of ethanol with petrol was recommended at supply locations of oil companies and the 5% blending was initiated in 9 states and 4 union territories (out of 29 states and 6 union territories) in 2003. Based on surplus sugarcane production in 2005-06 and 2006-07, the Government of India made 5% ethanol blending mandatory for 20 states and 4 union territories in November 2006, and in October 2007 it was made mandatory across the country in second phase (except Northeast, Jammu & Kashmir and island territories) [112]. Though, because of the shortage in sugarcane supply in 2007-08 the 5% blending target of ethanol in petrol was not achieved, still in 2008 the third phase 10% blending of ethanol was announced by Government of India [112]. In 2007 the Government of India has permitted to sugar industries to produce the ethanol directly from sugarcane juice instead of the molasses to achieve the minimum required supply of ethanol for mandatory blending targets. However, the fluctuating prices and availability of feedstocks, affecting the production of ethanol, and still remains the major threat to meet the targeted ethanol blending mandates in India. Thus, this is only the reason that the oil companies have been able to achieve only an average of 1.37% ethanol blending by July 2014 [113]. Therefore, alternate technologies are being developed for bioethanol production which uses biomass feedstocks that has nonfood value such as waste lignocellulosic agro residue biomass which includes rice husk, wheat straw, sugarcane topes and bagasse [110,111]. To promote and support the production of ethanol from cellulosic biomass, the Government of India planning commission has also adapted a new policy in 2008 called "Ethanol Blended Petrol Programme (EBPP)" and targeted a mandate of E20 by 2017 (*i.e.* blending of 20% ethanol to gasoline by 2017), and has set a target to produce more than 4 million gallons per year of ethanol by 2017 to meet this milestone [109,114,115].Though, various other alternatives for ethanol production have been developed and demonstrated, the success of mandatory ethanol blending still dependents on the production of sugarcane [109,111,112].

1.5.3.2.Biodiesel

Likewise bioethanol, the Planning Commission of India (GOI, 2003) has also recommended the "National Mission on Biodiesel" for biodiesel production from non-edible oils sources. The biodiesel production in India is primarily focused on using Jatropha, Pongamia, Karanja, Polanga, Neem, Mahua and other non-edible oils. Similar to ethanol, the Planning Commission of India in 2006 has also proposed the phase wise blending of biodiesel in high speed diesel and started with

5% blending of biodiesel with high speed diesel, and set a target to achieve the 20% blending of biodiesel by 2011-12. To meet with the proposed targets of 20% blending in 2011-12, the Government of India targeted the plantation of Jatropha over 11.2 million hectare of land for availability of required feedstock for biodiesel production; however, plantation of Jatropha was done only over 0.5 million hectare of land [116]. As a result the lack of assured supplies of crude vegetable oil is the major concern for the private sector to set up biodiesel plants in India [117]. That is only the reason why the most of the biodiesel production units in India are not operating throughout the year. Presently, the total Jatropha based biodiesel production in India is estimated varying from 100 to 300 million liters per year [105]. Besides, Jatropha various other non-edible oil feedstocks are also utilized for biodiesel production in India like Karanja oil, Mahua oil, Neem oil etc., however the timely availability of feedstocks to biodiesel production unit is still a matter of concern. Thus due to these constraints for biodiesel production in India the phase 1 of National Biofuel Mission More has not given the expected results.

Recently the research and development on algal based biodiesel production has been received a great attention in India and has exposed newer sight for biodiesel production that can be a more sustainable feedstock for biodiesel [117,118,119,120]. Algae, an important ecological plant species, is considered food and nutrition source for many animals and other members of food chain that can produce oxygen on earth [119]. Besides, Algae have a great biomass potential for biodiesel production and biodiesel can be easily derived from algae in comparison to oil derived from vegetable and tree borne oil seeds [118,120]. However, the biodiesel development from microalgae in India is still in demonstration stage. The major constraint in biodiesel production from microalgae is to find out an algal strain with a significant lipid content and excellent growth rate. Though, India is facing a lot of barriers in domestic biodiesel production, still the efforts are being made to maximum utilization of available biodiesel. Indian oil corporation (IOC) Ltd., has taken various initiatives to develop the technologies for the production of biodiesel from non-edible feedstock and their application in transportation sector [105]. A 60kg/day biodiesel production plant has been established by IOC at Faridabad (India), where 10% and 20% biodiesel blending has been used in diesel vehicles of Haryana state government (India) to study the emissions and engine impacts. In continuation, IOC in association with Indian Railways also running almost 10 trains across India by using biodiesel in locomotives with 5% blend of biodiesel [105]. Besides, Karanja oil based biodiesel pilot plant has been installed by Mahindra & Mahindra at Mumbai in association with Tata Motors Ltd., and Lubrizol India Pvt Ltd., to investigate the feasibility and impact of 10% biodiesel blending in diesel engines [105]. Gujarat in association with Central Salt and Marine Chemicals Research Institute-CSIR (CSMCRI-CSIR) has also been started using 5% biodiesel blending in commercial buses. CSMCRI-CSIR in association with Daimler Chrysler has successfully completed a 5000 km trial run with Mercedes cars using neat biodiesel as fuel. To enhance the India’s biofuel production and its commercial utilization, the Govt. of India is financially supporting the advance research and development programs across the country. The detail of some ongoing biofuel research projects funded by Govt of India and implemented by various esteemed research institutes/laboratories across the country is summarized table 1.6.

Table 1.6: Biofuel projects running currently in India

S. No.	Project Name	Executing Institution	Objective	Funding Agency
1	Enhanced butanol production from lignocellulosic biomass using improved pre-treatment and integrated saccharification, fermentation and separation in a membrane bioreactor	National Environmental Engineering Research Institute (NEERI)**, Nagpur**	Development of improved process for Bio-butanol production from lignocellulosic biomass	MNRE
2	Biodesel fuel production from microalgae	Jawaharlal Nehru Technological University Anantapuram (AP)	Identification of suitable strains of algae that can perform uniformly during all seasons	DST
3	Studies of chemo-enzymatic treatment of black liquor for recovery of reducing sugars for bio-ethanol production	Forest Research Institute, Dehradun	To establish more economical process of bio-ethanol production	DBT
4	Stabilization and up gradation of biomass derived bio-oils over tailored multifunctional catalysts in a dual stage catalytic process to produce liquid hydrocarbon fuels and its application studies	The Energy and Resources Institute (TERI), New Delhi	To establish technical feasibility of stabilizing bio oil to increase the storability and enhance the properties to be blended with petro fuel and upgrading bio oils to transport fuels	MNRE
5	Sorghum Stover based Biorefinery for Fuels and Chemicals	NIIST- Trivandrum, MNNIT-Allahabad, TERI-New Delhi, IICT-Hyderabad	To scale-up integrated technology for converting Sorghum Stover to Biofuels and value added chemicals	MNRE
6	Cost effective mass production of robust thermo tolerant, halophilic	Vinayak Ganesh Vaze College, Mumbai	Cost effective biofuel production	DBT

	microalgae strains and utilization of biomass for biofuel production			
7	Hydropyrolysis of lignocellulosic biomass to value added hydrocarbons	Indian Institute of Petroleum, Dehradun	To convert lignocellulosic biomass into value added hydrocarbons/fuels that can be used in the transportation sector and chemicals	MNRE
8	Biocrude Production: Hydro-cracking of non-edible vegetable oil	SardarSwaran Singh National Institute of Renewable Energy, Kapurthala, Punjab	Development of Process for the production of bio-crude by hydrocracking of the vegetable oils	MNRE
9	Process development for bioethanol production from agricultural residues Phase-I: Development of process for co-fermentation of hexose and pentose sugars of agricultural residues	SardarSwaran Singh National Institute of Renewable Energy, Kapurthala-144 601	Development of Process for co-fermentation of hexose and pentose sugars of agricultural residues by selected isolates of co-fermenting mesophilic and thermophilic strains for ethanol production	MNRE
10	Development of pretreatment strategies and bioprocess for improved production of cellulolytic enzymes and ethanol from crop byproduct for demonstration at pilot plant	Department of Microbiology, University of Delhi South Campus, New Delhi	Development of hyper cellulose producer and a fermentation process for production of bio-alcohol from lignocellulosic biomass	MNRE

1.6.Problems and challenges

Diesel is the major fuel source for transport and heavy-duty engines due to high combustion efficiency, reliability and cost effectiveness. However, in respect of environmental concerns, emission of pollutants is the major problem associated with the diesel fuel. It is well accepted that in diesel engines, clean combustion can be fulfilled only by engine development coupled with diesel fuel formulation [121-

122].Due to increase in demand, depletion of petroleum reserves as well as increasing environmental concerns, there is an urgent need for the search of renewable energy, hydroelectricity, or nuclear energy resources as alternative has been raised in recent years [123-124]. One of the environmental friendly renewable energy sources is biodiesel [125]. Biodiesel is a mixture of methyl esters of long chain fatty acids derived from vegetable oil and animal fats, and is similar to the commercial diesel in terms of fuel quality and combustion properties [126-127]. The biodiesel production from edible oil resources in India is very less, as the indigenous edible oil production is much less than its actual demand. Therefore non-edible oils(e.g. *Jatropha*, *Pongamia (Karanja)*,*Mahua*, and *Sal*) seems the only possible sourceof biodiesel in India [102].Biodiesel is non-flammable, nonexplosive, biodegradable,non toxic and free from sulphur and aromatics fuel source.Biodieselalso provides less harmful emissions compared to petroleum diesel fuel, [41,128]which makes biodiesel a good alternative to substitute the petroleum diesel [129].However; the long term storage of biodiesel is being a problem.The presence of unsaturated fatty acids ester in biodiesel makes it more susceptible to oxidation or autoxidation during long term storage [130-131] It is well reported in literature that oxidation stability does not correlate with the total number of double bond, but with the total number and position of allylic and bis-allylic carbon that are adjacent to double bond [132].These oxidation processes are less pronounced in the parent oil due to the presence of natural antioxidants which get partially lost during refining [133]. Reports have been found stating that, after oxidation of biodiesel and its diesel blends, the acid value, density and viscosity increased, while iodine value decreased with increasing storage time [134]. Thus biodiesel instabilities results formation of sediment and gum along with the fuel darkening, which causes filter plugging, injector fouling, depositions in the engine combustion chamber and malfunctions in various components of the fuel system [135-136].The use of antioxidant additives not only slow down the oxidation processes but also improve the fuel stability up to a certain extent [137]. Several reports have been found on the stabilities of diesel biodiesel blends [137-145].However, very limited reports are available on the impact of antioxidant additives on oxidation behavior of biodiesel/diesel blends, especially when biodiesel is derived from non-edible oil source [102,146-164].The aim of this study is to provide the experimental results on the effects of antioxidant additives on *Jatropha and Karanja* biodiesel and its blends with diesel fuel sold in Northern India. Andeffectiveness of binary combination of the commercial antioxidants which could provide the best synergistic effect, stabilization factor and oxidation stability when added to the biodiesel. The goal was to find out the optimum additive which could significantly improve the storage stability of both, the neat biodiesel and its diesel blends. These results will help to support the development of biodiesel specification and technology.

Objective -

- To prepare the biodiesel from various non-edible sources by using conventional basic catalyst and metal mediated waste eggshell derives heterogeneous catalyst.
- To prepare various blends of synthesized biodiesel and commercial diesel.
- To study the effect of various antioxidants on the oxidation stability and other related fuel characteristics of jatropha biodiesel-diesel blends.
- To study the effect of various antioxidants on the oxidation stability and other related fuel characteristics of karanja biodiesel-diesel blends.
- To study the impact of antioxidant combinations, *i.e.*, binary and / or ternary antioxidant mixtures on oxidation stability and other related fuel characteristics of jatropha and karanja biodiesel.

1.7.Literature Review

It is documented that the oxidation of stored biofuels and diesel blends is directly associated with increase in acid value, density and viscosity. However, the iodine value decreases with increasing storage time 102]. The instability of biodiesel means the formation of sediment and gum formation which causes filter plugging, injector fouling, depositions in the engine combustion chamber and breakdowns in several components of the fuel system [135-136]. The use of antioxidant additives improve the fuel stability as well as slow down the oxidation process [137]. Several reports on the stabilities of diesel biodiesel blends are available in literature [138-145]. It is found that natural antioxidants give primary oxidation stability to biodiesel but most of the biodiesels produced do not meet the oxidation stability specifications (6hrs) [146]. Several reports have established that synthetic antioxidants such as 2-tert butyl hydroquinone (TBHQ), 2-tert butyl-4-methoxy phenol (BHA), 2,6-di-tert butyl-4-methyl phenol (BHT), 1,2,3 tri-hydroxy benzene (PY), and 3,4,5-tri hydroxy benzoic acid (PG) as highly effective antioxidants [130,138,149,151,159]. However, very few reports are available on the impression of antioxidant additives on oxidation behaviour of biodiesel-diesel blends, particularly when biofuels developed from non-edible oils [146-164].

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Chapter 2: Materials and Methods

2.1. Introduction

This chapter deals with adopted methodology for biodiesel synthesis and selection of commercial diesel fuels and antioxidants. In addition, analytical methods used to detect fuel properties of diesel, biodiesel and its blends with and without antioxidants were discussed here in details.

2.2.Biodiesel

Biodiesel is prepared from Jatropha and Karanja oil from transesterification method using homogenous (KOH) and heterogeneous (waste eggshell) catalyst. The details of preparation method and characterization of produced biodiesel are discussed in chapter 3. The general properties of prepared biodiesel are mentioned in Table. 2.1.

2.3.Diesel fuel

Three commercial diesel fuel samples (D1, D2 and D3) were selected as base fuel. These diesel samples were purchased from the retail outlets of different oil companies in Northern India. The diesel sold by these outlets, received from respective refineries and was not known to contain cold flow or lubricity additives. The difference in their properties (Table. 2.1) may be because of the difference in origin of crude oil, its processing and quality control.

Table 2.1: General Properties of base diesel and biodiesel

S. No	Property (unit)	D1	D2	D3	***Jatropha Curcas* biodiesel**	**Std. Limits**		**Test Method**
						Diesel	**Jatropha Biodiesel**	
1	Flash point (°C)	68.0	79.0	84.0	161.5	55 min	100 Min	ASTM D 93
2	Moisture content (mg/kg)	0.004%	0.010%	0.011%	0.041%	Max. 0.02%	Max. 0.05%	ASTM-D 2709
3	Cloud Point (°C)	+3	0	0	+12			ASTM–D 2500
4	Pour point (°C)	0	-3	-3	+3			ASTM–D 97
5	Total Sulphur (ppm)	310 (±2)	336 (±2)	340 (±2)		350 max		ASTM D 1266 & IP 336
6	Calorific value (kJ/kg)	43358	41929	42848	39071			
7	Density (g/cm^3) at 15°C	0.8309	0.8288	0.8373	0.8811	0.820-0.845	0.880-0.890	ASTM-D 4052
8	Kinemetic viscosity (mm^2/s) at 40°C	3.07	2.88	2.82	4.71	2.00-4.50	1.90-6.00	ASTM-D 445
9	Oxidation stability (IP, at 140 °C, h)	-	-	-	4.21	-	3 (min)	ASTM-D 7545 & prEN16091

2.4.Antioxidants

The use of antioxidant additives improve the fuel stability up to a certain extent and slow down the oxidation process. Butylated hydroxy anisole (BHA) 98%, Butylated hydroxy toluene (BHT) 99%, Pyrogallol (PY), Propyl-gallate (PrG) 98%, tert-Butylhydroxyquinone (TBHQ) 97% and Diphenylamine (DPA) 99% were used as antioxidant additives. All additives were analytical grade and procured from

Sigma Aldrich, India and used as received. 300 ppm, 400 ppm and 500 ppm antioxidants was found to dissolve in the biodiesel and its blends. The chemical structrures of antioxidants are shown in figure 2.1.

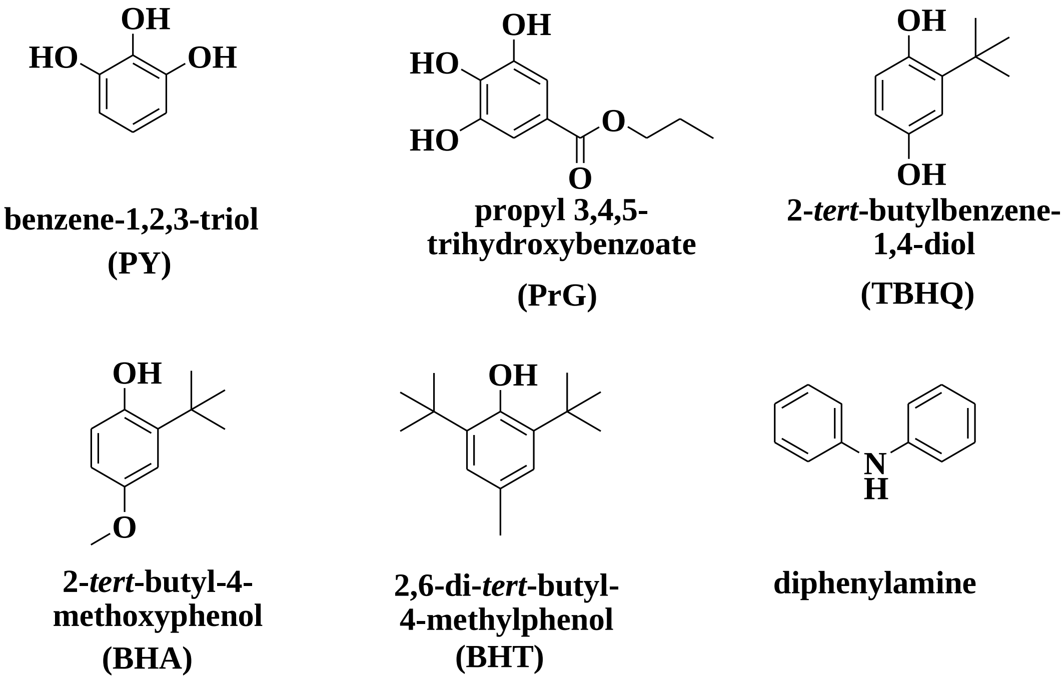

Figure 2.1: Chemical structures of antioxidants

2.5.Characterization method of prepared heterogeneous catalyst

The X-ray diffraction patterns of CaO (cesp) and metal impregnated CaO (sesp) based catalysts prepared were recorded on X-pert PRO multi-purpose X-ray diffractometer, PAN analytical with monochromated Cu, Kα radiation (λ-1.54Ά). The scanning range of 2θ was set between 2^o and 70^o. N$_2$ adsorption-desorption ion using a Belsorp instrument of samples evacuated at 350^{o}C for 3 h before exposure to nitrogen gas at 77 K. The Brunauer-Emmett-Teller (BET) equation was used to determine specific BET surface area and pore-volume. The pore size was calculated from desorption isotherms by using Barrett-Joyner-Halenda (BJH) method. The FTIR spectra were recorded in KBr (0.3% w/w) disks in the wavelength region of 4000 – 400 cm^{-1} with a Perkin Elmer 1760 X FTIR spectrometer. The surface morphology of the prepared catalysts was analyzed by SEM using scanning electron microscope Quanta 200 F (30 kv) instrument. Basic strength of the CaO (cesp) and other metal impregnated CaO (cesp) catalysts was determined by using Hammett indicators. To optimize the calcination temperature range TG analysis of the waste egg shell powder was done by using NETZSCH TG 209F1 Libra TGA209F1D-0105-L Thermal analysis machine under a flow of nitrogen. The sample weight used was about 20 mg, and the temperature ranged from 35^{o}C to 950^{o}C with a ramping rate of 10.0 (^{o}C/min).

2.6.Analysis and characterization method of biodiesel and diesel blends

Analysis and characterization of biodiesel and its various blends were evaluated as per standard method.

2.6.1. Acid value determination

The acid value means the weight of potassium hydroxide (KOH) in mg required to neutralize the acid present in 1gm of oil. During storage stability, the acid value of biodiesel and their blends increases due to oxidation and resulting higher viscosity, density leading to poor atomization and incomplete combustion. Therefore, the acid value of fuel should be analyzed during storage stability. The acid values of fuel blends were determined using Potentiometer titrator AT 28 (Spectralab make).

2.6.2. Density determination

Density is one of the important properties of biodiesel and its blend. High density of fuel means half finished combustion and increase the particulate matter emissions. Increase the density means increase the viscosity. The average density valuesof jatropha biodiesel arelies in between 0.820 – 0.850 g/cm^3 and karanja biodiesel density are lies inbetween0.880 – 0.890 g/cm^3.The Density of biodiesel and diesel blends was analyzed at 15°C by Anton Paar density meter DMA-35 Version 3, according to ASTM-D 4052 method.The density (p) of a sample is defined as its mass divided by its volume:

$$P = m/v$$

Density is a temperature-dependent measuring unit.

Figure 2.3: Anton Par – Density meter

2.6.3. Viscosity determination

Viscosity means internal friction or resistance of fuel to flow. As the temperature of the fuel is increased, the viscosity decreases and it flows more freely. Viscosity is one of the key property of biodiesel meanwhile increase viscosity disturbs the fluidity of fuel.

Kinematic viscosity of the biodiesel and its diesel blends were analyzed at 40°C temperature and 50% Torque by Brookfield viscometer (DV2T series), according to ASTM-D 445 method.

The Brookfield DV2T viscometer measures fluid viscosity at given shear rates. Viscosity is a measure of a fluids resistance to flow.

Figure 2.4: Brookfield Viscometer

The principle of operation of the DV2T is to drive a spindle (which is immersed in the test fluid) through a calibrating spring. The viscous drag of the fluid against the spindle is measured by the spring deflection. Spring deflection is measured with a rotary transducer. The measurement range of a DV2T (in centipoise or milliPascal seconds) is determined by the rotational speed of the spindle, the size and shape of the spindle, the container the spindle is rotating in, and the full scale torque of the calibrated spring.

2.6.4. Oxidation stability determination

Oxidation stability is one of the key fuel properties. The long term storage of biodiesel is being a problem.The presence of unsaturated fatty acids ester in biodiesel makes it more susceptible to oxidation or autoxidation during long term storage [1-2] It is well reported that oxidation stability does not correlate with the total number of double bond, but with the total number and position of allylic and bis-allylic carbon that are adjacent to double bond [3].These oxidation processes are less pronounced in the parent oil due to the presence of natural antioxidants which get partially lost during refining [4]. The biodiesel instabilities results formation of sediment and gum along with the fuel darkening, which causes filter plugging, injector fouling, depositions in the engine combustion chamber and malfunctions in various components of the fuel system [5-6].The use of antioxidant additives not only slow down the oxidation processes but also improve the fuel stability up to a certain extent [7].There are two methods for finding the oxidation stability of fuels:

2.6.4.1.Rancimat method (EN14112)

The oxidative stability of the biodiesel samples was evaluated using Rancimat equipment (Metrohm, model 743). Essentially, the oxidation process happens inside a reaction vessel heated at 110 °C (with 3 g of biodiesel sample) under air flow of 10 L h^{-1}. The volatiles oxidation products formed during the oxidation experiment are collected in a vessel containing 50 mL of distilled water, and the water conductivity is monitored continuously. A sudden change in electric conductivity of this water is noticed in the induction period point, indicating the propagation launch of an oxidation process. After that, a rapid increase in oxidation rate, peroxide value and oxygen absorption are observed.

2.6.4.2.PetroOXY method (ASTM D7545 and prEN 16091)

The oxidation stability (induction period *i.e.* IP) of neat *Jatropha* biodiesel and its diesel blends were investigated by Petrotest "PetroOXY(e)-VERSION: 10.08.2011" instrument made in Germany. The IP of biodiesel and its diesel blends was estimated according to the ASTM-D 7545-09 and prEN 16091 "Oxidation stability of fuel". IP was calculated for 5 ml fuel sample in hermetically sealed test chamber. The chamber was automatically pressurized with oxygen up to 700 kPa (~7 bar/101.5 psi) and heated to a temperature of 140 °C. This initiates a very fast oxidation process. As the fuel oxidizes, it consumes the oxygen in the sealed test chamber resulting in a 10% pressure drop that is displayed. The length of the induction period is a measure of how long the antioxidant will protect the biodiesel and its diesel blends from oxidation. The obtained IP values were converted to their corresponding Rancimat time by multiplying the Petrotest time with a correction factor 20 (as recommended by the test method and was automatically displayed). All determinations were performed in duplicate and the mean value is reported.

Figure 2.2: Petrotest – PetroOXY meter

2.6.5. Flash point determination

The flash point is signals of the flammability of the fuel. It can be defined as the lowermost temperature at which a combustible liquid fuel produced flammable vapors which ignites on providing of flammable source. If higher the flash point, it will be easy to transport fuels from one place to another. The flash point of biodiesel is higher than diesel. The flash point is also affected during storage stability which is due to oxidations of biodiesel fuels. The flash point of fuel were determined by Pensky-Martens Closed Cup apparatus (Hamco make) using ASTM D 93 method.

2.6.6. Moisture content determination

Water content in diesel and biodiesel is found in free, emulsionated, and soluble form. The presence of moisture/ water in fuels leads to accelerate microorganism's growth and cause corrosion in storage tanks, enhancing sediment deposition. In case of biodiesel and their blends with diesel, the moisture content results into hydrolysis leading the formation of free fatty acids. Therefore, it is very essential to analysis the moisture content during long-term stability of biodiesel fuels. Here the moisture content of the fuels and their blends was examined by TITRASYS 352 (Systronics make) using ASTM D 2709 method.

2.6.7. Calorific value determination

Calorific value is the measurement of energy produced by combustion of per unit gram of fuel at normal temperature and pressure. The fuel with higher calorific value is considered as better fuel. Generally, the calorific value of diesel is higher than biodiesel due to difference in composition of these fuels. As diesel is fuel is a mixture of hydrocarbons while biodiesel is the mixture of esters. the presence of oxygen in biodiesel fuels lead its lower calorific value. Calorific value of the fuels and their blends was analysed by a digital bomb calorimeter (Rajdhani make) using standard ASTM methods.

2.6.8. Cloud and Pour point determination

The cloud point and pour point displays the cold flow properties of the fuel. The cloud point is the minimum temperature at which crystals of wax appears first in the fuel while the pour point is the temperature at which there is no flow of fuel. Different biodiesel have different cold properties, which are generally due to their chemical composition (i.e presence of saturated and unsaturated fatty acid esters). The Cloud and pour point of diesel and biodiesel fuels and their blends were examined by a digital cloud and pour point apparatus (Hamco make) using ASTM D 2500 and ASTM D 97 methods.

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Chapter 3: Experimental

3.1.Introduction

This chapter describes about the synthesis methods of biodiesel from jatropha and karanja oil. Biodiesel was prepared using homogenous catalyst (potassium hydroxide) by transesterification. In addition, a heterogeneous catalyst based on metal mediated waste egg shell based CaOwas also used for the synthesis of biodiesel. The composition of prepared biodiesel was analyzed by using Gas chromatograph.In addition,the chapter also discuss about the biodiesel – dieselblending techniques, antioxidant combinations and storage conditions.

3.2. Acid value

Initially acid values of the jatropha and karanja oils were examined. The acid value of jatrropha oil is 2% conferring to the titrimetric method. In this method take 5 ml crude oil in a conical flask, add 2-3 drops of phenolphthalein indicator, and titrate against standard 0.5 N NaOH solution. The acid value of karanja oil is 12% so required to reduce the acid value of karanja oil by degumming.

3.3. Degumming of Jatropha and Karanja oil

The crude vegetable oils contain some of the impurities such as uncrushed seed cake and other impurities particulates. Therefore, it was essential to refine the crude vegetable oils before the conversion process. The crude Jatrophacurcas oil not required degumming process because its acid value is up to mark. In karanja oil required degumming process because its acid value is more than 2%. The karanja crude oil was refined in the laboratory through simple filtration methods. In this process, 0.5% (v/v) of phosphoric acid (H_3PO_4 20% concentration) was added to 300 ml karanjaoil at a temperature of 60^{o}C for 30 min. After that, the mixture was separated in a separation funnel by density separation in which the gum compounds drop down at the bottom. Gums and impurities were separated from the oil. Now the oils were filtered using Whattmanfilter paper No.42.The oil were stored in the air tight bottle at ambient temperature (25^{o}C) to avoid oxidation.

3.4.Preparation method of Jatropha curcas Biodiesel

Initially, Experiments were conducted in a laboratory set up which consists of heating mantle, reaction flask (made of glass) and mechanical stirrer. The working capacity of reaction flask is 500mL. It consists of three necks: one for stirrer, and the others for condenser & inlet of reactant as well as for placing the thermocouple to observe the reaction temperature. The flask has a stopcock at the bottom for collection of the final product. Process parameters such as reaction temperature, reaction duration, stirring speed, amount of catalyst and volume of methanol were optimized in 300 ml per batch capacity biodiesel reactor.

3.4.1. **Transesterification:** The product of first step having FFA less than 2% was used as the raw material for the final stage. The reaction was carried out with 300 ml karanja oil (obtained after degumming) using methanol (40%, v/v) and 2 % base catalyst of KOH (w/v) at 65°C and 400 rpm for 3 hr.However, in case of jatropha oil, the reaction conditions were different *i.e.* temperature 60°C, mixing speed-300rpm, catalyst-2% (w/v), methanol

(40%, v/v) and time-3hr. After the completion of reaction, the products were allowed to separate in two layers by gravimetric method. The lower layers contained impurities and glycerol. The top ester layer has ester with some impurities. To get purify biodiesel; the upper layer was separated and washed 4-5 times using warm water. After washing, the final product was keptwith silica crystals forovernightto remove any moisture in biodiesel. Now the biodiesel was again filtered through Whatmann filter paper no. 42 and stored in air tightborosilicate bottle for further experiment. The main physical properties of prepared jatrophabiodiesel are listed in (Table 2.1. Chapter 2).

3.5.GC-MS analysis of Jatropha biodiesel

The GC–MS analysis of FAME (biodiesel sample) was carried out on a QP2010 gas chromatography mass spectrometer (GC-2010 coupled with GC–MS QP-2010) equipped with an auto sampler (AOC-5000) from Shimadzu (Japan) using a RTX-5 fused silica capillary column, 30 m x 0.25 mm x 0.25 µm (Rastek).

Helium (99.9% purity) was used as the carrier gas with a column flow rate of 1 ml/min and a pre-column pressure of 49.7 kPa. The column temperature regime was 40 °C for 3 min, followed by a 5°C/min ramp up to 230°C, followed by 40 min at 230 °C. The injection volume and temperature were 0.2 µl and 240 °C and the split ratio was 1/30. The mass spectrometer was operated in electron compact mode with electron energy of 70 eV. Both the ion source temperature and the interface temperature were set at 200 °C. FAME peaks were identified by comparison of their retention times with authentic standards by GC–MS post run analysis and quantified by area normalization. Analysis revealed that the prepared *Jatropha curcas* biodiesel contains methyl esters of *Palmiticacid* (16:0) [17.52%], *Palmitoleicacid* (16:1) [0.74%], *Stearicacid* (18:0) [8.62%], *Oleicacid* (18:1) [41.78%] and *Linoleicacid*(18:2) [31.12%]. Linolenic methyl ester (18:3) was not observed at all by GC-MS analysis. The GC-MS results obtained were also supported by the existing literature where the composition of biodiesel from *Jatropha curcas*has been reported.[1-2] The prepared biodiesel was used to constitute the diesel-biodiesel blends with B10, B15, B20, B25 and B40 (volume/volume) with diesel fuel to study their physico-chemical properties (oxidation stability, viscosity and density) during long term storage.

Table 3.1: GC data for fatty acid composition of biodiesels

Jatropha biodiesel	**GC area %**	**Karanja biodiesel**	**GC area %**
Octanoic acid, methyl ester (C 8:0)	0.21	Hexadecanoic acid, methyl ester (C 16:0)	2.21
9-Hexadecenoic acid, methyl ester (C 16:1)	0.74	Octadecanoic acid, methyl ester (C 18:0)	4.81
Hexadecanoic acid, methyl ester (C 16:0)	17.52	9-Octadecenoic acid, methyl ester (C 18:1)	56.09
9,12-Octadecadienoic acid (Z,Z)-, methyl ester (C 18:2)	31.13	Octadecenoic acid, methyl ester (C 18:1)	3.81
9-Octadecenoic acid (Z)-, methyl ester (C 18:1)	41.78	9,12-Octadecadienoic acid, methyl ester (C 18:2)	25.21
Octadecanoic acid, methyl ester (C 18:0)	8.62	9-Octadecenoic acid (Z)-methyl ester (C 18:1)	1.34
		11-Eicosenoic acid, methyl ester (C 20:1)	1.25
		Eicosenoic acid, methyl ester (C 20:0)	0.89
		Docosanoic acid, methyl ester (C 22:0)	2.83
		Tetracosanoic acid, methyl ester (C 24:0)	1.44

3.6.Preparation method of Karanja Biodiesel (KOME)

The Karanja biodiesel is prepared from the base catalyzed transesterification of *Karanja* oil. The main physical properties of biodiesel are listed in (Table 2.1. chapter 2). The GC–MS analysis of FAME (biodiesel sample) was carried out on a QP-2010 gas chromatography mass spectrometer (GC-2010 coupled with GC–MS QP-2010) equipped with an auto sampler (AOC-5000) from Shimadzu (Japan) using a RTX-5 fused silica capillary column, 30 m x 0.25 mm x 0.25 µm (Rastek). Helium (99.9% purity) was usedas the carrier gas with a column flow rate of 1 ml/min and a pre-column pressure of 49.7 kPa. The column temperature regime was 40 °C for 3 min, followed by a 5°C/min ramp up to 230°C, followed by 40 min at 230 °C. The injection volume and temperature were 0.2 µl and 240 °C and the split ratio was 1/30.The mass spectrometer was operated in electron compact mode with electron energy of 70 eV. Both the ion source temperature and the interface temperature were set at 200 °C. FAME peaks were identified by comparison of their retention times with authentic standards by GC–MS post run analysis and quantified by area normalization. Analysis revealed that the prepared *KOME* contains methyl esters of *Palmiticacid* (16:0) [2.2%], *Stearicacid* (18:0) [4.8%], *Oleicacid* (18:1) [61.2%], *Linoleicacid*(18:2) [25.5%] Eicosanoic (20:0) [2.1%], Docosanoic (22:0) [2.8%], Tetracosanoic (24:0) [1.4%]. The GC-MS results obtained were also supported by the existing literature [1-3].The prepared biodiesel was used to constitute the diesel-biodiesel blends with B5, B10, B15, B20, B25 and B40 (volume/volume) with diesel fuel to study their physico-chemical properties (oxidation stability, viscosity and density) during long term storage.

3.7.Preparation of jatropha and karanja biodiesel by using waste egg shell

The transesterification of non-edible, high free fatty acid containing Jatropha and Karanja oils was also studied by using waste chicken egg shell derived calcium(*i.e.*CaO(cesp)) based mixed metal oxides (M-CaO; M= ZnO, MnO_2, Fe_2O_3 and Al_2O_3)as heterogeneous catalyst.

3.7.1. Preparation of catalyst

The collected chicken shell (UPES, Dining Hall)were rinsed thoroughly with tap water until the organic matter was removed. The washed egg shells were again rinsed twice with distilled water and were dried in hot air oven at 100 – 120^{o}C for 24 hr. the dried egg shell were powdered in an agate mortar and the powder form was calcined at three different temperatures 500, 700 to 900^{o}C in muffle furnace for 4 hr (heating rate 2^{o} minute $^{-1}$) and then stored in desiccator. Material thus obtained was the CaO (cesp) and used for transesterification and preparation of metal impregnated CaO (cesp) based catalysts. The incorporation of metals was carried out by impregnation of the metal oxide on CaO support by using wet incipient method with aqueous solutions of their metal nitrates 5 gm of CaO (cesp) was suspended in 30 ml of deionized water. To this 5 ml of aqueous solution of 3 wt% of metal nitrate was added. The reaction mixture thus obtained was stirred for 4 hr at room temperature. The reaction mixture was filtered and the solid material was dried in air, then in oven at 120^{o}C for 4 hr and finally calcined in a muffle furnace for 4 hr (heating rate 2^{o} minute $^{-1}$). The catalysts thus prepared were characterized by powder XRD, BET surface area measurement, SEM and FTIR techniques.

3.8. Transesterification of jatropha and karanja oils with heterogeneous catalyst

Transesterification of jatropha and karanja oils with methanol were carried out in a transesterification reactor with 250 ml three-neck round bottom flask fitted with an overhead stirrer and water-cooled reflux condenser. The reactor was also equipped with an oil bath with digital temperature controller for heating purpose. Optimized amount of catalyst was suspended in required volume of methanol and heated under a control temperature of 65^{o}C for 5 min, and then the desired amount of oil was added to the reaction mixture. The reaction mixture was stirred at 500 rpm for required time duration (1 h for jatropha and 1.5 h for karanja). After the completion of the reaction the catalyst was separated by filtration and the excess methanol was recovered by evaporation at reduced pressure. The mixture was then washed three to four times with Lukewarm distilled water to remove the glycerol formed. The mass thus obtained was dried with anhydrous sodium sulphate. The transesterification of oil was carried out under different reaction conditions in order to optimize the best condition, such as catalysts loading from 1 to 10 wt%, reaction time from 0.5 to 2 hr, reaction temperature from 50^{o}C to 70^{o}C and methanol to oil ratio from 5:1 to 18:1. The reaction condition for maximum conversion of oil into biodiesel was optimized by analyzing the reaction mixture by GC-MS.

3.9.Blending techniques

To make a blend of ethanol to gasoline, the E10-E20 compositions are mainly focused blends to minimize the side effect of emission, of the fuel. The mixing technique of the ethanol to the gasoline is key factor to get a homogenous and proper blend fuel. Presently the following two techniques, sequential and splash blending, are generally used at large scale based mixing of the ethanol to gasoline at production site, delivering site and fuel stations etc. Sequential blending is performed at the wholesale terminal, involves addition of a measured quantity of ethanol to a tank truck first and then addition of a known amount of gasoline. Splash blending involves pouring gasoline and ethanol, together in the tank truck which being loaded or enroute.Both the above blending technique are density based mixing methodology to prepare blended fuel. At lab scale level as well for research purpose, the above blending techniques are not feasible, as they required bulk amount of the ethanol as well as gasoline. To attain the desired mixing composition, ratio blending is the mostly used technique at lab scale method. This involves mixing of the ethanol to fuel in volume-by-volume ratio. In the present study, biodiesel was mixed with diesel (in volume/volume ratio), followed by vigorous mixing for 15 minutes using ratio blending technique. No phase separation was observed during the experimental work, as both are miscible to each other. To carry out experiments, 07 blends of diesel-biodiesel were prepared on basis of volume/volume ratio and denoted as B5, B10, B15, B20, B25, B30 and B40. The composition of diesel and biodiesel blends were shown in table 3.2.

Table: 3.2. Composition of diesel and biodiesel blends used for storage stability study

Blend (v/v)	Blend ratio (D - Diesel / BD - Biodiesel)
B 05	D = 95 ml; BD = 05 ml
B 10	D = 90 ml; BD = 10 ml
B 15	D = 85 ml; BD = 15 ml
B 20	D = 80 ml; BD = 20 ml
B 25	D = 75 ml; BD = 25 ml
B 30	D = 70 ml; BD = 30 ml
B 40	D = 60 ml; BD = 40 ml

3.10. Antioxidant concentration for binary combination

Since, the addition of synthetic antioxidants generally improves the oxidation stability of biodiesel; however the use of large concentration of additives makes the process uneconomical. The effectiveness of binary antioxidants to improve the oxidation stability of Jatropha and Karanja biodieselswere also studied. Antioxidant synergy was investigated using 500, 600 and 700 ppm of antioxidant combinations namlyPyrogallol:Propylgallate (PY:PrG), Pyrogallol:tert-butyl hydroquinone (PY:TBHQ) and Pyrogallol:Butylatedhydroxyanisole (PY:BHA) in their different proportions.

The different binary combinations those were usedare shown in table 3.3.

Table: 3.3: Combinations of binary antioxidants used for storage stability

Concentration (ppm)	A:B (1:9)	A:B (1:3)	A:B (1:2)	A:B (1:1)
500	A = 50 ppm B = 450 ppm	A = 125 ppm B = 375 ppm	A = 167 ppm B = 333 ppm	A = 250 ppm B = 250 ppm
600	A = 60 ppm B = 540 ppm	A = 150 ppm B = 450 ppm	A = 200 ppm B = 400 ppm	A = 300 ppm B = 300 ppm
700	A = 70 ppm B = 630 ppm	A = 175 ppm B = 525 ppm	A = 233 ppm B = 467 ppm	A = 350 ppm B = 350 ppm

3.11. Storage conditions

Storage condition classified into two types:

3.11.1. Long term storage stability of biodiesel (JOME & KOME)–diesel blend with the use of individual antioxidants

500 ml of biodiesel and its diesel blend with the use of antioxidant (500 ppm) were stored in closed Borosil glass bottles of 1 Lit capacity for 90 days and were kept indoors condition, at a room temperature of 20°C and 30°C. 500 mL space in the bottle was occupied by air. Samples were taken out periodically every 15 days to study the additive effects.

3.11.2. Long term storage stability of biodiesel with use of binary antioxidants

500 ml of biodiesel and its diesel blend with the use of antioxidant concentration 500 ppm, 600 ppm and 700ppm of PrG : PY, TBHQ : PY and PY: BHA (ratio 1 : 1, 1 : 2, 2 : 1, 1 : 3, 3 : 1, 1 : 9, 9 : 1) were stored in closed Borosil glass bottles of

1 Lit capacity for 90 days and were kept indoors condition, at a room temperature of 20°C and 30°C. 500 mL space in the bottle was occupied by air. Samples were taken out periodically every 15 days to study the additive effects.

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Chapter 4. Result and Discussions

4.1.Introduction

This chapter divided into three parts

(A) Characterization of the catalysts

(B) Study the oxidation stability of prepared biodiesel and diesel blends with antioxidants

(C) Study the oxidation stability of jatropha and karanja biodiesel with binery antioxidants

In **part (A)** catalyst characterized by powder XRD, BET surface area measurement, SEM and FTIR techniques. In **part (B)** to analysis the storage stability of jatropha and karanja biodiesel using different antioxidants. Here, a screening process was conducted to determine the suitable antioxidants for oxidation stability of prepared biodiesel and its blends. The selected antioxidants were further utilized for long term storage study. For that, jatropha and karanja biodiesel and their blends with commercial diesel are mixed with selected antioxidants in different concentration and kept for 90 days in a borosilicate bottle under indoor condition. The fuel properties such as oxidation stability, viscosity and density were examined at a particular time intervals. **Part (C)** includes the effect of binary antioxidants on jatropha and karanja biodiesel under long term storage study. Here, two antioxidants were mixed with neat jatropha and karanja biodiesel in different ratio and the samples were kept for the period of 90 days under indoor condition. The physico-chemical properties such as antioxidant synergy, stabilization factor and oxidation stability were examined at the time interval of every 15 days.

4.2.Characterization of the catalysts

4.2.1. XRD analysis

The XRD patterns of CaO(cesp) calcined at 900 °C was investigated and it showed the complete transformation of $CaCO_3$ to CaO(cesp) (Fig. 4.1a). The intense and sharp peaks at 2θ (°): 31.35, 36.58, 52.96, 61.64 and 66.27 were observed, which can be indexed in the in the cubic structure of CaO(cesp) (JCPDS 00-001-1160). The XRD patterns of Zn/CaO(cesp) which was calcined at three different temperatures 500, 700 and 900 °C showed the combined diffraction pattern along with the formation of ZnO in hexagonal phase (JCPDS 00-003-0888) with low intensity peaks at 2θ(°): 31.84, 32.33, 34.51, 37.37, 38.55, 40.82, 41.31, 43.39, 47.62, 48.71, 52.17, 55.81, 56.60 and 62.39. Better hexagonal phase formation was observed for ZnO calcined at 900°C. The XRD pattern with important peaks and their corresponding planes are presented in Fig. 4.2a. Similarly, the XRD patterns of MnO_2/CaO(cesp) (JCPDS 00-005-0600), Fe_2O_3/CaO(cesp) (JCPDS 00-002-0272) and Al_2O_3/CaO(cesp) (JCPDS 00-002-1124) were also recorded for the catalysts calcined at 500, 700 and 900°C; and the important peaks along with their corresponding planes are presented in Fig. 4.2b, 4.2c and 4.2d respectively. Calcination of the Mn/CaO(cesp), Fe/CaO(cesp) and Al/CaO(cesp) at 900°C exhibited better diffraction patterns in comparison to the samples calcined at lower temperatures *i.e.* 500 and 700°C. Peaks observed at 2θ(°): 39.5, 43.5, 47.7 and 48.8 indicate the presence of Mn (Fig. 4.2b); peaks at 2θ(°): 26.0, 35.9, 40.1, 43.1, 47.7, 48.3 and 57.5 show the presence of Fe (Fig. 4.2c); whereas peaks at 2θ(°): 33.0, 35.0, and 43.0 due to presence of Al (Fig. 4.2d). The occurrence of peaks for the catalysts calcined at 900°C reveals their crystalline structures and also indicates that the catalysts should be thermally activated before being used for transesterification reactions[1].

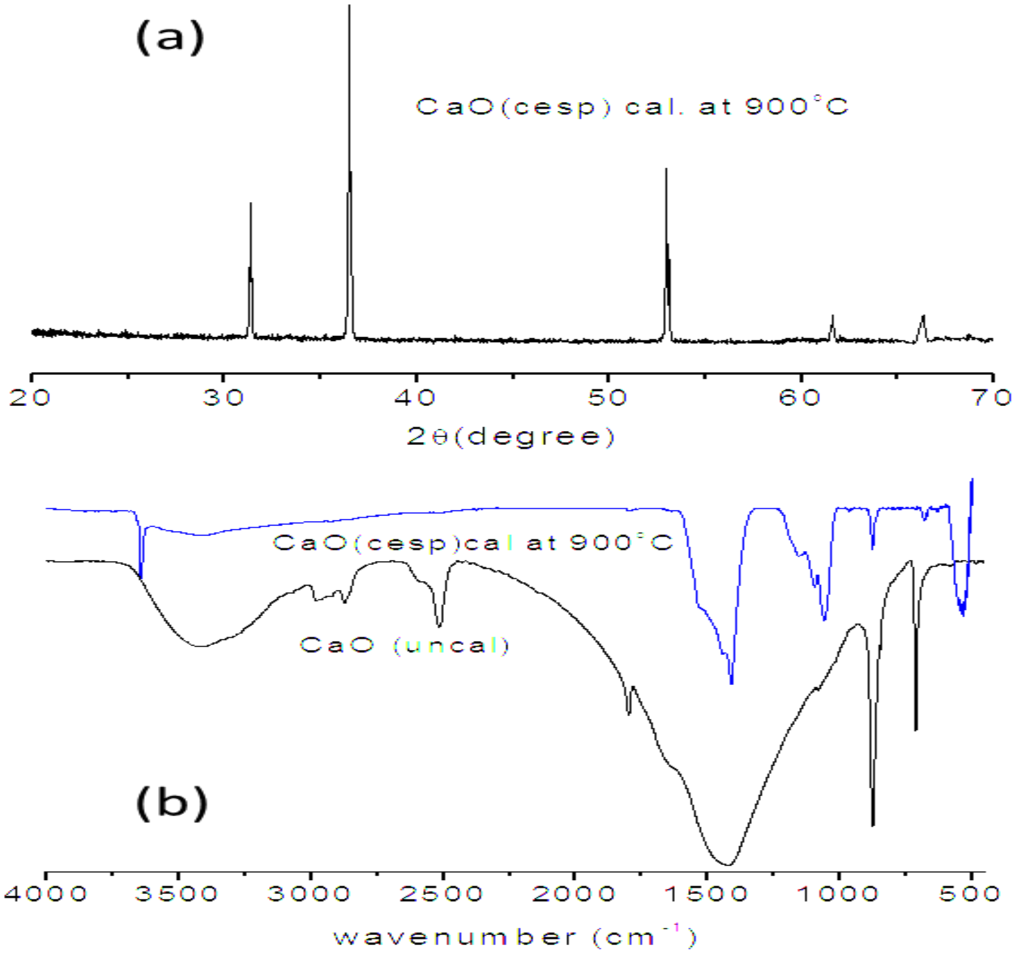

Fig. 4.1 (a)X-ray diffraction spectrogram of CaO(cesp); (b) FTIR spectra of CaO(cesp)

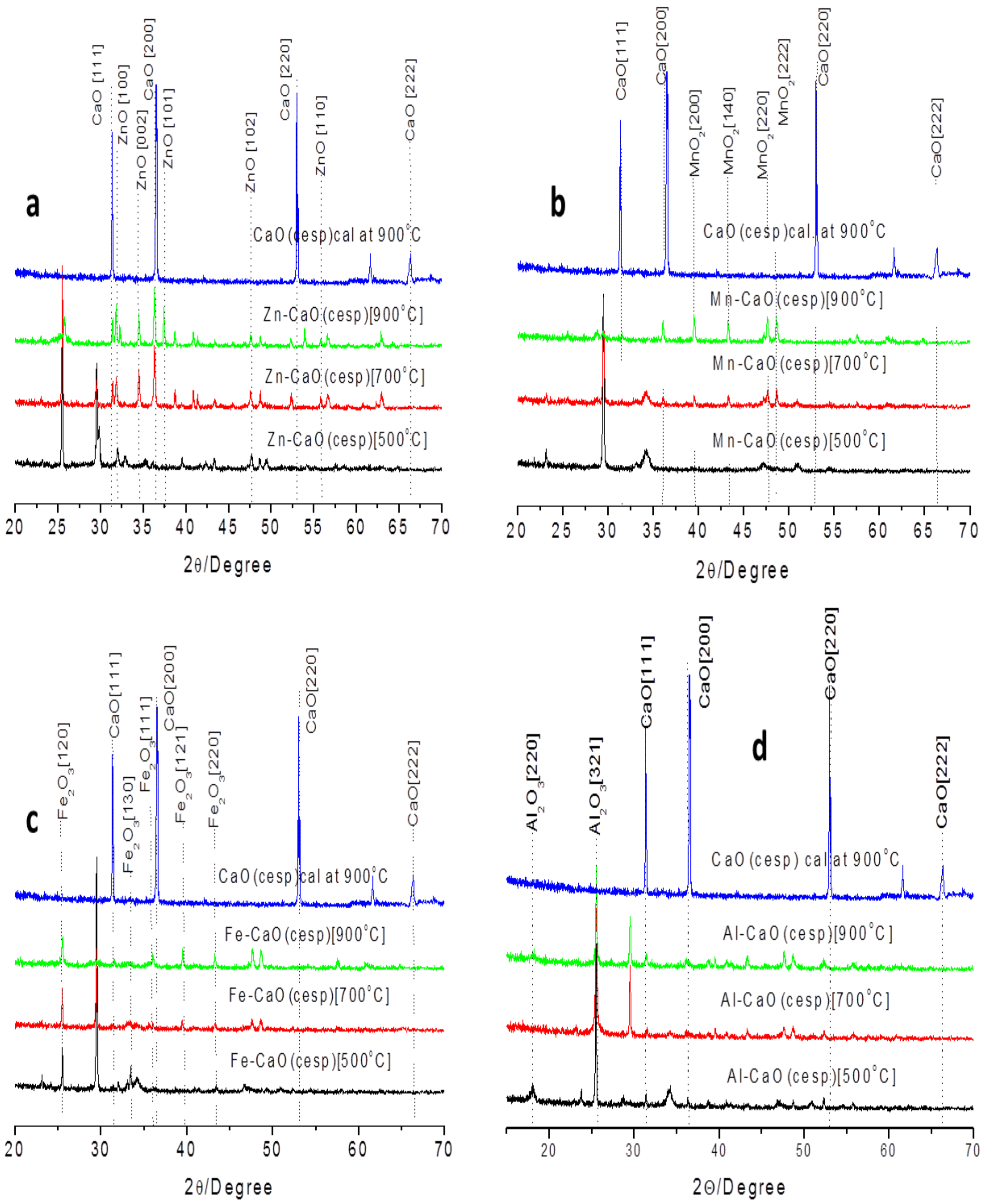

Fig. 4.2X-ray diffraction spectrogram of Zn-CaO(cesp) (a), Mn-CaO(cesp) (b), Fe-CaO(cesp) (c) and Al-CaO(cesp) (d)

4.2.2. FT-IR analysis

The FT-IR spectra for un-calcined and calcined CaO(cesp) are shown in (Fig. 4.1b). Un-calcined CaO(cesp) exhibited the sharp absorption bands for CO_3^{2-} at 1422 (asymmetric stretching), 875 (out of plane bending) and 707 cm^{-1} (for in plane bending) respectively. However, a shift to higher energy of absorption bands for CO_3^{2-} was observed at 1450, 1050, 875 and 525cm^{-1} respectively, due to decrease in reduced mass of the group CO_3^{2-} upon calcination at 900°C. The moderate to weak absorption bands at 2980, 2875 and 2515 cm^{-1} correspond to organic matters, were observed for un-calcined CaO(cesp), which disappeared completely when the catalysts was calcined at 900°C. A broad absorption band around 3432 cm^{-1} was observed due to the stretching vibration mode of associated water molecule. However, absorption band for associated water molecule was disappeared when the catalyst was calcined at 900°C and a sharp absorption band for OH stretching was appeared at 3640 cm^{-1}. The IR absorption band pattern for uncalcined and calcined eggshells agrees with the reported literature[2].The FT-IR was also recorded for all the metal impregnated catalysts calcined at 500, 700 and 900 °C, and are presented in Figs. 4.3a, 4.3b, 4.3c and 4.3d respectively. For Zn impregnated CaO(cesp) catalyst moderate to sharp absorption bands at 678, 612, 597, 528, 510 and 483cm^{-1} correspond to the stretching vibrations for Zn-O bond (Fig. 4.3a). The less intense band at 3642 correspond to OH stretching of CaO(cesp), while the absorption bands at1534, 1408, 1155 and 873 cm^{-1} corresponds to bending vibration modes of CaO(cesp). Similarly, the FT-IR of MnO_2/CaO(cesp), Fe_2O_3/CaO(cesp) and

Al_2O_3/CaO(cesp), calcined at 500, 700 and 900 °C respectively, were also recorded (Figs. 4.3b, 4.3c and 4.3d, respectively). Calcination of the MnO_2/CaO(cesp), Fe_2O_3/CaO(cesp) and Al_2O_3/CaO(cesp) at 900°C exhibited better absorption bands in comparison to the samples calcined at lower temperatures. Besides, the characteristic bands of CaO(cesp), absorption bands at 677, 613, 594 and 519 cm^{-1} for Fe impregnated CaO(cesp); absorption bands at 737, 679, 613, 595 and 526 cm^{-1} for Mn impregnated CaO(cesp); absorption bands at 2137, 674, 647, 613, 595 for Al impregnated CaO(cesp) were observed. These absorption bands correspond to respective metal-oxygen stretching vibration modes.

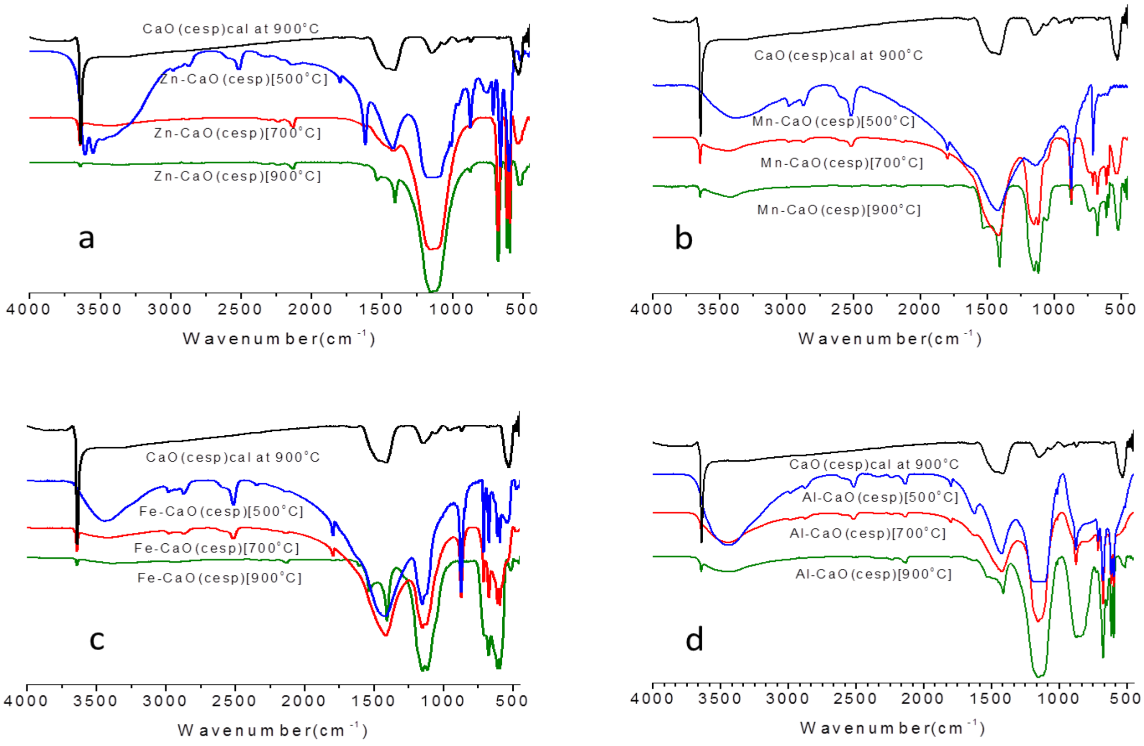

Fig. 4.3 FTIR spectra of Zn-CaO(cesp) (a), Mn-CaO(cesp) (b), Fe-CaO(cesp) (c) and Al-CaO(cesp) (d)

4.2.3. BET surface area determination

The specific surface areas of prepared catalysts were determined by BET surface area measurement. The surface areas of CaO(cesp) and M-CaO(cesp) (M: ZnO, MnO_2, Fe_2O_3 and Al_2O_3) were determined. The results are brief in Table 4.1.

Table 4.1: BET surface areas, pore volume, pore diameter and basicity of catalysts

S. No	**Catalyst**	**Cal. Temp. (°C)**	**Surface area (m^2g^{-1})**	**Pore Volume (cm^3g^{-1})**	**Pore Diameter (Å)**	**Basic strength (H_)**
1	CaO(cesp)	**900**	**1.4**	0.01732	nd	7.2<H_<9.8
		700	1.3	0.01462	nd	Nd
		500	1.1	0.01202	nd	Nd
2	ZnO-CaO(cesp)	**900**	**12.1**	0.16671	116.4	15.0<H_<18.4
		700	11.6	0.14712	nd	15.0<H_<17.2
		500	10.7	0.11671	nd	15.0<H_<17.2
3	MnO_2-CaO (cesp)	**900**	**9.5**	0.10844	232.4	15.0<H_<17.2
		700	8.4	0.07542	nd	12.2<H_<15.0
		500	6.9	0.06104	nd	12.2<H_<15.0
4	Fe_2O_3-CaO (cesp)	**900**	**7.3**	0.08816	268.1	15.0<H_<17.2
		700	6.8	0.05987	nd	15.0<H_<17.2
		500	6.1	0.05313	nd	10.0<H_<12.2
5	Al_2O_3-CaO (cesp)	**900**	**3.1**	0.03314	271.0	10.0<H_<12.2
		700	2.9	0.02342	nd	10.0<H_<12.2
		500	2.4	0.01932	nd	9.8<H_<10.2
6.	ZnO-CaO (cesp) after **4th cycle**	**900**	9.8	0.10057	nd	12.2<H_<15.0

The results from Table 4.1 clearly indicate that the specific surface area of metal impregnated CaO(cesp) catalysts is higher than neat CaO(cesp). It was also observed that the surface areas of the catalysts were increased with the calcination temperature. This may because of the maximum conversion of $CaCO_3$ to CaO at 900 °C. ZnO impregnated CaO(cesp) has the maximum surface area and pore volume. Whereas the surface area and pore volume of other metal impregnated CaO(cesp) catalysts were comparatively less than that of Zn impregnated CaO(cesp). This may because of the higher dispersion ability of Zn metal in comparison to rest of the metals used [3].The differences in surface areas of M-CaO(cesp) and CaO(cesp) indicate that the metal impregnated catalysts should have greater activity than neat CaO(cesp).

4.2.4. **Basicity determination of prepared catalysts**

Basicity of the catalysts was measured conducting Hammett indicator experiments. The experiments were conducted to determine the H range of basic sites in each catalyst. 20 mg of sample was shaken with 5 ml of moisture free ethanolic solution of Hammett indicator and left to attain equilibrium for 2h. Bromothymol blue, pKa =7.2; phenolphthalein, pKa = 9.8; 2,4,6-Trinitrobenzene amine, pKa = 12.2; 2,4-dinitroaniline, pKa= 15.0; 4-chloride-2–nitroaniline, pKa = 17.2 and nitroanilinepKa =18.4 are the Hammett indicators used for this experiments. The basicity of the catalyst was determined by titrating with 0.02 mol/L anhydrous ethanolic solution of benzoic acid using Hammett indicator. The color change of the solution was observed. When the solution exhibits a color change, this indicates that the basic strength of the catalyst is stronger than the indicator used. However, when the solution produces no color change, the basic strength of the catalyst is weaker than that of the indicator used [4-5]. The results obtained for basicity of the catalysts are shown in Table 4.1. The data reveals that the Zn-CaO(csep) catalyst have shown better basic strength in comparison to neat CaO(cesp) and other metal impregnated catalysts. The basicity of transition metal impregnated CaO(cesp) is comparatively greater than that of neat CaO(cesp) may be because of the synergistic relation between multi-metal ions which generally enhances the basicity on active site of the catalyst [4-5]. The synergistic effect of multi-metal ions may also be explained as the basicity of an metal oxide surface is closely related to the electron donating property of oxygen anion which increases with the increase in electropositive character of combined metal ion which will probably form more Lewis base sites (-O-) on CaO(cesp) surface [6].

4.2.5. **SEM Analysis**

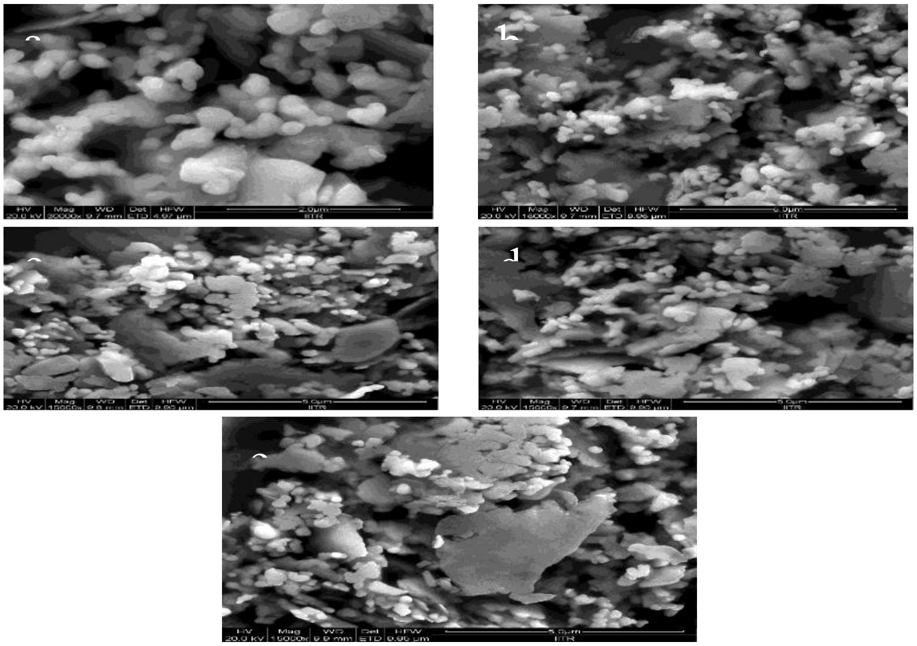

Fig. 4.4SEM images of CaO (a), Zn/CaO (b), Mn/CaO (c), Fe/CaO (d) and Al/CaO (e) calcined at 900°C

The surface morphology of the calcined catalysts was studied by *scanning electron microscopy* (SEM) and the images obtained are shown in Figs. 4.4a, 4.4b, 4.4c, 4.4d and 4.4e, respectively. The calcined eggshell surface contained irregular shapes of particle such as rod, dumbbells etc., thus they constructed a net like porous structure. However, the surfaces of metal impregnated catalysts generally comprise the formation of smaller aggregates of variable morphologies. The irregularities in the morphologies of metal impregnated catalysts may be due to the formation of clusters of M- CaO(cesp) particles during their preparation and calcination. The smaller size of aggregates could provide the higher specific surface areas. The fact can also be supported by the XRD pattern and surface area analysis obtained for those M- CaO(cesp) catalysts.

4.2.6. TGA Analysis

In order to explain the effect of calcination temperature, we have investigated the calcination process of waste eggshell powder with Thermogravimetric analysis (TGA). The results are shown in Fig. 4.5. TGA results showed that the temperature at which the waste eggshell powder decomposed when heated in a controlled environment. Water and other organics were removed up to 500 °C, whereas carbon dioxide CO_2 was lost 600-800 °C. Only one dominant step of weight loss was found over a temperature range of 600-800°C. Above 850 °C, the weight of the sample kept almost constant. Since, the chicken eggshell generally contains $CaCO_3$ as main calcium based component. Thus it is clear from the TG analysis that the high temperature >800°C is required for the transformation of the $CaCO_3$ to CaO(cesp) which could be confirmed by Tg and DTG analysis. Therefore, in perspective of preparation temperature and time, and energy consumption, the temperature of 900°C was selected as a suitable calcination temperature to produce the CaO(cesp) catalyst from the waste chicken egg shell. Similar observations were also reported for the material derived from waste shells 7-8].

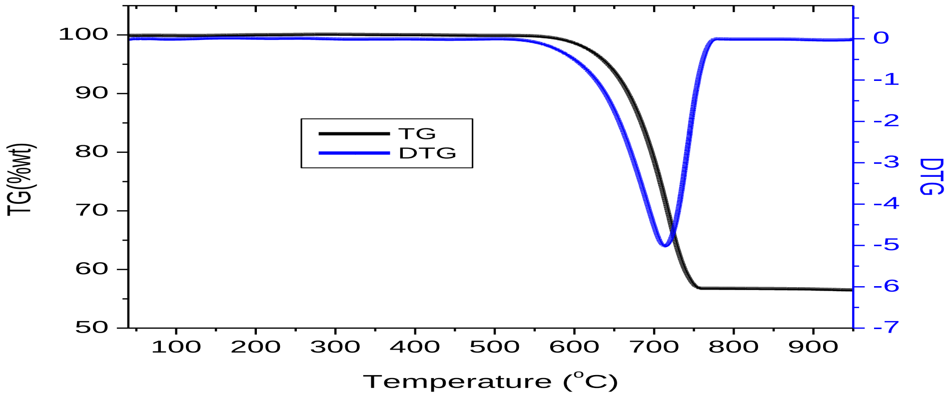

Fig. 4.5TGA analysis of egg shell powder

4.3.Transesterification of Jatropha and Karanja oils with methanol by using prepared catalysts

The activity of prepared catalysts including the CaO(cesp) was established by performing transesterification reactions of Jatropha and Karanja oils according to the procedure described in section 3.7 chapter - 3. The effect of catalysts loading, methanol-to-oil ratio, and reaction time and reaction temperature on transesterification reactions was also studied. The optimization results are shown in Table 4.2 and Fig. 4.6. Table 4.2 represents the optimization of reaction conditions (catalyst loading, methanol-to-oil ratio reaction time and reaction temperature) for transesterification of Jatropha and Karanja oils. The transesterification of Jatropha and Karanja oil was started using 1 wt % of catalysts loading at 50°C using 5:1 methanol-to-oil ratio for 0.5 h; a GC conversions of 28.2% for Jatropha and 25.4% for Karanja biodiesel were obtained (entry 1 Table 4.2).

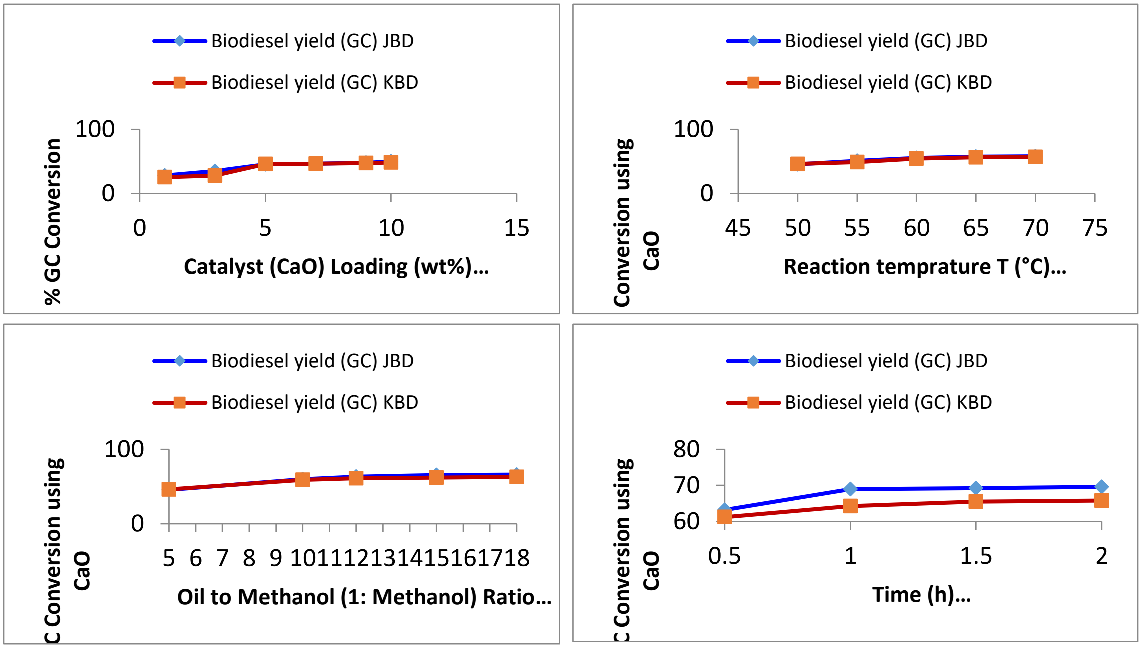

Fig. 4.6. The effect of catalysts loading, methanol-to-oil ratio, reaction time and reaction temperature on transesterification reactions of Jatropha and Karanja Oil: (a) Optimization of catalyst loading at temp 50°C, oil/methanol ratio (1:5) and reaction time 0.5h; (b) Optimization of temperature for catalyst loading of 5 wt%, oil/methanol ratio (1:5) and reaction time 0.5h; (c) Optimization of oil:methanol ratio for catalyst loading of 5 wt%, T=65°C and reaction time 0.5h; (d) Optimization of time for catalyst loading of 5 wt%, T=65°C and oil:methanol ratio (1:12)

It is clear from the Table 4.2 that maximum GC conversions of 69.0% (reaction time, 1h)for Jatropha and 65.5% (reaction time, 1.5h) for Karanja biodiesels were obtained using 5 wt% of CaO(cesp) catalyst at 65°C with 12:1 molar ratio of methanol-to-oil (entries 15 and 16, Table 4.2). Karanja oil has high acid value in comparison to Jatropha oil [3], because of that it may react with base catalysts to form soap or insoluble scum and water during reaction. The formation of such insoluble scum may decrease both the biodiesel yield and the CaO catalytic activity [9].The optimized reaction conditions (5 wt% catalyst, 65°C temperature and 12:1 methanol/oil ratio) used for CaO(cesp) were extended to carry out the transesterification reactions for both Jatropha and Karanja oils using the prepared metal impregnated catalysts. It was found that all the metal impregnated CaO(cesp) shown better activity for transesterification in comparison to neat CaO(cesp). Zn impregnated CaO(cesp) has shown maximum activity among all metal impregnated catalysts for transesterification of both Jatropha and Karanja oils (Fig. 4.7).

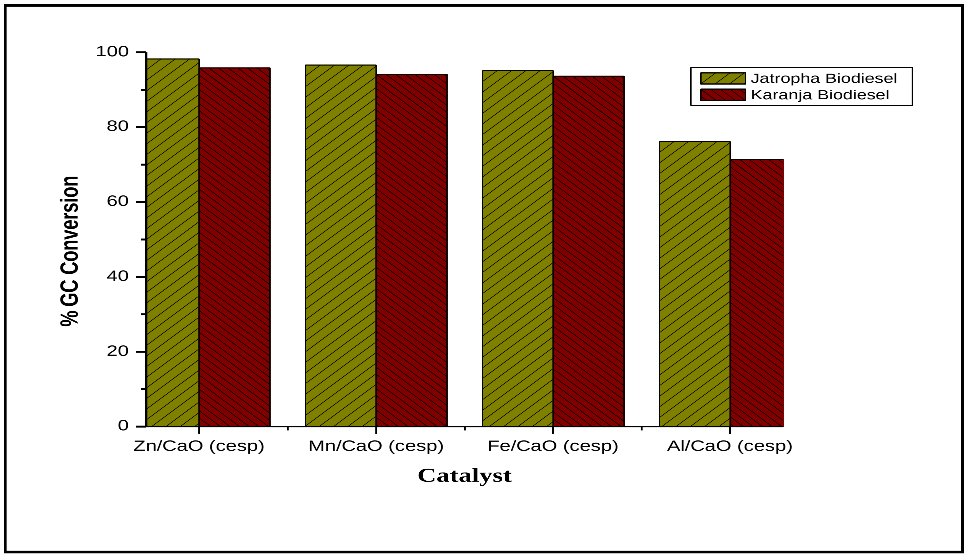

Fig. 4.7. The effectiveness of catalysts (M-CaO) for transesterification of Jatropha and Karanja Oils

This may be because of the greater surface area and more basic strength of the ZnO-CaO mixed oxide in comparison to others. Also it is well accepted that higher basic strength of the solid base catalysts is directly related to their effectiveness towards the transesterification reactions [3].

Table 4.2 The effect of catalysts loading, reaction time, temperature and methanol-to-oil ratio on transesterification reactions

S. no	**Catalysts**	**Catalysts amount (wt %)**	**Reaction temperature (°C)**	**Methanol/oil ratio**	**Reaction time (h)**	**Biodiesel yield (GC)**	
						JBD	**KBD**
1	**CaO(**cesp)	1	50	5:1	0.5	28.2	25.4
2		3	50	5:1	0.5	35.2	28.3
3		**5**	50	5:1	0.5	**45.6**	**46.2**
4		7	50	5:1	0.5	46.7	46.4
5		9	50	5:1	0.5	47.8	47.4
6		10	50	5:1	0.5	49.8	48.3
7	**CaO(**cesp)	5	55	5:1	0.5	48.9	51.2
8		5	60	5:1	0.5	55.6	54.3
9		5	**65**	5:1	0.5	**57.4**	**56.7**
10		5	70	5:1	0.5	58.1	57.1
11	**CaO(**cesp)	5	65	10:1	0.5	60.0	59.1
12		5	65	**12:1**	0.5	**63.2**	**61.2**
13		5	65	15:1	0.5	65.3	62.0
14		5	65	18:1	0.5	66.1	63.1
15	**CaO(**cesp)	5	65	12:1	**1**	**69.0**	**64.3**
16		5	65	12:1	**1.5**	**69.2**	**65.5**
17		5	65	12:1	2	69.6	65.8
18	**ZnO/CaO(**cesp)	**5**	**65**	**12:1**	**1**	**98.2**	
19	**ZnO/CaO(**cesp)	**5**	**65**	**12:1**	**1.5**		**95.8**
20	MnO_2/CaO(cesp)	5	65	12:1	1	95.1	
21	MnO_2/CaO(cesp)	5	65	12:1	1.5		93.6
22	Fe_2O_3/CaO(cesp)	5	65	12:1	1	96.6	
23	Fe_2O_3/CaO(cesp)	5	65	12:1	1.5		94.1
24	Al_2O_3/CaO(cesp)	5	65	12:1	1	76.2	
25	Al_2O_3/CaO(cesp)	5	65	12:1	1.5		71.3

Therefore, based on the results of BET surface area and basicity determination of the prepared catalysts it is clear that why the ZnO-CaO(cesp) has shown maximum activity towards the transesterification reactions of Jatropha and Karanja oils. The maximum conversion of 98.2% for Jatropha and 95.8 % of Karanja biodiesels were obtained with Zn impregnated CaO(cesp) under the optimized reaction conditions (entries 18 and 19, Table 4.2).

4.4.Study the oxidation stability of prepared jatrophabiodiesel and diesel blends with antioxidants

4.4.1. Effect of antioxidants on the oxidation stability of Jatropha biodiesel samples

The effects of additives on the oxidation stability of the neat *Jatropha* biodiesel samples were investigated for 90 days indoor storage conditions. The antioxidants were screened by adding 300 ppm, 400 ppm and 500 ppm, concentration of each antioxidant in 500 mL of neat *Jatropha* biodiesel. The results are shown in Fig. 4.8. A significant difference in the efficiencies of tested antioxidants was observed. It is clear from the Fig. 4.8, that the induction period of biodiesel with additives was improved significantly. Screening study of antioxidant additive was also reveled that the 500 ppm concentration of additive was the optimum concentration at which maximum stability was obtained. Therefore 500 ppm additive concentration was used for further studies of oxidation stability of diesel/biodiesel blends. Pyrogallol (PL) was found most effective antioxidant with maximum IP of 10.4 hrs whereas Diphenylamine (DPA) was found to be least effective during the course of study. On the basis of screening data the effectiveness of antioxidants used was observed in order of PL > PG > TBHQ > BHA > BHT > DPA. Study revealed that the phenolic antioxidants were found more effective. As the active hydroxyl group provides free proton easily to inhibit the formation of free radicals or interrupt the propagation of free radical and thus slow down the rate of oxidation, also the phenolic additives offer more sites for the formation of the complex between the free radical and antioxidant radical for the stabilization of the ester chain [10-12]. It can also be stated that the stability of prepared *Jatropha* biodiesel is lower due to the presence of ~84% of unsaturated fatty acid.

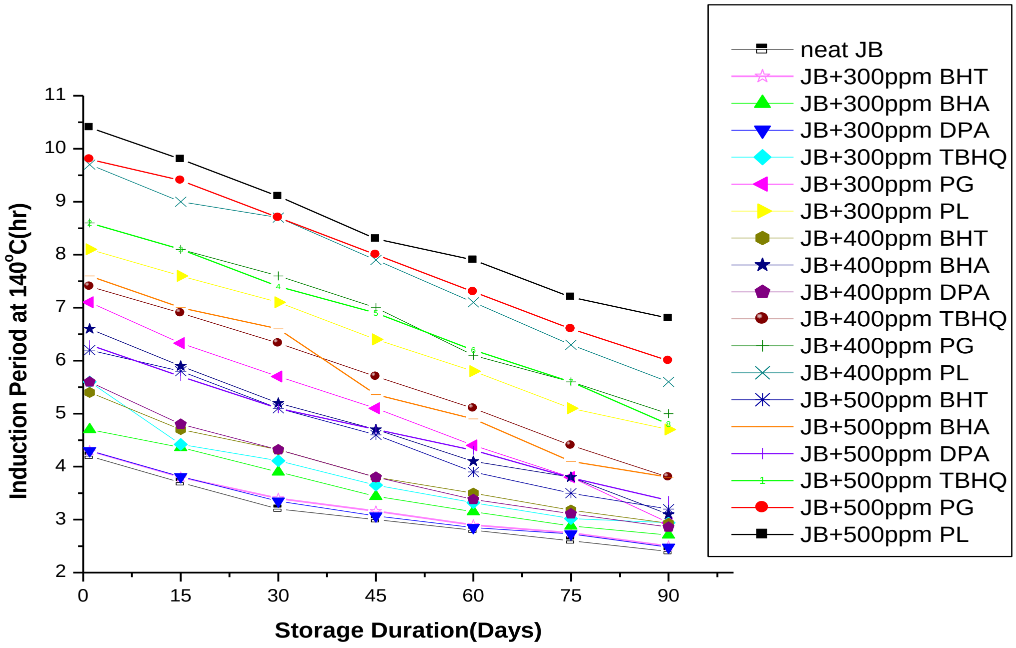

Fig. 4.8. Oxidation stability of *Jatropha* biodiesel with additives

4.4.2. Effects of antioxidants on the oxidation stability of diesel biodiesel blends.

Oxidation stability of neat diesel biodiesel blends (B10, B15, B20 and B25) was investigated under the storage conditions and the results obtained are shown in Fig. 4.9.

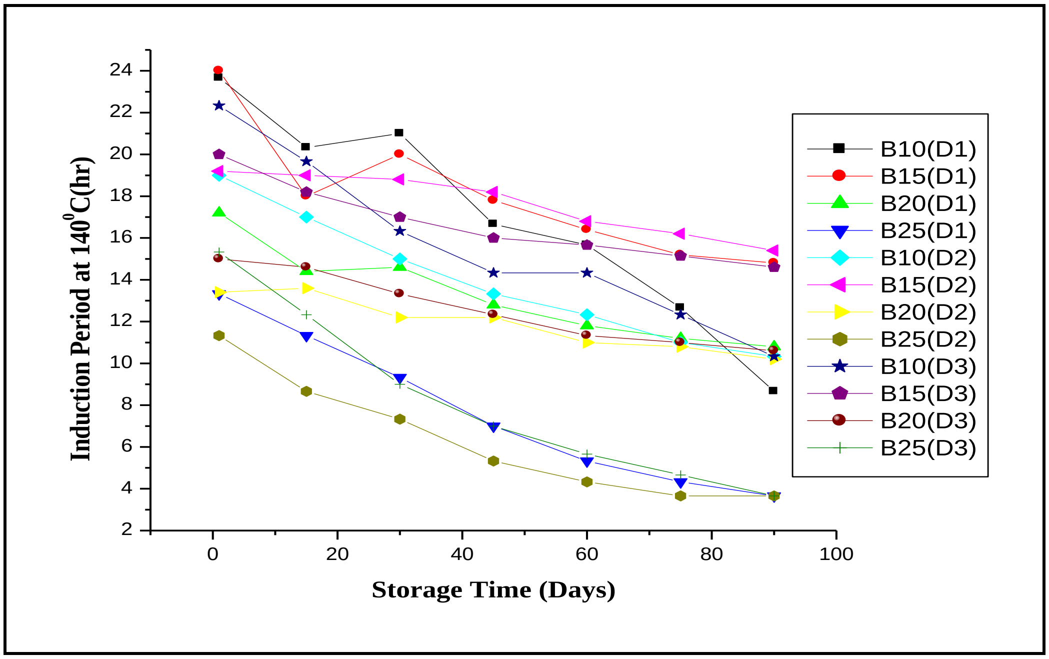

Fig. 4.9. Oxidation stability of Diesel/Biodiesel blends without antioxidants

Results from Fig. 4.9 revealed that only B10 blends with all diesel samples and B15 blends with D1 and D3 were stable for induction period of 20 h or more than this (at day1) rest were failed to meet the minimum induction period. The oxidation stability was further decreases for next 15, 30....90 days storage duration, due to the decomposition of unsaturated fatty acids present in of biodiesel.

Whereas Fig. 4.10, 4.11, 4.12 and 4.13 shows the oxidation stability of B10, B15, B20 and B25 diesel biodiesel blends after the addition of optimized concentration of each antioxidant additives separately in 500ml test solution of these blends.

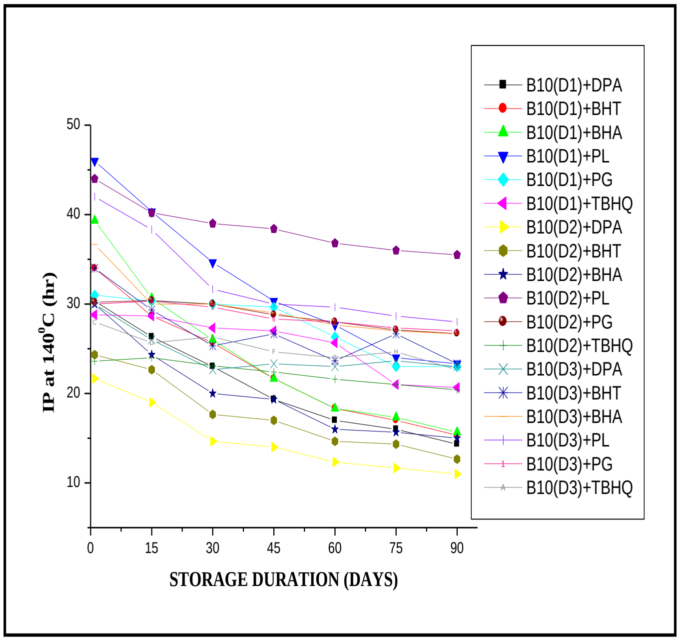

Fig. 4.10

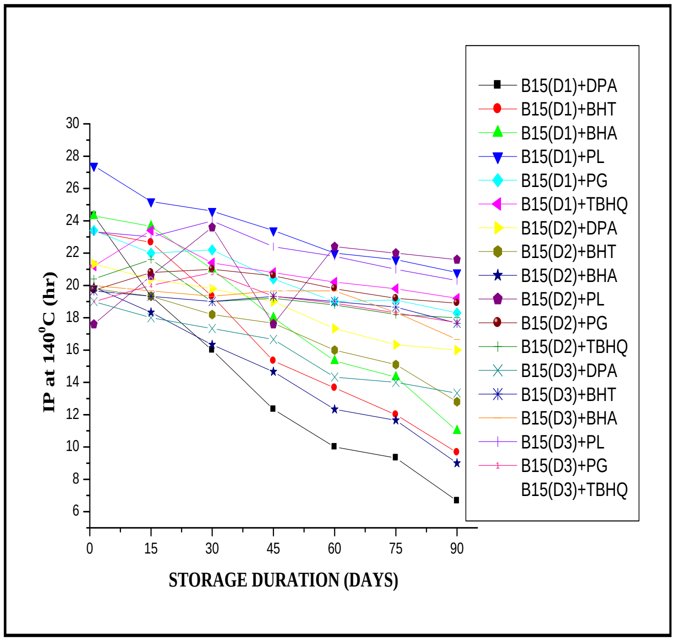

Fig. 4.11

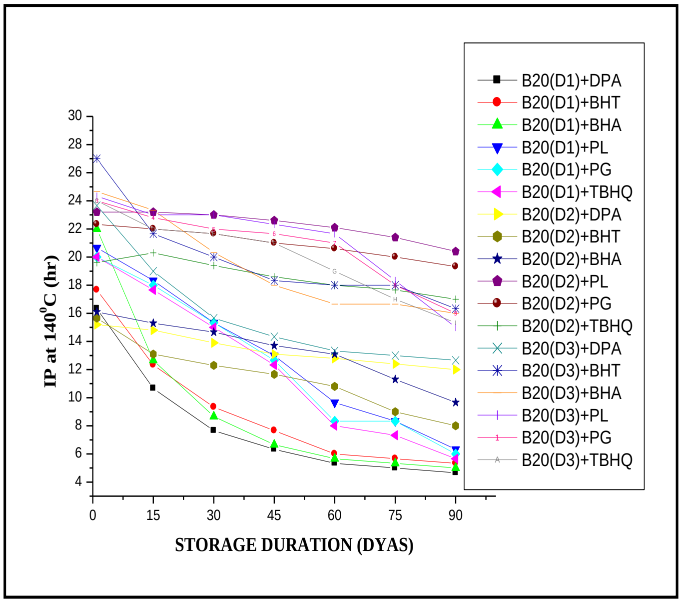

Fig. 4.12

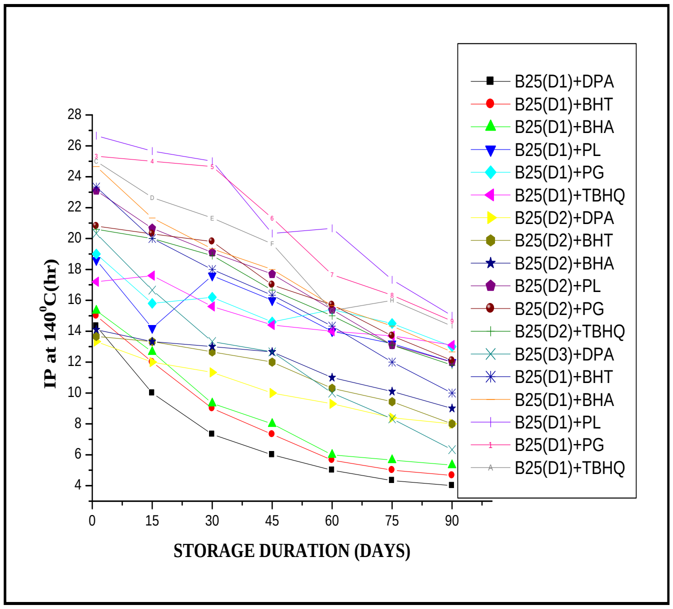

Fig. 4.13

Fig. 4.10 – 4.13 Oxidation stability of biodiesel blends of D1, D2 and D3 with different antioxidants [Fig 4.10 for B10, Fig 4.11 for B15, and Fig 4.12 for B20 and Fig 4.13 for B25]

Fig.4.10 shows the effect of antioxidant additives of oxidation stability of B10 blends of D1, D2 and D3 diesel samples. It is clear from the study that all the B10 blends of D3 diesel sample were stable during the 90 days storage time with all additives. However, B10 blends of D1 and D2 were stable up to 90 days only with PL, PG, and TBHQ. The B15 blends of D1, D2 and D3 using additive PL were found stable up to 90 days whereas these blends could be stored up to maximum 60 days with PG and TBHQ (Fig. 4.11). Rest additives were not shown their effectiveness on long term storage of B15 blends. When the similar study was performed for B20 Blends of D1, D2 and D3 (Fig. 4.12) using antioxidant additives, it was observed that B20 blends of D1 could not gave the satisfactory results, whereas B20 blends of D2 with additives PL and PG were found stable up to 90 days. B20 blends of D3 with antioxidants PL and PG were stable up to 60 days only. Finally, oxidation stability of B25 blends of D1, D2 and D3 (Fig. 4.13) were also investigated and it was observed that only B25 blend of D3 using additive PL was stable for 60 days. Among the antioxidants investigated PL and PG shown a greater effect on the stability of diesel biodiesel blends of D1, D2 and D3. This was expected because both the additives have shown good stabilizing potential with neat *Jatropha* biodiesel sample. Although the use of TBHQ showed good performance in neat *Jatropha* biodiesel but undesirable results were obtained with the biodiesel blends this may be due to *pro-oxidantinteraction* [11]of TBHQ. On the other hand, BHA, BHT and DPA were found least effective. Since the properties of diesel fuel samples were not found the same (Table 2.1 chapter2), which may be the reason for the variation in oxidation stabilities of similar blends.

It needs further research to know the effect of diesel fuel properties on the oxidation stability of its biodiesel blends.

4.4.3. Density measurement of diesel biodiesel blends

A density measurement reflects stability and consistency of a fuel sample. It is a property for developing adequate storage methods for diesel biodiesel blends [13-14]. In diesel biodiesel blends the density of fuel increases with the increase of amount of biodiesel in the mixture. The density of all the blends was observed within the range mentioned by standard ASTM-D 445.

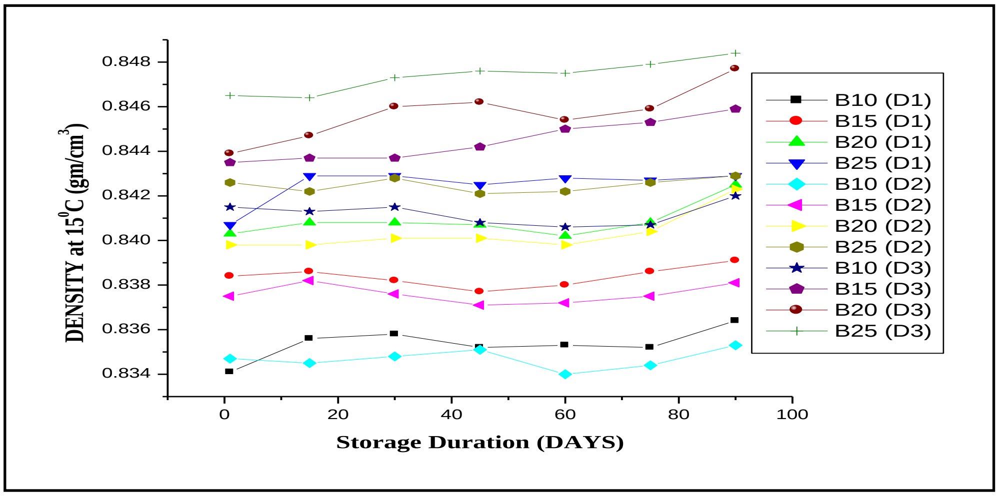

Fig. 4.14. Density of diesel/biodiesel blends without antioxidants

The initial density value for neat blends (B10, B15, B20 and B25) of D1, D2 and D3 ranged from 0.834 gm/cm^3 - 0.846 gm/cm^3 with an average density value of 0.8399 gm/cm^3 while as the final density value for the same were ranged from 0.835 gm/cm^3 - 0.848 gm/cm^3 with an average of 0.841 gm/cm^3 (Fig.4.14). Similarly, densities of all the blends were also investigated with antioxidant additives and the results are shown in Fig. 4.15. The average density of B10 blends (Fig. 4.15a) with additives ranged from 0.834 gm/cm^3 - 0.842 gm/cm^3. Whereas, the average density of B15 and B20 blends with additives ranged between 0.838 gm/cm^3 - 0.846 gm/cm^3(Fig. 4.15b and 4.15c).

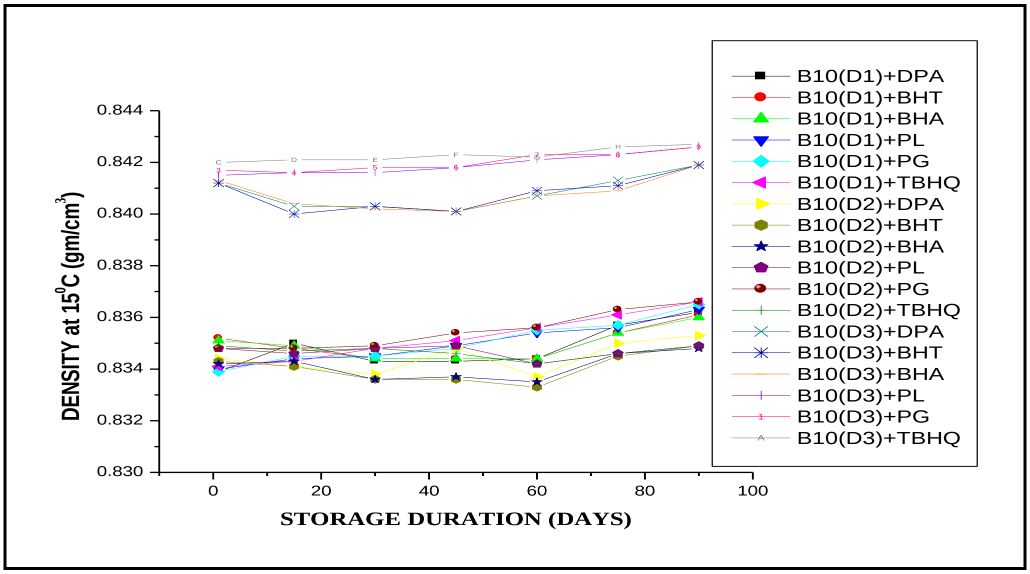

Fig. 4.15a. Effect of antioxidant additives on density of blends of *Jatropha* biodiesel with D1, D2 and D3 (B10)

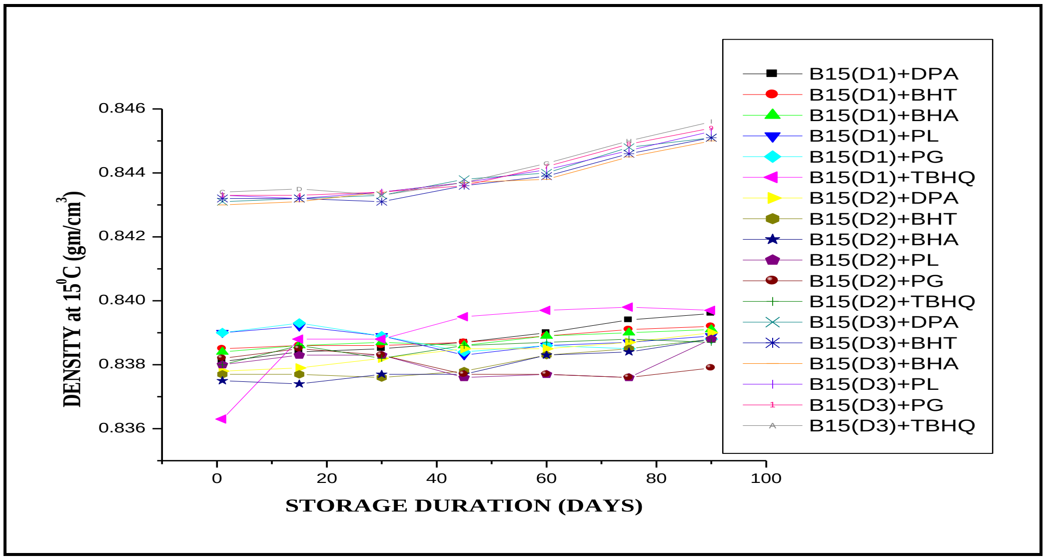

Fig. 4.15b. Effect of antioxidant additives on density of blends of *Jatropha* biodiesel with D1, D2 and D3 (B15)

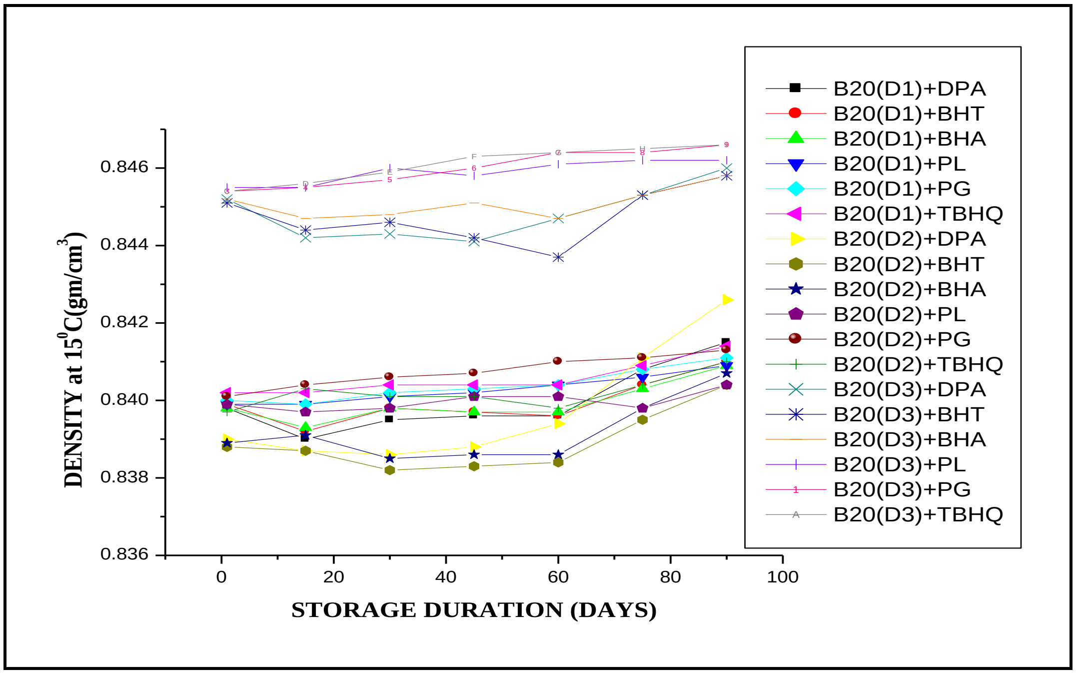

Fig. 4.15c. Effect of antioxidant additives on density of blends of *Jatropha* biodiesel with D1, D2 and D3 (B20)

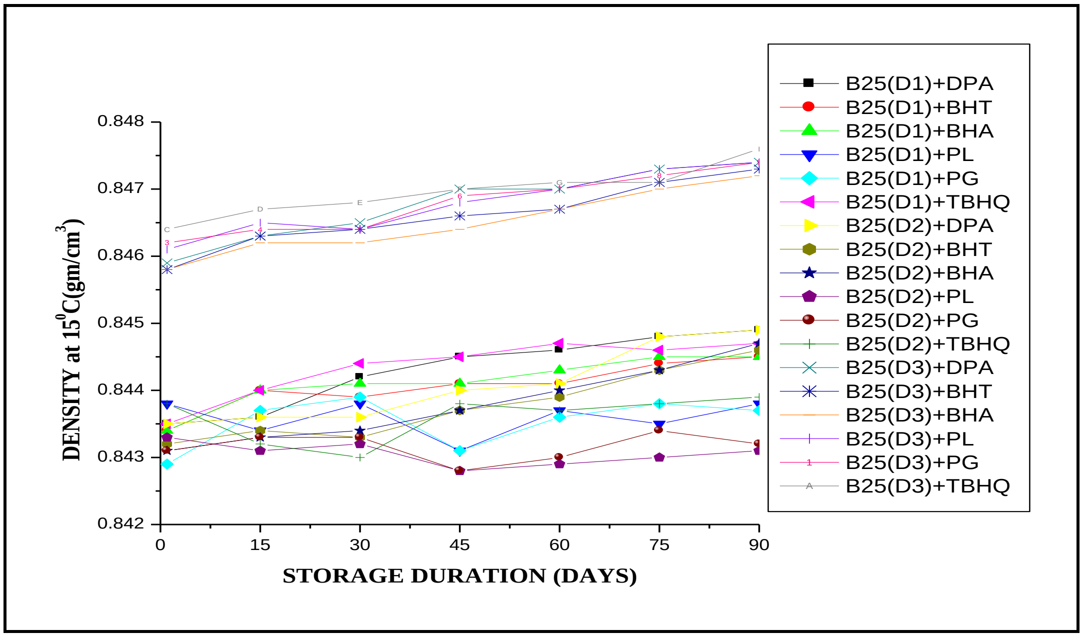

Fig. 4.15d. Effect of antioxidant additives on density of blends of *Jatropha* biodiesel with D1, D2 and D3 (B25)

4.4.4. Kinematic viscosity measurement of diesel biodiesel blends

Kinematic viscosity of all the blends was also investigated with and without antioxidant additives and the results are summarised in Fig. 4.16 and 4.17 respectively. As during oxidation of biodiesel the viscosity starts to increase due to the formation of oxidized products which lead to the formation of sediments and gum [15].

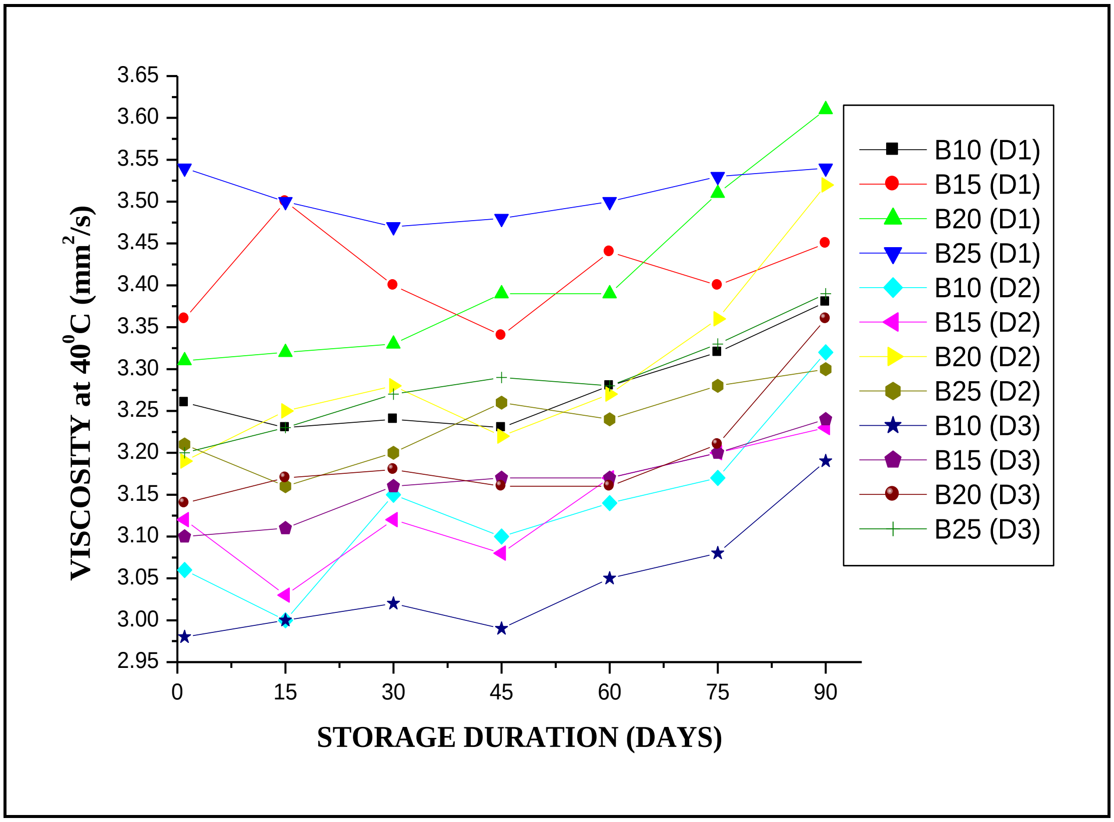

Fig. 4.16.Kinematic Viscosity of diesel/biodiesel blends without antioxidants

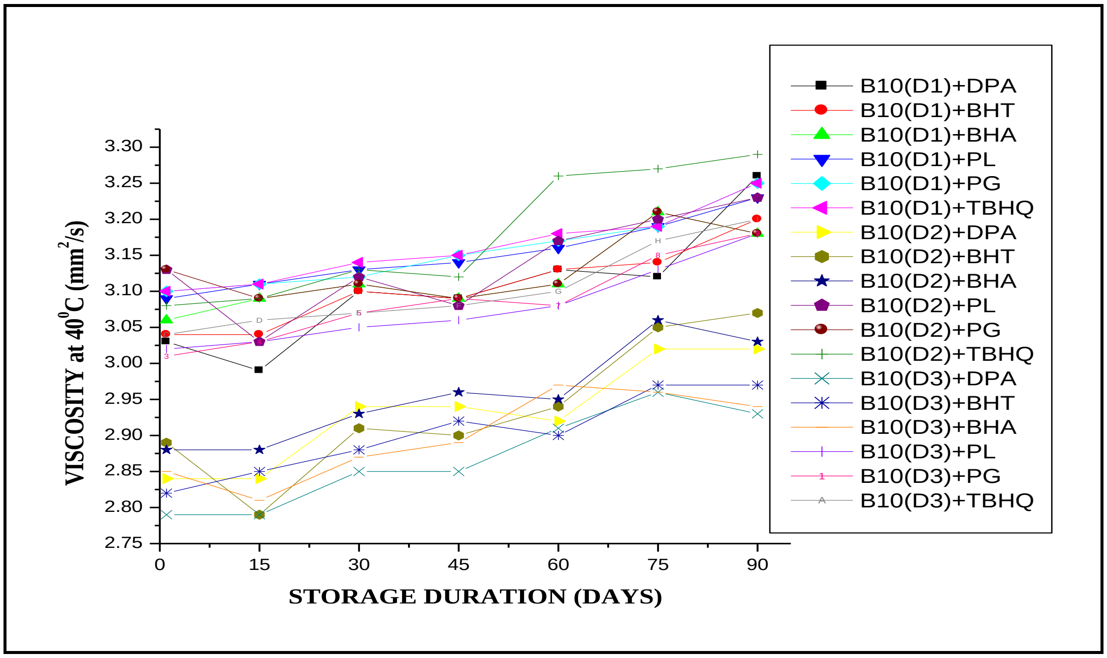

Fig. 4.17a. Effect of antioxidant additives on kinematic viscosity of blendsof *Jatropha* biodiesel with D1, D2 and D3 (B10)

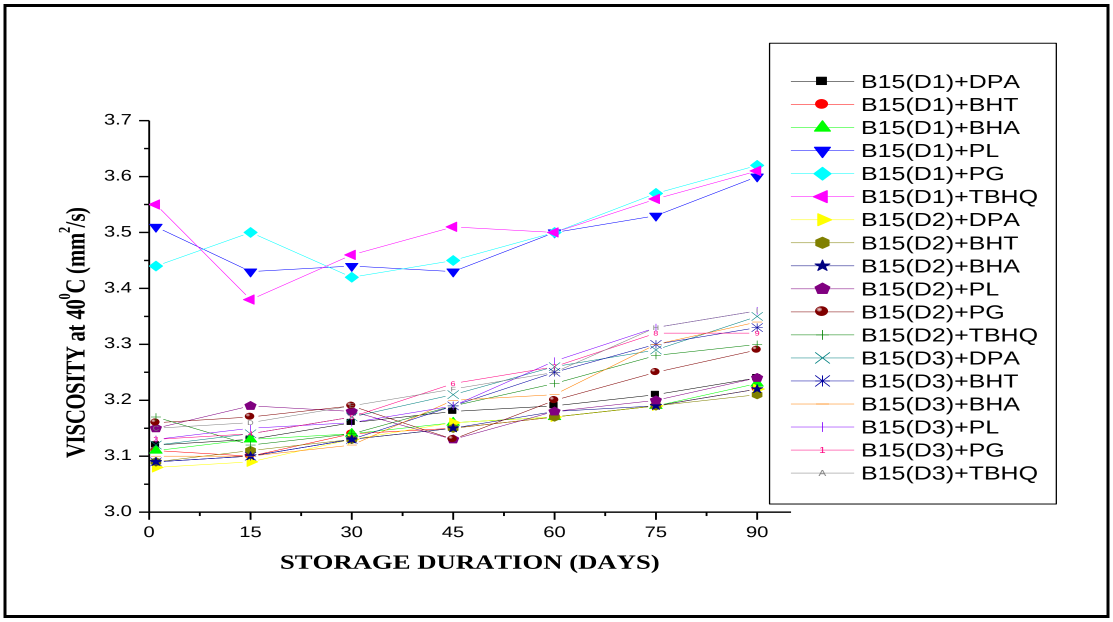

Fig. 4.17b. Effect of antioxidant additives on kinematic viscosity of blendsof *Jatropha* biodiesel with D1, D2 and D3 (B15)

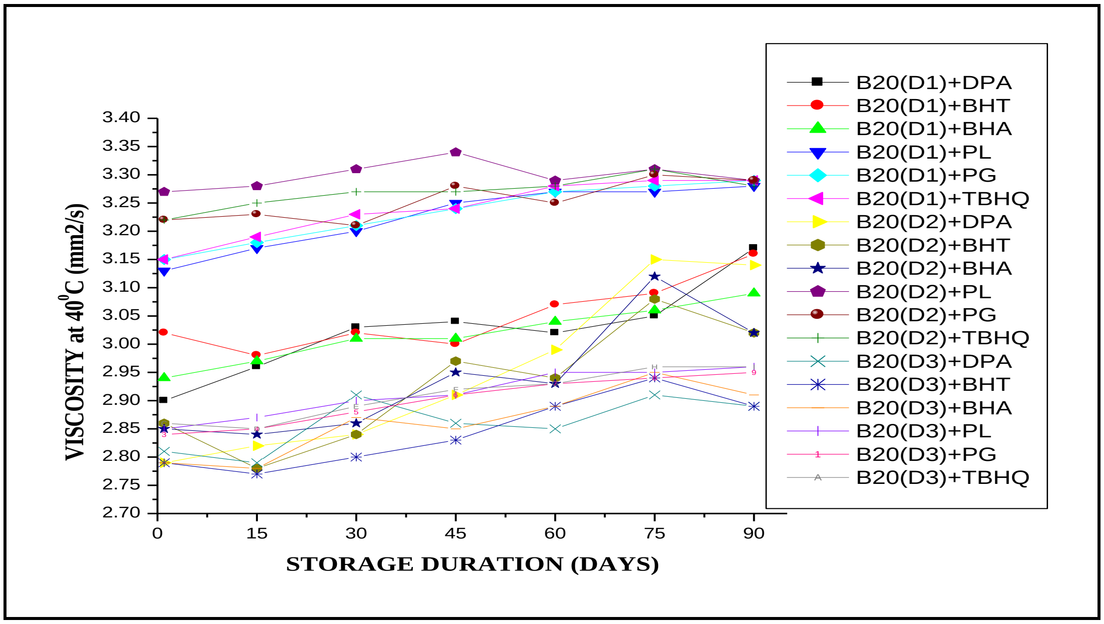

Fig. 4.17c. Effect of antioxidant additives on kinematic viscosity of blendsof *Jatropha* biodiesel with D1, D2 and D3 (B20)

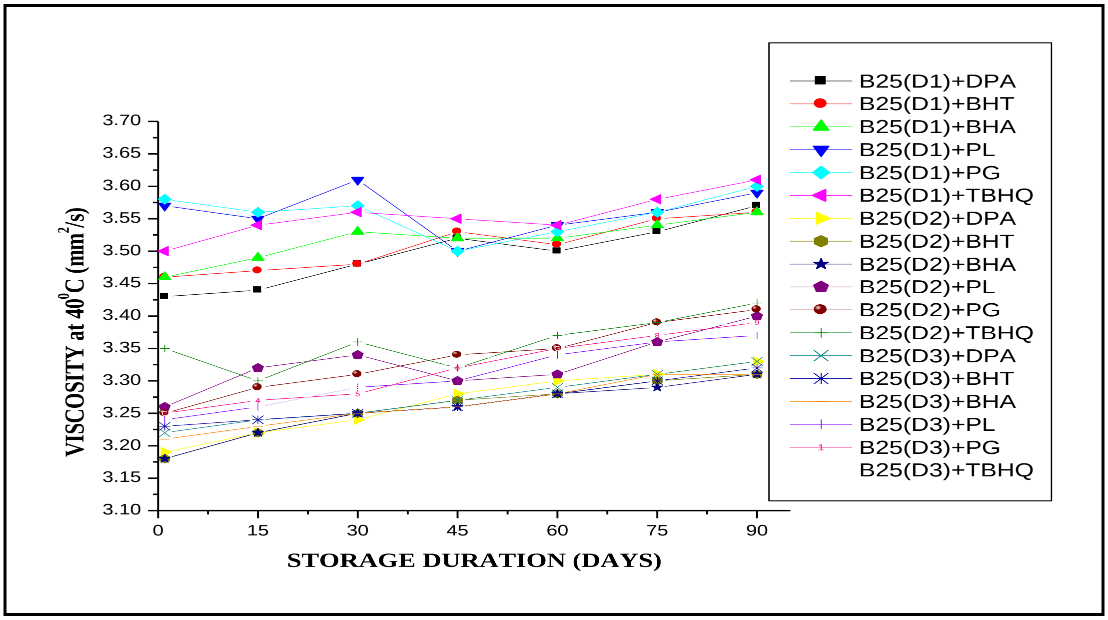

Fig. 4.17d. Effect of antioxidant additives on kinematic viscosity of blendsof *Jatropha* biodiesel with D1, D2 and D3 (B25)

The initial kinematic viscosity of neat diesel biodiesel blends ranged from 2.98 - 3.54 mm^2/s with an average value of 3.20 mm^2/s whereas the final value for the same were ranged from 3.19 - 3.61 mm^2/s with an average of 3.37 mm^2/s (Fig.4.16). The initial and final average kinematic viscosity of B10 blends with additives (Fig. 4.17a) ranged from 3.03 - 3.29 mm^2/s, whereas the same of B15 and B20 blends with additives (Fig. 4.17b and 4.17c) ranged between 3.02 - 3.62 mm^2/s over the course of storage. The viscosity of blends was within the range of standard ASTM-D445.

4.5. Study the oxidation stability of prepared karanja biodiesel and diesel blends with antioxidants

4.5.1. Effect of antioxidants on the oxidation stability of karanja biodiesel samples

As per IS-15607 and prEN-16091 standards the biodiesel must retain its fuel characteristics over a minimum period of 6 hr. under test conditions. The oxidation stability of neat biodiesel (*KOME*) was analyzed by Petrotest method and it gave an induction period of 2.98 hr. which indicates that, it is not possible to use neat biodiesel (*KOME*) as an alternate fuel directly. However, improvement in induction period can be achieved by the use of antioxidant additives. Therefore effect of antioxidants on the oxidation stability of the neat *KOME* sample was investigated for 90 days indoor storage conditions. The antioxidants were screened by adding 300 ppm, 400 ppm and 500 ppm of each antioxidant in 500 mL of neat *KOME* and samples were taken out periodically every 15 days to study the additive effects. The results are shown in Fig. 4.18. A significant difference in the efficiencies of tested antioxidants was observed.

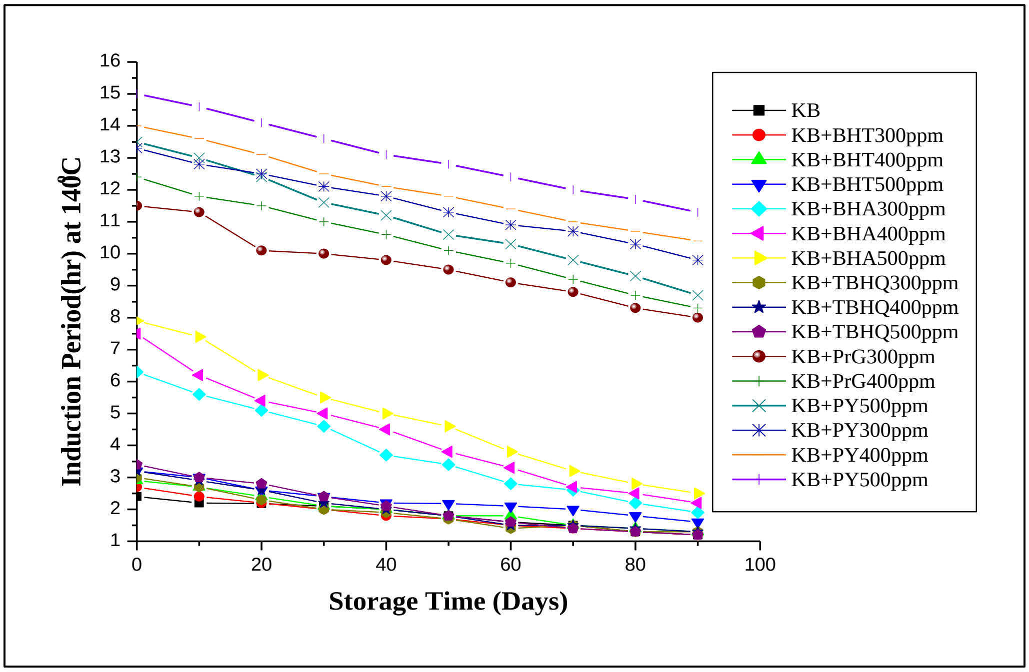

Fig. 4.18. Oxidation stability of *Karanja*biodiesel with antioxidants

It is clear from the Fig. 4.18 that, after the addition of antioxidants, a significant improvement in the induction period of biodiesel was observed. Screening study was also revealed that the 500 ppm concentration of additive was the optimum concentration at which maximum stability was achieved. Therefore 500 ppm additive concentration was preferred for further studies of oxidation stability of diesel/biodiesel blends. From the screening data obtained, PY was found the most effective antioxidant with maximum induction period of 15.0 hrs whereas TBHQ was found to be the least effective during the course of study. On the basis of screening study the effectiveness of antioxidants used was observed in order of PY

>PrG> BHT > BHA > TBHQ. Similar additive response was also observed by other researchers [16-18].The screening study also revealed that the phenolic antioxidants were found more effective. As the active hydroxyl group provides free proton easily to inhibit the formation of free radicals or interrupt the propagation of free radical and thus slow down the rate of oxidation, also the phenolic additives offer more sites for the formation of the complex between the free radical and antioxidant radical for the stabilization of the ester chain [11-12]. It can also be stated that the stability of neat *KOME* is lower in compare to *Jatropha* methyl ester due to the presence of ~86% of unsaturated fatty acid.

4.5.2. Effects of antioxidants on the oxidation stability of diesel biodiesel blends.

Diesel-biodiesel blend stability is best described by determination of its induction period (IP). Blends with an IP of ≥ 20 h has been demonstrated to be sufficiently stable for standard usage conditions and considered as EN 590:2009 limit. Induction period of neat diesel biodiesel blends (B5, B10, B15, B20, B25 and B40) was investigated under the test conditions and the results obtained are shown in Fig. 4.19.

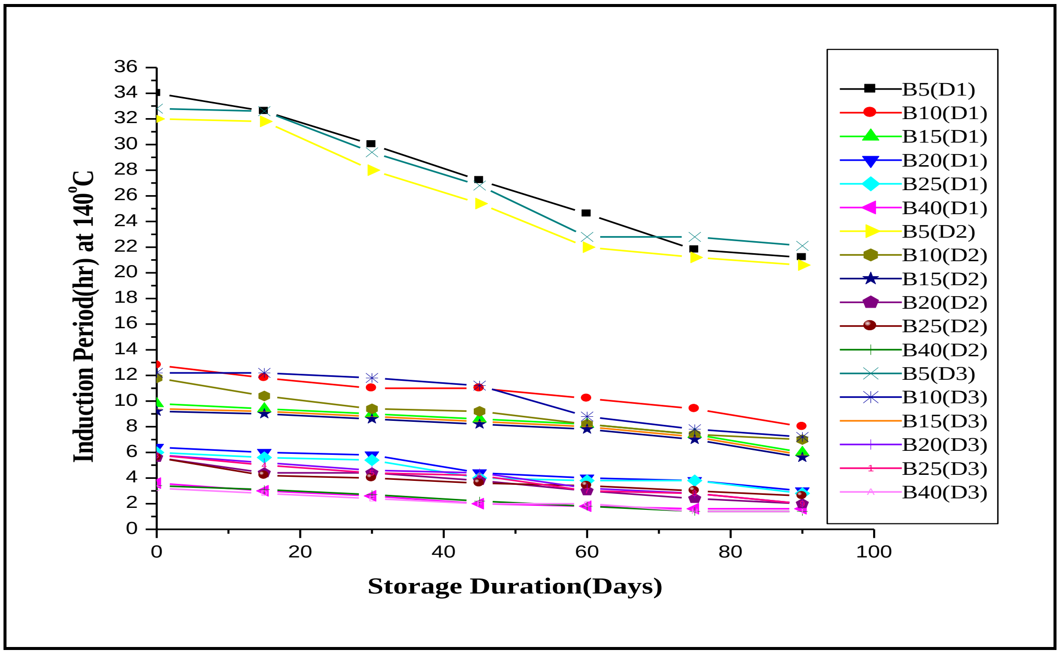

Fig. 4.19. Oxidation stability of Diesel/Biodiesel blends without antioxidants

From Fig. 4.19 it is clear that only B5 blends of all diesel samples were shown the induction period more than 20 h, whereas B10, B15, B20, B25 and B40 blends were failed to meet the minimum induction period (EN 590 limit). However, a sharp drop in the induction period of B5 blend was also observed for next 15, 30....90 days storage duration due to rapid degradation of biodiesel in blended samples. Further to see the antioxidant additives response on oxidation stability of the blends, the optimized amount (500 ppm) of antioxidants was added in 500 mL of each test solution and the oxidation stability was measured.

Fig. 4.20 shows the additive effects on oxidation stability of B5, B10, B15, B20, B25 and B40 diesel-biodiesel blends. Fig.4.20a shows the effect of antioxidant additives of oxidation stability of B5 blends of D1, D2 and D3 diesel samples. It is clear from the Fig. 4.20a that, the maximum induction period of ~75 hrwas shown by the diesel D1 and D3 with PY. However, B5 blends of all three diesels were stable during the 90 days storage time with all additives and has shown the induction period more than 20 hr (EN 590 limit). The B10 blends of D1, D2 and D3 (Fig.4.20b) with antioxidants PY, PrG and BHT were found stable up to 90 days as all the B10 blends with these three additives has shown the induction period >20h. However, these blends were failed to meet the minimum induction period limit (20h as per EN590 limit) with BHA and TBHQ.

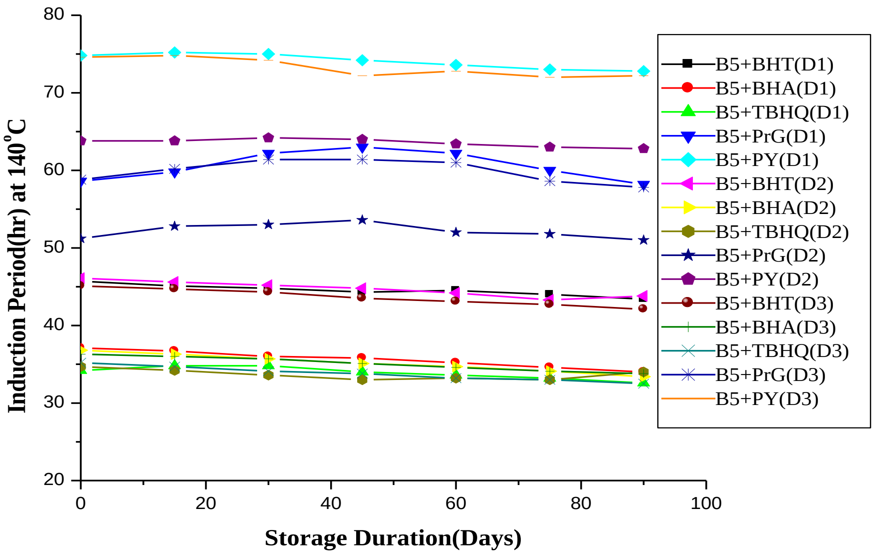

Fig. 4.20a. Additive effects on Oxidation Stability of *Karanja* Biodiesel blends with diesels D1, D2 and D3

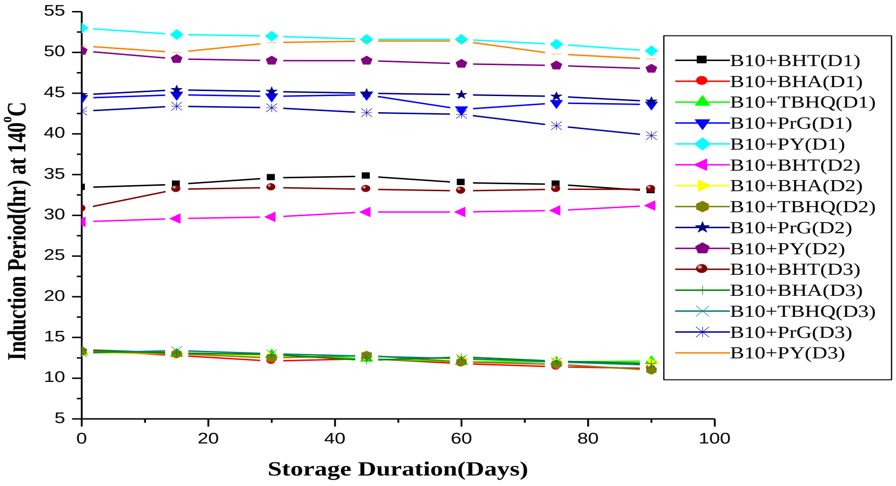

Fig. 4.20b. Additive effects on Oxidation Stability of *Karanja* Biodiesel blends with diesels D1, D2 and D3

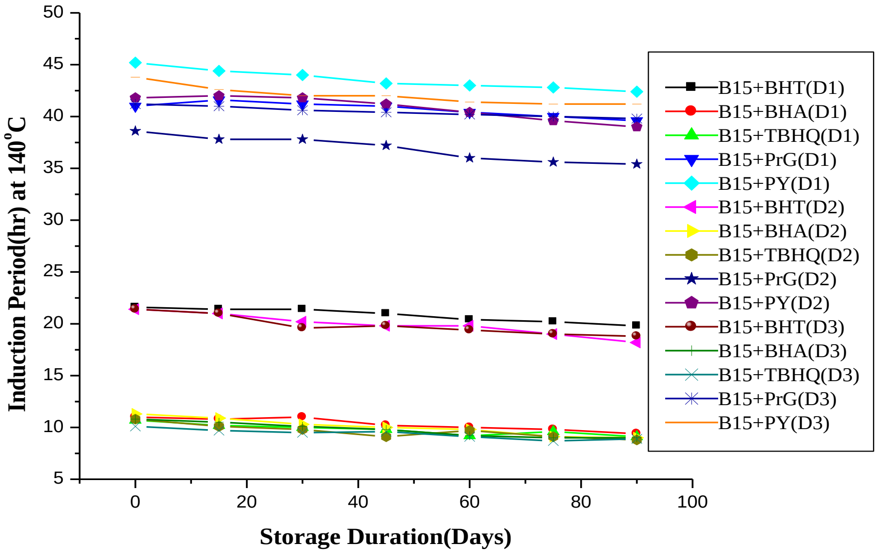

Fig. 4.20c. Additive effects on Oxidation Stability of *Karanja* Biodiesel blends with diesels D1, D2 and D3

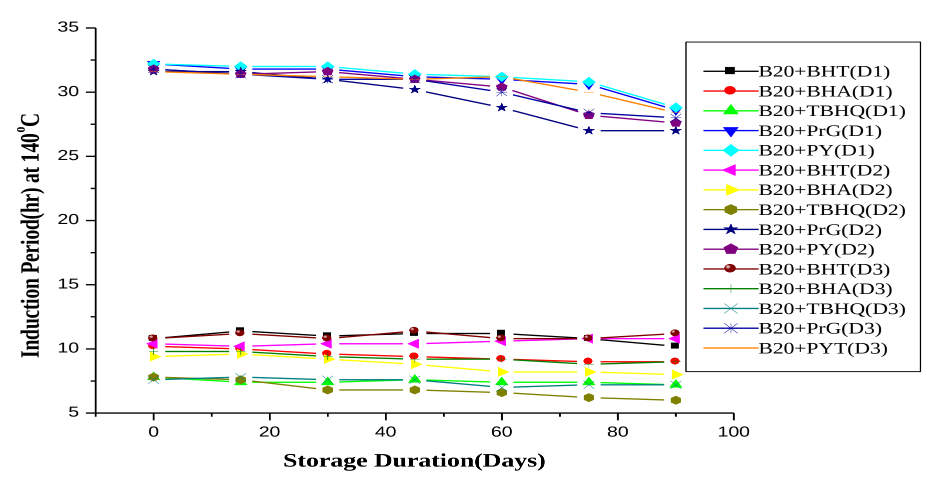

Fig. 4.20d. Additive effects on Oxidation Stability of *Karanja* Biodiesel blends with diesels D1, D2 and D3

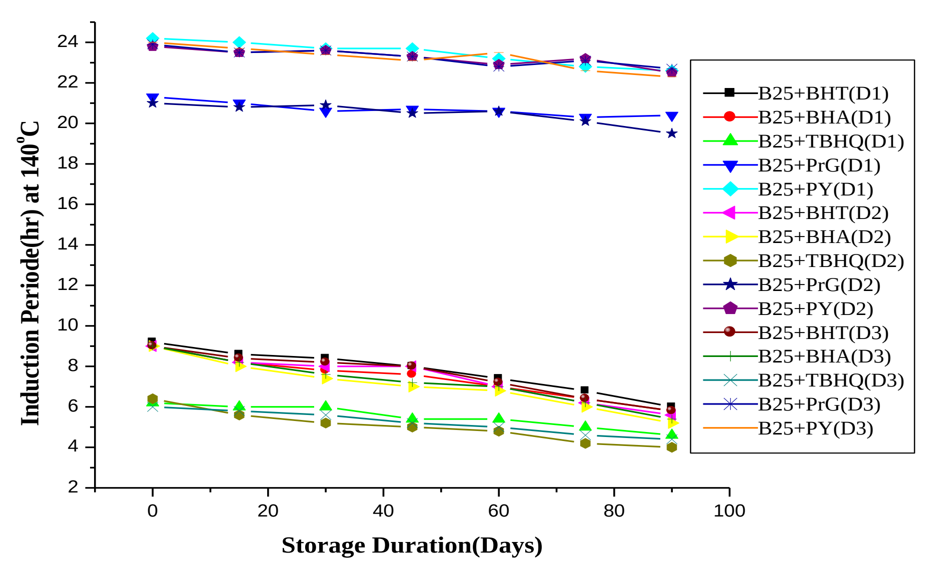

Fig. 4.20e. Additive effects on Oxidation Stability of *Karanja* Biodiesel blends with diesels D1, D2 and D3

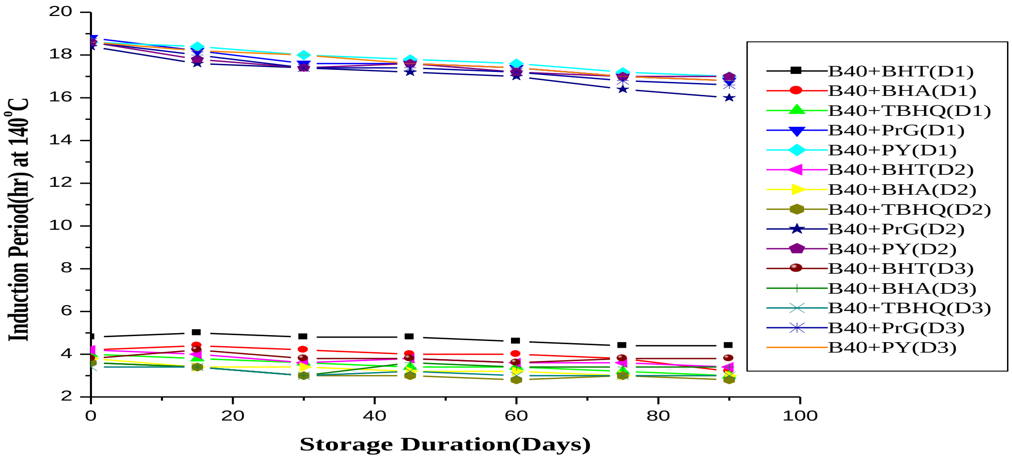

Fig. 4.20f. Additive effects on Oxidation Stability of *Karanja* Biodiesel blends with diesels D1, D2 and D3

The B15 blends of D1, D2 and D3 were found stable up to 90 days with antioxidant PY and PrG, whereas these blends could be stored up to maximum ~75 days with BHT (Fig. 4.20c). However, BHA and TBHQ were not shown the desired effectiveness on long term storage of B15 blends. When the additive effect studies were performed for B20 and B25 blends of diesels D1, D2 and D3 (Fig. 4.20d and 4.20e), it was observed that both; B20 and B25 blends of diesels D1, D2 and D3 with antioxidants PY and PrG were stable up to 90 days study duration. B20 blend has shown the maximum induction period of ~32 hr with both PY and PrG antioxidants, on the other hand induction period of ~24 hr and ~23 hr has shown by B25 blend with PY and PrG antioxidants respectively. However, these blends with BHT, BHA and TBHQ were failed to meet the minimum induction period (20 hr;

EN590 limit). Finally, oxidation stability of B40 blends of D1, D2 and D3 (Fig. 4.20f) was investigated and it was observed that with the optimized doses of antioxidants none of the blend were meet with the minimum stability limit. Among the antioxidants investigated PY PrG and BHT has shown a greater stabilizing effect on the oxidation stability of diesel biodiesel blends of D1, D2 and D3. This was expected because all three additives have already shown their stabilizing potential with neat *Karanja* biodiesel. BHA and TBHQ were failed to mark their effectiveness in all the diesel-biodiesel blends tested. The difference in properties of diesel fuel samples (Table2.1 chapter2) may be the reason for the variation in oxidation stabilities of similar blends. Additionally, the lower sulphur in the base diesel may responsible to decrease the oxidation stability of the final blend [16]. From Table 2.1 chapter2, diesel D1 and D3 have more sulphur content in compare to the diesel D2, therefore the blends of D1 and D3 have shown comparatively more induction period.

4.5.3. Density measurement of diesel biodiesel blends

A density measurement reflects stability and consistency of a fuel sample. It is a property for developing adequate storage methods for diesel biodiesel blends [13-14]. In diesel biodiesel blends the density of fuel increases with the increase of amount of biodiesel in the mixture. The density of all the blends was observed within the limit as mentioned in ASTM-D 445 and IS 1448, P:16 standards. The initial density value for neat blends (B5, B10, B15, B20, B25 and B40) of D1, D2 and D3 ranged from 0.830 gm/cm^3 - 0.844 gm/cm^3 with an average density value of 0.8365 gm cm^3; while as the final density value for these blends were ranged from 0.831 gm/cm^3 - 0.843 gm/cm^3 with an average of 0.8379 gm/cm^3 (Fig.4.21).

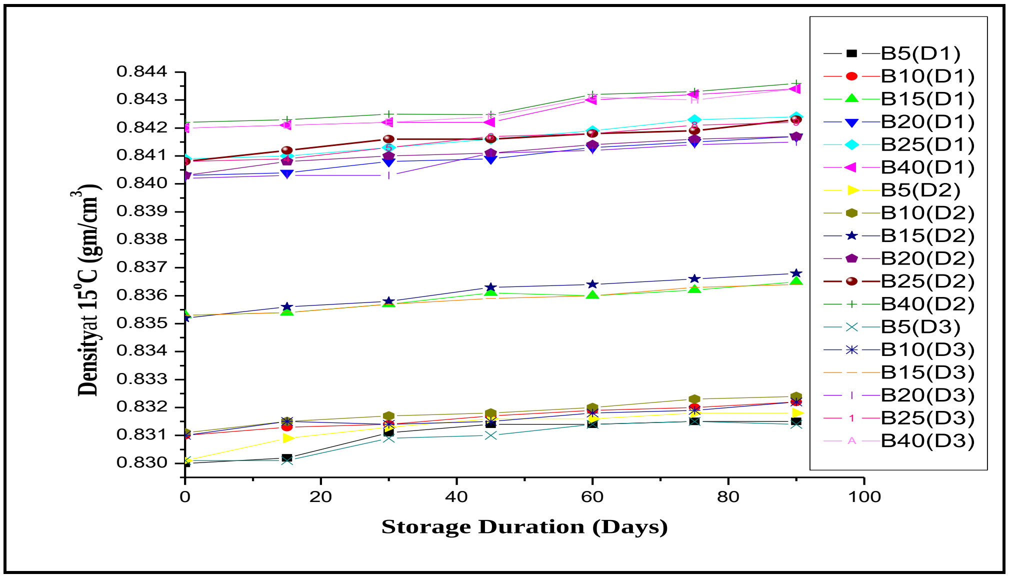

Fig. 4.21. Density of neat *Karanja* biodiesel blends of diesels D1, D2 and D3

Similarly, density of all the diesel blends was also investigated with antioxidant additives and the results are shown in Fig. 4.22. The initial densities of the blends were ranged between 0.831 gm/cm^3 - 0.844 gm/cm^3, whereas the final densities were found within the range of 0.833 gm/cm^3 - 0.846 gm/cm^3.

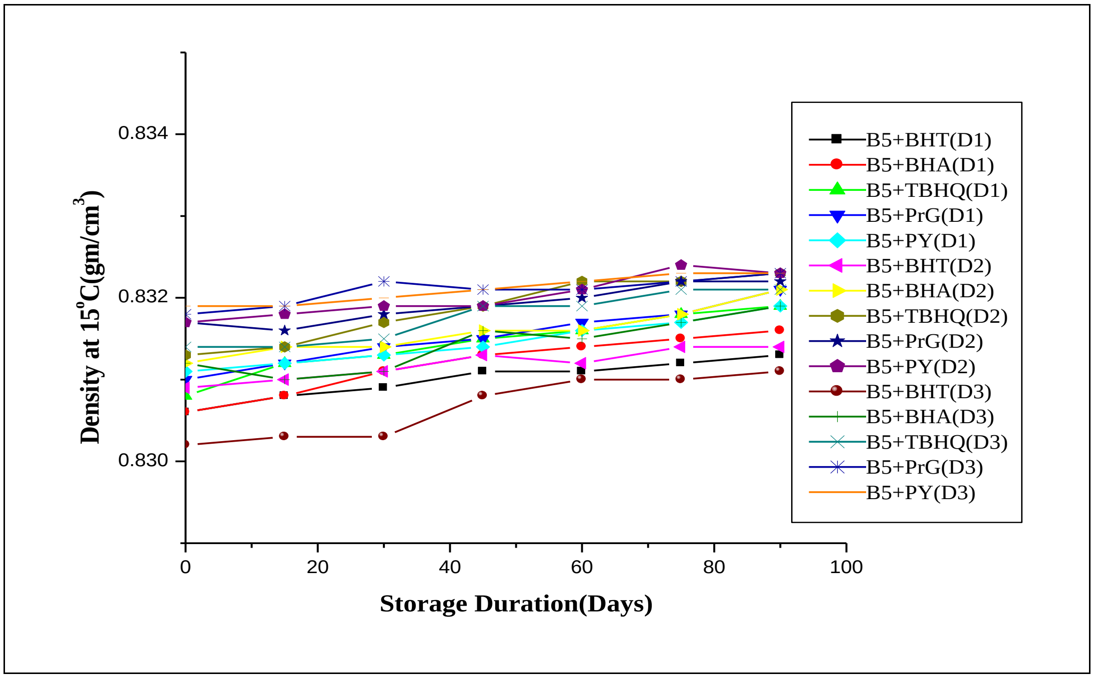

Fig. 4.22a. Additive effects on Density of *Karanja* Biodiesel blends with diesels D1, D2 and D3

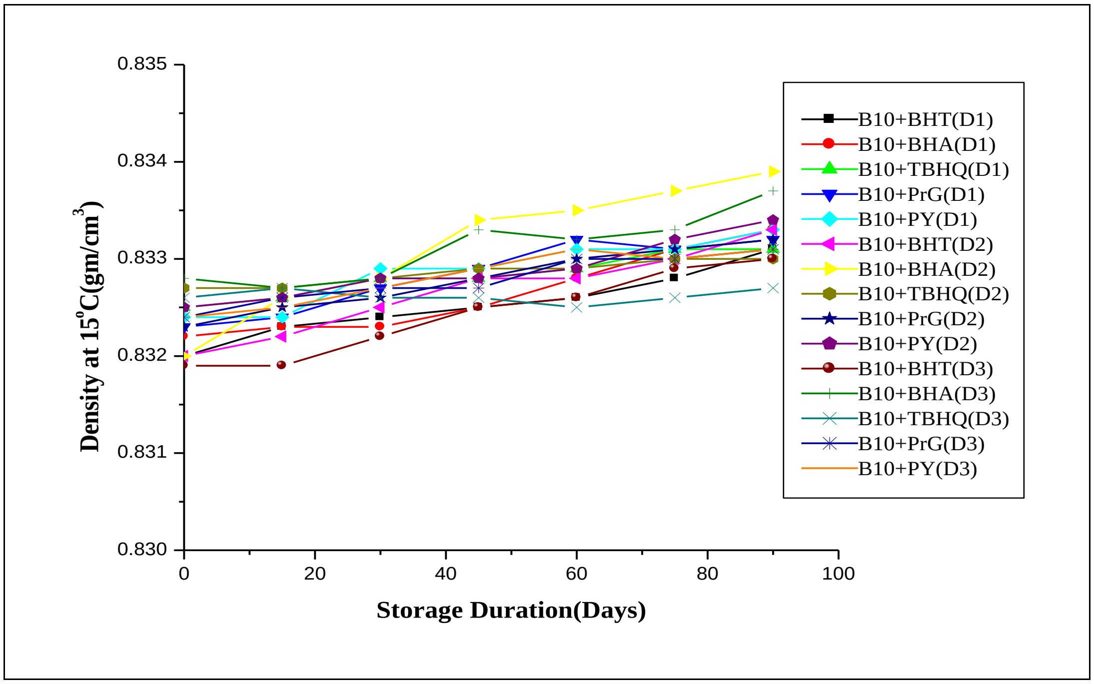

Fig. 4.22b. Additive effects on Density of *Karanja* Biodiesel blends with diesels D1, D2 and D3

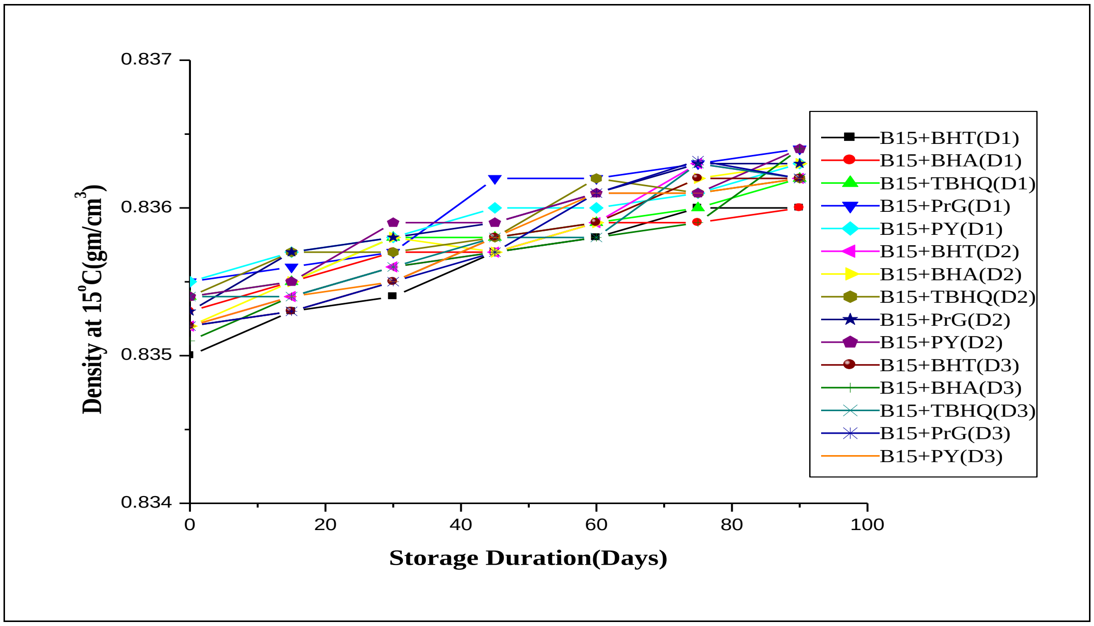

Fig. 4.22c. Additive effects on Density of *Karanja* Biodiesel blends with diesels D1, D2 and D3

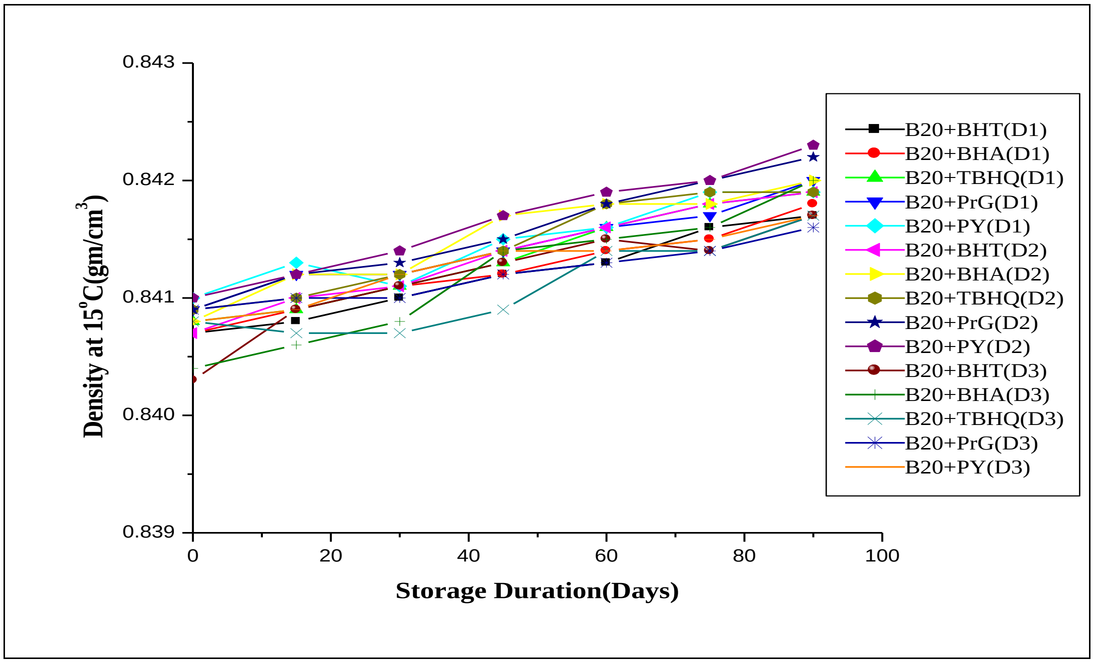

Fig. 4.22d. Additive effects on Density of *Karanja* Biodiesel blends with diesels D1, D2 and D3

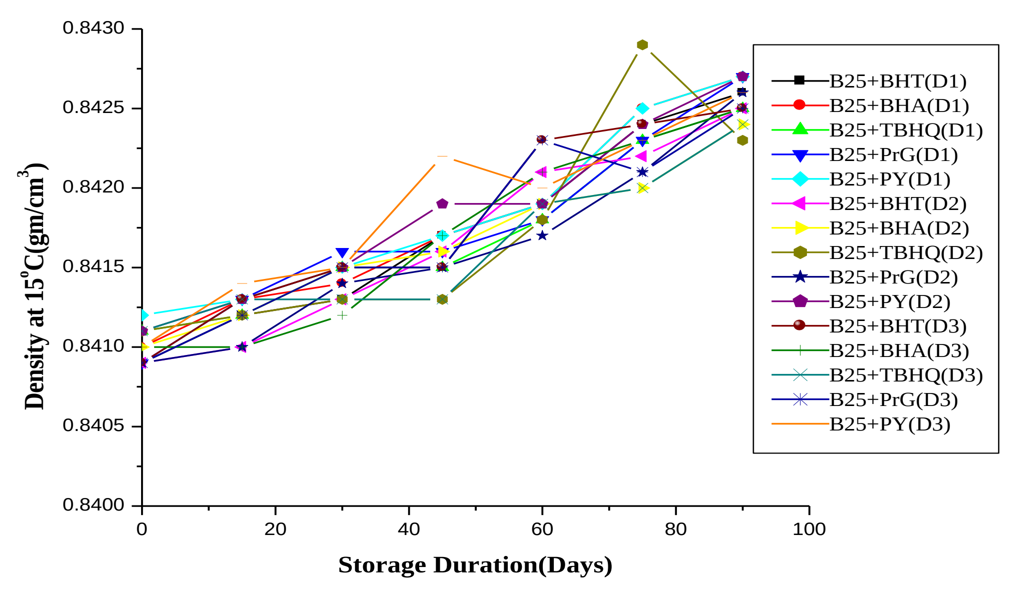

Fig. 4.22e. Additive effects on Density of *Karanja* Biodiesel blends with diesels D1, D2 and D3

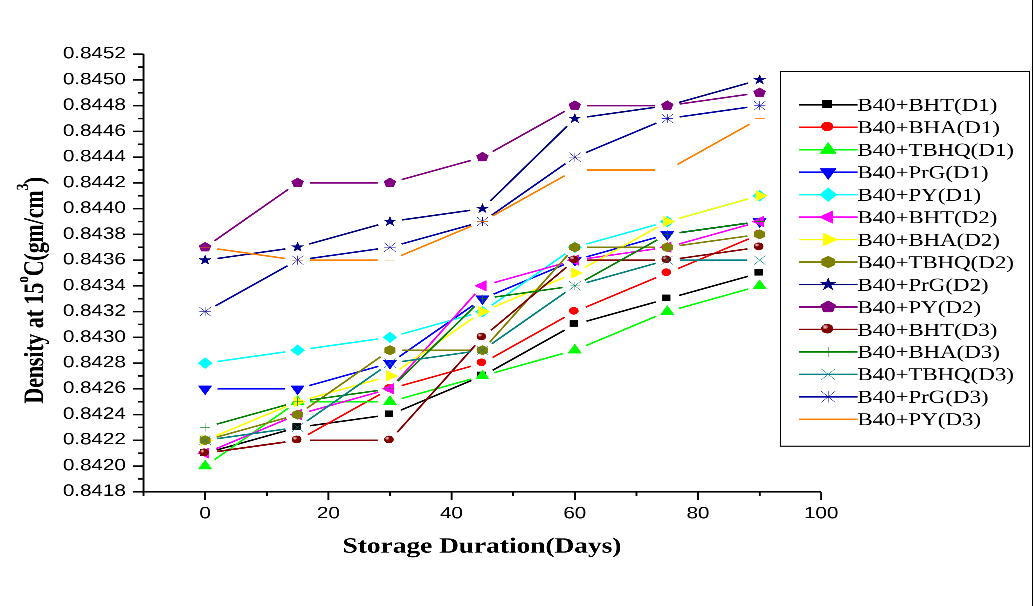

Fig. 4.22f. Additive effects on Density of *Karanja* Biodiesel blends with diesels D1, D2 and D3

4.5.4. Kinematic viscosity measurement of diesel biodiesel blends

Kinematic viscosity of all the blends was also investigated with and without antioxidant additives and the results are summarized in Fig. 4.23 and 4.24 respectively. During oxidation of biodiesel the viscosity increases due to the formation of oxidized products which lead to the formation of sediments and gum [15].

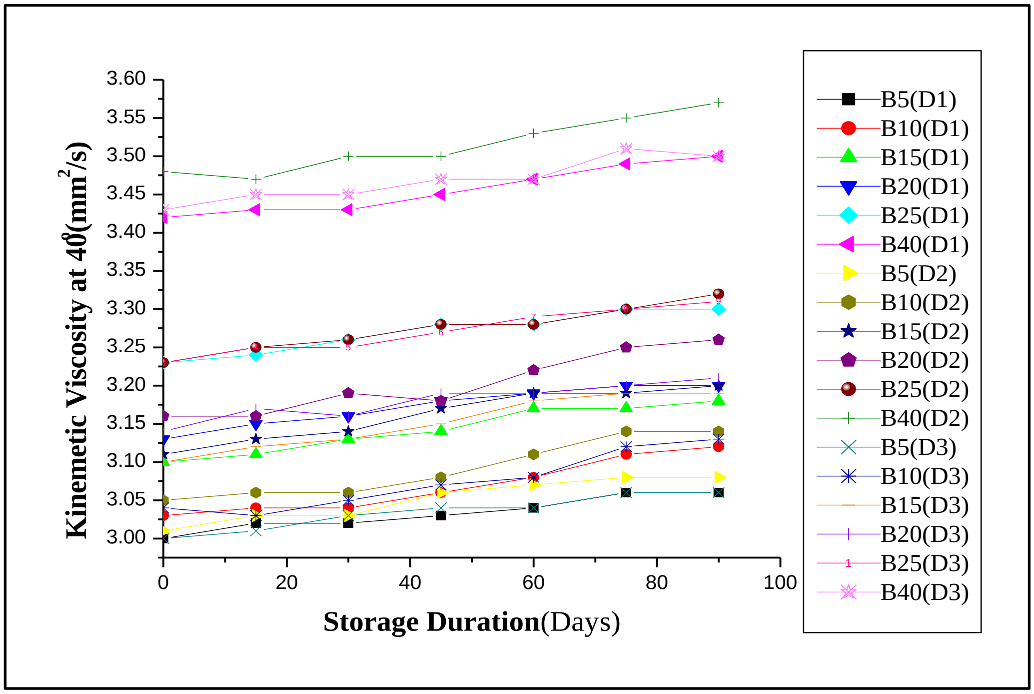

Fig. 4.23.Kinematic Viscosity of diesel/biodiesel blends without antioxidants

The initial kinematic viscosity of neat diesel biodiesel blends ranged from 3.0 - 3.48 mm^2/s with an average value of 3.17 mm^2/s whereas the final value for the same were ranged from 3.06 - 3.57 mm^2/s with an average of 3.24 mm^2/s (Fig.4.23). Similarly, the initial kinematic viscosity of the blends were ranged between 3.01 - 3.47 mm^2/s, whereas the final densities were found within the range of 3.06 - 3.59

mm^2/s (Fig. 4.24). The viscosity of all the blends was observed within the limit as mentioned in ASTM-D445 and IS 1448, P:25 standards.

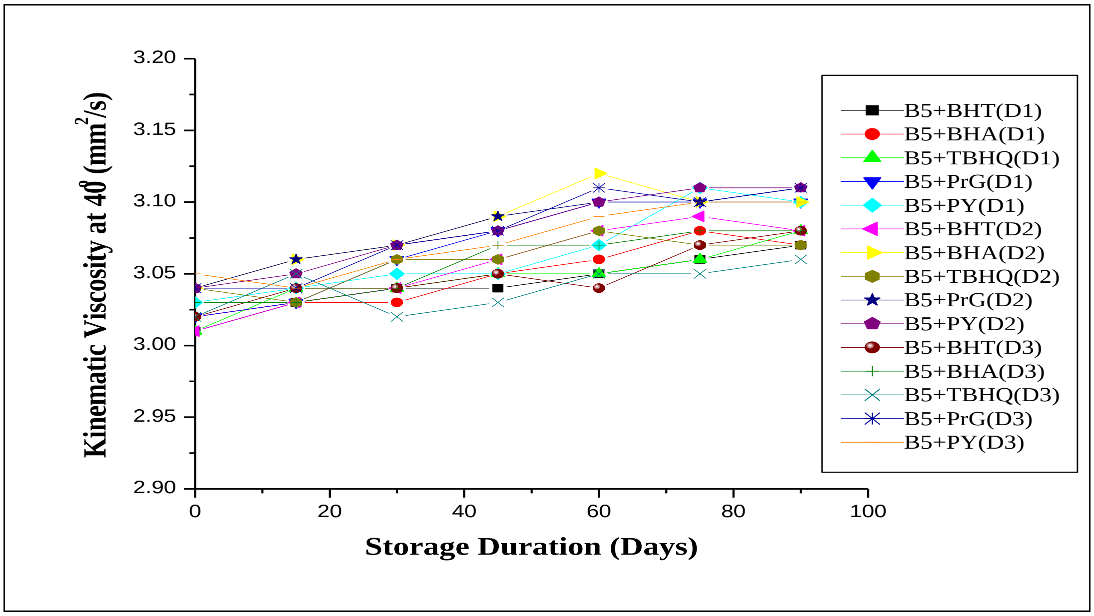

Fig. 4.24a. Additive effects on kinematic viscosity of *Karanja* biodiesel blends with diesels D1, D2 and D3

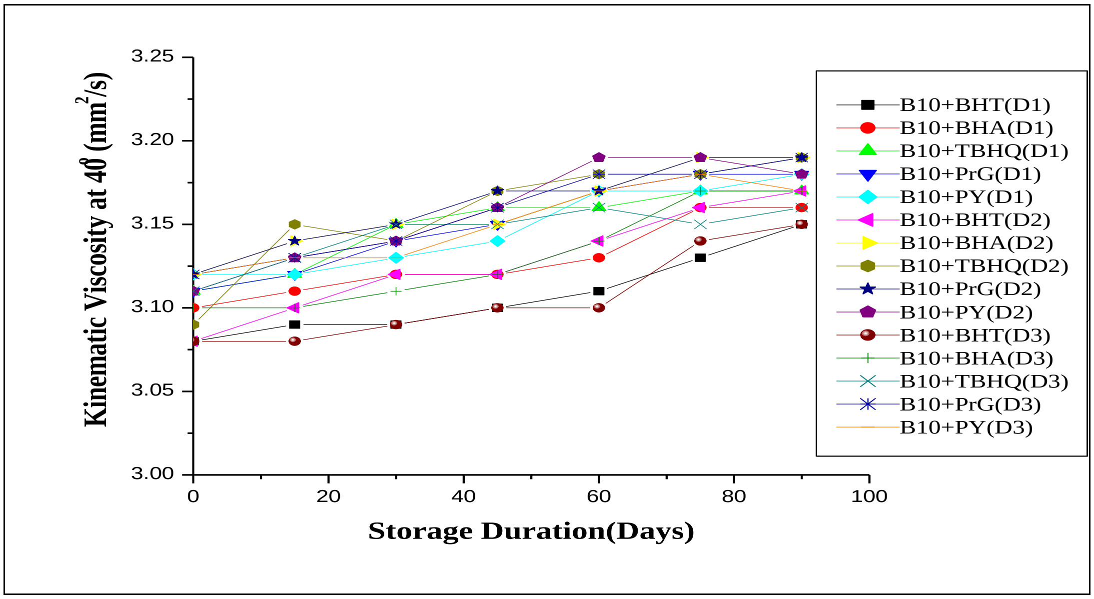

Fig. 4.24b. Additive effects on kinematic viscosity of *Karanja* biodiesel blends with diesels D1, D2 and D3

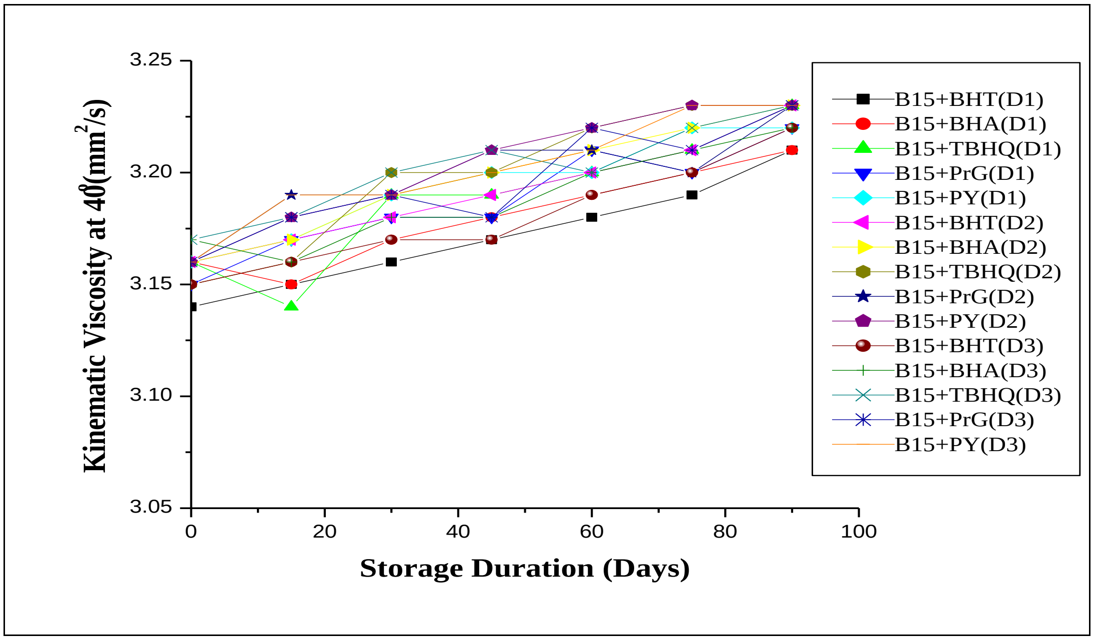

Fig. 4.24c. Additive effects on kinematic viscosity of *Karanja* biodiesel blends with diesels D1, D2 and D3

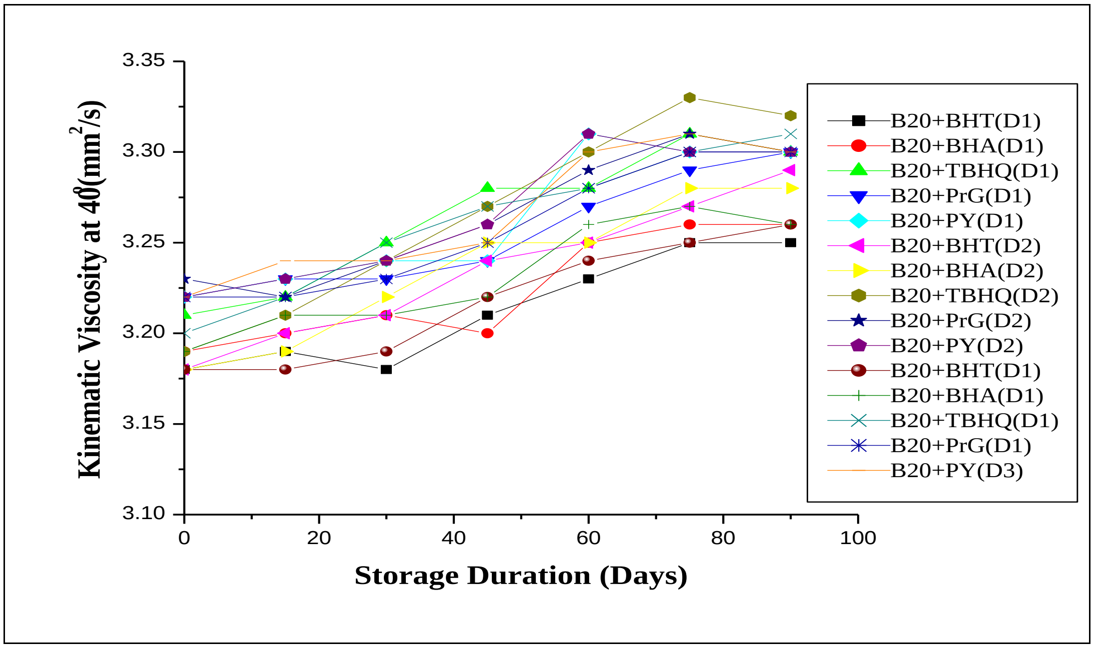

Fig. 4.24d. Additive effects on kinematic viscosity of *Karanja* biodiesel blends with diesels D1, D2 and D3

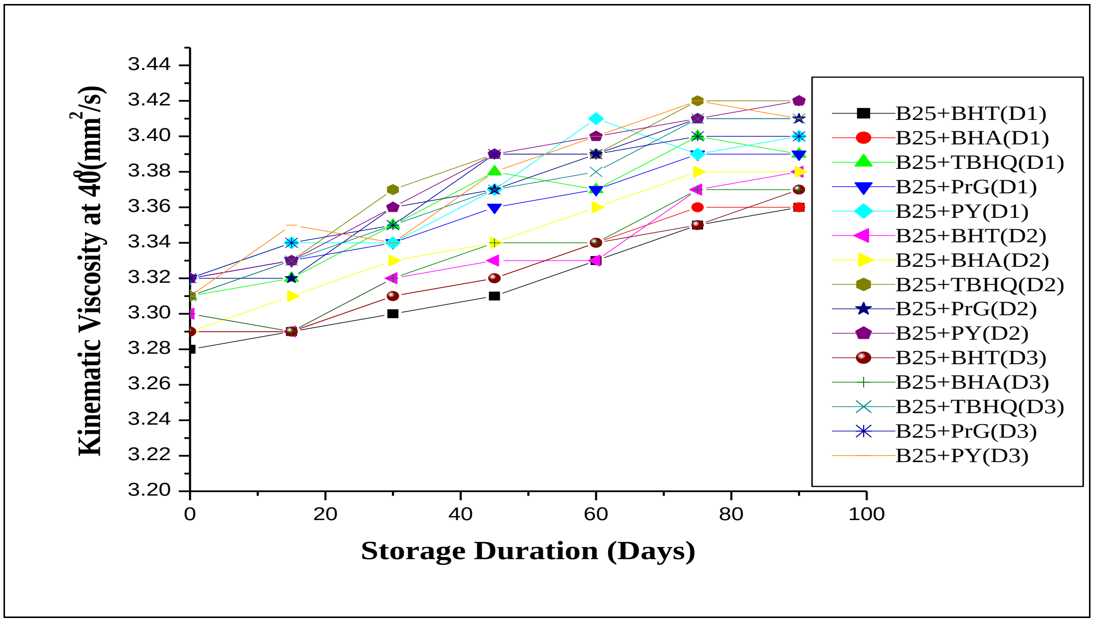

Fig. 4.24e. Additive effects on kinematic viscosity of *Karanja* biodiesel blends with diesels D1, D2 and D3

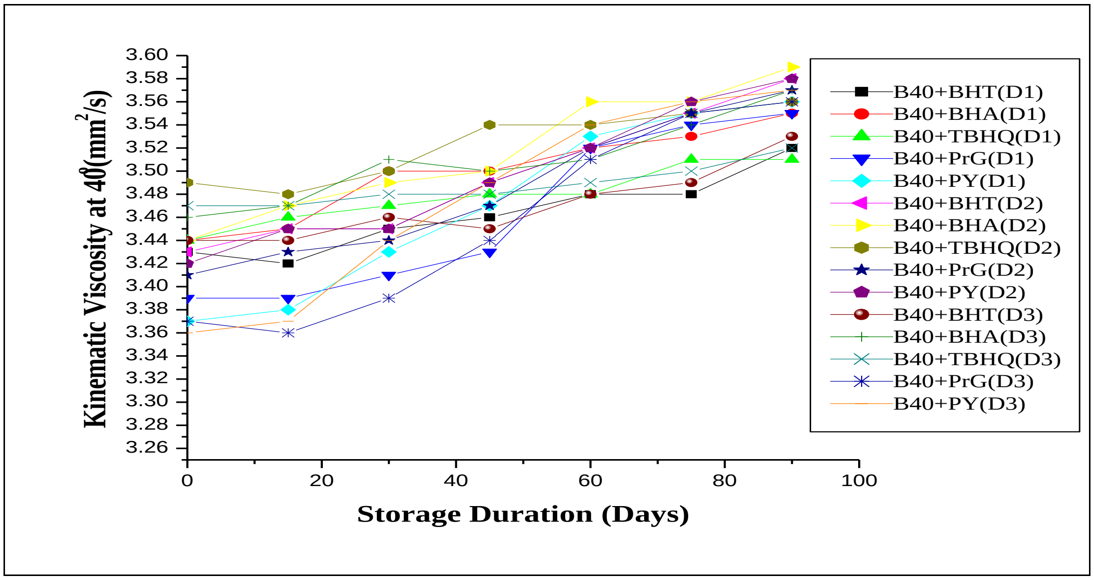

Fig. 4.24f. Additive effects on kinematic viscosity of *Karanja* biodiesel blends with diesels D1, D2 and D3

4.6.Study the oxidation stability of jatropha and karanja biodiesel with binary antioxidants

4.6.1. Binary antioxidant and their effect on antioxidant synergy, stabilization factor and oxidation stability of Jatropha and Karanja biodiesel

Based on the improvement on oxidation stability of both Jatropha and Karanja biodiesels with individual antioxidants; biodiesel blends with binary mixtures of antioxidants were prepared in various proportions of antioxidants, and the role of different additive proportions on antioxidant synergy, stabilization factor and oxidation stability of Jatropha and Karanja biodiesels was investigated.

4.7.Study for Jatropha biodiesel

Fig. 4.25 shows the comparison between improvement in IP of Jatropha biodiesel with individual and binary combination of antioxidants. Better improvement was observed in IP of Jatropha biodiesel using binary mixture of antioxidants in comparison to their individual dosage of equal concentration. Oxidation stability of Jatropha biodiesel was tested using 500, 600 and 700 ppm of binary antioxidantsystem in above mentioned proportions and results are shown in Fig 4.25a, 4.25b and 4.25c.

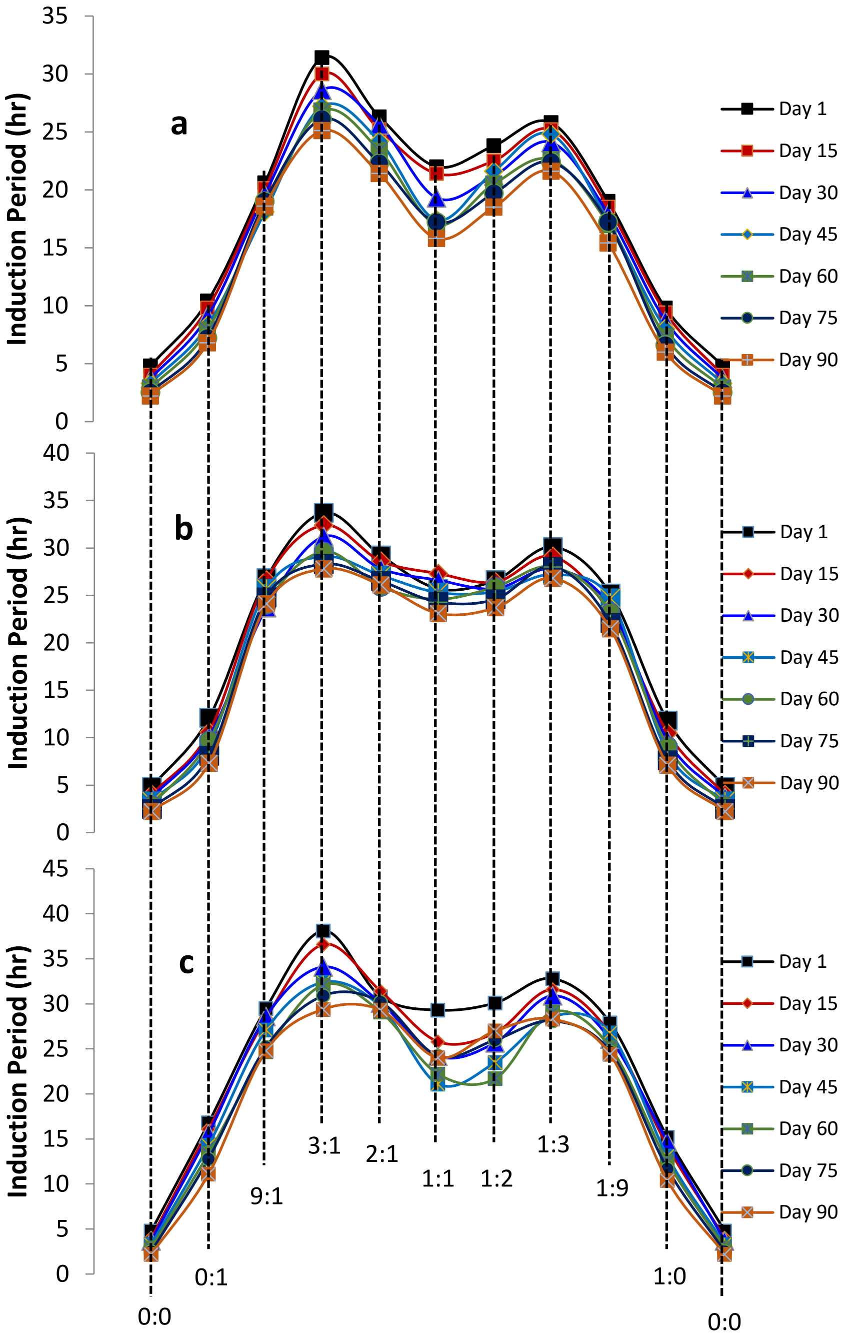

Fig. 4.25: Variation in Induction Period of Jatropha biodiesel with binary antioxidants; a) 500 ppm, b) 600 ppm and c) 700 ppm total additive (PrG:PY) concentration in different ratios

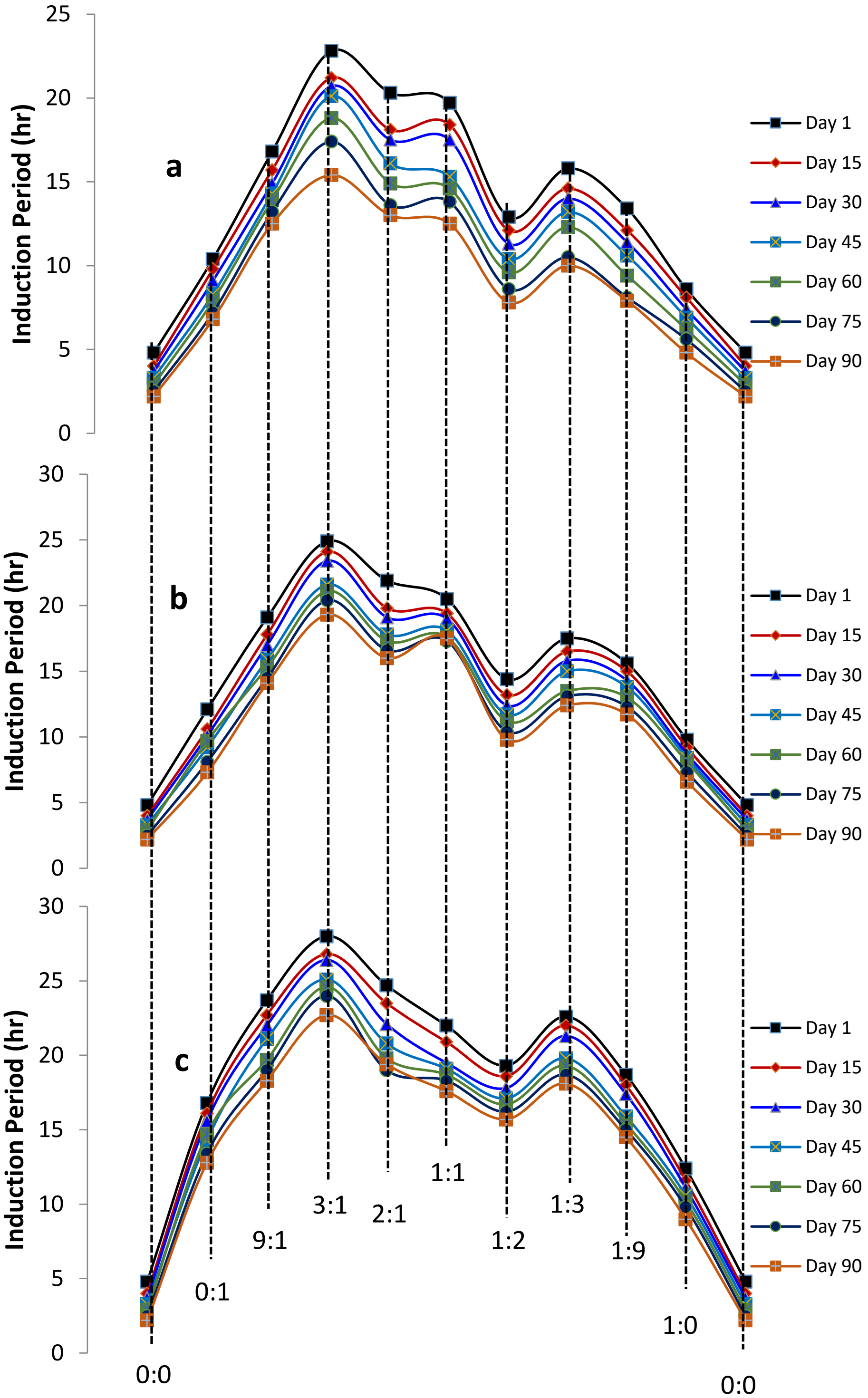

Fig. 4.26 Variation in Induction Period of Jatropha biodiesel with binary antioxidants; a) 500 ppm, b) 600 ppm and c) 700 ppm total additive (TBHQ:PY) concentration in different ratios

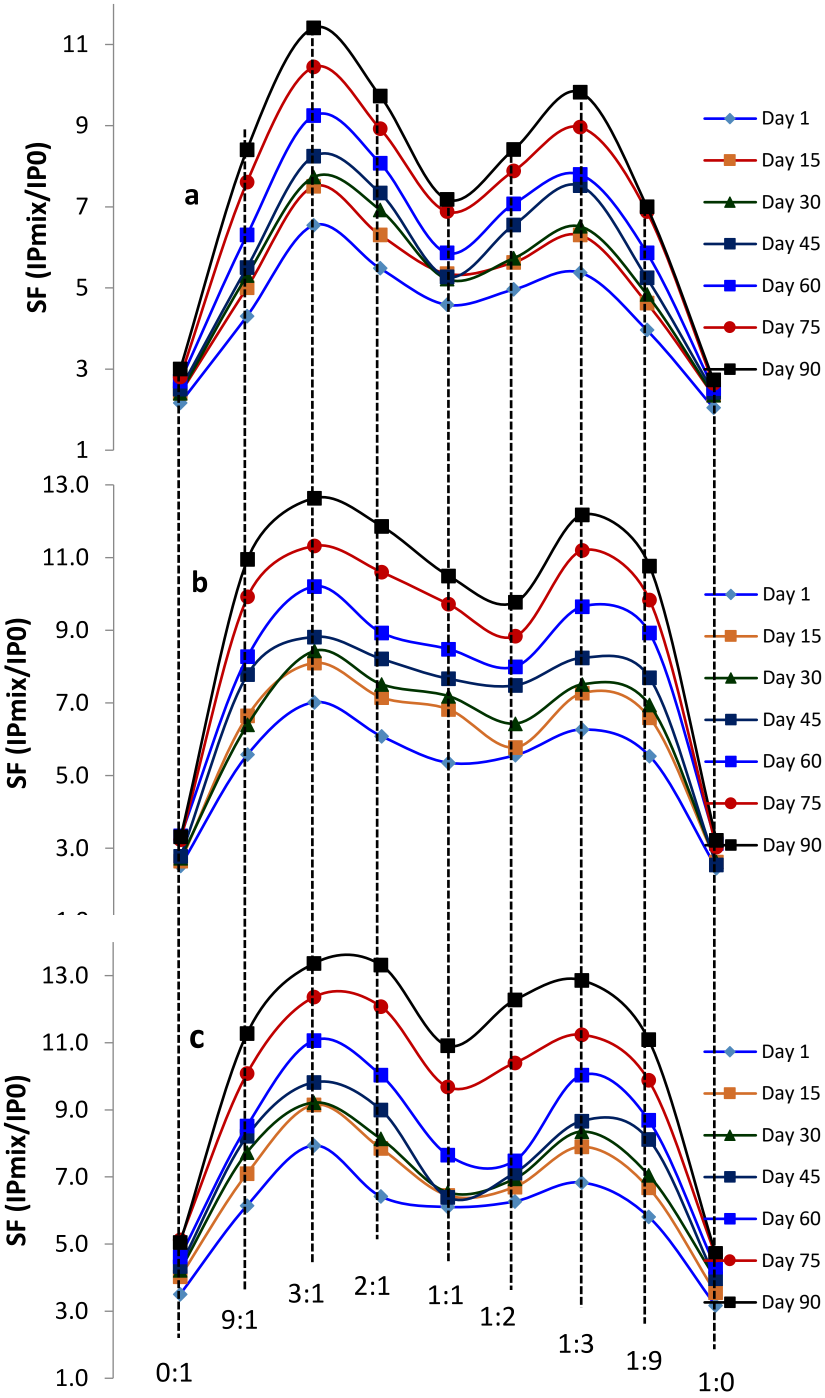

Fig. 4.27Variation in stabilization factor for Jatropha biodiesel with a) 500; b) 600 and c) 700 ppm total additive (PrG:PY) concentration in different ratios

The maximum IP (31.4 hr for 500ppm; 33.7hr for 600 ppm; 38.1 hr for 700 ppm) was achievedwith 3:1 weight ratio of PrG:PY in all concentrations of additives for Jatrophabiodiesel. Similarly,the effect of binary mixture of PY:TBHQ on oxidation stability of Jatropha biodiesel was also determined (Fig.4.26).

It was also observed that for Jatropha biodiesel TBHQ:PY mixture shows less effectiveness as compared to PY:PrG. The maximum IP of 22.8, 24.9 and 28 hrwere achieved with 500, 600 and 700 ppm of 3:1 weight ratios of TBHQ: PY respectively (Fig. 4.26a, 4.26b and 4.26c). However, gradual decrease in IP was observed with all binary composition during storage period.

Stabilization factor or protection factor represents the increase in oxidation period caused by the antioxidant. It is determined as the ratio between the induction periods of biodiesel in the presence of antioxidant (IP_A) to the induction periods biodiesel in the absence of antioxidant (IP_0) [19-20].

$$\mathbf{SF = IP_A/IP_0}$$

Effect of binary combination of antioxidants PY:PrG and PY:TBHQ on stabilization factor for Jatropha biodiesel was also calculated and the results are summarized in Fig. 4.27 and Fig. 4.28.With increase in antioxidant concentration the stabilization factor also increases. Also the binary combinations have shown a significant improvement in SF values in comparison to the individual antioxidants, it may be because of the synergy between both the antioxidants which results the continuous regeneration of primary antioxidant during the storage period.

Furthermore, the synergistic behavior of these binary antioxidant combinations (*i.e.*PY:PrG and PY:TBHQ) on biodiesel stability was also determined. The synergistic effect is the oxidation inhibiting effect of binary mixture of antioxidants. If the induction period of biodiesel using binary mixture of antioxidants is higher than the sum of the induction periods of the individual antioxidants, it is called +ve synergy [19-20].

$$\mathbf{IP_{mix} >> IP_1 + IP_2}$$

Where; IP_{mix}= Induction period of biodiesel using binary mixture; IP_1 = Induction period of biodiesel with antioxidant1; IP_2 = Induction period of biodiesel with antioxidant 2.

The % synergism can be calculated by the formula developed by Shahidi et al. [21].

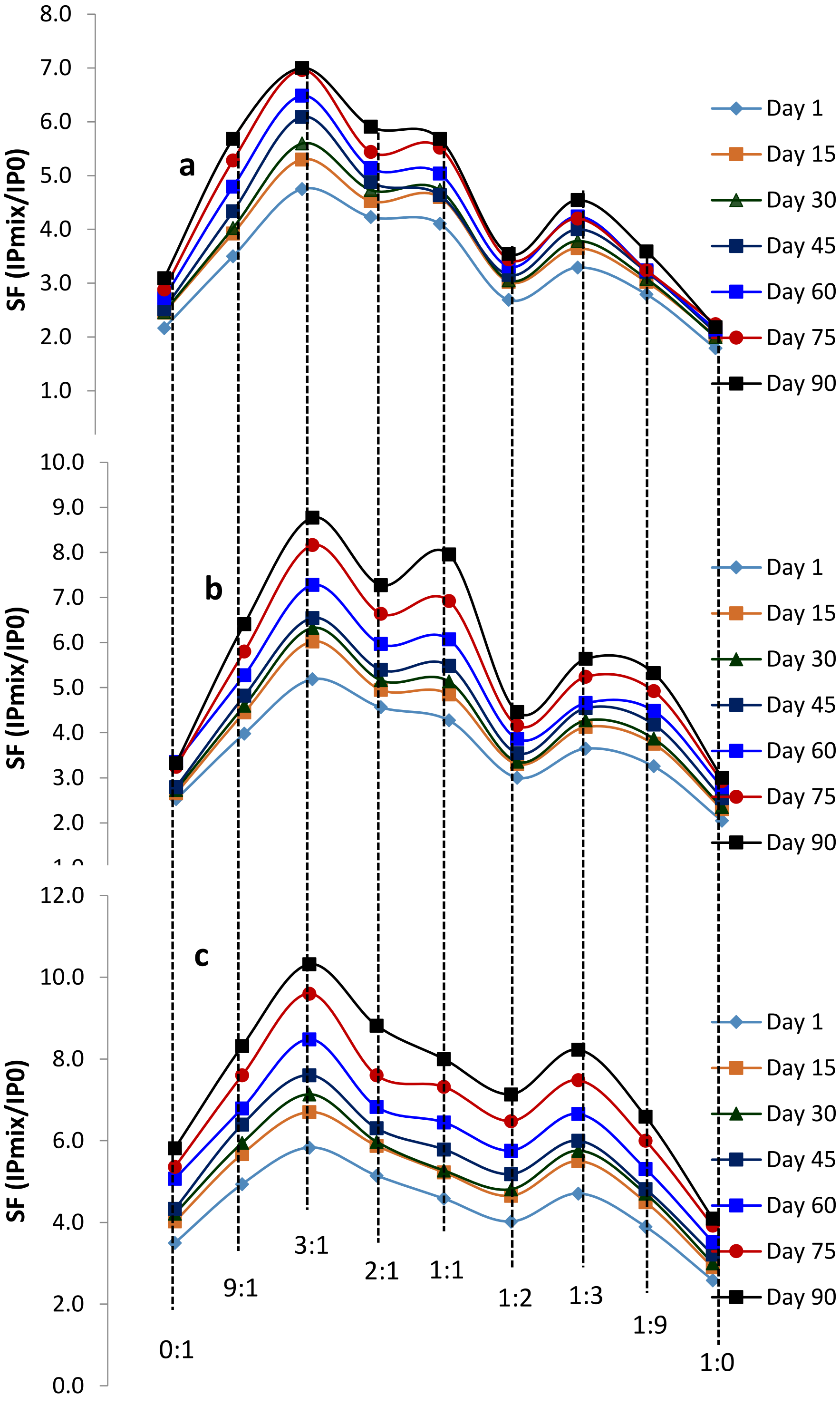

Fig. 4.28 Variation in stabilization factor for Jatropha biodiesel with a) 500; b) 600 and c) 700 ppm total additive (TBHQ:PY) concentration in different ratios

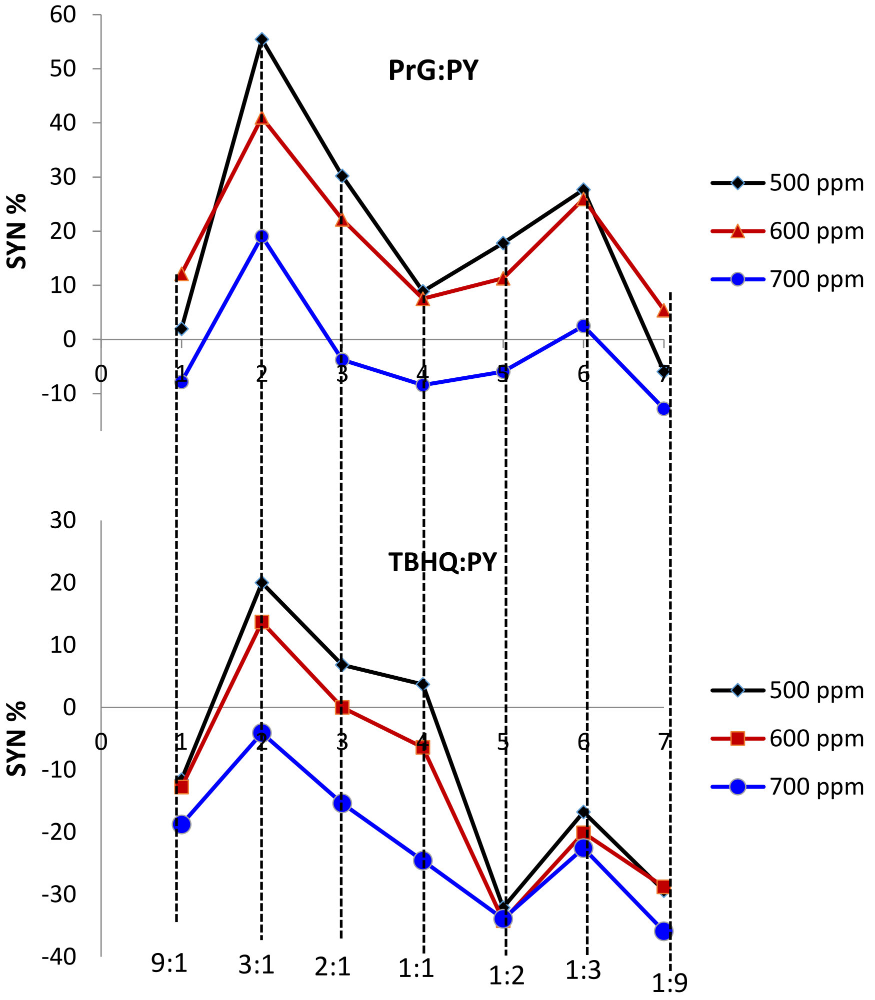

Fig. 4.29 Variation in %SYN of binary mixtures of antioxidants for oxidation stability of Jatropha biodiesel

$$\% \mathrm{SYN} = [\mathrm{IP}_{mix} - (\mathrm{IP}_1 + \mathrm{IP}_2)]/(\mathrm{IP}_1 + \mathrm{IP}_2)] \times 100\%$$

Antioxidant synergy was also calculated based on collected data of induction period. It was observed that the induction period and stabilization factor have shown dependency on binary antioxidant concentration, but the same was not found true for antioxidant synergy. Lower concentration of binary antioxidants has generally shown +ve antioxidant synergy while the –ve antioxidant synergy was observed with higher concentrations. This may be because of the saturation of biodiesel with antioxidants and/or dissolution solid phase of binary antioxidant mixture with biodiesel [22]. Fig. 4.29 represents the %SYN shown by the different additive proportions and binary concentrations of PY:PrG and PY:TBHQ. It is clear from Fig. 4.29 that 500 ppm of 1:3 and 3:1 weight ratios of PY:PrG have shown maximum % SYN of 55.4% and 27.7% respectively; while higher concentrations of PY:PrG in similar proportions resulted maximum %SYN of 41% and 25.94 % (for 600 ppm); and 19.06% and 2.5% (for 700 ppm). It was also observed that for 700 ppm of PY:PrG all binary combinations except 1:3 and 3:1 weight ratios have shown –ve synergy. Whereas for binary combination TBHQ:PY, positive synergy was shown only by 3:1 (20.0%), 2:1 (6.84%), 1:1 (3.68%) weight ratios with 500 ppm; and 3:1 (13.69%) weight ratio with 600 ppmonly. While other TBHQ:PY binary combinations of 500 and 600 ppm including all binary combinations of 700 ppm were resulted in –ve synergy.

4.8.Study for Karanja biodiesel

The study was further extended to explore the effect of binary antioxidants on the oxidation stability of Karanja biodiesel having different fatty acid composition than Jatropha biodiesel (Table 3.1 chapter 3). Based on previous study [23] it was found that, besides, PY and PrG the third most effective antioxidant was BHA for Karanja biodiesel. Likewise for Jatropha biodiesel; the antioxidant combination of PrG:PY showed a better improvement in IP of Karanja biodiesel than PrG and PY alone (Fig.4.30). It is clear from Fig.4.30 that for Karanja biodiesel the highest IPs of 27.8 hr, 29.2 hr and 31.6 hrwere achieved by using 500, 600 and 700 ppm of 3:1 weight ratios of PrG: PY (Fig. 4.30a, 4.30b and 4.30c). Further, Karanja biodiesel was blended with similar concentrations (500, 600 and 700 ppm) of binary mixture of PY:BHA at similar weight proportions. The results are summarized in Fig. 4.31 (a, b and c).

Though, the PY:BHA combination also improved the IP of Karanja biodiesel in comparison with PY and BHA alone, but it was not found as effective as PrG:PY and TBHQ:PY.It can be attributed from the results that the highest IP of 14.4hr, 16.1 hr and 19.1 hr were obtained with 500, 600 and 700 ppm of 3:1 weight ratios of PY:BHA respectively. As stated previously, a gradual decrease in IP was also observed for binary combination of PY:BHA. Both, PY:PrG and PY:BHA have shown good stabilization factor for Karanja biodiesel when used in difference proportions under study (Fig. 4.32 and 4.33).

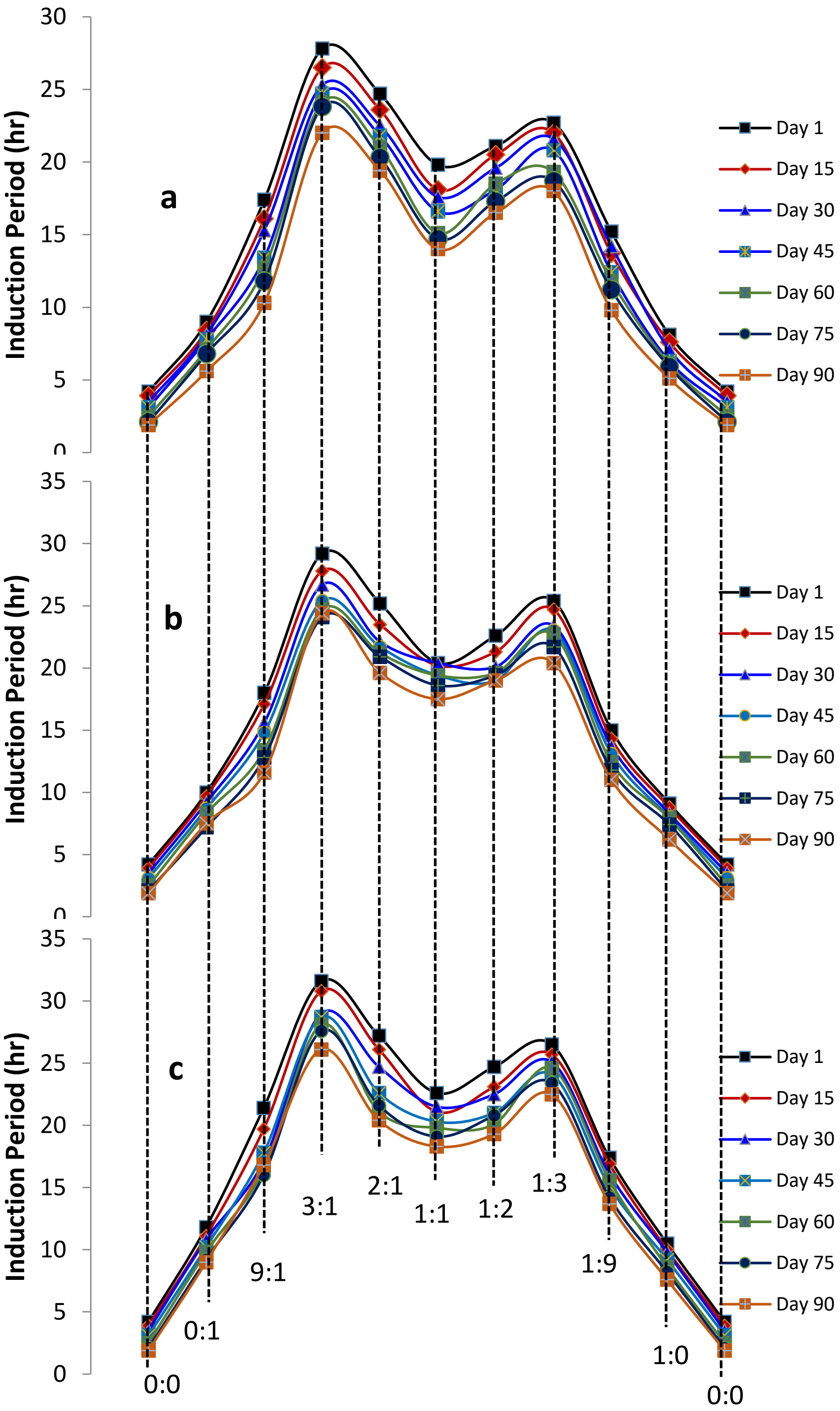

Fig. 4.30: Variation in Induction period for Karanja biodiesel with a) 500; b) 600 and c) 700 ppm total additive (PrG:PY) concentration in different ratios

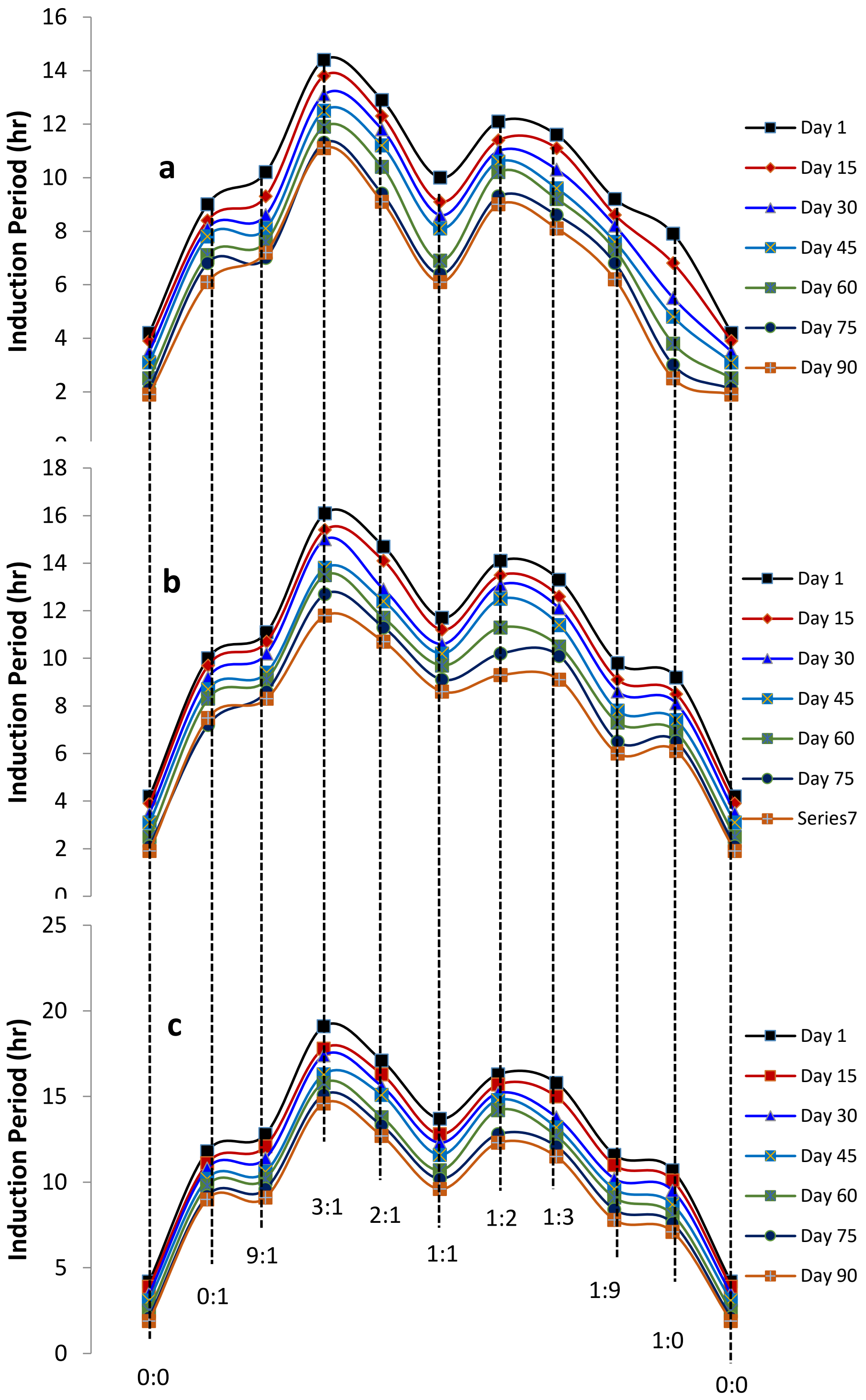

Fig. 4.31: Variation in Induction period for Karanja biodiesel with a) 500; b) 600 and c) 700 ppm total additive (BHA:PY) concentration in different ratios

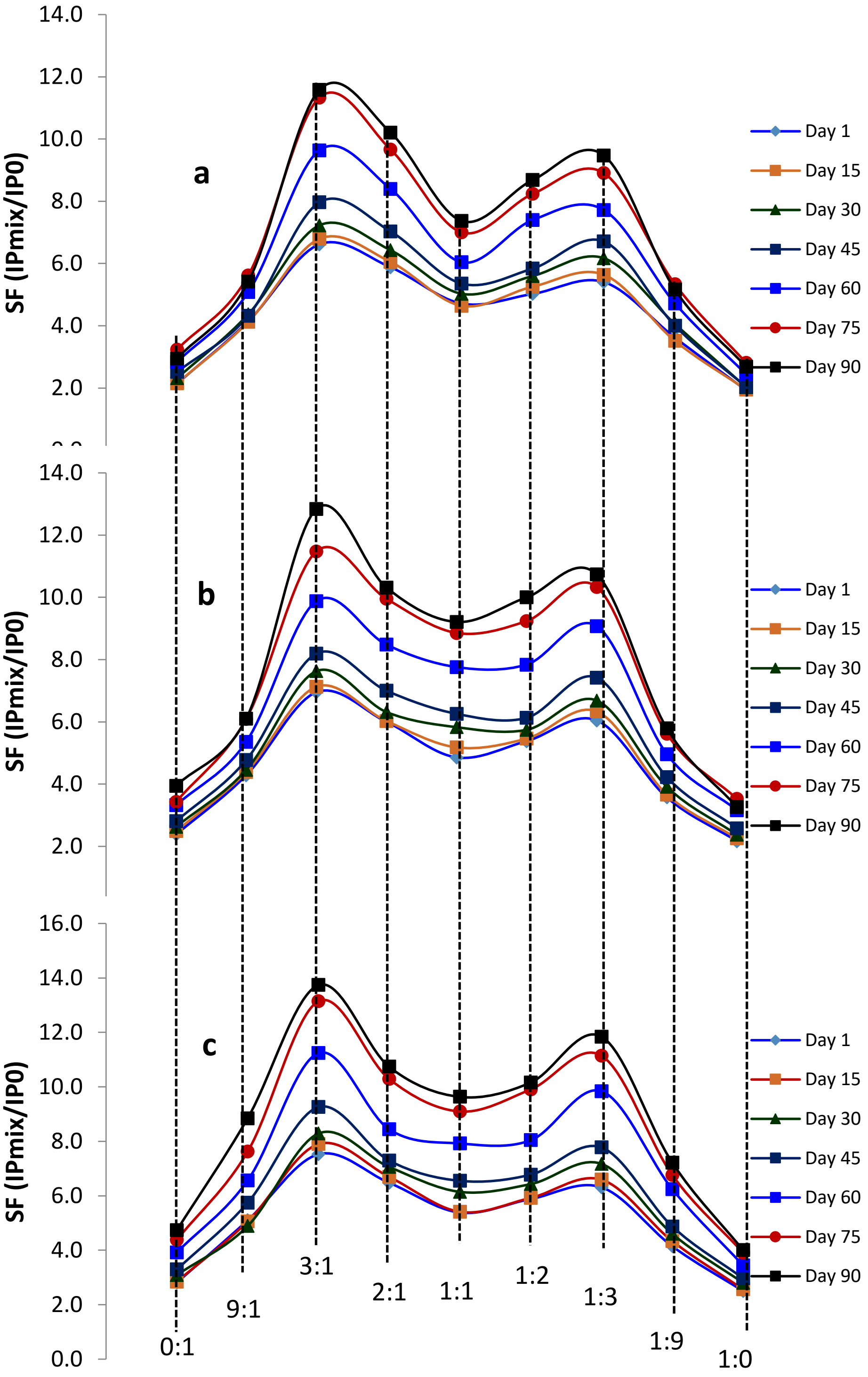

Fig. 4.32: Variation in stabilization factor for Karanja biodiesel with a) 500; b) 600 and c) 700 ppm total additive (PrG:PY) concentration in different ratios

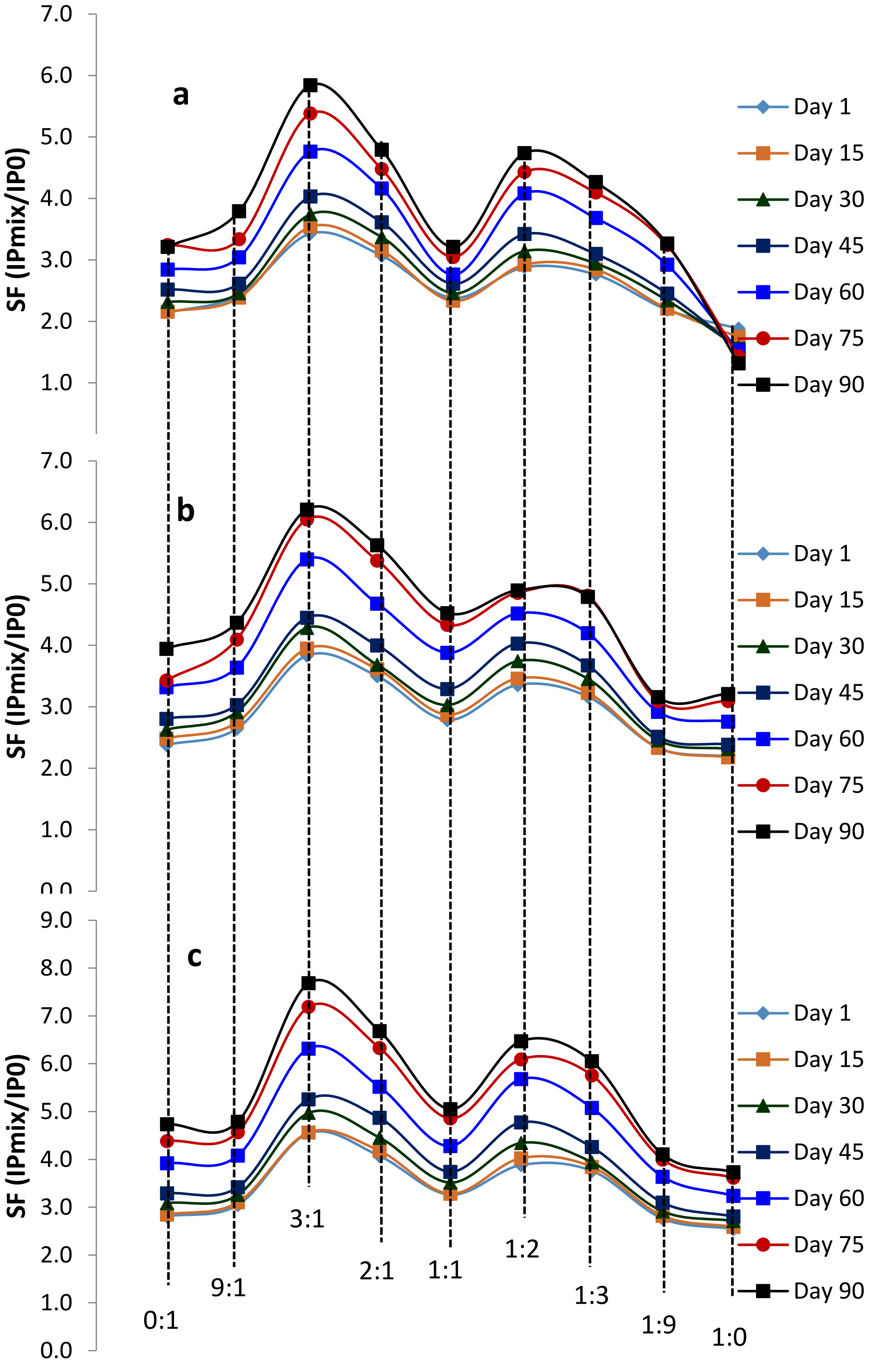

Fig. 4.33: Variation in stabilization factor for Karanja biodiesel with a) 500; b) 600 and c) 700 ppm total additive (BHA:PY) concentration in different ratios

All binary proportions of PY:PrG at all concentrations have shown more stabilization power in comparison to that when they were usedfor Jatropha biodiesel (Fig. 4.32). However, the PY:BHA combination has shown less effectiveness in comparison to PY:PrG and PY:TBHQ in general.

Finally the antioxidants synergy (%SYN) of binary combinations of PY:PrG and PY:BHA was also calculated for stabilization of Karanja biodiesel. The results are summarized in Fig. 4.34. It is clear from Fig. 4.34, in contrast of Jatropha biodiesel, the binary combination of PY:PrG exhibited more positive synergy when blended with Karanja biodiesel. All proportions of PY:PrG with 500 ppm produced positive synergy, except 9:1 (% SYN -11.1%) weight ratio of PY:PrG. The 500 ppm 3:1 PrG:PY showed the maximum positive synergy (62.6%) followed by the 2:1 (44.4%), 1:3 (32.7%) and 1:2 (23.39%) weight ratios of PrG:PY. Similar trends of positive synergy were observed with binary mixture of 600 ppm at 3:1 (52.9%), 1:3 (32.9%), 2:1 (31.9%) 1:2 (18.3%); and 700 ppm 3:1 (41.7%), 2:1 (21.9%), 1:3 (18.8%), 1:2 (10.8%) weight ratios of PrG:PY. However, PY:BHA binary combination resulted in –ve synergy with all concentrations of antioxidants.

In general with the present study it was observed that the order of effectiveness of binary combination of the antioxidants PrG, TBHQ and BHA with primary antioxidant PY was PrG:PY>TBHQ:PY>BHA:PY. Primary antioxidant (PY) acts as free radical scavenger that inhibits the oxidation [24-33]. PY donate H radical to the free radicals which were generated in fatty acid chain due to auto-oxidation and thus inhibit the rate of oxidation. The resulting antioxidant free radical was stabilized by conjugation of aromatic ring as well as hydrogen bonding with adjacent hydroxy group [34]. This radical can react again with other fatty acid free radicals and can further contribute to inhibit the oxidation. In a binary combination of antioxidant, the primary antioxidant acts as hydrogen radical donor for fatty acid free radical to inhibit the oxidation process; at the same time the other partner supplies the hydrogen radical to regenerate it. Thus, the cyclic process continue till the secondary antioxidant get consumed completely [24].

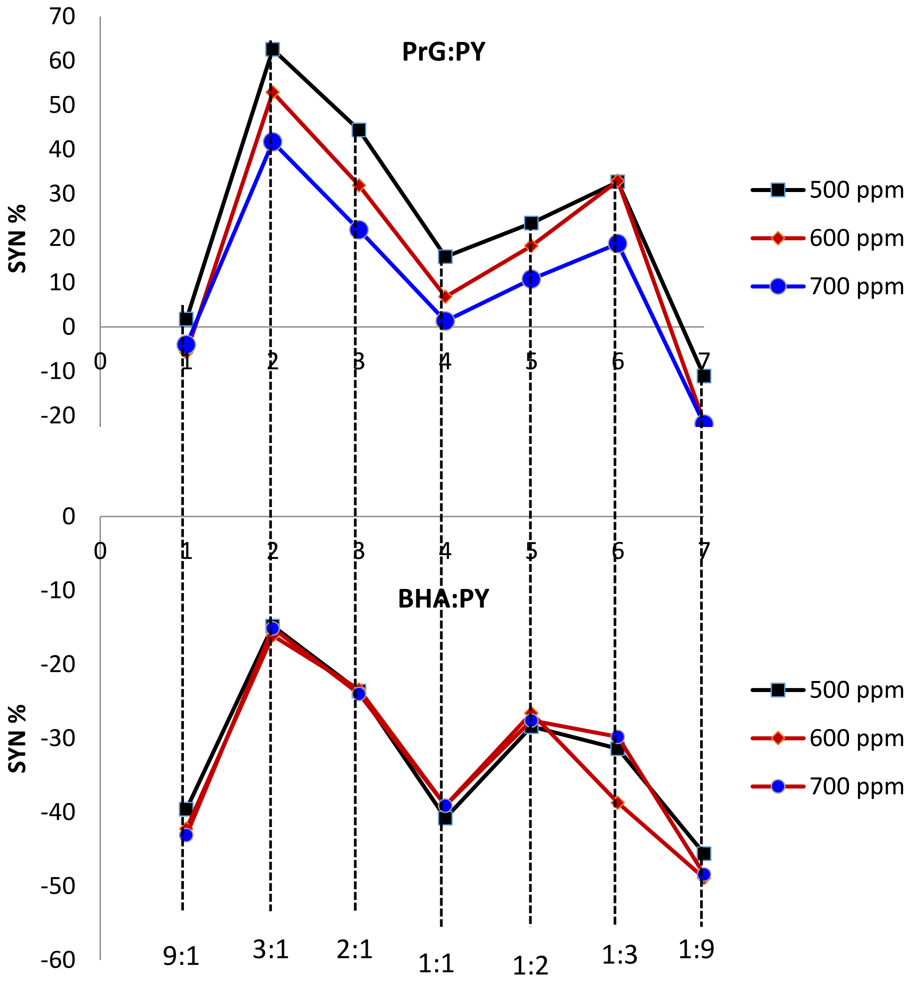

Fig. 4.34 Variation in %SYN of binary mixtures of antioxidants for oxidation stability of Karanja biodiesel

It may also possible that during inhibition process, the primary and secondary antioxidants can combine together and generate a heterodimer which again can act as another antioxidant since the heterodimer contains active hydroxy group [15]. Therefore, binary antioxidants exhibit much better antioxidant behavior than the individual antioxidants. Hydrogen radical donation ability of secondary antioxidants (PrG, TBHQ and BHA) depends on the stabilization of oxy free radical generated. Since the electron withdrawing groups on aromatic structure generally better stabilize the radical when compared to electron donating groups. The oxy radical of PrGcan be stabilized through *ortho*-quinone formation as well as by electron withdrawing carbonyl group at *para* position. ThusPrG showed a good synergy with PY. The TBHQ stabilizes respective hydroxy free radical through conversion of its hydroquinone form to quinone form. However, BHA which has more electron donating group –OMe at *para* position, comparatively less stabilizes the generated oxy radical. Hence the order of effective hydrogen radical donation to primary antioxidant can be considered as PrG>TBHQ>BHA. From the above discussion it was observed that like other properties, antioxidant synergy is also feedstock dependent. Similar trends are reported by K. Y. Simon Ng et al. It was also observed that with the four commercial antioxidants (PY, PrG, TBHQ and BHA) at equal concentrations, the IPs, stabilization factor and antioxidant synergy with 1:3 ratios of PY:PrG and PY:TBHQ in both Jatropha and Karanja biodiesels were maximum. However, in general, all binary formulations studied have shown better improvement in IPs, stabilization factor and antioxidant synergy in comparison with the individual antioxidants.

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Chapter 5: Summary and Conclusions

This study investigated the synthesis of biodiesel using homogenous and heterogeneous catalyst. In addition, this investigation also studied effectiveness of various antioxidants like Butylated hydroxy anisole (BHA), Butylated hydroxy toluene (BHT), Pyrogallol (PL), Propyl-gallate (PG), tert-Butylhydroxyquinone (TBHQ) and Diphenylamine (DPA) to improve the oxidative stability ofjatropha oil and karanja oil based biodiesel at the varying concentrations between 300, 400and 500 ppm. Besides, the effect of mixture of two antioxidant (500, 600 and 700 ppm) on storage stability of kranja and jatropha biodiesel were also examined. The conclusion derived from the study are given below:

- Biodiesel is prepared from homogenous (KOH) and heterogeneous (CaO(cesp)) catalyst. The heterogeneous catalyst CaO(cesp) was prepared and modified by metal impregnation. The effectiveness of different Ca based mixed metal oxides (CaO-ZnO, CaO-MnO_2, CaO-Fe_2O_3 and CaO-Al_2O_3) for methanolysis of Jatropha and Karanja oils, was studied. Higher surface areas of the catalysts were observed when they calcined at 900°C and therefore have shown the higher catalytic activity. Metal oxide impregnated catalysts have shown better activity in comparison to that of neat CaO(cesp). The ZnO-CaO(cesp) catalyst was found to be the best among all. The biodiesel yield was not much affected by the increase in optimized catalyst loading, reaction temperature and methanol:oil molar ratio. The catalyst has shown good reusability. The biodiesels derived from Jatropha and Karanja oils have also shown good fuel characteristics which were under the limits prescribed by fuel standards (EN and ASTM). By using $CaO_{(cesp)}$ based mixed oxides reduced the catalyst cost and made the process more economic and also more environmental benign.

- *Jatropha* biodiesel was blended with diesel obtained from the retail outlets of three different Oil companies in northern India, and the effectiveness of six antioxidants on the storage stability (oxidation stability, density and viscosity) of these blends were studied over a period of 90 days. B10, B15, B20 and B25 diesel biodiesel blends were tested in present study. The experimental results revealed that PL, PG, and TBHQ were most effective in neat biodiesel as well as its diesel blends, whereas BHA, BHT and DPA were found less effective. It was also observed that with increasing the concentration of biodiesel the oxidation stability decreases. The increase in density and viscosity of diesel biodiesel blends revealed that storage stability can be affected by the storage condition and time. Study showed that the tested physico-chemical properties of blended fuel were not consistent. These variations may be due the composition of biodiesel, nature of antioxidant additives, and quality of diesel fuel. However, further study is required to understand the role of the diesel fuel in the oxidation stability of diesel biodiesel blends, especially when there is a difference in the physical properties of the diesel fuel used for the blend preparation.
- Karanja biodiesel was blended with diesel obtained from the retail outlets of three different Oil companies in northern India, and the effectiveness of five

antioxidants on the storage stability (oxidation stability, density and kinematic viscosity) of these blends were studied over a period of 90 days. The B5, B10, B15, B20, B25 and B 40 diesel biodiesel blends were tested under the present study. The experimental results revealed that the 500 ppm dosages of PY, PrG, and BHT were most effective in neat biodiesel as well as its diesel blends. The neat biodiesel with 500 ppm of PY has shown the maximum stability (IP=15 hr). Except B40, all other blends with 500 ppmconcentration of PY could be stored up to 90 days duration. However, B5 blend with 500 ppm of PY was found to be the most stable among all. Regarding biodiesel blends it was observed that with increasing the biodiesel concentration the oxidation stability decreases. Also the increase in density and viscosity of diesel biodiesel blends revealed that storage stability can be affected by the storage condition and time, leading to induction times below the minimum specification limit (EN590) of 20 h after 5-6 weeks. Studies showed that the induction period of blended fuel were not consistent. These variations may be due the composition of biodiesel, nature of antioxidant additives, and quality of diesel fuel. Diesel with higher sulphur content was found the most suitable for blend preparation in respect of oxidation stability. However, further study is required to understand the role of the diesel fuel in the oxidation stability of diesel biodiesel blends, especially when there is a difference in the physical properties of the diesel fuel used for the blend preparation.

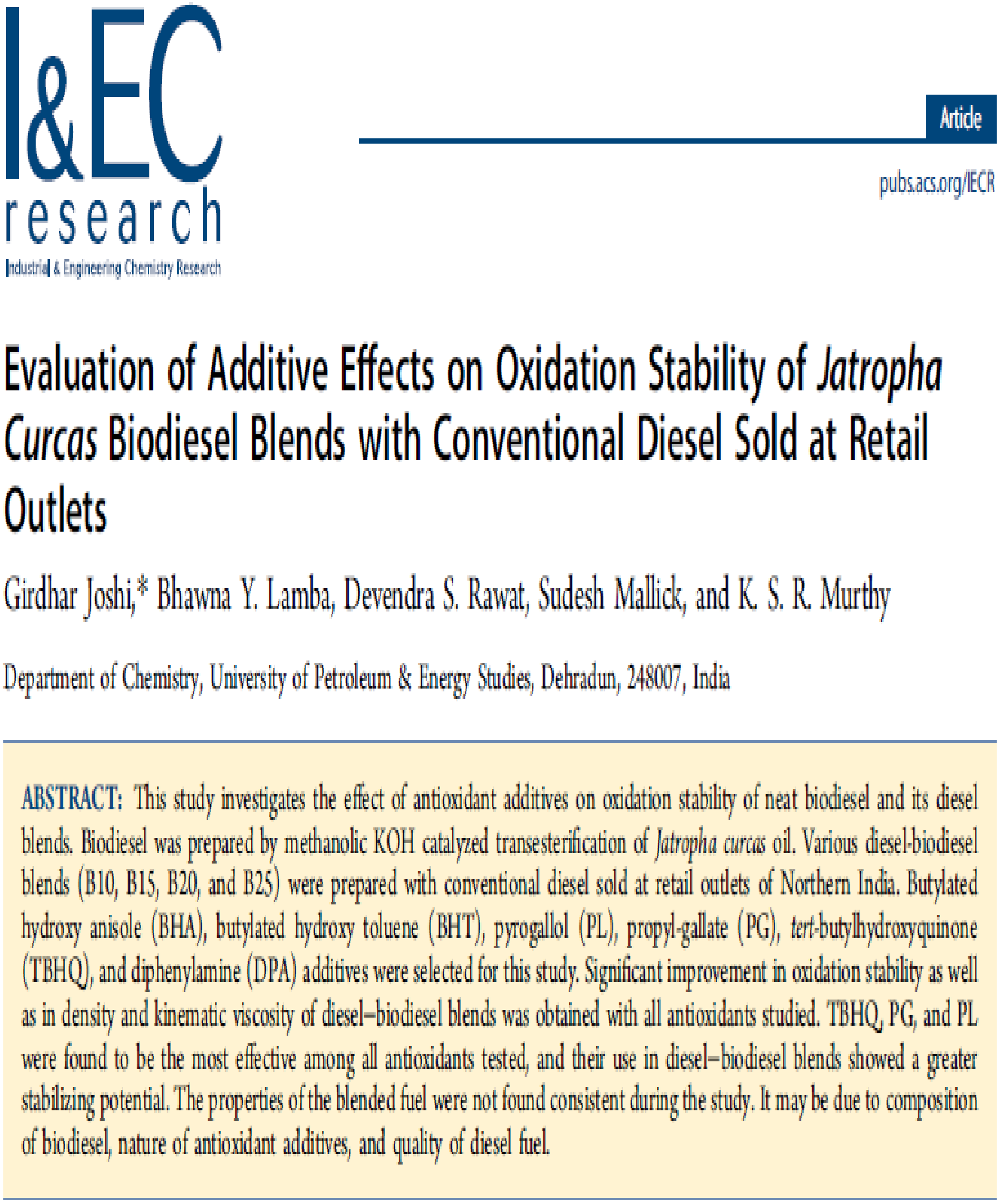
- The effectiveness of 1:3 weight ratios of antioxidants on their synergy, stabilization factor and oxidation stability determination for Jatropha and

Karanja biodiesels was studied over 90 days period of indoor storage. Antioxidants synergy was investigated by using 500, 600 and 700 ppm of additives at 9:1, 3:1, 2:1, 1:1, 1:2, 1:3, 1:9 weight ratios of Pyrogallol:Propylgallate (PY:PrG), Pyrogallol:tert-butyl hydroquinone (PY:TBHQ) and Pyrogallol:Butylatedhydroxyanisole (PY:BHA). It was observed that oxidation stability and stabilization factor generally increases with increase in antioxidant dosage; but the antioxidant synergy decreases with increase in concentration of binary antioxidants. This may be because of the saturation and/or dissolution of solid binary antioxidant mixture with biodiesel. The Binary combinations of 500 ppm concentration at 1:3 and 3:1 weight ratios of PY:PrG for both Jatropha and Karanja biodiesels; and PY:TBHQ for Jatropha biodiesel has shown maximum effectiveness in all aspects *i.e.* oxidation stability, stabilization factor and antioxidant synergy. Probably because of the best molecular interaction was achieved with 1:3 ratios of antioxidants, which could be able to regenerate the primary antioxidant more effectively. Further research is required to understand the reason behind the most effective synergy between antioxidants at 1:3 weight ratios. From the present study, it can also be concluded that 500 ppm of 1:3 and/or 3:1 binary formulations of antioxidants could be a good choice for long-term storage of Jatropha and Karanja biodiesel.

Recommendations for further research

The utilization of binary antioxidants not also shown great improvement in storage stability of Jatropha and Karanjabiodiesel. Also, play a major role in reduction of cost of antioxidants used. However, the use of ternary oxidant for improvement of storage stability may be studied in future. In addition, there is also need to see the effect of binary and ternaryantioxidants on the mixture of biodiesel blended with diesel for long term.

List of publications



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Evaluation of Additive Effects on Oxidation Stability of *Jatropha Curcas* Biodiesel Blends with Conventional Diesel Sold at Retail Outlets

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ABSTRACT: This study investigates the effect of antioxidant additives on oxidation stability of neat biodiesel and its diesel blends. Biodiesel was prepared by methanolic KOH catalyzed transesterification of *Jatropha curcas* oil. Various diesel-biodiesel blends (B10, B15, B20, and B25) were prepared with conventional diesel sold at retail outlets of Northern India. Butylated hydroxy anisole (BHA), butylated hydroxy toluene (BHT), pyrogallol (PL), propyl-gallate (PG), *tert*-butylhydroxyquinone (TBHQ), and diphenylamine (DPA) additives were selected for this study. Significant improvement in oxidation stability as well as in density and kinematic viscosity of diesel–biodiesel blends was obtained with all antioxidants studied. TBHQ, PG, and PL were found to be the most effective among all antioxidants tested, and their use in diesel–biodiesel blends showed a greater stabilizing potential. The properties of the blended fuel were not found consistent during the study. It may be due to composition of biodiesel, nature of antioxidant additives, and quality of diesel fuel.

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Effect of antioxidants on physico-chemical properties of EURO-III HSD (high speed diesel) and *Jatropha* biodiesel blends

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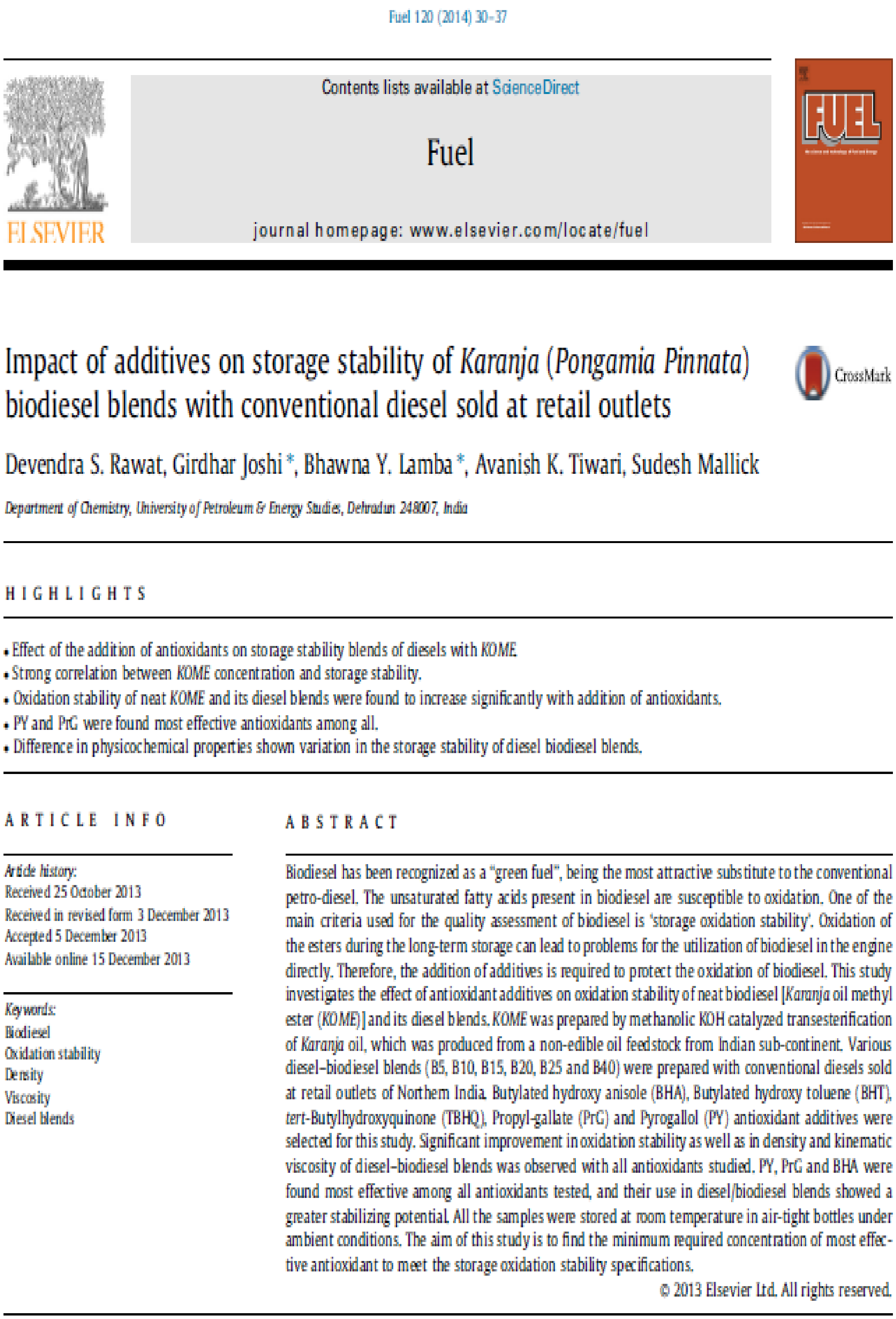
ABSTRACT

The stability of fuel during storage is an important consideration for bulk users. Storage instability leads to solids formation which can plug nozzles and filters. This work focuses on the effect of the addition of antioxidants on **EURO-III and *Jatropha* Biodiesel blends**. The changes in physico-chemical properties were observed for **these blends** after addition of antioxidants. BHA (butylated hydroxy anisole), BHT (butylatedhydroxy toluene), TBHQ (tert-butylhydroxyquinone) and DPA (diphenylamine) were the antioxidants used for this study. The rate of change in kinematic viscosity and density of **EURO-III-*Jatropha* Biodiesel blends** with antioxidants were found to be less as compared to the neat samples. The oxidation stability of the neat samples, after addition of antioxidants, was found to increase significantly. It was also observed that addition of antioxidant significantly improved the oxidation stability of biodiesel-diesel fuel blends however in some case may act as pro-oxidants. The results showed that the addition of an antioxidant to diesel fuel blends influenced beneficially most of the important fuel properties.



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Impact of additives on storage stability of *Karanja* (*Pongamia Pinnata*) biodiesel blends with conventional diesel sold at retail outlets

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HIGHLIGHTS

- Effect of the addition of antioxidants on storage stability blends of diesels with *KOME*.
- Strong correlation between *KOME* concentration and storage stability.
- Oxidation stability of neat *KOME* and its diesel blends were found to increase significantly with addition of antioxidants.
- PY and PrG were found most effective antioxidants among all.
- Difference in physicochemical properties shown variation in the storage stability of diesel biodiesel blends.

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ABSTRACT

Biodiesel has been recognized as a "green fuel", being the most attractive substitute to the conventional petro-diesel. The unsaturated fatty acids present in biodiesel are susceptible to oxidation. One of the main criteria used for the quality assessment of biodiesel is 'storage oxidation stability'. Oxidation of the esters during the long-term storage can lead to problems for the utilization of biodiesel in the engine directly. Therefore, the addition of additives is required to protect the oxidation of biodiesel. This study investigates the effect of antioxidant additives on oxidation stability of neat biodiesel [*Karanja* oil methyl ester (*KOME*)] and its diesel blends. *KOME* was prepared by methanolic KOH catalyzed transesterification of *Karanja* oil, which was produced from a non-edible oil feedstock from Indian sub-continent. Various diesel–biodiesel blends (B5, B10, B15, B20, B25 and B40) were prepared with conventional diesels sold at retail outlets of Northern India. Butylated hydroxy anisole (BHA), Butylated hydroxy toluene (BHT), *tert*-Butylhydroxyquinone (TBHQ), Propyl-gallate (PrG) and Pyrogallol (PY) antioxidant additives were selected for this study. Significant improvement in oxidation stability as well as in density and kinematic viscosity of diesel–biodiesel blends was observed with all antioxidants studied. PY, PrG and BHA were found most effective among all antioxidants tested, and their use in diesel/biodiesel blends showed a greater stabilizing potential. All the samples were stored at room temperature in air-tight bottles under ambient conditions. The aim of this study is to find the minimum required concentration of most effective antioxidant to meet the storage oxidation stability specifications.

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Transesterification of Jatropha and Karanja oils by using waste egg shell derived calcium based mixed metal oxides

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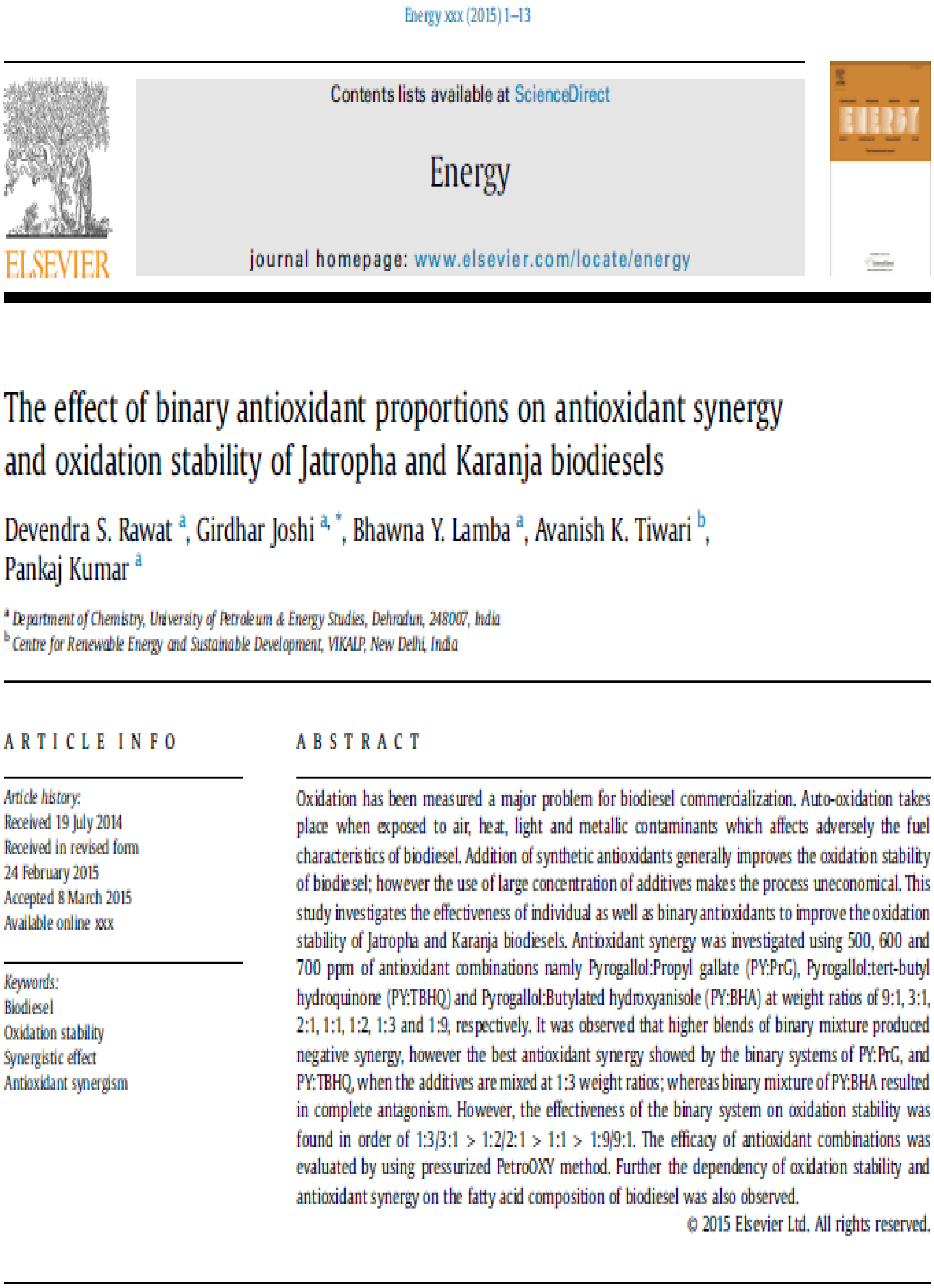
ABSTRACT

Solid base heterogeneous catalysts are one of the promising materials for the transesterification of vegetable oils because these catalysts are generally more reactive than solid acid catalysts which require very severe operating conditions. Calcium oxide has shown good catalytic activity due to its high basicity which is required for transesterification of triacylglycerides (TAGs). In the present study, the transesterification of non-edible, high free fatty acid containing Jatropha and Karanja oils was studied by using waste chicken egg shell derived calcium (i.e. CaO(cesp)) based mixed metal oxides (M-CaO; M = ZnO, MnO_2, Fe_2O_3 and Al_2O_3) as heterogeneous catalyst. A comparison was also made on the catalytic performance of these prepared catalysts. The catalyst characterizations were done by XRD, SEM, TGA, FT-IR and BET techniques. The effectiveness of the catalysts was highly influenced by the calcination temperature. ZnO–CaO(cesp) catalyst was found to be the most efficient catalyst among all. The maximum conversion for the transesterification of Jatropha and Karanja oils were achieved using 5 wt% catalyst, 65 °C temperature and 12:1 methanol/oil ratio. The catalyst could be re-used effectively during four cycles. Use of the CaO(cesp) based mixed oxides made the process more environmental benign and economical. The biodiesel prepared has shown good fuel characteristics as per EN, ASTM and IS standards.



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The effect of binary antioxidant proportions on antioxidant synergy and oxidation stability of Jatropha and Karanja biodiesels

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ABSTRACT

Oxidation has been measured a major problem for biodiesel commercialization. Auto-oxidation takes place when exposed to air, heat, light and metallic contaminants which affects adversely the fuel characteristics of biodiesel. Addition of synthetic antioxidants generally improves the oxidation stability of biodiesel; however the use of large concentration of additives makes the process uneconomical. This study investigates the effectiveness of individual as well as binary antioxidants to improve the oxidation stability of Jatropha and Karanja biodiesels. Antioxidant synergy was investigated using 500, 600 and 700 ppm of antioxidant combinations namly Pyrogallol:Propyl gallate (PY:PrG), Pyrogallol:tert-butyl hydroquinone (PY:TBHQ) and Pyrogallol:Butylated hydroxyanisole (PY:BHA) at weight ratios of 9:1, 3:1, 2:1, 1:1, 1:2, 1:3 and 1:9, respectively. It was observed that higher blends of binary mixture produced negative synergy, however the best antioxidant synergy showed by the binary systems of PY:PrG, and PY:TBHQ, when the additives are mixed at 1:3 weight ratios; whereas binary mixture of PY:BHA resulted in complete antagonism. However, the effectiveness of the binary system on oxidation stability was found in order of 1:3/3:1 > 1:2/2:1 > 1:1 > 1:9/9:1. The efficacy of antioxidant combinations was evaluated by using pressurized PetroOXY method. Further the dependency of oxidation stability and antioxidant synergy on the fatty acid composition of biodiesel was also observed.

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Microwave enhanced alcoholysis of non-edible (algal, jatropha and pongamia) oils using chemically activated egg shell derived CaO as heterogeneous catalyst

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HIGHLIGHTS

- Microwave enhanced alcoholysis of algal, jatropha and pongamia oils were achieved.
- Chemically activated waste egg shell derived CaO was used as heterogeneous catalyst.
- Effect of aliphatic chain of alcohol on biodiesel yields was observed.
- ZnO-CaO(cesp) was found the best among all.
- ZnO-CaO(cesp) has shown good reusability up to 4 cycles without significant loss of catalytic activity.

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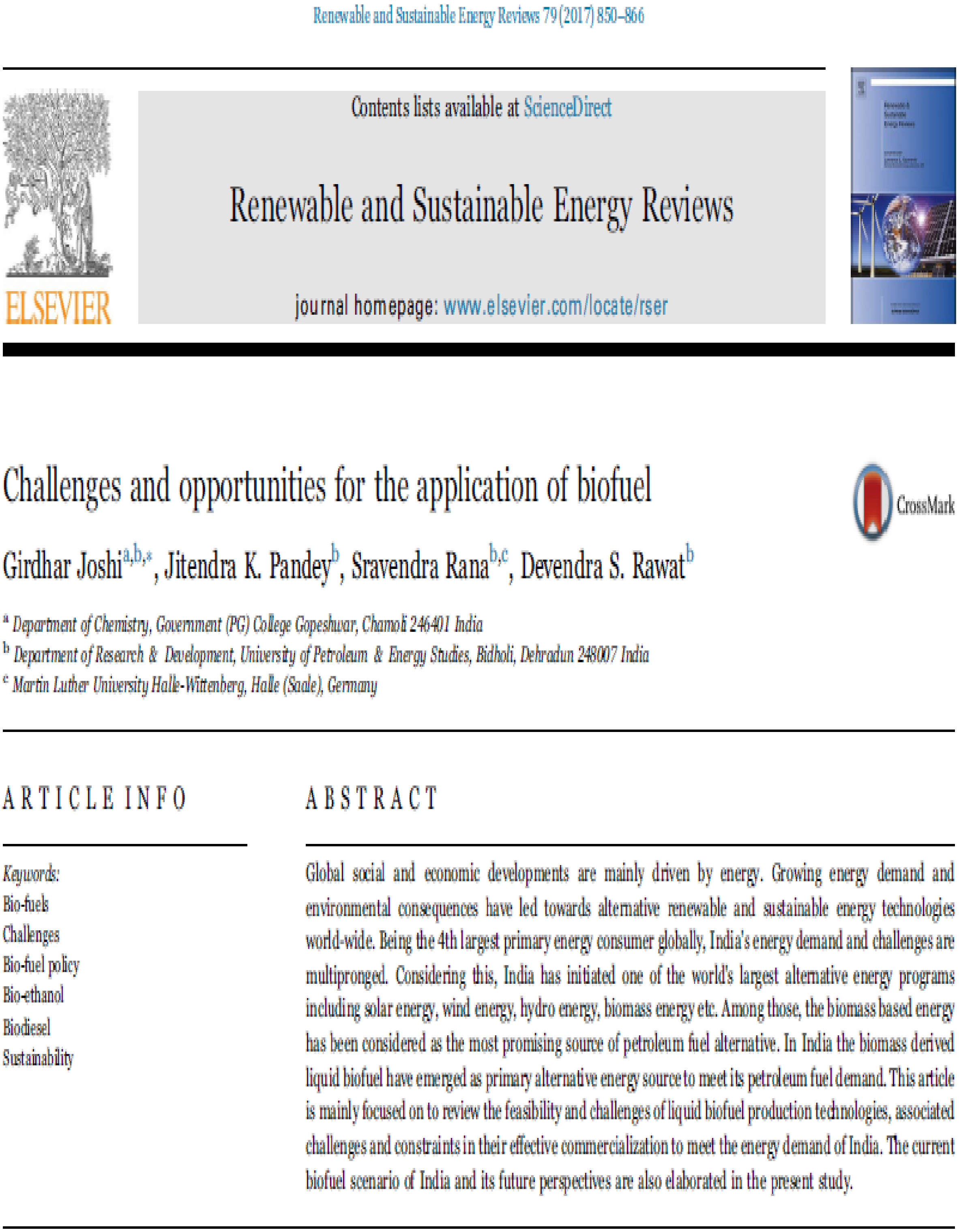
ABSTRACT

Microwave enhanced fast and efficient alcoholysis (methanolysis and ethanolysis) of non-edible oils (*algal, jatropha* and *pongamia*) is achieved using chemically activated waste egg shell derived CaO (i.e. CaO(cesp)) as heterogeneous catalyst. CaO(cesp) was extracted from waste chicken egg shell and further activated chemically by supporting transition metal oxide. The maximum conversion was achieved using 3 wt% catalysts under 700 W microwave irradiation and 10:1 alcohol/oil ratio in 6 min. Alcoholysis using ZnO activated CaO(cesp) catalyst has shown higher reaction yields in comparison to other modified catalysts. Methanolysis has shown better biodiesel conversion in comparison to ethanolysis. The catalyst has shown longer lifetime and sustained activity after being used for four cycles. Due to more saturated fatty acid content; algal biodiesel has shown improved fuel properties in comparison to other biodiesels.



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Challenges and opportunities for the application of biofuel

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ABSTRACT

Global social and economic developments are mainly driven by energy. Growing energy demand and environmental consequences have led towards alternative renewable and sustainable energy technologies world-wide. Being the 4th largest primary energy consumer globally, India's energy demand and challenges are multipronged. Considering this, India has initiated one of the world's largest alternative energy programs including solar energy, wind energy, hydro energy, biomass energy etc. Among those, the biomass based energy has been considered as the most promising source of petroleum fuel alternative. In India the biomass derived liquid biofuel have emerged as primary alternative energy source to meet its petroleum fuel demand. This article is mainly focused on to review the feasibility and challenges of liquid biofuel production technologies, associated challenges and constraints in their effective commercialization to meet the energy demand of India. The current biofuel scenario of India and its future perspectives are also elaborated in the present study.

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Full Length Article

Algal biodiesel stabilization with lower concentration of 1:3 ratios of binary antioxidants – Key factors to achieve the best synergy for maximum stabilization

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ABSTRACT

Poor storage stability of biodiesel is considered a major problem for its commercialization. The use of commercial antioxidants has been proven very effective for biodiesel stabilization; hence these are frequently being used for long term storage of biodiesel. Moreover, in comparison to individual antioxidants, use of their binary combinations with their optimized concentrations could be more economical and highly effective to improve the storage behavior of biodiesel. In present report the effectiveness of lower concentration of binary antioxidants on the oxidation stability of algal biodiesel was studied. The 500, 600 and 700 ppm concentrations of binary combinations of three antioxidants [*i.e.* Pyrogallol (PY); Propylgallate (PrG) and *tert*-butyl hydroquinone (TBHQ)], are prepared at weight ratios of 1:1, 1:2, 1:3 and 1:9 and vice-versa. Although, storage stability was increased with increase in antioxidant concentration; however, the best synergy was obtained with 1:3 ratios of binary antioxidants with 500 ppm concentration of binary antioxidants.

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ORIGINAL RESEARCH ARTICLE

Study of oxidation behavior of Jatropha oil methyl esters and Karanja oil methyl esters blends with EURO-IV high speed diesel

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Poor oxidation stability of methyl esters is the major problem associated with its worldwide acceptance. As per the standards EN 14214 and prEN16091; and ASTM-D 7545-09 the oxidation stability limit should be 20 h for the blends and 8 h for neat methyl ester. One approach for increasing resistance of fatty acid methyl ester derivatives against autoxidation is to treat them with oxidation inhibitors known as antioxidants. This study examines the effectiveness of five such commercial antioxidants [*viz. tert*-butylhydroquinone (TBHQ), butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PrG) and pyrogallol (PY)] on the storage stability of Jatropha methyl ester (JOME), Karanja methyl ester (KOME), and their 5%, 10%, 20% and 40% blends with low sulphur EURO-IV High speed Diesel (HSD) using Petrotest PetrOxymeter. The impact of the antioxidants strongly depends on the feed-stock used for biodiesel production. PY was found to be the most effective antioxidant for JOME and its EURO-IV blends; however, PrG has shown maximum effectiveness with KOME and its EURO-IV HSD blends. 500 ppm was found to be the most optimum concentration for both the antioxidants.