PRODUCTION, CHARACTERIZATION AND TESTING OF BIODIESEL FROM *TERMINALIA BELERICA* R. AND *SAPINDUS MUKOROSSI* G. OIL SEEDS AVAILABLE IN NORTH EAST INDIA

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

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APRIL, 2012

I dedicate this thesis to my parents Mrinal Kanti Chakraborty and Nanda Chakraborty whose love inspired me to complete this work successfully.

Maumita

DECLARATION

I do hereby declare that the thesis entitled "**Production, Characterization and Testing of Biodiesel from *Terminalia belerica* R. and *Sapindus mukorossi* G. oil seeds available in North East India**", being submitted to the Department of Energy, Tezpur University, is a record of original research work carried out by me. All sources of assistance have been assigned due acknowledgment. I also declare that neither this work as a whole nor a part of it has been submitted to any other University or Institute for any other degree, diploma or award.

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This is to certify that the matter embodied in the thesis entitled ***"Production, Characterization and Testing of Biodiesel from Terminalia belerica R. and Sapindus mukorossi G. oil seeds available in North East India"*** submitted by Maumita Chakraborty for the award of degree of Doctor of Philosophy of Tezpur University is a record of bona-fide research work carried out by her under my supervision and guidance. The results embodied in this thesis have not been submitted to any other University or Institute for the award of any degree or diploma.

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The committee recommends for the award of the degree of Doctor of Philosophy.

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ABSTRACT

There has been an increase in research activities on biofuel in recent times due to urgent requirement for a viable alternative to conventional petroleum fuel. There are several important research issues related to biodiesel which are varied in forms amongst the different countries. In some countries, like India, identification of new feedstock addressing food-fuel conflict has been a major area of emphasis. Government of India has formulated policy for growth of biodiesel from non-edible feedstocks. Search for such new feedstock is also an important area of National Bio-Fuel Policy of the government. With the limited available land resources, forest based tree species could be one of the sustainable sources for biodiesel feedstock in India. However, target oriented research is required to ascertain such possibility.

Objectives of the present study are (i) to identify some oil bearing tree seeds of Northeast India having potential for biodiesel production, (ii) to investigate the fuel properties of biodiesel produced from oils of selected species, (iii) to study the oxidation and storage stability of biodiesel obtained from oils of selected species and investigation of efficacy of some phenolic antioxidants and (iv) to investigate the engine performance and emission characteristics of CI engine fueled with biodiesel obtained from the oils of selected species.

Two forest origin oilseeds of *Terminalia belerica* R. and *Sapindus mukorossi* G. trees are selected for this study. Oil content (w/w% of kernels) of *Terminalia belerica* and *Sapindus mukorossi* are found as 43% and 39%, respectively. *Terminalia belerica* oil composes of 39.5% saturated fatty acid and 60.5% unsaturated fatty acid. Palmitic (32.8%), oleic (31.3%) and linoleic (28.8%) acids are dominant in *Terminalia belerica* oil. On the other hand, *Sapindus mukorossi* oil composes of 16.5% saturated and 83.5% unsaturated fatty acids. Oleic (58.4%), linolenic (17.1%) and arachidic (7.5%) acids are the major constituents of *Sapindus mukorossi* oil. Overall, fatty acid profiles of both the oils are found as suitable feedstock for biodiesel production.

Oil samples of both the oils are also characterized as per the standard procedure. Acid value of *Terminalia belerica* oil is found as 8.01 mgKOH/g, which is less than the acid value of *Sapindus mukorossi* (15.6 mgKOH/g) oil. There are also differences in characteristics of these two oils which are expected to reflect in varying fuel properties of the resultant biodiesel. Moreover, the transesterification requirement would also vary between *Terminalia belerica* and *Sapindus mukorossi*, as they have varying level of acid values. However, overall results of vegetable oil characterization show both of these seed oils as prospective feedstock for biodiesel production.

Alkaline catalytic transesterification process is chosen for production of biodiesel from *Terminalia belerica* oil. A Molar ratio of 10:1 (alcohol: oil) and 1 wt% catalyst ($NaOCH_3$) concentration results 93% yield for *Terminalia belerica.* Two step transesterification is followed for *Sapindus mukorossi* oil as its acid value is higher. Conversion yield of 92.5% is obtained with 8:1 (alcohol: oil) and 1 wt% catalyst ($NaOCH_3$) concentration for *Sapindus mukorossi* oil. ^1H NMR and ^{13}C NMR spectral analyses are conducted to ensure production of biodiesel.

Standard experimental procedures are followed to investigate the fuel quality parameters (*viz.*, density, viscosity, calorific value, acid value, flash point, cloud point, pour point, ash content, carbon residue, copper strip corrosion, IBP/FBP, water content, sulphur content, cetane number, lubricity and oxidation stability) of biodiesels obtained from both the seed oils. Moreover, elemental analysis for determination of carbon, hydrogen and oxygen for both the biodiesel samples are also carried out. Overall, almost all the above fuel quality parameters for both the biodiesels are found to confirm the existing biodiesel norms except sulphur content and oxidation stability.

Induction period (IP) is considered as an index for evaluation of oxidation stability of biodiesel in the present investigation. Efficacy of six phenolic antioxidants *viz.*, vitamin E (α-tocopherol), butylated hydroxyanisole (BHA), pyrogallol (PY), propyl gallate (PG), tert-butylhydroxytoluene (BHT) and tert-butylhydroxyquinone (TBHQ) and their concentrations (*viz.*, 100 ppm, 500 ppm, 1000 ppm, and 1500 ppm) are investigated for freshly prepared samples of biodiesel on the basis of IP. Overall, the efficacy of antioxidants are summarized as, PG>PY>TBHQ>BHT>BHA>α-tocopherol for *Terminalia belerica* biodiesel and PG>PY>BHT>TBHQ>BHA>α-tocopherol for *Sapindus mukorossi* biodiesel. Oxidation stability of biodiesel (B100) and its different blends (B5, B10, B20 and B30) are also assessed with and without antioxidant additives up to a storage period of 12 weeks considering three specific antioxidants *viz*., PG, TBHQ and BHT, with a concentration of 1000 ppm. For freshly prepared biodiesel blends, the activities of antioxidants are in the order of, PG>BHT>TBHQ for both the biodiesels.

The blended biodiesel (B5, B10 and B20) of both the types are tested in a 39 kW CI type test engine. Results of blended biodiesel are compared with the performance results of petro-diesel. Brake power, brake thermal efficiency and specific fuel consumptions are determined at some arbitrarily varying load conditions. Overall, acceptable performances are observed for both the types of biodiesel (*Terminalia belerica* and *Sapindus mukorossi*) up to 20% blending. Experiments are also performed to assess the engine exhaust emission of CO, NO_X and HC during engine operation fueled with blended biodiesel of both the types. It is found that with increase in biodiesel percentage in blends, the emission of CO and HC decreases for both the cases. However, increase in NO_X emission with biodiesel fuel is observed compared with diesel fuel.

Both the non-edible oil seeds are suitable feedstock for biodiesel production. The outcomes of this study would be useful to stimulate the growth of biodiesel based on the forest resources which otherwise remain unused. Entrepreneurial activities at nearby forest areas could be enhanced and this is important for the economically backward regions like North-Eastern India. Economic analysis and long term engine testing could not incorporate in the present study and suggested for future work.

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LIST OF ABBREVIATIONS

AOCS	American oil chemists' society
ASTM	American standard testing of material
BHA	Butylated hydroxyanisole
BHT	Butylated hydroxytoluene
BSFC	Brake specific fuel consumption
BTE	Beef tallow ester
BTE	Brake thermal efficiency
CCR	Conradson carbon residue
CFTRI	Central Food Technological Research Institute
CI	Compression ignition
CME	Canola methyl ester
CN	Cetane number
CO	Carbon mono-oxide
CO_2	Carbon di-oxide
CV	Calorific value
DI	Direct ignition
DPF	Distilled poultry fat
DSBO	Distilled soybean oil
DU	Degree of unsaturation
EN	European nations
FBP	Final boiling point
FFA	Free Fatty acid
FOME	Anchovy fish oil
GHG	Green house gas
h	Hour
HFRR	High frequency reciprocating rig
HSD	High sulphur diesel
IBP	Initial boiling point
IOC	Indian oil corporation
IP	Induction period

JCO	*Jatropha curcas* oil
KME	Karanja methyl ester
LME	Linseed methyl ester
MOME	Manketti oil methyl ester
MPa	Mega pascal
NE	North East
NEDFi	North Eastern Development Finance Corporation Ltd.
NMR	Nuclear magnetic resonance spectroscopy
NO_x	Oxides of Nitrogen
NRL	Numaligarh Refinery Ltd.
OOME	Okra oil methyl ester
OS	Oxidation stability
OT	Oxidation onset temperature
PAME	Palmitic acid methyl ester
PBD	Palm biodiesel
P-DSC	Pressurized differential scanning calorimetry
PG	Propyl gallate
PM	particulate matter
PME	Palm oil methyl ester
PoME	Pongamia methyl ester
PY	Pyrogallol
R & D	Research and development
RME	Rapeseed methyl ester
RPR	Reserve to production ratio
SF	Stabilization factor
SFC	Specific fuel consumption
SME	Sunflower methyl ester
SME	Soybean oil methyl ester
SO_X	Oxides of sulphur
TBHQ	Tert-butylhydroquinone
UFOME	Used frying oil methyl ester

CHAPTER 1

INTRODUCTION

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1.1 Need for alternative fuel

Petroleum has been a dominating fuel for the development of human civilization during the last 150 years. August 27, 1859 is considered as historically significant day for petroleum fuel when, for the first time, Edwin L. Drake in Pennsylvania became successful in drilling petroleum well[1, 2]. There have been lots of activities in research, industry and commerce for the promotion of this precious commodity during this one and half century, almost all over the World. In true sense, petroleum has affected and expedited the development of all the major sectors including industry and transport[3]. Besides energizing the industrial engines and automobiles, petroleum also becomes major source of chemicals for many industries. Till recent times, this naturally occurring commodity could be conveniently used for the prosperity and development of mankind. However, there have been serious threat and uncertainties of continuing with petroleum as a reliable fuel. Amongst the uncertainties, three major issues have compelled the modern world to search for a sustainable alternative fuel. These issues are (i) diminishing reserves against growing demand; (ii) uneven distribution leading to political conflict and (iii) emission of greenhouse gases related to combustion of fossil based petroleum fuel.

There have been many estimates of the reserve to production ratios (RPR) of petroleum fuel and all such estimates are alarming, indicating that the reserves will last for only few decades. There are regional variations of estimated RPR, but overall, the scenario is very gloomy. The reserve to production ratio for Central and South America is approximated to be around 94 years and for Middle-east, RPR is estimated as 82 years[4]. With the exponential increase in rate of production, the figures could come down further. Overall, it is estimated that with the current rate of production, world oil reserve will last approximately for about 46 years[4].

Non-uniform occurrence and distribution of petroleum reserves amongst the geographical regions have been considered as another issue resulting in serious conflict. It is estimated that Middle-east has the maximum share of petroleum reserve (about 102 thousand million tonnes) followed by South and Central America (34 thousand million tonnes) and Europe and Eurasia (19 thousand million tonnes)[4]. The uneven distribution of petroleum amongst the countries is viewed as the cause of political unrest in the Middle-east. The dependency of the rest of the nations on those resourceful countries for petroleum also affects the development programme of the developing countries like India. For example, the fluctuation of global petroleum prices disturbs the domestic economy of India.

The third and the most important risk due to petroleum and other fossil fuel combustion is the emission of greenhouse gas (GHG) causing climate change catastrophe at accelerated rate. It is now conclusively evidenced that the emission of GHG (CO_2) is linked with the consumption of fossil fuel[5]. Therefore, there has been a worldwide effort to reduce the GHG emission through multi-dimensional strategies. It is also believed that reduction of petroleum consumption could effectively reduce the GHG emission[6]. Thus, shifting from petroleum fuel to some carbon neutral alternative fuel has been considered as one of the global strategies to mitigate climate change.

All the three issues, *viz.*, declining stock, uneven distribution and GHG emission, as discussed above, necessitate search for a carbon neutral alternative fuel. There could be variations in such need and hence strategy amongst the countries of the World for such search. India is a developing nation having aspiration to prosper further. The ever increasing demand for importing petroleum has already made situation critical for India. A brief account on the petroleum consumption and related economic implication in India are discussed in later section.

1.2 Petroleum consumption in India *vis-à-vis* its economic implication

India has emerged as one of the strongest economies of the World. With the growth of major sectors of economic importance (industry, transport, communication, agriculture etc), the country's petroleum consumption has also increased year by year. With limited domestic production, the major share of its requirement is fulfilled through import. As can be seen from Table 1.1, the consumption as well as import of petroleum has been increased year by year causing burden on the economy. Reliance up to the extent of 75% of total oil requirement on foreign import is considered as a serious energy insecurity issue[7]. It is also anticipated that with a current trend of economic growth, the demand of petroleum will further rise, making the situation worse in future.

The exponential growth of crude oil import bill is shown in Fig 1.1. The hike in international oil price along with increased demand causes for this exponential increase in import bill putting heavy pressure on India's economy.

Table 1.1 Production and import of crude oil in India

Year	Production (Mt)	Import (Mt)	Total (Mt)	Import share (% of total)
1971	6.8	11.7	18.5	63
1981	10.5	16.2	26.7	61
1991	33.0	20.7	53.7	39
2000	32.0	57.9	89.9	64
2004	33.4	90.4	123.8	73
2005	33.4	100.0	133.4	75
2008	34.1	121.6	155.7	78
2011	37.7	163.5	201.2	81

Source: Ministry of petroleum and natural gas[8]

Diesel and gasoline are the two major liquid fuels used in India. It is further noted that requirements of diesel is higher in India compared to gasoline[8]. This is primarily because of extensive uses of diesel in transport and industrial sectors. It is interesting to note that demand ratio of diesel to gasoline remains uniform at a little over than 5 as seen in Table 1.2. This implies the possible adverse impact on Indian economy due to any crisis relating to diesel fuel.

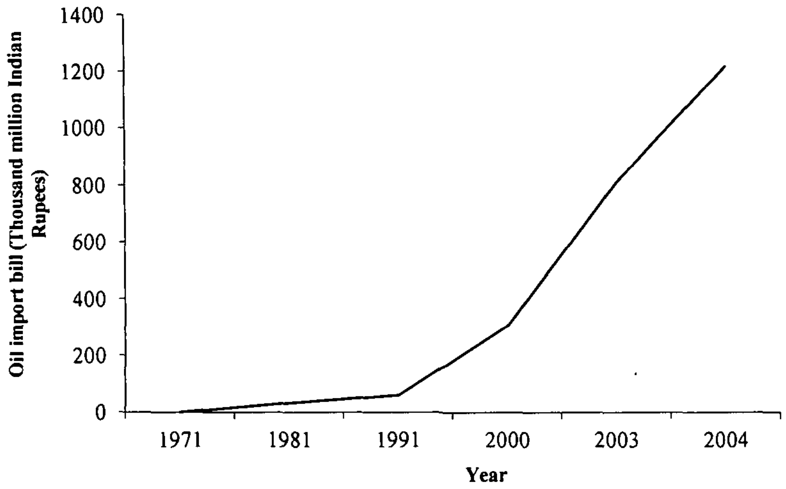


Fig. 1.1 Increase in Indian oil import bill during 1971-2004[8]

Table 1.2 Demand of gasoline and diesel in India

Year	Gasoline demand (Mt)	Diesel demand (Mt)	Demand ratio, diesel/gasoline
2002-2003	7.62	42.15	5.53
2003-2004	8.2	44.51	5.42
2004-2005	8.81	46.97	5.33
2005-2006	9.42	49.56	5.26
2006-2007	10.07	52.33	5.20
2010-2011	12.85	66.9	5.21

Source: Planning Commission, Government of India[9]

1.3 Biodiesel: A potential alternative fuel

Biodiesel is a type of biofuel produced from oils or fats through chemical conversion process and it resembles diesel in terms of fuel properties. Biodiesel is identified as a potential candidate to substitute petroleum diesel and therefore, it is drawing worldwide attention in research and development (R & D). A lot of activities concerning biodiesel production at national level in different regions of the world have been reported[10-12].

The commercial production of biodiesel has also been started in many countries. Germany, Brazil, France, Argentina, USA, Spain, Italy, Belgium, Poland and Malaysia are the top ten biodiesel producing countries ranked in that order of volume of production as per the record of the year 2010. It is further reported that about 2.86 million tonnes of biodiesel were produced by Germany in 2010[13]. Annual production capacity of 27 European nations has been estimated as more than 22 million tonnes, with a current production of more than 9.6 million tonnes[13]. Amongst the non-European regions, USA, Argentina and Brazil are the three major biodiesel producing countries. The efforts of both Argentina and Brazil during the past few years are also noticeable[14-16]. The feedstock availability, appropriate research and development intervention, Government policies and environmental concern are favourably acting to increase in the growth of biodiesel industry.

Biodiesel activities are also visible amongst the Asia pacific regions *viz.*, Thailand, Malaysia, Philippines, Singapore, Taiwan, India and Japan[16]. However, compared to European and other countries (*viz.*, USA, Argentina, Brazil), commercial production in Asia pacific region is relatively low. Therefore, special emphasis would be required to increase the production capacity in this region also. Objective oriented research and development activities will be required to address region specific issues of biodiesel production.

1.4 Present status on the Research and Development (R & D) on biodiesel

Several issues pertaining to (i) identification of feedstock, (ii) optimization of production process, (iii) safer storage and handling, and (iv) quality assessment vis-à-vis engine performance of biodiesel are drawing R & D attention till now. The current statuses of these issues are discussed below.

1.4.1 Biodiesel feedstock

Availability of low cost and quality feedstock is of major consideration for biodiesel production. In general, oilseeds, animal fats, waste cooking oils, greases, soapstocks etc. are used as biodiesel feedstock[11, 17]. Recently, algae, an aquatic plant are also attempted as feedstock for biodiesel production[17]. In most of the countries edible vegetable oils are used for commercial production of biodiesel. As per the currently available report, rapeseed (contributing 84% of total commercial production), sunflower oil (13%), soybean oil (2%) and palm oil (1%), are the major vegetable oils used for commercial production of biodiesel[16,18]. However, other sources are also attempted for obtaining biodiesel with varying degree of success.

Table 1.3 Feedstock used for biodiesel production

Plant origin		Animal origin	Other sources
Edible oils	**Non-edible oils**		
Apricot[19]	Desert Date[39]	Beaf Tallow[60]	Algae[65]
Coconut[20]	Ethiopian mustard[40]	Duck tallow[61]	Bacteria[66]
Coffee[21]	Hemp[41]	Fish oil[62]	Fungi[67]
Corn[22]	Hingan[42]	Poultry fat[63]	Microalgae[68]
Coriander[23]	Igiri Tree[43]	Lard[64]	
Cottonseed[24]	Indian almond[44]		
Grapeseed[25]	Jatropha [45]		
Hazelnut[26]	Jojoba [46]		
Linseed[27]	Karanja[47]		
Olive/pomace[28]	Koroch[48]		
Soybean[29]	Luganda[49]		
Sunflower[30]	Mahua[50]		
Tall[31]	Milkweed[51]		
Tobacco[32]	Moringa[52]		
Palm[33]	Nahar[53]		
Peanut[34]	Neem[54]		
Pumpkin seed[35]	Osage orange[55]		
Rapeseed[36]	Polonga[56]		
Rice bran[37]	Poon[57]		
Sesame[38]	Rozelle[58]		
	Rubber [59]		

Overviews of the feedstock used for commercial production as well as for R & D are presented in Table 1.3. It can be seen that edible vegetable oil (19 species), non-edible vegetable oil (22 species), animal fats (5 species), algae and similar sources are under investigation and are in different stages of biodiesel research.

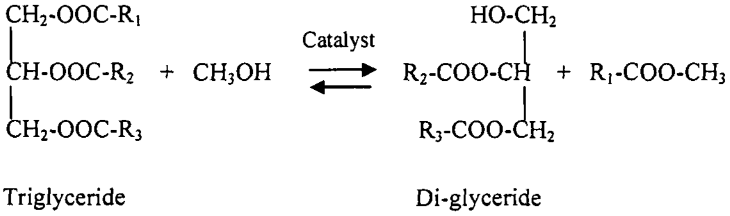
Sustainable production of feedstock without creating fuel-food conflict is ideally required for successful biodiesel programme. The choice mostly depends upon regional dynamics. Thus, identification of feedstock suitable for a given region requires research intervention.

The conversion of raw material into biodiesel passes through some distinct chemical processes, nature of which depends upon the characteristics of feedstock. The R & D work on feedstock identification is related with the mechanisms of conversion process. Therefore, a brief account of the biodiesel production process is given below.

1.4.2 *Biodiesel production process*

All naturally occurring oils and fats are triglycerides or triacylglycerides. Studies have shown that triglycerides hold promise as alternative fuel for diesel engine[69,70]. However, the direct use of oil/fat is unsatisfactory for diesel engine due to its higher viscosity and free fatty acid content. Moreover, formation of gum due to oxidation and polymerization, combustion carbon deposit, lubricating oil thickening are some of the obvious problems[60]. Several processes have been evolved to convert viscous and thick oil into biodiesel. Pyrolysis, micro-emulsification and transesterification are some of the commonly cited conversion process. However, transesterification has been the most commonly used conversion process amongst the three.

Transesterification, commonly known as alcoholysis, is the reaction of an oil or fat with an alcohol to form esters (Biodiesel) and glycerol[10]. The overall transesterification reaction is composed of three consecutive reactions where di-glycerides and mono-glycerides are formed as intermediates (Fig 1.2).



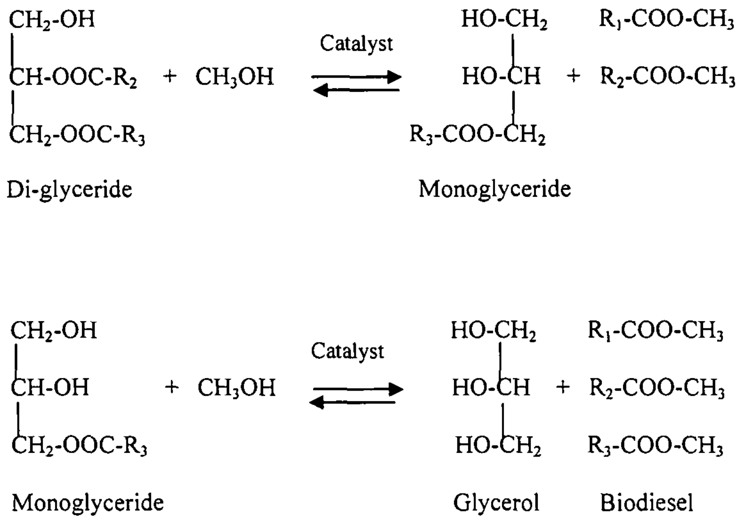


Fig 1.2 Transesterification reaction showing intermediate steps[10]

Theoretically, the transesterification reaction is an equilibrium reaction in which excess alcohol is required to shift the reaction equilibrium to the right side and produce more methyl esters as product. A catalyst is usually used to improve the reaction rate and hence yield. The overall chemical reaction of the transesterification process is summarized in Fig 1.3.

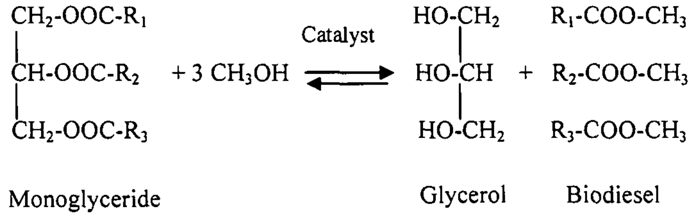


Fig 1.3 Overall transesterification reaction

There are several parameters such as, (i) type of catalyst, (ii) concentration of catalyst, (iii) type of alcohol, (iv) alcohol to oil molar ratio (v) reaction time, (vi) reaction temperature and (vii) reaction pressure by which transesterification process can be described. A wide range of variations of these transesterification parameters are possible. Selection of optimum parameters is mostly governed by the nature and composition of feedstocks. There have been many studies aimed at determination of optimal parameters to achieve maximum yield[36,61,71-73]. A process called supercritical methanol transesterification is done at elevated pressure such as 35–40 MPa, and a temperature of 300^{0}C is required to complete the reaction. Although esterification of FFA and triglycerides happen simultaneously in this type of reaction, still it is an energy consuming process[74].

A number of catalysts have been reported as successful for transesterification process. Primarily the catalysts can be classified as either alkaline or acidic type. Now-a-days heterogeneous types of catalysts are gaining attention because of their superiority over homogeneous catalysts. Heterogeneous catalysts are less corrosive which can be separated from the reaction mixtures and can be reused. A number of studies have shown the use of heterogeneous type of catalyst[75-77].

Free fatty acid (FFA) content of the feedstock governs the selection of appropriate type of catalyst. The reaction mechanism of alkaline and acidic transesterification reported elsewhere[78, 79] is produced in Fig 1.4 and Fig 1.5, respectively.

In general, FFA content of feedstock is an index for selection of type of catalyst. Acid catalysts are preferred for feedstocks containing higher amount of FFA. However, there are differences among the reports of recommending catalyst selection. Some reports [80] recommend the use of alkaline catalyst up to 5% FFA content of feedstock, whereas other suggests avoiding alkaline catalyst beyond 0.5% FFA level[81-83].

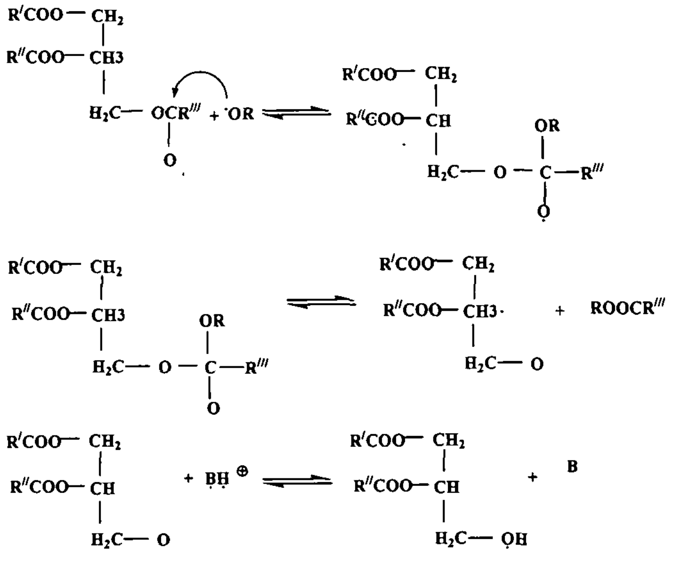
In addition to FFA, vegetable oil used for transesterification process may contain various minor contaminants such as phospholipids, colouring pigments, waxes, which might require some refining steps. It is reported that poor quality vegetable oil inactivates the catalyst used for transesterification reaction[84,85].

Further, it is reported that high quality feedstock (refined vegetable oil) can be easily converted into biodiesel by alkaline catalytic transesterification, because of the low level of FFA content[86]. NaOH, KOH, Na-metal are the alkali catalysts generally used in this type of reaction. Alkali catalyst (either NaOH or KOH or Na-metal) when mixed with alcohol, the actual catalyst, alkoxide group is formed[87,88]. As shown in the Fig 1.4, the reaction is completed in three different steps[64,88]. The first step is an attack on the carbonyl carbon atom of the triglycerides molecule by the anion of the alcohol (methoxide ion) to form a tetrahedral intermediate which reacts with an alcohol (methanol) to regenerate the anion of alcohol (methoxide ion). Finally, rearrangement of tetrahedral intermediate results in the formation of a fatty acid ester and a di-glyceride. A small amount of water is also generated in the reaction, which may produce soap during transesterification reaction.

It is reported that some low quality feedstocks *viz.*, used frying oils, animal fats, soapstocks and greases, are available for the production of biodiesel which reduces the feedstock cost. But these types of feedstocks contain more amount of FFA and therefore, cannot be converted to biodiesel using alkaline catalytic transesterification[89,90]. Because FFAs react with an alkaline catalyst, forms soap and water, which decrease the ester yield and also create problems in ester separation[82,86,91]. For such feedstocks, acid catalysis is preferred.

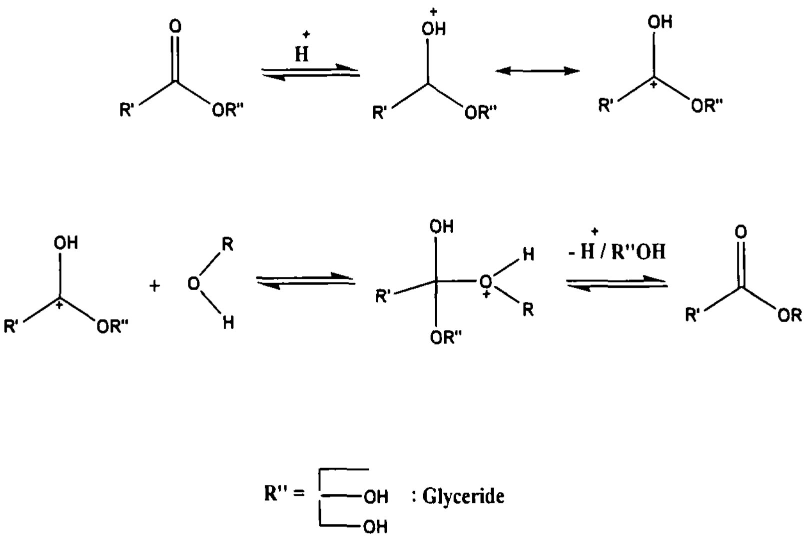
The acid catalyzed transesterification process is catalyzed by acids, preferably by hydrochloric and sulfuric acids (Fig 1.5). The protonation of the carbonyl group of the ester leads to the carbocation which, after a nucleophilic attack of the alcohol, produces the tetrahedral intermediate, which eliminates glycerol to form the new ester[88].

Methanol to oil molar ratio is another important parameter affecting transesterification reaction. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of glycerides to yield three moles of biodiesel and one mole of glycerol. However, practically the alcohol to oil molar ratio requirement differs from the stoichiometric molar ratio. Wide range of researches are reported with objectives to determine the optimum molar ratio for maximum conversion[71-73,86]. The type of catalyst, the type of alcohol, the characteristics of feedstock and reaction environment (temperature and pressure) govern the requirement of optimum molar ratio.



B: alkaline catalyst

Fig 1.4 Mechanism of alkaline catalytic transesterification[78,79,88]



R' = Carbon chain of fatty acid

R = alkyl group of alcohol

Fig 1.5 Mechanism of acid catalytic transesterification[78,79,88]

For a new feedstock, determination of optimum molar ratio has been considered as an important part of investigation. For instance, while varying the molar ratio from 6:1 to 15:1 in steps of 3:1 for rice bran oil, the highest yield of about 90% was reported with 9:1 molar ratio[36]. Similar studies are also reported optimizing to maximize the conversion at economic production under specific conditions[92,93].

Time of transesterification is another important factor affecting the transesterification reaction. There are reports indicating variation of reaction time requirement as it is affected by major reaction parameters[71-73, 94,95]. It is reported that acid catalytic process requires more time as compared to alkaline catalytic process for conversion of triglycerides to biodiesel[17]. Reaction completion time is also dependent on the alcohol to oil molar ratio. The reaction is found faster with high molar ratio, whereas longer time is required for lower molar ratio to get the same conversion[96,97].

Reaction temperature and pressure are important considerations as these are related to economy of biodiesel production. It is desired to produce biodiesel at ambient pressure and temperature to reduce the cost of production. However, experimental studies are reported at elevated temperature to improve the conversion process which also varies from situation to situation[72,73,95-100]. Nahar (*Mesua ferrea*), Rubber (*Hevea brasiliensis*), Mahua (*Madhuca indica*) and Koroch (*Pongamia glabra*) are some of the trees, seeds of which have been attempted as feedstock for biodiesel production. A reaction temperature of 65^0C is almost uniformly reported for the production of biodiesel with these feedstocks[48,53].

Determination of optimal reaction parameters has been seen as the major areas of biodiesel R & D till now. This is more important when attempting to explore the possibilities of new feedstocks.

Fuel quality has been another major area of biodiesel research, brief account of which is discussed below.

Fuel quality of biodiesel

It is desired to produce good quality biodiesel in terms of some well defined and standard parameters. Viscosity, density, cetane number, oxidation stability, acid value, cold flow properties, flash point, are the quality parameters which have standard definition as well as assessment procedures. Assessments of these quality parameters are imperative while reporting a new variety of biodiesel. There are also well established standards *viz.*, ASTM 6751-07 and EN 14214-07 available for assessment of these quality parameters. With an ideal production procedure, the quality of biodiesel depends upon the characteristics of feedstock.

Feedstocks are characterized by its composition identified by fatty acid profile. Some common fatty acids which are found in vegetable oil are presented in Table 1.4.

Table 1.4 Chemical structures of some common fatty acids

Acid chain	No. of carbon atoms	Structure
Caprylic	8	$CH_3(CH_2)_6COOH$
Capric	10	$CH_3(CH_2)_8COOH$
Lauric	12	$CH_3(CH_2)_{10}COOH$
Myristic	14	$CH_3(CH_2)_{12}COOH$
Palmitic	16	$CH_3(CH_2)_{14}COOH$
Palmitoleic	16	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$
Stearic	18	$CH_3(CH_2)_{16}COOH$
Linoleic	18	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$
Linolenic	18	$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$
Arachidic	20	$CH_3(CH_2)_{18}COOH$
Eicosenoic	20	$CH_3(CH_2)_7CH=CH(CH_2)_9COOH$
Behenic	22	$CH_3(CH_2)_{20}COOH$
Erucic	22	$CH_3(CH_2)_7CH=CH(CH_2)_{11}COOH$

Fatty acid composition (percentage) of six different types of vegetable oils (corn, cottonseed, linseed, peanut, rapseed and soybean) is also presented in Table 1.5. Majority of the vegetable oils are rich in unsaturated fatty acids (oleic, linoleic and linolenic acid) as seen from Table 1.5. For instance, cottonseed oil contain 78% unsaturated fatty acids, whereas linseed and peanut contain 93% and 81%, respectively.

Table 1.5 Fatty acid composition (percentage) of some commonly used biodiesel feedstock[10]

Vegetable oil	14:0	16:0	18:0	20:0	22:0	24:0	18:1	18:2	18:3
Corn	0	12	2	<1	0	0	25	6	<1
Cottonseed	0	28	1	0	0	0	13	58	7
Linseed	0	5	2	0	0	0	20	18	55
Peanut	0	11	2	1	2	1	48	32	1
Rapeseed	0	3	1	0	0	0	64	22	8
Soybean	0	12	3	0	0	0	23	55	6

The characteristics of oil (feedstock) and the resultant biodiesel depend upon the composition of fatty acid profile. A given fatty acid is characterized in terms of chain length and number of double bonds. It is conclusively evidenced that quality of biodiesel depends upon such fatty acid characteristics of parent material. Viscosity, density, calorific value, cetane number, cold flow properties are the properties influenced by the fatty acid profile of parent material. Several literatures are available reporting the correlation between the fatty acid profile and the properties of biodiesel[101-105]. It is reported that viscosity, density and calorific value increases with increase in chain length and saturation level. With the increasing chain length, decreasing branching and unsaturation, cetane number increases. These chemical structures increase the heating value as well, so there is a tendency for cetane number to increase with viscosity and heating value. The fatty acid composition also influences cold-flow properties of fuel. The freezing point of a biodiesel fuel increases with increasing carbon atoms in the carbon chain and decreases with increasing double bonds.

As a fuel commodity, biodiesel would be required to store and transport under some specific conditions. It is desirable to keep the fuel quality unchanged during storage and handling. This aspect has also drawn considerable amount of R & D attention, a brief account of which is presented below.

1.4.3 Storage of biodiesel: Mechanism of degradation and action of antioxidant additives

Stability of biodiesel refers to the general resistance of biodiesel to changes in its fuel properties. Oxidation stability (OS), storage stability and thermal stability are the indicators associated with biodiesel stability. Oxidation stability refers the influence of oxygen or air, thermal stability expresses the influence of temperature on biodiesel in the absence of oxygen and storage stability measures the time factor and storage conditions[106]. Fuel quality of biodiesel may be deteriorated either due to exposure of oxygen or temperature. Deterioration of fuel quality is resulted during storage, which may vary depending on the duration of storage and storage condition[107,108].

Standard definition and standard procedure are available to assess the storage stability of biodiesel (*viz.*, EN 14214, EN 14112 and ASTM D6751). Biodiesels containing higher percentage of unsaturated fatty acid are more prone to oxidation than saturated fatty acid[103,109]. The mechanism of oxidation degradation is now understood[110] and a typical scheme of oxidation degradation is presented in Fig 1.6.

Fatty acid methyl esters contain unsaturated fatty acids, which impart their relatively low storage stability having a tendency to undergo hydrolysis and oxidative changes. In presence of moisture, biodiesel hydrolyze to produce alcohols and acids. The presence of alcohols decreases the flash point, and the presence of acids increases total acidity. Thus, high degree of unsaturation is a factor affecting the stability of biodiesel. Double bonds are susceptible to the attack from oxygen/air to form a mixture of various products from polymers to short-chain compounds. Methylene groups adjacent to the double bonds are particularly susceptible to the free-radical attack. It is reported that the stability of fatty acid present in a particular species is of the sequence oleate > linoleate > linolenate[111,112].

Initiation $RH \longrightarrow R^{\cdot}$

Propagation $R^{\cdot} + O \longrightarrow ROO^{\cdot}$

Termination $ROO^{\cdot} + RH \longrightarrow ROOH + R^{\cdot}$

$ROO^{\cdot}, R^{\cdot} \longrightarrow$ Stable product

Fig 1.6 Mechanism of oxidation

The allylic hydrogen of unsaturated fatty acid chain can be easily removed to form a carbon-based radical ($R^{\cdot}$), during initiation step. This radical then reacts with oxygen in a propagation step to form a peroxy radical ($ROO^{\cdot}$) and a hydroperoxide (ROOH). Two free radicals can react with one another in a termination step. The ROOH concentration is very low during the initial period. In the propagation period, the ROOH level increases rapidly, indicating the onset of the overall oxidation process. The hydroperoxide species can form acids, aldehydes, and dimers, finally resulting in polymer formation even at ambient temperatures. It is reported that these polymers can potentially plug fuel filters and injection systems[113,114].

There have been several research reports on oxidation and storage stability of biodiesel[113-116]. Long duration storage stability tests revealed the changes in induction time, viscosity, acid value of biodiesel sample. Physical changes of biodiesel *viz.*, change in colour and formation of insolubles of biodiesel samples are also reported [110,112].

There are instances of using additive in fuel including petro-diesel for improving fuel quality. Use of appropriate additive to inhibit oxidation tendency of biodiesel is a new area of research[117-121]. These additives are known as antioxidants. In the presence of oxygen, oxidation can neither be prevented nor be reversed, but it can be inhibited, delaying the buildup of oxidized products to unacceptable limit. Antioxidants are free radical scavengers that remove reactive radicals formed in the initiation and propagation steps of autoxidation, by delaying the formation of oxidation products. The reaction mechanism of oxidation and autoxidation of fatty acid methyl ester presented elsewhere[122] is reproduced in Fig 1.7.

Investigation of the efficacy of antioxidants has also been a major area of biodiesel R & D[117-120]. A number of natural and phenolic antioxidants are used now-a day to improve the oxidation stability of biodiesel and diesel/biodiesel blends.

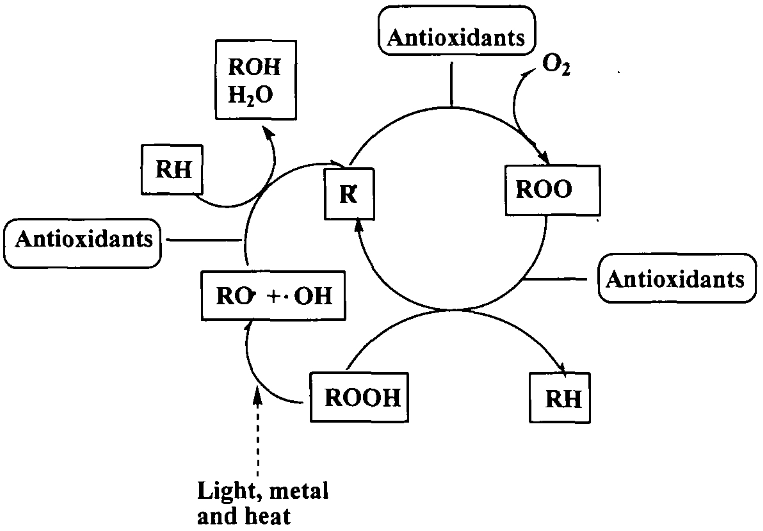


Fig 1.7 Reaction mechanisms of oxidation and autoxidation of fatty acid methyl ester[122]

RH: fatty acid methyl ester; ROOH: Hydroperoxide; ROO˙ : Hydroperoxyl radical;
R˙ : Alkyl radical; RO˙ : Alkoxy radical; ˙OH: Hydroxyl radical

The testing of fuel in engine is required to ensure full confidence on quality assessment. A brief account on the engine performance is discussed below.

1.4.4 Performance of engine fuelled with biodiesel

It is observed that conventional diesel engine are operated using biodiesel or blends of biodiesel and petro-diesel. Three distinct aspects *viz.*, (i) combustion efficiency, (ii) emission characteristics and (iii) engine health require attention while investigating engine performance using biodiesel fuel either neat or blended with petro-diesel. Differences in engine performance behaviour are reported while comparing diesel fuel with biodiesel with respect to above aspects. In most of the cases, the fuel characteristics of biodiesel are linked with the varying engine performance[123,124]. In general higher viscosity and lower calorific value of biodiesel are considered as attributing factors of poor atomization vis-à-vis improper combustion and lower rate of heat release. In contrast, compared to conventional diesel fuel, higher cetane number of biodiesel is believed to result in shorter ignition delay, and longer combustion duration, and hence, low particulate emission. If engine is operated on biodiesel for longer time, adjustment of injection timing is recommended for better thermal efficiency. Studies have shown that diesel-biodiesel blends reduce smoke opacity, particulates, unburnt hydrocarbons, carbon dioxide and carbon monoxide emission[125-127]. Limitation of using biodiesel is also reported as it has tendency to form crystal at low temperature. Such crystals can plug fuel lines and filters, causing problems in fuel pumping and engine operations. However, uses of appropriate additive are shown to decrease the crystallization temperature and hence overcome the problem[128].

A comprehensive overview of biodiesel research in global perspective could be known from the discussion presented so far. The research issues have reflection of the regional needs. As discussed earlier, the requirements in India have region specific dimension and needs special mention.

1.5 Biodiesel research in India with reference to present research problem

Along with the rest of the world, the Government of India has also taken initiative towards the growth and development of renewable energy aiming to reduce the country's dependency on conventional energy with focused programmes and investment. Biofuel including biodiesel is also in the renewable energy agenda of the country. Government of India has announced its National Biofuel Policy in 2008 with an objective to meet 20% of India's diesel demand with fuel derived from plants[129]. Due to deficit domestic production of edible vegetable oils in India, the country has emphasized non-edible feedstock for biodiesel production. A national mission of the Government of India has aimed the controlled cultivation of non-edible plant species for generating feedstock for biodiesel production. There are reports of the initiatives and involvements of some private parties in biodiesel production and commercialization in India including the Indian Oil Corporation (IOC), Mahindra & Mahindra Ltd., Tata Motors, General Motors India Pvt. Ltd. and Central Salt and Marine Chemical Research Institute[130,131].

There have also been lot of research activities concerning production of biodiesel from a variety of non-edible plant seed oil including *Pongamia glabra* (Koroch)[48], *Madhuca indica* (Mahua)[50], *Mesua ferrea* L. (Nahar)[132], *Hevea brasiliensis* (Rubber)[59], *Calophyllum inophyllum* (Polonga)[56], *Schleichera triguga* (Kusum)[72], *Thevetia peruviana* (Karabi)[133] and *Jatropha curcus* (Ratanjyot)[134]. Identification of new feedstock, characterization of new variety of vegetable oil with an aim to assess the suitability for biodiesel production, optimization of the production process and assessment of engine performance have been the major focus of Indian biodiesel research till now. Identification of new feedstock for biodiesel production has been found to have regional perspective. For country like India, it is better if renewable energy initiatives like biodiesel programme are planned with integration of regional needs.

Northeastern (NE) region of India comprising eight states is endowed with rich forest resources. The region is economically backward and is typically dominated by an agrarian ethos. As per the assessment by the Forest Survey of India, the total forest area of Assam, the major state of NE India, is over 35% of the geographical area[135]. It is also seen that, vast areas of forest have been degraded during the last twenty years due to various biotic factors. As a result, considerable rich biodiversity has been lost which need to be restored. Effort to utilize the vast forest resources of the North-eastern states for economic exploitation is likely to bring in rich dividends. If the effort is directed towards the identification of biodiesel feedstock, it would strengthen the biodiesel programme and re-insertion of identified species into the forest will effectively restore the forest cover.

Considering the above discussion pertaining to need of alternate fuel and current trend of research activities, it can be concluded now that target oriented research and developmental activities on biodiesel will be the thrust area to continue. With reference to Indian mandate to search for non-edible feedstock, regional factors need to be considered for identification of feedstock. The assessment of the identified feedstock in terms of quality and utility of biodiesel is pre-requisite for its further promotion.

1.6 Objectives

The background stated above provide the basis to carry out the present research work with the following objectives:

- To identify some oil bearing tree seeds of Northeast India having potential for biodiesel production
- To investigate the fuel properties of biodiesel produced from seed oils of selected tree species
- To study the oxidation and storage stability of biodiesel obtained from seed oils of selected tree species and investigation of efficacy of some phenolic antioxidants
- To investigate the engine performance and emission characteristics of CI engine fueled with biodiesel obtained from the seed oils of selected tree species.

1.7 Organization of Thesis

The flowchart for organization of the Thesis is presented in Fig 1.8 and briefly highlighted below.

- **Chapter 2**

Literatures pertaining to biodiesel production processes, its feedstocks, oxidation and storage stability, engine performance and emission characteristics have been reviewed and presented in Chapter 2.

- **Chapter 3**

Chapter 3 covers in detail the methodologies adopted for preparation and characterization of vegetable oils and biodiesels. Moreover, the procedure of

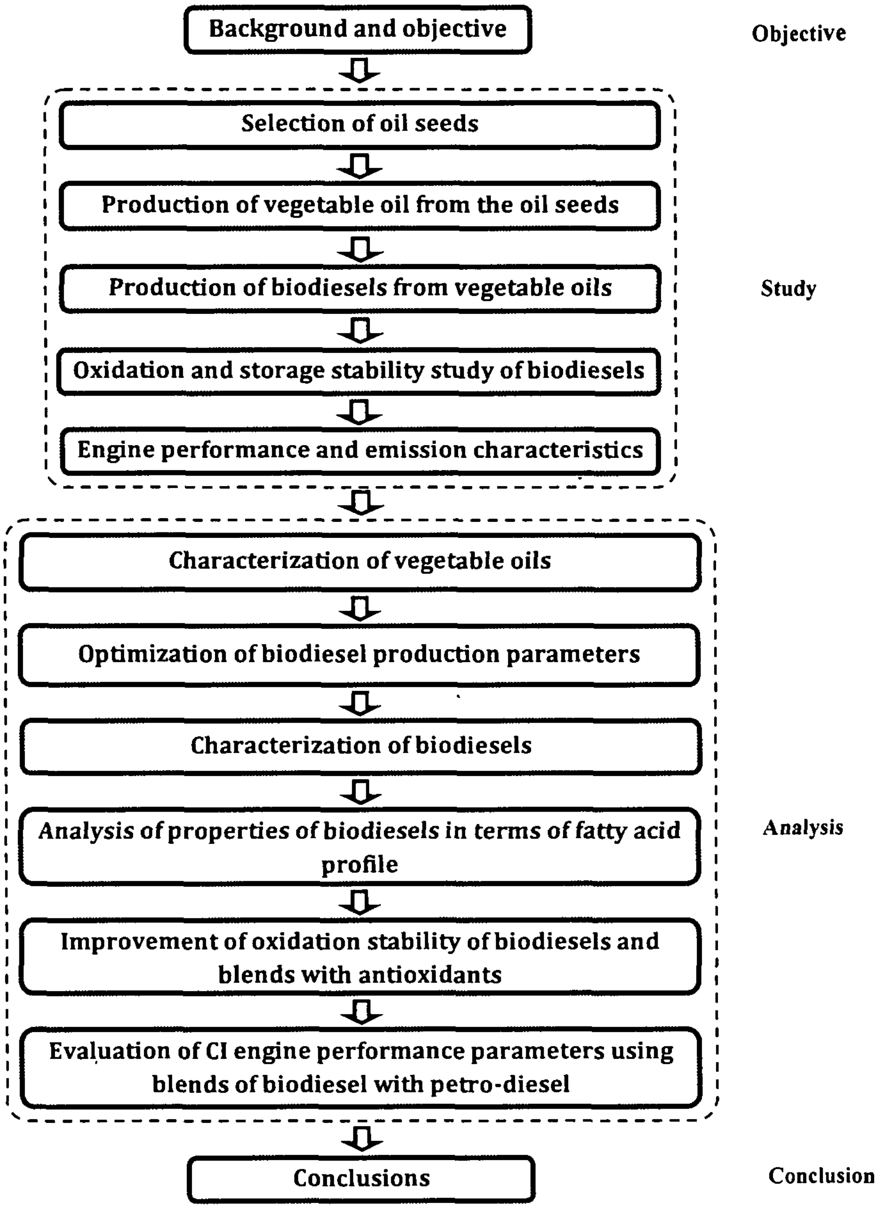


Fig 1.8 Organization of Thesis

storage stability analysis, procedure of investigation of efficacy of suitable antioxidant additives and procedure of engine performance testing are provided in Chapter 3.

- **Chapter 4**

The results obtained in the present study are presented and discussed in four distinct parts in Chapter 4.

- **Chapter 5**

This chapter enlists the summary of the results obtained to achieve the objectives of the Thesis. It also discusses the scope, limitations and possible future extensions of the work.

CHAPTER 2

REVIEW OF LITERATURE

CHAPTER 2

REVIEW OF LITERATURE

The first report of using vegetable oil as a fuel for IC engine is perhaps attributed to Rudolf Diesel when peanut oil was used to power one of the exhibited diesel engines in Paris in the year 1900[136]. There are similar reports of use of vegetable oil as engine fuel later also. However, the inherent technical difficulties of using raw vegetable oil as fuel for diesel engine compelled to think for processing of vegetable oil to improve its fuel characteristics. Perhaps a Belgian patent issued to Chavanne in 1937, could be the first documented use of processed vegetable oil (biodiesel) where palm vegetable oil was shown to be converted into ethyl ester[137]. Productions of petroleum like fuel by "cracking" of cottonseed, palm and fish oils were also documented in several other literatures[138-140]. Though sporadic attempts of converting vegetable oils into engine fuel were made in several places, the focused and organized deliberation on this alternative fuel could be seen only in recent time. The international conference on plant and vegetable oils as fuels which was held in Fargo, North Dakota, in August 1982 discussed several important issues including economy and technical aspects of using biodiesel in engine[141].

Now, focus on biodiesel has been increased worldwide due to several factors details of which are discussed in Chapter 1. Literature on biodiesel research is now regularly available from almost all parts of World. It is commonly observed that research issues are region specific but have global relevance.

The literature on biodiesel research concerning (i) identification of new feedstock and process optimization for transesterification of vegetable oil; (iii) oxidation and storage stability and (iv) engine testing and emission characteristics are reviewed for the present investigation and presented in two parts. In the Part 1, the major research and development aspects are presented in global context. Focus of biodiesel in India is centered on non-edible feedstock. Literature on the Indian biodiesel research is separately presented in Part 2 of this Chapter.

2.1 Biodiesel research: Global scenario

2.1.1 Identification of new feedstock vis-à-vis it's processing and assessment of fuel quality

Processing of vegetable oil to convert into diesel like fuel *i.e.* biodiesel has been the theme of many research activities all over the World. Varieties of feedstock have been investigated for its suitability and hence for identification of optimum process parameters. The consensus of almost all the research works is the reliance on catalytic transesterification of oil or fats using suitable alcohol under certain conditions of pressure and temperature[142-144]. Besides alkaline and acid catalysts, certain enzymes are also reported as catalyst for transesterification process[145-148]. Literature on these aspects is presented below.

Wright *et al.* (1944) reported that for an alkali-catalyzed transesterification the glycerides and alcohol must be substantially anhydrous, because water makes the reaction partially change to saponification[149]. The choice of catalyst was suggested by another researcher stating that acid catalyzed transesterification can be used if more water and free fatty acids are present in triglycerides[150]. Bradshaw and Meuly (1944)[97] and Feuge and Grose (1949)[151] also stressed on the quality of raw oils (dry and free of fatty acids). Bradshaw and Meuly (1944) also suggested practical ranges of molar ratio (methanol to vegetable oil) as between 3.3:1 and 5.25:1. Further, they stated that higher molar ratios result in quicker ester conversion. Similar findings were also reported by other researchers. For example, in the ethanolysis of peanut oil, a 6:1 molar ratio liberated more glycerin than did a 3:1 molar ratio[151]. Similarly, Sprules and Price (1950)[152] reported that when large amount of free fatty acids was present in the oil, a molar ratio of 15:1 was needed under acid catalysis. Nye and Southwell (1983)[153] methanolysed rapeseed oil using 1wt% NaOH and found that a molar ratio of 6:1 (methanol to oil) gave the best conversion. Freedman *et al.* (1984)[86] applied a molar ratio of 6:1 (alcohol to oil) while transesterifying soybean, sunflower, peanut and cottonseed oils and achieved highest conversion (93-98%) with refined vegetable oil. The study also compared the yield of methyl ester using crude vegetable oils instead of refined vegetable oils. A decrease in yield of methyl ester (67-85%) was observed while preparing biodiesel using crude vegetable oil. Thus, the effects of quality of raw material on conversion process were evidenced. It is also reported that alkali catalyzed transesterification was much faster than acid catalyzed transesterification. However, if the glycerides contain higher free fatty acid and water, acid-catalyzed transesterification is more suitable. It was also observed that sodium methoxide ($NaOCH_3$) was more effective catalyst than sodium hydroxide (NaOH).

Ahn *et al.* (1995)[154] followed a two-step reaction processes to produce canola methyl ester (CME), rapeseed methyl ester (RME), linseed methyl ester (LME), beef tallow ester (BTE) and sunflower methyl ester (SME) in a batch reactor taking sodium hydroxide, potassium hydroxide and sodium methoxide as catalysts. Cvengro and Povaz (1996)[155] described biodiesel production by using two-stage low-temperature transesterification of cold pressed rapeseed oil with methanol at temperatures up to 70^0C. Ma *et al.* (1998)[156] studied the effects of free fatty acids and water on transesterification of beef tallow and reported that free fatty acids content should be kept below 0.06 w/w% in order to get the best conversion.

Masaru *et al.* (1999)[148] developed a new enzymatic method of synthesizing methyl esters from plant oil and methanol in a solvent-free reaction system. Uosukainen *et al.* (1999)[146] presented statistical and experimental design to evaluate interdependence of process variables in enzymatic transesterification by studying the alcoholysis of rapeseed oil methyl ester. Kamini *et al.* (2000)[157] investigated the factors affecting the methanolysis of rice bran oil in aqueous medium by *Cryptococcus* spp. S-2 lipase. The crude lipase from the yeast efficiently catalyzed the methanolysis of vegetable oils (oil/methanol molar ratio of 1:1) in the presence of 40 wt% water. It was found that the methyl ester content was high at 30°C for 96 h. Dizge and Keskinler (2008)[145] reported the production of canola oil methyl ester using an immobilized lipase *T. lanuginosus*, which yielded 90% biodiesel by optimizing oil/alcohol molar ratio (1:6), water concentration (0.1 g) and temperature (40^{0}C).

Turck *et al.* (2002)[158] reported the negative influence of base catalyzed transesterification of triglycerides containing substantial amount of free fatty acid. Free fatty acids reacted with the basic catalyst added in reaction and produced soap, as a result of which, one part of the catalyst was neutralized making it unavailable for transesterification.

Rashid *et al.* (2008)[159] reported the production of *Moringa oleifera* biodiesel by two step catalytic transesterification method. Viscosity, Cetane number, cloud point, pour point, oxidative stability, lubricity were determined in that study. The viscosity, oxidative stability, cetane number were reported as 4.83 mm^2/s at 40^{0}C, 3.61 h and 67, respectively. Kufuku and Mbarawa (2010)[92] reported the alkaline catalytic transesterification of the *Moringa oleifera* oil, and an optimum biodiesel yield of 82% was reported, after optimization of the process parameters (1 wt% catalyst, 30 wt% methanol and 60^{0}C reaction temperature). However, this is disagreement with earlier report of using 2-stage transesterification by Rashid *et al.* (2008). Da Silva *et al.* (2010)[52] also studied the production of biodiesel from *Moringa oleifera* (MO) seed oil. They evaluated properties and chemical composition of oil and biodiesel and suggested that this material may be used as fuel in diesel engines, mainly as a mixture to petro-diesel. Ejigu *et al.* (2010)[160] reported the production of biodiesel from another variety of the feedstock *Moringa stenopetala*. Base catalyzed transesterification of M. stenopetala seed oil was carried out with methanol, ethanol and a mixture of methanol and ethanol (1:1 molar ratios) with an alcohol to oil molar ratio of 6:1. The physio-chemical characteristics of the esters were assessed to evaluate their suitability for use in standard diesel engines. Overall, the physio-chemical properties of the ester mixture of M. stenopetala oil were better than that of methyl ester. The recommended way to use the oil as a fuel was as a mixture of esters.

Qian *et al.* (2008)[161] produced cottonseed oil methyl ester by direct *in situ* alkaline catalyzed transesterification and reported a detailed description of the experimental conditions. About 99% of the cottonseed oil was dissolved in methanol resulting 98%

conversion. Raw material (cottonseed flour) contained about 2% moisture content and had 0.3–0.335 mm particle size. Other parameters were: 0.1 mol/L NaOH concentrations in methanol, 135:1 methanol/oil mole ratio, 40^0C reaction temperature and 3 h reaction time. Saydut *et al.* (2008)[38] reported the transesterification of sesame oil (*Sesamum indicum* L.) to produce methyl ester taking molar ratio as 6:1 with 1.5 g NaOH as catalyst. Sesame seed oil was obtained in 58 w/w%, by traditional solvent extraction.

Kaya *et al.* (2009)[34] reported about the transesterification of peanut oil. Oil was obtained in 50 w/w%, by solvent extraction. Biodiesel was prepared from peanut by transesterification of the crude oil with methanol in the presence of NaOH as catalyst. The comparison shows that the methyl ester has relatively closer fuel properties to diesel than that of raw peanut seed oil. Oleveira *et al.* (2009)[45] reported the biodiesel production from two species of Jatropha genus *viz.*, *Jatropha gossypiifolia* and *Jatropha curcas*. Resulting fuel properties were found to confirm all the norms of ASTM and European standard specifications.

Dias *et al.* (2009)[162] investigated the production of biodiesel from industrial waste (waste lard) mixing with soybean oil. Alkali transesterification of the mixture of waste lard and soybean oil resulted in a product with a purity of 99.8 wt% and a yield of 77.8 wt%. However, the raw material mixture required selected pre-treatment at 65^0C with 2.0 wt% H_2SO_4 for 5 h to result in a product with a viscosity of 4.81 mm^2/s. Similarly, Gűrű *et al.* (2009)[163] investigated the production of biodiesel using waste animal fat. The maximum yield of 89% was obtained in two steps with 0.35 (w/w) methanol/fat, at 62 ± 1^0C reaction temperature for a reaction period of 2 h. Catalysts used were 0.08 (w/w) H_2SO_4/fat and 0.01 (w/w) NaOH/fat. It is further reported that reduction of pour point of fuel was achieved by adding organic based nickel and magnesium compounds with biodiesel. Optimum conversion processes was also reported by Caynak *et al.* (2009)[28] while using pomace (obtained from waste olive oil plants) oil for production of biodiesel. The maximum yield was obtained at 30% of methanol/oil ratio (8:1), 60^0C temperature for 1 h reaction time with NaOH catalyst. The study also reported the use synthetic manganese additives to improve fuel properties. Nakpong and Wootthikanokkhan

(2010)[20] reported the two-stage transesterification reaction of coconut oil having 12.8% free fatty acid. Effects of parameters including methanol-to-oil ratio, catalyst concentration, reaction temperature, and reaction time on yield were studied. Methyl ester content of the coconut biodiesel was 98.4% under the optimum conditions. It is further reported that viscosity of coconut biodiesel was very close to petroleum diesel and other measured properties met the Thai biodiesel (B100) specification. Kufuku *et al.* (2010)[164] reported the production of *Croton megalocarpus* biodiesel with an optimum yield of 95% using sulphated tin oxide enhanced with SiO_2 as super acid solid catalyst. *Croton megalocarpus* oil reportedly contained high FFA but could be transesterified to yield satisfactory conversion. In a related study, Kufuku and Mbarawa (2010)[165] also reported about production of *Croton megalocarpus* biodiesel using two step transesterification processes with KOH as catalyst. The fuel properties were also found to meet the minimum requirement criteria.

Sinha *et al.* (2008)[37] reported the production of biodiesel from rice bran oil with optimized process parameters. The optimum conditions for transesterification of rice bran oil with methanol and NaOH as catalyst were found to be 55^{0}C reaction temperature, 1 h reaction time, 9:1 molar ratio (rice bran oil to methanol) and 0.75% catalyst (w/w). Results showed that biodiesel obtained under the optimum conditions had comparable properties to substitute mineral Diesel. Shiu *et al.* (2010)[166] reported the production of biodiesel from two varieties of rice bran oil using two step *in situ* processes yielding more than 96% conversion. The method involves an *in situ* acid-catalyzed esterification followed by an *in situ* base-catalyzed transesterification.

Anwara *et al.* (2010)[167] described the production of biodiesel from okra (*Hibiscus esculentus*) seed oil by methanol-induced transesterification using an alkali catalyst. Using optimized production parameters, 96.8% of okra oil methyl esters (OOMEs) yield of appropriate standard (as per ASTM D6751 and EN 14214) was reported. Chen *et al.* (2010)[168] reported the use of tung (*Vernicia montana*) oil with respect to the transesterification yield and biodiesel properties. The tung oil biodiesel had low cold filter plugging point of -11^{0}C, ester content of 94.9 wt%, and oxidation stability (110^{0}C) of 0.3 h. Moreover, the tung oil biodiesel exhibits the higher density (903 kg/m^3 at 15^{0}C) and kinematic viscosity (7.84 mm^2/s at 40^{0}C) needing appropriate blending to be used for engine operation.

There are also some other reports available on new feedstock vis-à-vis selection of optimal feedstock parameters and fuel quality analysis. Identification of promising feedstock and investigation of optimal production parameters have been found as common objectives of majority of researches. Moreover, the assessments of fuel quality of freshly prepared samples through standard procedures (ASTM D6751 and EN 14214) have been almost common in all the reported studies. However, there are number of reports which indicated deterioration of biodiesel with time due to action of oxygen. Some selected and relevant studies on this aspect are discussed below.

2.1.2 Oxidation and storage stability of biodiesel

Literature involving oxidation as well as storage stability of biodiesel and improvement of the property using different synthetic antioxidants is discussed below.

Mittelbach and Gangl (2001)[115] investigated the physical and chemical deterioration of biodiesel produced from rapeseed and waste frying oil (both distilled and undistilled) keeping the samples under different storage conditions. The viscosity and acid numbers rose during storage owing to the formation of dimers and polymers and also due to hydrolytic cleavage of methyl esters into acids. Induction period (IP) has been considered as an index for assessment of oxidation stability of biodiesel samples in most of the research works. The IP values for the un-distilled samples were found to decrease very rapidly during storage, especially with exposure to light and air.

There are also reports of using antioxidant additives to enhance oxidation stability. The effects of natural and synthetic antioxidants on the oxidative stability of refined and crude biodiesels obtained from rapeseed, sunflower, used frying oil and beef tallow oil were investigated by Mittelbach and Schober (2003)[117]. In that study, five synthetic antioxidants pyrogallol (PY), propylgallate (PG), tert-butylhydroquinone (TBHQ), butylated hydroxyanisole (BHA), and butylated hydroxytoluene (BHT) are used to enhance the IP. Out of those, BHT is found to be least effective as compared to others, for rapeseed, used frying oil and beef tallow oil. Dunn (2005)[169] studied the effectiveness of five antioxidants *viz*., TBHQ, BHA, BHT, PG and α-tocopherol with soybean oil fatty acid methyl esters (SME). Antioxidant activity in terms of increasing oxidation onset temperature (OT) was determined by non-isothermal pressurized-differential scanning calorimetry (P-DSC). Overall, this study recommended either BHA or TBHQ (at 3000 ppm loading) to safeguard biodiesel from effects of autoxidation during storage. Loh *et al.* (2006)[170] also investigated the effect of antioxidants on the oxidative stability of used frying oil biodiesel (UFOME). The order of increasing antioxidant effectiveness with respect to the oxidative stability of UFOME was reported as vitamin E < BHT <TBHQ < BHA < PG.

In another related study, Tang *et al.* (2008)[118] also investigated the effectiveness of individual and binary synthetic antioxidants to improve the oxidative stability of different types of biodiesels. Synthetic antioxidants could enhance the oxidative stability of biodiesel and antioxidant activity increases as a function of its concentration. However, the effective activity level of antioxidant is dependent on characteristics of biodiesel feedstock. It was also reported that binary antioxidant formulations (TBHQ + PY) have a synergistic effect on oxidative stability of biodiesel. Guzman *et al.* (2009)[120] studied the effectiveness of blends of antioxidants amongst the combinations of BHA, PG, PY and TBHQ to increase oxidative stability. Results indicated that binary antioxidant formulations *viz*., TBHQ+BHA, TBHQ+PG and TBHQ+PY were most effective at 2:1, 1:1, 2:1 weight ratio, respectively in both distilled soybean oil (DSBO) and distilled poultry fat (DPF) based biodiesel. It is further stated that the best synergistic effect was observed with the TBHQ+BHA blends while the best stabilization factors (SF) were achieved by using the TBHQ+ PY blends. Lin and Chiu (2009)[116] also investigated the dependence of fuel properties of palm oil biodiesel on oxidative degradation.

Similarly, Karavalakis *et al.* (2010)[171] investigated the impact of various synthetic phenolic antioxidants on the oxidation stability of biodiesel blends. Butylated hydroxytoluene (BHT) and butylated hydroxyanisol (BHA) displayed the lowest effectiveness in neat biodiesel, whereas their uses in blended biodiesel showed greater stabilizing potential. Propyl gallate (PG) and pyrogallol (PY) additives showed the strongest effectiveness in both the neat biodiesel and the biodiesel blends.

Kivevele and Mbarawa (2010)[119] studied the effect of antioxidants on the oxidation stability of biodiesel prepared from Manketti seeds (*Schinziophyton rautanenii*) oil (MOME). While majority of the fuel properties of MOME fulfilled the minimum requirements of ASTM D6751 and EN 14214 biodiesel standards, failed to meet EN 14214 oxidation stability requirements (6 h). This study evaluated the effectiveness of three antioxidants *viz.*, pyrogallol (PY), propyl gallate (PG) and butylated hydroxyanisole (BHA) on the oxidation stability of MOME. The result showed that the effectiveness of these antioxidants was in the order of PY>PG >BHA.

Overall, it is observed from the above assessment on oxidation stability that biodiesel require additional treatment to improve its oxidation stability. Storage conditions are found to have effect on oxidation stability of biodiesel. Antioxidant additives can improve oxidation stability of biodiesel. However, identification of appropriate antioxidant additives suiting specific chemistry of biodiesel has been matter of research.

2.1.3 Engine performance and emission characteristics of biodiesel fuel

Biodiesel is tested in conventional diesel engine to assess its performance. Literature pertaining to engine performance and emission characteristics of biodiesel fuel are reviewed and presented below.

There are several attempts of using vegetable oil as alternative fuel for diesel engine. The use of sunflower, safflower and rapeseed oils as liquid fuels was investigated by Bettis *et al.* (1982)[172]. They found the engine power output of these liquid fuels as equivalent to that of diesel fuel, but long-term durability tests indicated severe problems which were attributed to carbonization. Strayer *et al.* (1983)[173] investigated the feasibility of using degummed canola oil and high erucic rapeseed oil as diesel fuel substitutes in small and large diesel engines. Pryor *et al.* (1983)[174] conducted short and long-term engine tests using neat soybean oil in a small diesel engine. Short-term tests with soybean oil indicated the performance similar to that of diesel. However, carbon build-up on the injectors hindered the long-term testing. Such problems of using neat vegetable oils necessitated further processing to improve fuel quality. Quick[175] used over 30 different vegetable oils to operate compression engines and reported that the use of raw vegetable oil as fuel can lead to premature engine failure. Blending vegetable oils with diesel fuel was found to be a method to reduce chocking and extend engine life.

Zhang and Van Gerpen (1996)[176] investigated the use of blends of methyl esters of soybean oil and diesel in a turbo-charged, four- cylinder, direct injection diesel engine with modified combustion chamber. They found that the blends gave a shorter ignition delay and similar combustion characteristics as diesel. Monyem and Van Gerpen (2001)[177] evaluated the impact of oxidized soybean biodiesel on engine performance and emission. A John Deere 4276 turbocharged DI diesel engine was fueled with oxidized and unoxidized biodiesel. The performance and emission were compared with No. 2 diesel fuel. The engine performance of the neat biodiesels and their blends was similar to that of No. 2 diesel fuel with similar level of thermal efficiency, but higher fuel consumption.

Kalam and Masjuki (2002)[178] carried out experiments to evaluate the effect of anticorrosion additive in palm oil biodiesel on diesel engines. In their investigation performance, emissions and wear characteristics were assessed and results were found comparable with similar biodiesel. In a related study Kalligeros *et al.* (2003)[179] investigated the performance of biodiesel/marine diesel blends testing in a stationary single cylinder diesel engine. The engine was fuelled with pure marine diesel fuel and blends containing two types of biodiesel prepared from sunflower and olive oil, at proportion up to 50%. Improvement of emission of the particulate matter, unburned hydrocarbon, nitrogen oxide and carbon monoxide emission was reported. Similarly, Dorado *et al.* (2003)[180] studied the emission characteristics of direct injection Perkins engine fueled with waste olive oil methyl ester. Results revealed that the use of biodiesel resulted in lower emissions of CO (up to 58.9%), CO_2 (up to 8.6%), NO (up to 37.5%), and SO_2 (up to 57.7%). However, increase in NO_2 emissions up to 81% was reported. Further, a slight increase in brake-specific fuel consumption (8.5%) was also reported.

There are also reports to test biodiesel in automobile engine. For example, Cetinkaya *et al.* (2005)[181] investigated performance of used cooking oil derived biodiesel fuel in a Renault Me´gane automobile four cylinder diesel engine. Results were compared with No. 2 diesel fuel. It was found that the torque and brake power output obtained during the operation with biodiesel application were 3 to 5% less than those of No. 2 Diesel fuel. The engine exhaust gas temperature with biodiesel was less than that of No. 2 Diesel fuel. Carbonization of the injectors was observed with biodiesel usage. Labeckas and Slavinskas (2006)[182] reported the performance of neat rapseed oil methyl eater (RME) and 5%, 10%, 20% and 35% blends of RME with diesel. It was found that the brake specific fuel consumption at maximum torque (273.5 g/kWh) and rated power (281 g/kWh) for RME is higher by 18.7% and 23.2% relative to diesel fuel. The maximum brake thermal efficiency varied from 35.6% to 39.8% for RME and from 37.3% to 38.3% for diesel fuel.

Emission characteristics of four types of diesel fuel *viz.*, biodiesel with and without an additional peroxidation process, a commercial biodiesel and ASTM No. 2D diesel were studied by Lin and Lin (2006)[183] to emphasis the need of processing. Biodiesel with addition of the peroxidation process exhibited the lowest equivalence ratio and emission indices of CO_2, CO and NO_x among the four test fuels. Therefore, the peroxidation process could be used to improve the fuel properties and reduce emissions when biodiesel is used. Later, Lin *et al.* (2007)[184] studied the formation of exhaust tail gas of a diesel engine while using restaurant cooking oil biodiesel, biodiesel/diesel blends, and normal diesel. The biodiesel and blended biodiesel produced higher NO_x for various engine speeds. It is also observed that SO_2 showed an increasing trend with increased engine speed and also increasing trend as the percentage of diesel increased in the fuels. Öner and Altun (2009)[185] observed decrease in engine performance of both pure and blended (with petroleum) biodiesel obtained from inedible animal tallow.

In another study, Keskin *et al.* (2010)[186] investigated Tall oil biodiesel and resinic acids as alternative diesel fuels. Performance and emission tests of the test fuels were carried out in an unmodified direct injection diesel engine on full load conditions. The results showed that the specific fuel consumption (SFC) with the blend fuels did not show any significant change. CO emission and smoke level decreased up to 23.91% and 19.40%, respectively. In general, NO_x emissions showed an increasing trend with the blended fuels (up to 25.42%).

Biodiesel prepared from waste anchovy fish oils (FOME) was investigated by Behçet (2011)[187] in a single cylinder direct injection compression ignition engine running at full load with variable speeds of 1000, 1500, 2000 and 2500 rpm. Reduction of engine torque (4.14%) and power (5.16%) with an associated increase in specific fuel consumption (4.96%) were reported with FOME. On one hand, there has been reduction of 4.6%, 21.3%, 33.42% in CO_2, CO, HC, respectively. Again, an increase of 9.63%, 29.37% and 7.54% in O_2, NO_x and exhaust gas temperature compared with diesel was also reported.

The deviation of fuel characteristics of biodiesel from petro-diesel has been shown as the primary cause of dissimilar engine performance of these two fuels. The fuel characteristics are mostly reflected in engine performance in almost all the reported studies. Both edible and non-edible feedstocks have been the subject matters of the above investigations. As mentioned earlier, the findings of the above works have global relevance. However, there are certain regional factors directing the research agenda at regional scale. For example, non-edible feedstock has been the priority in India. Some selected literature pertaining to Indian biodiesel research has been discussed below.

2.2 Biodiesel research in India

Vegetable oils obtained from some tree seeds have been identified as promising source of biodiesel in India. Oil seeds of trees like *Mesua ferrea*, *Pongamia pinnata*, *Pongamia glabra*, *Madhuca indica*, *Schleichera triguga*, *Hevea Brancillis* have been identified as a source of biodiesel feedstock.

De and Bhattacharya (1999)[188] produced biodiesel from *Mesua ferrea* and *Pongamia pinnata* and then assessed their fuel properties such as density, viscosity, flash point, pour point and cetane index. In terms of flashpoint and calorific value, *Mesua ferrea* biodiesel is found superior than *Pongamia pinnata.* A detail production procedure of biodiesel from *Pongamia pinnata* seed oil was also reported by Karmee and Chadha (2005)[47]. A maximum conversion of 92% (oil to ester) was achieved using a 1:10 molar ratio of oil to methanol at 60^0C. Sarma *et al.* (2005)[48] reported that the preparation of biodiesel from Koroch (*Pongamia glabra,* another species under genus Pongamia) seed oil with 6:1 molar ratio and 1 g of $NaOCH_3$ Viscosity, density, cetane number, calorific value, IBP/FBP etc of resultant biodiesels was also evaluated. Similarly, Sharma and Singh (2008)[189] reported the transesterification of Karanja (*Pongamia pinnata*) oil expelled from the seeds. Both acid as well as alkaline esterification was subsequently performed to get the final product. NaOH was found to be a better catalyst than KOH in terms of yield. Maximum yield of 89.5% was achieved at 8:1 molar ratio for acid esterification and 9:1 molar ratio for alkaline esterification with 0.5 wt% catalysts (NaOH/KOH) using mechanical stirrer.

Ghadge and Raheman (2005)[190] reported a technique to produce biodiesel from Mahua oil (*Madhuca indica*) having high free fatty acids (19% FFA). The high FFA level of Mahua oil was reduced to less than 1% by a two-step pretreatment process.

Sarin *et al.* (2009)[191] investigated *Guizotia abyssinica* seeds oil as a potential biodiesel production feedstock. According to this study, the maximum yield of ester (98.7%) can be obtained with optimized sodium methoxide catalyst dosage (0.6 wt %) at an operational temperature of 65^0C. Singh and Singh (2010)[192] reported the lost cost production of *Argemone mexicana* methyl ester. Fuel properties and economic assessment of the oil and its methyl ester were determined and compared to that of commercial diesel fuel. The analysis of the properties in comparison to commercial diesel fuel showed that transemethylation improves the fuel properties of the oil.

Jain and Sharma (2010)[193] reported the kinetic study of two-step acid (H_2SO_4) base (NaOH) catalyzed transesterification process of *Jatropha curcas* (JCO) oil carried out at an optimum temperature of 65^0C and 50^0C for esterification and transesterification respectively under the optimum methanol to oil ratio of 3:7 (v/v), catalyst concentration 1% (w/w) for both H_2SO_4 and NaOH. The maximum yield of 21.2% of methyl ester during esterification and about 90.1% during transesterification of pretreated JCO were obtained.

Sharma and Singh (2010)[72] reported a non-edible oil bearing plant Kusum (*Schleichera triguga*) for the preparation of biodiesel with the optimization of paramaters. Molar ratios (methanol to oil) were optimized at 10:1 for acid esterification, and at 8:1 for alkaline transesterification. The amounts of H_2SO_4 and KOH, 1% (v/v) and 0.7% (w/w), respectively, were found to be optimum for the reactions. The optimum time requirement for completion of acid esterification was 1 h, followed by another 1 h for alkaline transesterification at $50 \pm 0.5\ ^0C$.

Sharma and Singh (2010)[194] reported the production of biodiesel synthesized from Karanja, Mahua and their mixture (Karanja and Mahua (50:50 v/v)) feedstocks. A high yield in the range of 95-97% was obtained with all the three feedstocks. Conversion of vegetable oil to fatty acid methyl esters was found to be 98.6%, 95.71% and 94% for Karanja, Mahua and mixed feedstocks respectively, with optimized reaction parameters. Conversion of the oil to biodiesel was ascertained using ^1H NMR.

Identification of promising feedstock and investigation of optimal production parameters were found as common features of the most of the researches as discussed above. Quality parameters were also assessed through standard procedure as evidenced from the literature. Deterioration of quality was reported as the main drawback associated with biodiesel while storing for longer time.

Limited literatures are available regarding oxidation and storage stability of biodiesel in Indian context.

Sarin *et al.* (2009)[195] determined the influence of the transition metal on oxidation stability of Jatropha biodiesel. Copper showed strongest detrimental and catalytic effect amongst all metals used. Sarin *et al.* (2010)[196] studied the oxidation stability of palm oil methyl ester (PME) adding some transition metal. Neat PME exhibited an oxidation stability of 9.24 h, while adding the transition metal, Copper showed the strongest detrimental and catalytic effect. Antioxidant TBHQ was most effective among the entire antioxidants used. In another study, Sarin *et al.* (2010)[197] reported the influence of metal contaminants along with antioxidants on OS of Jatropha biodiesel. It was found that usage of antioxidant could be reduced by 30-50%, even if very small amount of metal deactivator is doped in Jatropha biodiesel to meet EN 14112 specifications. Again, Sarin *et al.* (2010)[198] reported the effect of biodiesel blends on OS, using three biodiesels such as Jatropha, Pongamia (synthesized from their respective non-edible seed oils) and PBD (Palm biodiesel) (synthesized from edible oil). Good correlation between OS and percentage share of PAME (palmitic acid methyl ester) was obtained. A negative correlation between the OS and total unsaturated fatty acid methyl ester was also observed. Using these correlations, OS of different biodiesel blends could be predicted.

Sarin *et al.* (2010)[199] also investigated the effect of the presence of transition metals on OS of neat Pongamia methyl ester (PoME). Like the previous study[196], Copper showed the strongest detrimental and catalytic effect on OS. It was also observed that OS of metal contaminated PoME was found to increase with an increase in the dosage of antioxidant but the dosage required for copper contaminated PoME became approximately four times than required for neat PoME.

From the review of literatures regarding oxidation and storage stability it can be concluded that selection of appropriate antioxidant and its loading doses are critical for its efficacy on a particular type of feedstock.

Biodiesel and its blends are also accessed in engine to check its suitability as diesel engine fuel. The studies concerning engine testing and emission performance are as discussed below. Some studies reveal the testing of pure oil and diesel blend in diesel engine. Though the performances are not satisfactory, still some observations are noticed.

Pramanik (2003)[200] evaluated the performance of a Kirloskar make single cylinder diesel engine using Jatropha curcus oil and its diesel blends. Higher BSFC (Brake

Specific Fuel Consumption) was found in the case of biodiesel blends in the entire range of load and it was attributed to the combined effects of the fuel density, viscosity and heating value of the blends. It was further observed that the B30 and B40 blends had BSFC close to diesel. The BTE (Brake Thermal Efficiency) of the blends were lower than diesel throughout the entire load range. Working on a single cylinder four stroke diesel engine with Jatropha oil, Agarwal and Agarwal (2007)[201] found performance and emission parameters very close to diesel for the lower blend concentrations. However, for higher blend concentrations, performance and emissions were observed to be marginally inferior.

Raheman and Phadatare (2004)[125] investigated the fuel properties of Karanja methyl ester (KME) and its blend with diesel from 20% to 80% by volume. These fuels were also tested for engine performance. It was found that the exhaust emissions were reduced together with increase in torque, brake power, brake thermal efficiency. Reduction in brake-specific fuel consumption made the blends of Karanja esterified oil (B20 and B40) a suitable alternative fuel for diesel with a promise to control air pollution. Ramadhas *et al.* (2006)[59] used Rubber seed biodiesel and its diesel blends in a single cylinder diesel engine observed that the blends containing 20-40% of Rubber seed oil in the blend yielded similar engine performance with that of diesel.

Raheman and Ghadge (2007)[50] reported the performance of biodiesel obtained from mahua oil and its blend with high speed diesel in a Ricardo E6 engine. These properties were found to be comparable to diesel and confirming to both the American and European standards.

Sahoo *et al.* (2007)[56] reported the performance of Polonga (*Calophyllum inophyllum*) oil in CI engine. The engine performance parameters such as fuel consumption, thermal efficiency, exhaust gas temperature and exhaust emissions (CO, CO_2, HC, NO_x, and O_2) were recorded. From emission point of view the neat POME was found to be the best fuel as it showed lesser exhaust emission as compared to HSD. Banapurmath *et al.* (2008)[127], while investigating a diesel engine operated with methyl esters of Honge, Jatropha and Sesame oils, found that, methyl esters of Honge, Jatropha and Sesame oils resulted in poor performance along with higher emissions compared to diesel operation.

Srivastava and Verma (2008)[202] reported transesterification of Karanja (*Pongamia pinnata*) oil and studied the physical and chemical properties of karanja biodiesel. Maximum thermal efficiency of biodiesel was determined through engine testing and found to be slightly less than that of diesel. The brake specific fuel consumption of biodiesel of karanja oil was slightly higher as compared to diesel. Carbon monoxide, hydrocarbon and NO_x emission of methyl ester and blends were determined and compared with that of the diesel. Methyl ester of Karanja oil was reported to be a suitable substitute of petroleum diesel fuel.

Sahoo *et al.* (2009)[126] made a performance analysis using neat biodiesel from Jatropha, Karanja, Polanga and their blends (B20 and B50) at different speed in a three cylinder tractor engine at full and part throttle operations. BSFC for all the biodiesel blends was higher compared to neat diesel operation. Among the biodiesel blends, the maximum increase in power was observed for B50 Jatropha blend at the rated engine speed of 2200 rpm. Devan and Mahalakshmi (2009)[57] conducted the performance, emission and combustion characteristics of a DI diesel engine using Poon oil (*Sterculia foetida*) based fuels. The reductions in smoke, hydrocarbon and CO emissions were observed for poon oil methyl ester and its diesel blend along with increased NO_x emission compared to those of standard diesel. The combustion characteristics of poon oil methyl ester and its diesel blend closely followed those of standard diesel. Puhan *et al.* (2010)[27] investigated the effect of using Linseed oil methyl ester having high linolenic acid in diesel engine. A constant speed diesel engine (4.4 kW) run with biodiesels and its performance were compared with diesel fuel. High oxides of nitrogen emission and low thermal efficiency were reported while using biodiesel.

2.3 Summary of literature review and scope of present work

Need of identification of new feedstocks are realized in India with a special emphasis on non-edible oil. Optimization of process parameters are also stressed in different literature for economic and efficient conversion of oil to biodiesel. Different fuel properties of biodiesels are needed to assessing using standard methods. Literature citing engine performance and emission characteristics of biodiesels and blends are also available. Procedures for selection of feedstocks, optimization of process parameters, evaluation of fuel qualities and engine performance are considered for the present study based on the relevant literatures. Deterioration of fuel quality *viz.*, viscosity, acid value, peroxide value and oxidation stability are also reported in various literatures. Improvement of oxidation stability was achieved by adding different synthetic antioxidants. It is found imperative to check the quality of the stored biodiesel in terms of oxidation stability. Therefore, investigation of oxidation stability is also considered as one aspects of the present study.

CHAPTER 3

MATERIALS AND METHODS

CHAPTER 3
MATERIALS AND METHODS

The prospect of biodiesel obtained from tree seed vegetable oil has been investigated in this research work. The methodologies of the research work are presented in this Chapter as below.

i. Feedstocks and their sources
ii. Extraction of vegetable oils
iii. Characterization of vegetable oils
iv. Transesterification of vegetable oils
v. Characterization of biodiesel and blends
vi. Oxidation stability study of biodiesel and blends
vii. Diesel engine performance and emission tests

3.1 Identification of feedstocks and their description

The oil seeds are collected from two different tree species available in the forests of the state of Assam, located in the North-East India. Assam is located between $24^0 8'$ to $28^0 9'$ N latitude and $89^0 42'$ to $95^0 16'$ E longitude. A warm and humid climate generally covers the entire area of Assam, except some region of middle Assam. The maximum and minimum temperature during summer is in the range of 30^0-35^0C and 22^0-27^0C, respectively. During winter, the maximum temperature varies from 25^0 to 30^0C while the minimum temperature varies from 10^0 to 15^0C. Relative humidity is in the range of 75-90% for the entire state throughout the year. The average annual rainfall varies from 1700-2100 mm[203]

Various oilseed bearing trees are found to grow in their natural habitat in the forest of Assam. For this study two forest origin tree species oilseeds from *Terminalia belerica* and *Sapindus mukorossi* are selected.

There are some reports of traditional usage of both of these tree species[204, 205] The fruit pulp of *Terminalia belerica* is traditionally used as medicinal ingredient in India. It is reported that in Aurvedic medicine (in Indian style of medicine), *Terminalia belerica* is used in the treatment of several ailments including dyspepsia, chronic diarrhea, dysentery, intestinal parasites, fever, sore throat, cough, bronchitis, skin diseases, edema, dropsy and piles[204]. Similarly, the prospect of conversion of oilcake into bio-fertilizer or animal feed has also been reported while investigation the physio-chemical and nutritional properties of *Terminalia belerica* seed oil and kernel.

Sapindus mukorossi seed is rich in saponin content. Saponin is a natural detergent commonly used for cleaning. The fruit pulp is used as traditional soap. The pulp has also other traditional medicinal usages like expectorant, emetic and contraceptive[205]. The saponins produced from the pulp are also used as a textile auxiliary and an emulsifier in insecticides.

Terminalia belerica and *Sapindus mukorossi* oil seeds have been chosen as feedstock for biodiesel production. We have no reports about the use of these two oils seeds for biodiesel production earlier. Moreover, these two trees are grown in North East India. Many parts of these trees have traditional medicinal usage, and kernels containing oil remain unutilized. These are reasons for selecting those seed oils as feedstock for biodiesel production.

The detail of the identification parameters of these tree species are given in Table 3.1

Table 3.1 Identification parameters of the selected tree species

Identification parameter	**Tree # 1**	**Tree # 2**
Botanical Name	*Terminalia belerica* Robx.	*Sapindus mukorossi* Garth.
Family	Combretaceae	Sapindeacea
English Name	Beleric myrobalan	Soapnut
Vernacular Name (Assam)	Bhumura	Monisal

Descriptions of *Terminalia belerica* and *Sapindus mukorossi* are available elsewhere[206] and brief descriptions are provided below.

Morphology of *Terminalia belerica* tree

Terminalia belerica is a large deciduous tree available in the forests of North-eastern region of India (Fig 3.1(a)). It attains a height of up to 40 m, with a girth and clear bole of 3 to 9 m respectively. Flower appears as greenish-white or greenish-yellow with honey like smell and spikes appear during April-May. Fruit harvesting period is during November-December. Commonly found in deciduous forest up to 900 m elevation and moist valleys. It grows well in moist situations. It can be grown in almost all types of soil. However, it prefers loamy soil, red soil, and silted soil of tropical and subtropical areas. It can also thrive in continuous water stagnation for up to 10-12 days after 3-4 years of age[207].

Terminalia belerica fruits and its characteristics

Fruits are globular; fleshy grey drupe and having an average diameter of 1.3-2.0 cm (Fig 3.1(b)). Fruits contain tannin, organic acids and alcohol[207].

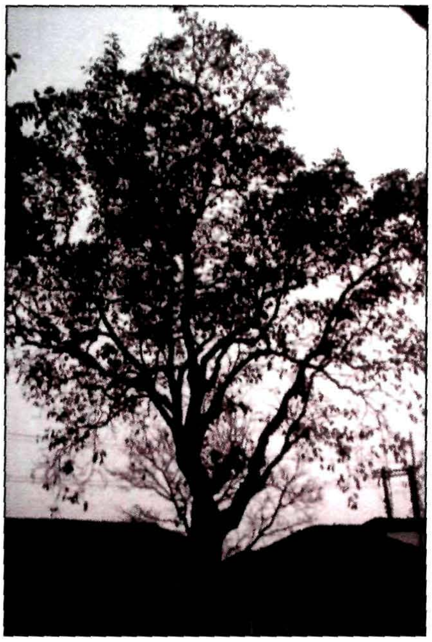


Fig 3.1(a) A matured *Terminalia belerica* tree

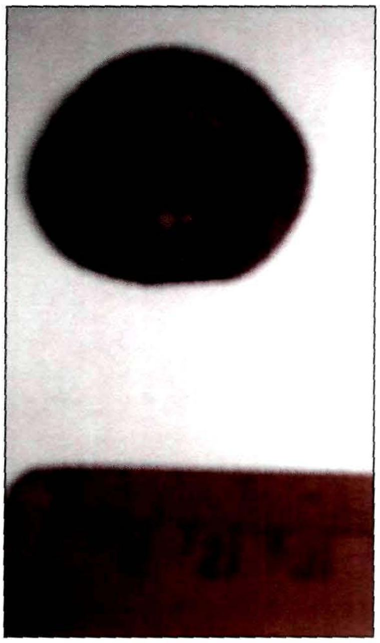


Fig 3.1(b) Matured fruit of *Terminalia belerica*

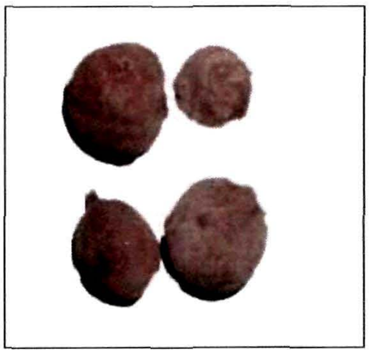


Fig 3.1 (c) Kernels of *Terminalia belerica*

A *Terminalia belerica* tree produces about 200 kg fruit after 10 years of planting. It is also reported that yield increases with maturity. Annually about 3.5-4.0 tonnes of fruits are expected from one hectare area under good management. The pulp of *Terminalia belerica* fruit has commercial value and the kernel remains as by-product.

Terminalia belerica trees are reported to contain different chemical compounds in different parts. Stem bark contains arjungenin and its glycosides, beleric acid, belericosides. Fruits contain hexa-hydroxydiphenic acid ester, β-sitosterol, gallic acid, ellagic acid, ethyl gallate, galloyl glucose, chebulagic acid, mannitol, glucose, galactose, and rhamnose. Fruits also contain certain phyto-chemicals such as alkaloid, antraquinone glycoside, saponins, flavonoids, polysaccharides, steroid and tannin[204].

North Eastern Development Finance Corporation Ltd. (NEDFi) estimated about $1850 as the net return from each hectare of *Terminalia belerica* grown area. The estimation is based on the prevailing market price of fruits and cost of planting and management[207].

Morphology of *Sapindus mukorossi* tree

Sapindus mukorossi is fairly large, deciduous tree usually with a height of up to 20 m and with about 1.8 m girth (Fig 3.2(a)). It is one of the important trees of tropical and subtropical regions of Asia. According to the report the species flourishes well in deep loam soil and does the best in areas experiencing nearly 1500 to 2000 mm of annual rainfall[205]. Flowers appear during May to June and the matured fruit harvesting period is

October-November. The wood is hard and light yellow in color and is utilized for rural building construction, oil and sugar presses, and agricultural implements[205].

Sapindus mukorossi fruits and its characteristics

Fruit is round shaped and is about 1.8-2.5 cm in diameter (Fig 3.2(b)). The fruit shells appear golden yellow when harvested but become darker red once dried.

Fig 3.2(a) A matured *Sapindus mukorossi* tree

Fig 3.2(b) Matured fruit of *Sapindus mukorossi*

Fig 3.2 (c) Kernels of *Sapindus mukorossi*

Fruits of *Sapindus mukorossi* are reported to contain sesquiterpenoidal glycosides and six different fatty ester oftetracyclic triterpenoids. Leaf of *Sapindus mukorossi* contains different type of flavanoids like quercetin, apigenin, kaempferol and rutin. Various types of triterpene, saponins of oleanane, dammarane and tirucullane type can also be isolated from the galls, fruits and roots of *Sapindus mukorossi*[205].

Although information regarding the yield could not be confirmed from literature, it is learnt that a single tree produces about 123 kg of fruits.

3.2 Extraction of vegetable oils

Identical method is adopted for extraction of vegetable oil from matured seeds (kernels) of both the trees. Detail of extraction process is presented through a flow chart in Fig 3.3 and discussed below.

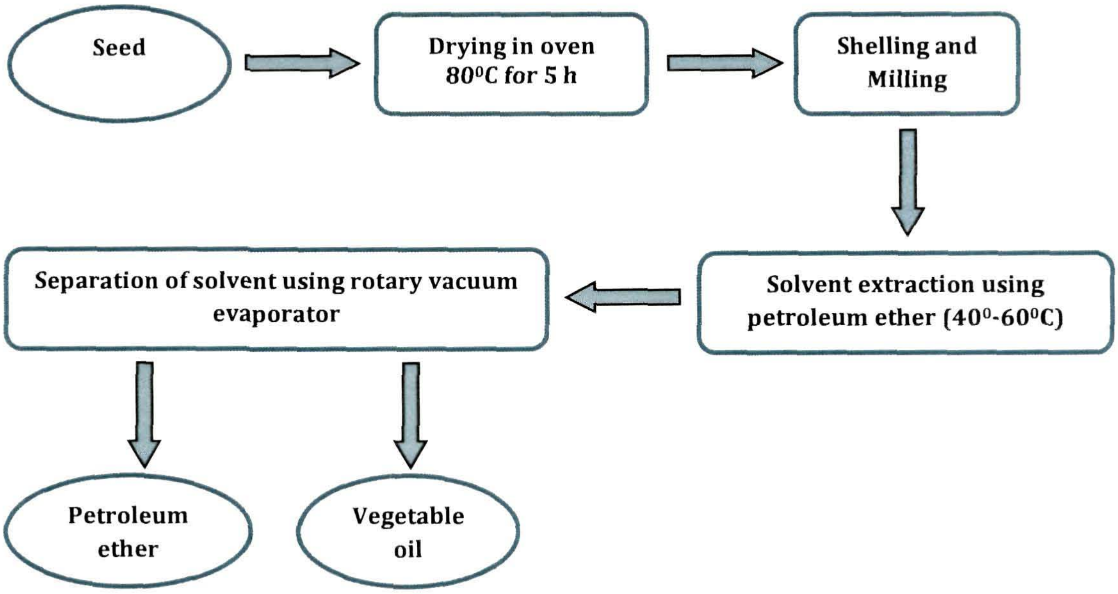


Fig 3.3 Flowchart for processes involving extraction of vegetable oil

About 300 kg of each type of seeds were collected from mature trees grown in the forests of Assam and dried at 80^{0}C for 5 h in a hot air oven. The dried seeds were shelled and milled separately. The oil was extracted from the milled kernels with petroleum ether

(40-60^{0}C) using the Soxhlet extraction method[48,50,53] (Fig 3.4(a)). Finally vegetable oil was obtained after removing the solvent from the extract with the help of rotary vacuum evaporator (Fig 3.4(b)).

About 5 litre of vegetable oil has been extracted using this method separately for both the seeds. The extracted oil was kept over anhydrous sodium sulphate for 3 days and filtered through glass wool to remove the particulate matter present in it. The filtered oil was then stored in glass bottles for further experiments.

Fig 3.4(a) Laboratory Soxhlet extraction

Fig 3.4(b) Rotary vacuum evaporator

Extracted vegetable oils from *Terminalia belerica* and *Sapindus mukorossi* are as shown

Fig 3.5(a) Vegetable oil prepared from *Terminalia belerica*

Fig 3.5(b) Vegetable oil prepared from *Sapindus mukorossi*

in Fig 3.5(a) and Fig 3.5(b).

3.3 Determination of properties of vegetable oils

Properties such as fatty acid profile, viscosity, density, calorific value, acid value, ash content, carbon residue, pour point, flash point for both the oils as well as biodiesel are determined using ASTM standards. The standards used for specific properties are mentioned in Table 3.2. Descriptions of the properties except fatty acid profile are presented in Section 3.6 while discussing the properties of biodiesel. A brief description of determination of fatty acid profile is presented below.

Fatty acid profile

Biodiesel properties are greatly influenced by the fatty acid composition that is present in the parent oil. Viscosity, cetane number, oxidation stability, low temperature flow ability are influenced by fatty acid profile as chain length and number of double bonds of the fatty acids are the key factors influencing those properties[105] .

In the present investigation, fatty acid composition is determined using AOCS method 1998, Ce 1-62 and Ce 2-26 by Gas Chromatograph at Central Food Technological Research Institute (CFTRI), Mysore.

3.4 Transesterification of vegetable oils

As discussed earlier (Chapter 1, section 1.4.2), depending upon the feedstock characteristics, either single stage or two stage transesterification process is adopted. The FFA content is a key parameter for deciding the transesterification process for vegetable oil[64]. Based on the earlier research work[80], a two stage transesterification process (acid catalysis followed by base catalysis) is decided to adopt if FFA content (acid value ~ 10 mgKOH/g) is equal or lower than 5%.

For the present study, it is found that the FFA content of *Terminalia belerica* oil is 8.1 mgKOH/g, and whereas for *Sapindus mukorossi* it is 15.6 mgKOH/g. Single stage alkaline transesterification is selected for conversion of *Terminalia belerica* oil to biodiesel. However two stage transesterification is selected for conversion of *Sapindus mukorossi* oil to biodiesel.

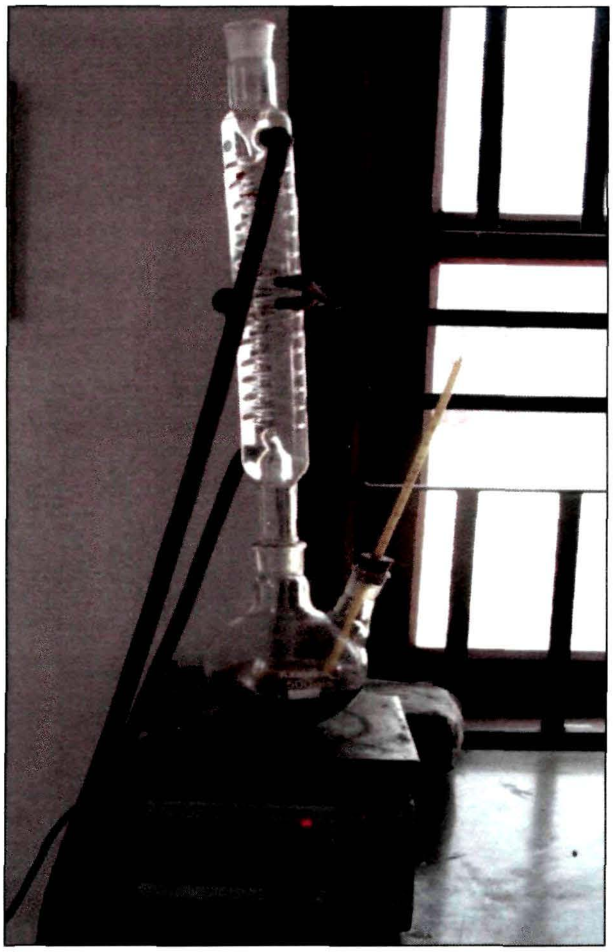


Fig 3.6 Setup for transesterification reaction

The detail of experimental setup for conversion of oil to biodiesel and selection of reaction parameters (*viz.*, alcohol to oil molar ratio, temperature, catalyst amount, reaction time and reaction stirring speed) are discussed below for both *Terminalia belerica* and *Sapindus mukorossi* oil.

The experimental setup for transesterification of vegetable oil to biodiesel consists of a 500 ml 2-necked reaction flask, equipped with a reflux condenser, a speed controlled magnetic stirrer with hot plate and a thermometer as shown in Fig 3.6.

Vegetable oil is taken in 500 ml reaction flask and kept over the hot plate magnetic stirrer at 65^0C for about 30 minutes. Methanol in specific (detail discussed later) proportion is then added into the oil. When the mixture temperature reaches 65^0C, freshly prepared sodium methoxide ($NaOCH_3$) in specific (detail later) proportion is added to the mixture as catalyst and allowed to stir up to 120 minutes at 600 rpm. After completion of the reaction, excess methanol is separated from the mixture with the help of rotary vacuum evaporator. The mixture is then transferred into a separating funnel and allowed to settle. After about 6 h of decantation, two distinct layers of methyl ester (biodiesel) and glycerol are formed. After separation of glycerol, unreacted methanol is removed by rotary vacuum evaporator. Biodiesel is washed for 7-8 times with distilled water to remove the trace amount of glycerol present in it. Finally, biodiesel is dried by passing over heated sodium sulphate. The measurements at each stage are recorded to determine the yield of biodiesel.

Optimizing reaction parameters for production of *Terminalia belerica* biodiesel

Several sets of experiments are performed by varying two parameters *viz.*, alcohol to oil molar ratio and catalyst (Na-metal, Qualigen) amount. Anhydrous methanol (Merck, Analytical grade, assay $\geq$ 99%, water $\leq$ 0.2%) with specific molar ratio (methanol: oil) is used for transesterification. Different molar ratios *viz.*, 4:1, 6:1, 8:1, 10:1, 12:1 are taken with different amount of $NaOCH_3$. $NaOCH_3$ was varied starting from 0.5 wt% up to 1.5 wt%, at an interval of 0.25 wt%. The biodiesel yield of each stage is monitored for each set of experiment. Reaction temperature, reaction stirring speed is kept constant throughout all the sets of experiments.

The flow chart for transesterification reaction is as shown in Fig 3.7.

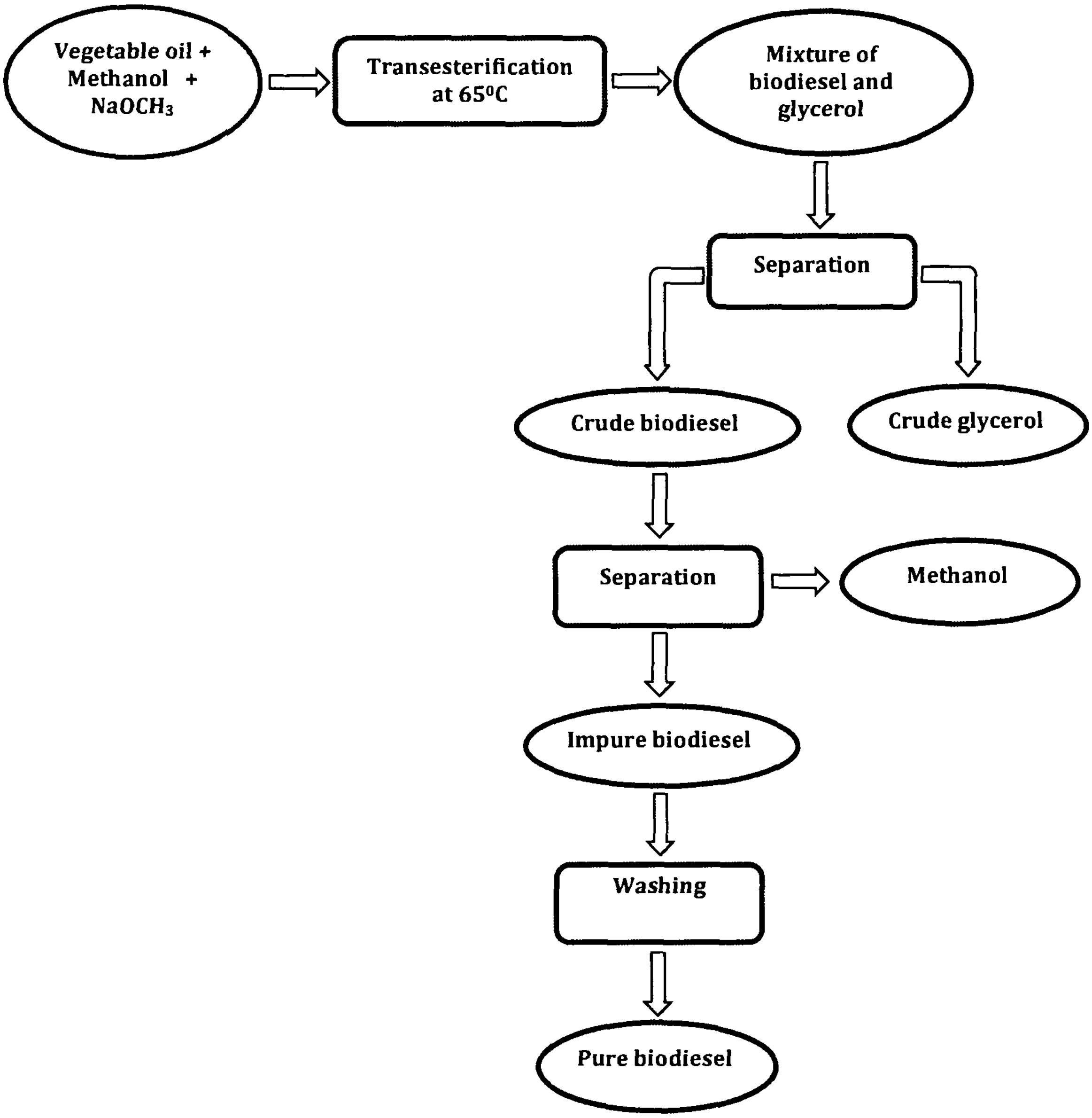


Fig. 3.7 Flowchart of single stage transesterification process

Fig 3.8(a) Biodiesel obtained from *Terminalia belerica* oil

Fig 3.8(b) Biodiesel obtained from *Sapindus mukorossi* oil

Pretreatment (acid esterification) process for production of *Sapindus mukorossi* biodiesel

Identical experimental setup (as discussed above) for is used for pretreatment of *Sapindus mukorossi* oil.

Methanol and vegetable oil at 6:1 ratio is taken in the reaction flask, and the mixture is heated up to 55^0C. After attaining the temperature, 1 wt% of anhydrous sulphuric acid is added drop-wise to the mixture. The reaction is continued for 60 minutes, maintaining a constant stirring speed of 600 rpm. After esterification, the product is shifted to a separating funnel, followed by 3 h of decantation. The upper layer contains mixture of unreacted methanol and free fatty acid. The lower layer containing mixture of mono, di- and tri-glycerides and water formed during reaction is settled at bottom[53]. The unreacted methanol is then removed from the mixture using rotary vacuum evaporator. The acid value of the product is determined (as described in Section 3.6) to ensure completion of the reaction, so that the product could be taken to the second stage of transesterification reaction. Acid value of the feedstock was reduced to 1.89 mg KOH/g (FFA~ 0.94%). The product obtained after acid esterification is dried in an oven for 3 h. After cooling to room temperature, it is passed over anhydrous sodium sulfate to remove the left over moisture.

Optimization of reaction parameters for production of *Sapindus mukorossi* biodiesel (alkaline transesterification)

The cooled dried product of first stage transesterification is subjected to alkaline transesterification. For alkaline transesterification, identical process is followed as that of *Terminalia belerica* oil.

The flow chart of 2-stage transesterification process of *Sapindus mukorossi* is shown in Fig 3.9. Series of repeated experiments are conducted for the second stage transesterification with varying molar ratio (alcohol: oil) and catalyst concentration to determine the optimum parameters for highest conversion.

3.5 Preparation of biodiesel blends

Biodiesel and petrodiesel are mixed in some specified proportions (v/v) to obtain blends. For example, 5% biodiesel is mixed with 95% petrodiesel to obtain B5. Similarly, B10, B20 and B30 blends are prepared.

The prepared B5, B10, B20 and B30 blends are used to investigate the oxidation and storage stability with the help of antioxidants. The diesel used for blending is obtained from Numaligarh Refinery Ltd. (Assam, India) having low sulphur content.

B5: 5% (vol.) biodiesel + 95% (vol.) NRL diesel
B10: 10% (vol.) biodiesel + 90% (vol.) NRL diesel
B20: 20% (vol.) biodiesel + 80% (vol.) NRL diesel
B30: 30% (vol.) biodiesel + 70% (vol.) NRL diesel

Similarly, blends (B5, B10 and B20) are also prepared with a typical petro-diesel for testing engine performance as well as for emission characteristics.

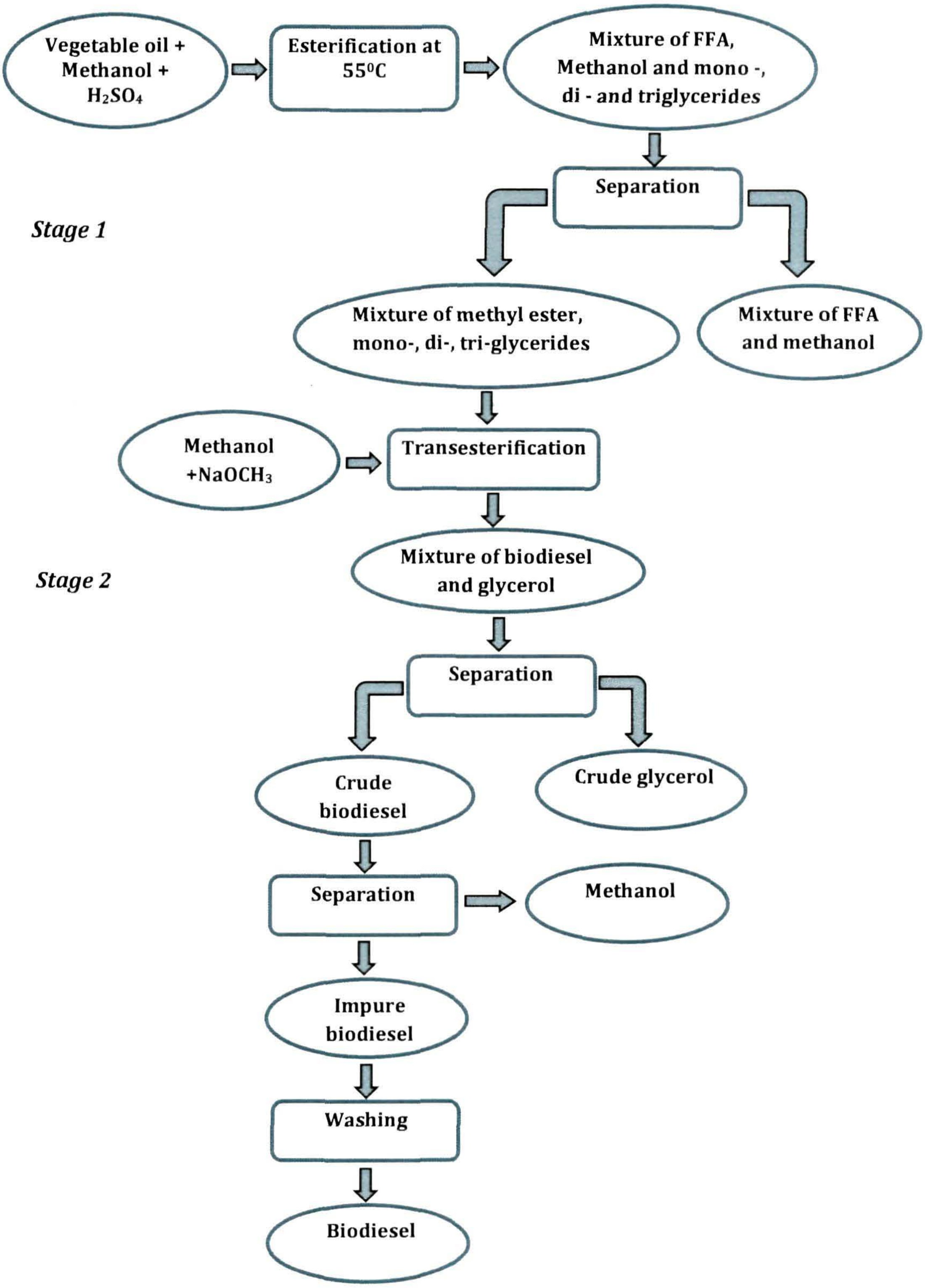


Fig 3.9 Flowchart of 2-stage transesterification process

3.6 Fuel characterization of biodiesel and blends

Characterization of fuels determining viscosity, density, pour point, flash point, carbon content, oxidation stability, distillation characteristics, low temperature flow properties and copper strip corrosion has determined according to the ASTM standards, which are listed in Table 3.2. Brief descriptions of the above properties are mentioned below.

Viscosity

Viscosity is a measure of internal fluid friction which opposes any dynamic change in the fluid motion. Higher viscosity of fuel has severe implication on engine operation due to poor atomization of the fuel spray and improper fuel injection[208]. It is reported that viscosity of any fuel is reflection of the chemical structure. As mentioned earlier, viscosity increases with increase in chain length and decreases with the increase in number of double bonds. It is also reported that viscosity and heat content of biodiesel fuel increases together[105]. Ideally biodiesels should have viscosity closer to diesel fuel.

For the present investigation, viscosities of oil as well as biodiesel sample are determined according to ASTM D445 specification using kinematic viscosity apparatus. For this purpose, 10 ml of sample is taken in "U" (viscometer tube) tube, and immerse it inside the viscometer bath, setting temperature of the bath at 40^0C. When the system acquires the desired temperature, viscosity of oil and fuel are calculated (mm^2/s) by recording the time taken by the fluid to traverse a required distance using the constant given for the particular tube.

Density

Density is an important property which influences the fuel injection system of engine. It is reported that fuel amount, injection timing, injected spray pattern are directly affected by viscosity as well as density[17]. A fuel having lower viscosity and density is preferred for improved atomization and better formation of air to fuel mixture. Molecular structure of fuel has some influence on the density of fuel. It has been seen that as the chain length and saturation level increases, the fuel density also increases[103]. There are certain correlations with the density of fuel with exhaust emissions, particularly particulate matter (PM) and nitrous oxide (NO_x). A greater increase in PM and NO_x emission is noticed in fuels having higher fuel density, as reported in some literature[209, 210].

In present investigation, density of oil as well as biodiesel sample is measured according to ASTM D287 using hydrometer. About 250 ml of sample is taken in a measuring flask. Hydrometer of appropriate density range is then put into the flask, and allowed to float free. Readings are taken after it attains the equilibrium position. The temperature of the fluid is also measured using a thermometer. Density of the sample measured at the prevailing temperature is converted into density at 15^0C (using standard conversion chart) for reporting.

Calorific value (CV)

Calorific value is the net heat content of fuel and it affects brake thermal efficiency and specific fuel consumption of diesel engine. Calorific value or heat content of a fuel is a function of its viscosity and density[211].

In the present investigation, calorific values of oil as well as biodiesel samples are measured by ASTM D5865, using auto bomb calorimeter.

Flash point

The flash point is the temperature at which the sample starts burning when it comes to contact with fire. This temperature can be directly correlated with its volatility; an important fuel feature for engine's starting and warming[212]. A fuel having high viscosity and low volatility leads to bad cold engine start up, misfiring and ignition delay[180]. It is reported that fuels having high flash point cause carbon deposit in the combustion chamber.

Using ASTM D93, flash point of oil as well as both the biodiesel samples is determined. Abel flash point apparatus is used to determine the flash point for the study.

Acid value (AV)

Acid value of oil is an important determining parameter for transesterification reaction. For the present investigation, acid value of oil, biodiesel and blends are determined using ASTM D664 standard. About 2 g of ethanolic sample is titrated against 0.1 N ethanolic KOH using indicator phenolphthalein to determine the titration end point. Acid value is then calculated using the standard formula.

Ash content

Ash content is a measuring parameter for suitability of the fuel in long term engine application. For the present investigation, ash contents of biodiesel samples are determined by ASTM D874 standard. A furnace having provision for temperature control is used for this measurement. Reduction in sample weight after keeping the sample in furnace at 900^0C for 5 minutes is measured with a sensitive balance. The difference in weight is expressed as the ash content of the sample.

Cetane number (CN)

The cetane number is an indicator which reflects the ignition quality of a fuel for diesel engine. It is reported that cetane number influences ignition delay time that is the time between the start of injection and start of combustion. CN of fuel should be within the optimum limit for better ignition properties. Both low and high cetane numbers of diesel fuel are not desirable for better ignition properties. Cetane number of fuel is also the reflection of the chemical composition of parent material. As mentioned earlier with increasing chain length, decreasing branching and unsaturation, cetane number increases[17].

In the present investigation, CN of both the samples of biodiesel are determined in the quality control laboratory of Numaligarh Refinery Ltd.

Low temperature flow properties

Low temperature flow properties are determined through measurement of cloud point and pour point. The cloud point is the temperature at which a cloud of wax crystals first appears in a liquid when cooled. The pour point is the lowest temperature after which the fuel ceases to flow. Fatty acid profile of the parent material has major implication on cold flow properties of biodiesel. It is reported that the cold flow properties of biodiesel fuel increases with increasing carbon atoms in the carbon chain and decreases with increasing double bonds[17].

Cloud and pour points of biodiesel fuel are determined by ASTM D2500 and ASTM D97 standard, respectively, using cloud and pour point bath. About 50 ml of biodiesel is taken in a container (provided with the instrument) fitted with a thermometer, and allowed to cool the sample keeping it inside the bath, setting the bath at -20^{0}C. There is a provision of gradual increase in temperature in this experimental setup. Formation of cloud is monitored visually, carefully taking out the sample from the bath, at an interval of 3^{0}C. Ones cloud point is reached, the sample is again kept inside the bath for determination of pour point based on the observation on flow-ability.

Distillation characteristics

It is reported that the distillation (volatility) characteristic of fuel affects engine performance and also this is important from safety point of view[48]. Distillation is also an indication of Cetane Index. In compression ignition (CI) engine, when atomized fuel comes in contact with the high temperature air, it vaporizes, and undergoes a series of spontaneous chemical reactions. Volatility of fuel determines the readiness to produce potentially explosive vapor.

In the present investigation, Sim-dis method is used using ASTM D287 and D86 correlation. Sim-dis is performed using 2 ml of sample using Gas chromatography technique, which provides the quantitative percent of mass yield as a function of the boiling points of the components present in the sample. The facilities available in Numaligarh Refinery Ltd. are used for determination of distillation characteristics.

Copper strip corrosion

The corrosion behavior of the fuel is tested through a standard test called ASTM D130 by using a copper strip. It is believed that free moisture, sulphur compound and similar impurities present in fuel could cause corrosion of the engine components, when it is acted upon on such fuel. Both the biodiesels and blends are tested in quality control laboratory of Numaligarh Refinery Ltd. as per the standard test procedure, dipping standard piece of copper into the fuel for 3 h.

Lubricity

Lubricity is an index of lubricating behavior of the fuel that ideal fuel should possesses certain level of lubricity. There are several procedures to determine the lubricity index of fuel. In this study, high frequency reciprocating rig (HFRR) is used to determine the lubricity index (ASTM D6079) of both the biodiesel samples. Wear scar on a spherical metal ball undergoing high frequency reciprocating load is measured as an index of the lubricity. The experiment was conducted in the set up available in NRL, quality control laboratory.

Sulphur content

Sulphur is an undesirable constituent of the fuel as the combustion of sulphur causes environmental problem. Sulphur may originate either from the feedstock or the chemical used in conversion process. The sulphur analyzer available in NRL, quality control laboratory is used for determining the sulphur content of both the samples of biodiesel by using ASTM D5453 standard.

Carbon residue

The carbon residue value is an indication of the deposit forming tendency of a fuel. It is the tendency of the fuel to form carbon deposits under high temperature conditions in an inert atmosphere, and is expressed as Conradson Carbon Residue (CCR). In the present investigation, carbon residue of fuel is measured by ASTM D4530 standard, using Conradson Carbon Residue apparatus available in NRL, quality control laboratory.

Water content

The amount of water content of any fuel is primarily required for determining its economic value[100]. Various methods are used for determination of water content such as evaporation, distillation, xylene and the Karl-Fisher titration method.

For the present investigation, water content is determined by direct measurement of mass of water evaporated during distillation, by the facilities available in Numaligarh Refinery Ltd. using ASTM D287.

Peroxide value (PV)

The magnitude of the peroxide value is an indication of the quantity of oxidizing constituents present. Deterioration of oil, biodiesel and blends result in the formation of peroxides and other oxygen-carrying compounds. The peroxide value measures those compounds that will oxidize potassium iodide, and is measured using ASTM D1832. Sample preparation has done by taking 2 g of sample mixed with 20 ml of solvent (mixture containing 3:2 ratio of glacial acetic acid and decanol), 0.2 ml of KI solution and 50 ml of distilled water; shake well and allowed to stand in a dark place. The prepared sample is then titrated against 0.01 M Na_2SO_4, to determine the titration end point. The peroxide number is then calculated using the standard formula.

NMR spectroscopy

One of the commonly used methods for analysis of biodiesel is ^1H and ^1C nuclear magnetic resonance spectroscopy (NMR).

For the present investigation, biodiesels prepared from *Terminalia belerica* and *Sapindus mukorossi* are confirmed by NMR spectroscopic study with the facilities available at Tezpur University laboratory.

Elemental analysis

Elemental analysis (C, H and O) has done by using standard CH analyzer, facility available in the Tezpur University laboratory.

Table 3.2 Methods and standards for property determination of oils, biodiesels and blends

Property	Apparatus and methods used	Laboratory
Fatty acid profile	AOCS official method, GC/MS	CFTRI, Mysore
Kinematic viscosity @40^{0}C	Kinematic viscosity meter, ASTM D445	Numaligarh Refinery Ltd
Density@15^{0}C	Hydrometer, ASTM D287	Numaligarh Refinery Ltd
Cloud point	Cloud and pour point bath, ASTM D2500	Numaligarh Refinery Ltd
Pour point	Cloud and pour point bath, ASTM D97	Numaligarh Refinery Ltd
Flash point	Able (closed cup) flash point analyzer, ASTM D93	Numaligarh Refinery Ltd
Conradson carbon residue	Carbon residue tester, ASTM D4530	Numaligarh Refinery Ltd
Ash content	Muffle furnace, ASTM D874	Numaligarh Refinery Ltd
Water content	Distillation method, ASTM D287	Numaligarh Refinery Ltd
Sulphur content	Sulphur analyzer, ASTM D5453	Numaligarh Refinery Ltd
IBP/FBP	GC-Sim Distillation, ASTM D287 and D86 correlation	Numaligarh Refinery Ltd
Cetane Number	Cetane Engine, ASTM D613	Numaligarh Refinery Ltd
Lubricity	HFRR, ASTM D6079	Numaligarh Refinery Ltd
Copper strip corrosion	Constant temperature water bath, ASTM D130	Numaligarh Refinery Ltd
Oxidation stability	Rancimat Apparatus, EN 14112	Tezpur University
Calorific value	Bomb calorimeter, ASTM D421	Tezpur University
Acid value	Titration method, ASTM D664	Tezpur University
Peroxide value	Titration method, ASTM D 1832	Tezpur University
Elemental analysis	CH analyzer	Tezpur University
NMR spectroscopy	NMR	Tezpur University

3.7 Oxidation and storage stability study of biodiesel samples

Investigation of oxidation and storage stability of biodiesel is another aspect of the present study.

Induction period (IP) is considered as an index for evaluation of oxidation stability of biodiesel in the present investigation. IPs are determined by using EN 14112 (Rancimat method) and EN 15751(Modified Rancimat method).

The Rancimat method is based on determination of the time for the sudden change of oxidation rate by measuring the increase in the conductivity of distilled water caused by the volatile acids in air bubbled from the heated sample. Use of modified Rancimat method in case of blends is necessitated due to higher rate of sample evaporation of blends, due to presence of diesel, as compared to pure biodiesel. An elongated reaction vessel along with more amounts of sample and distilled water is used to check volatilization in modified Rancimat method.

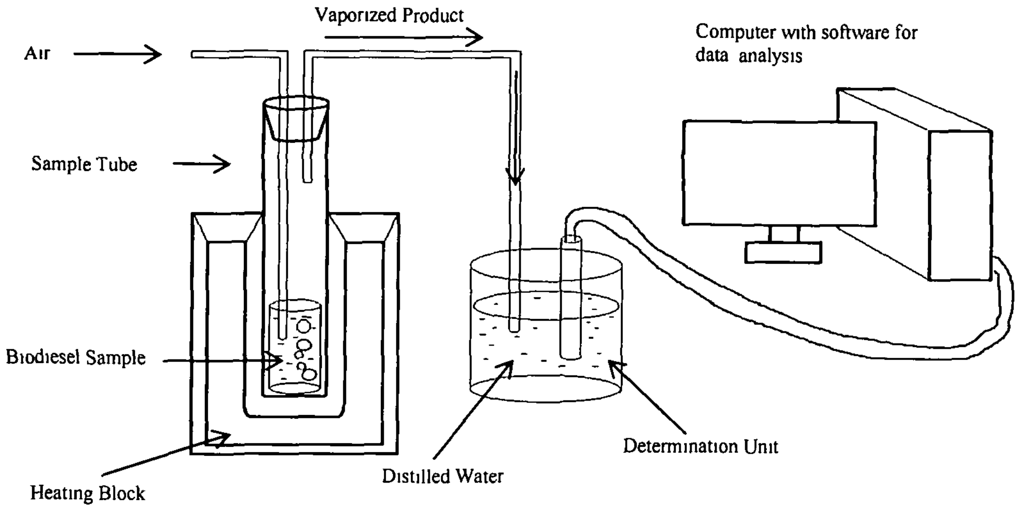


Fig 3.10 Line diagram of Rancimat apparatus

As shown in Fig 3.10, the samples are kept in the heating block to heat up to 110°C. Purified air is circulated through the hot sample and then passed to another unit containing distilled water. The conductivity of distilled water is expected to change by volatile short chain carboxylic acids from decomposed samples of hydroperoxide, and thus gives the Induction point (IP). The change of conductivity with elapsed time is sensed and recorded by a computer attached with the Rancimat.

IPs of pure biodiesel (B100) and biodiesel blends (B5, B10, B20, B30) of *Terminalia belerica* and *Sapindus mukorossi* are determined by using Rancimat apparatus

(Fig 3.11). Experiments are conducted with and without antioxidant additives. Further, IPs are assessed for freshly prepared as well as for stored samples, the details of which are presented below.

3.7.1 Effects of antioxidant additives on IP of freshly prepared samples

To inhibit the oxidation process, generally antioxidants are added with biodiesel. Two types of antioxidants are available (chain breakers and hydroperoxide decomposers) amongst which, chain breaking antioxidants are more popular. Chain breaking antioxidants are of two types *viz.*, phenolic types and amine types. The detail of antioxidant working mechanism is available elsewhere[213] and mentioned in Chapter 1.

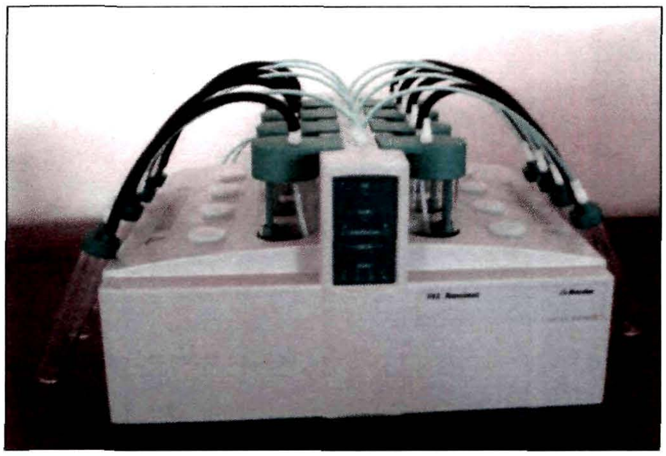


Fig 3.11 Determination of oxidation stability of biodiesel and blends using Rancimat Apparatus

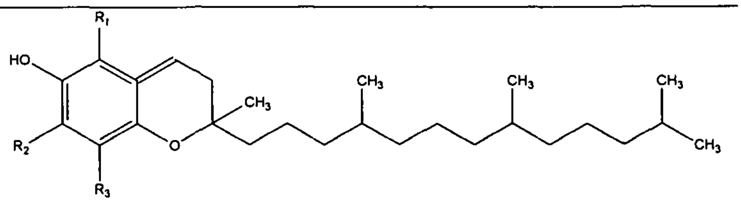
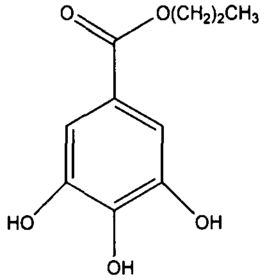
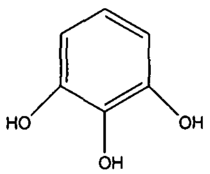
For the present study, six phenolic antioxidants *viz.*, α-tocopherol (Vitamin E), Butylated hydroxyanisole (BHA), Pyrogallol (PY), Propyl gallate (PG), Tert-butylhydroxytoluene (BHT) and Tert-butylhydroxyquinone (TBHQ) are added in some specific concentration (100 ppm, 500 ppm, 1000 ppm, 1500 ppm) with B100 of both the biodiesels to investigate the effect of these antioxidants on IP. The chemical structures of these antioxidants are presented in Table 3.3.

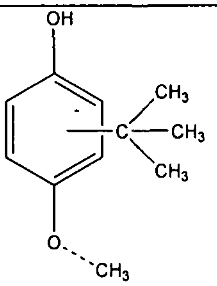
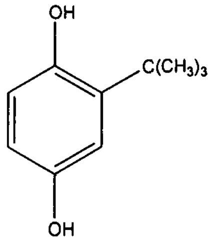
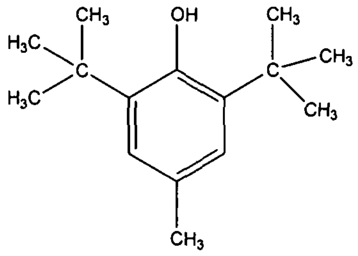
3.7.2 Effects of antioxidant additive on IP of stored samples

Storage stability of biodiesel (B100) and its different blends (B5, B10, B20, B30) with and without antioxidant additives are also assessed through determination of IPs.

Based on the results of freshly prepared sample, three specific antioxidants are sorted *viz.*, PG, TBHQ and BHT for testing on stored samples. For that purpose, 300 ml of each sample is stored in glass bottles for 12 weeks in laboratory, with in a temperature variation of 17^{0}C to 25^{0}C, for both the samples. The information of exact temperature variation and relative humidity for the study period is presented in Appendix 1. Oxidation stability of the samples is (after 2 weeks) assessed periodically. Viscosity, acid value and peroxide value of both the biodiesel samples without antioxidants during storage are also simultaneously ascertained to examine the quality of biodiesel.

Table 3.3 Chemical structures of the antioxidants used[213]

Antioxidant Name	Structure
α-tocopherol	
Butylated hydroxyanisole (BHA)	
Pyrogallol (PY)	

Propyl gallate (PG)	
Tert-butylhydroxyquinone (TBHQ)	
Tert-butylhydroxy toluene (BHT)	

3.8 Diesel engine performance and emission tests

Diesel engine performance tests and emission characteristics of three biodiesel blends namely B5, B10, B20 and also the typical petroleum diesel are carried out in an Indica, 4-cylinders, 4-strokes, water cooled CI engine. Technical details of the diesel engine are given in Table 3.4.

Table 3.4 Basic technical specifications of the test engine

Items	Specifications
Model	Tata Indica
Engine power	39 kW
Cylinder bore	75 mm
Stroke length	79.5 mm
Compression ratio	22:1
No of cylinders	Four
Stroke type	Four
Dynamometer type	Eddy current, water cooled, with loading unit

The test engine is equipped with measuring arrangement such that all the required parameters could be recorded simultaneously and feed into computer for further analysis through software. For assessment of engine performance, the fuel consumption was recorded along with shaft load and speed. The test engine is provided with measuring arrangement such that all the required parameters could be recorded with minimum errors. A loading arrangement is provided in the test engine to vary loads at engine crankshaft. Temperature, pressure, speed, torque, volume flow rate of fuel and air are some of the basic measurements done in the test engine. The measuring devices *viz.*, calorimeter, orificemeter, dynamometer, rotameter and fuel flow meter are provided with the standard test engine. The computerized engine test set-up is shown in Fig 3.12.

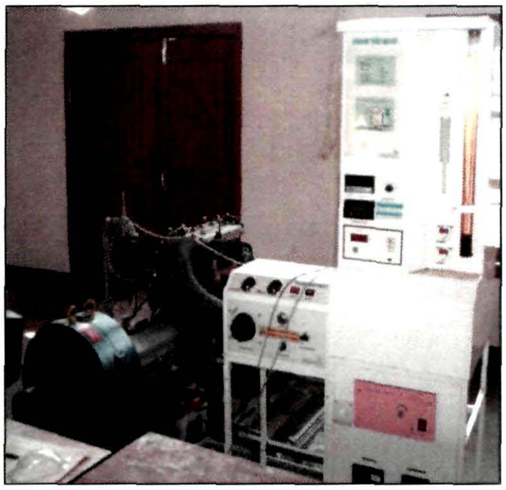


Fig 3.12 Laboratory test engine set up

The performance results in terms of brake power (kW), brake specific fuel consumption (kg/kWh), brake thermal efficiency (%) were taken as output of the engine shaft for each set of testing. The each biodiesel and each level of blending the experiments are carried out at varying engine load conditions. The results were then compared with similar results published elsewhere.

In the present investigation the composition of engine exhaust gases are also analyzed for each of the samples as mentioned in section 3.5. An exhaust gas analyzer (Indus 5 gas analyzer, PEA 205) was used to measure the composition of exhaust gas such as CO, NO_X, Unburned hydrocarbons (HC) (Fig 3.13).

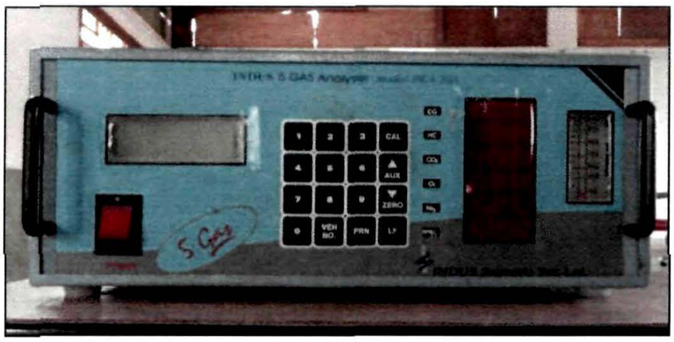


Fig 3.13 Laboratory exhausts gas analyzer

The arrangement of experimental set up for exhaust gas measurement is illustrated in Fig 3.14.

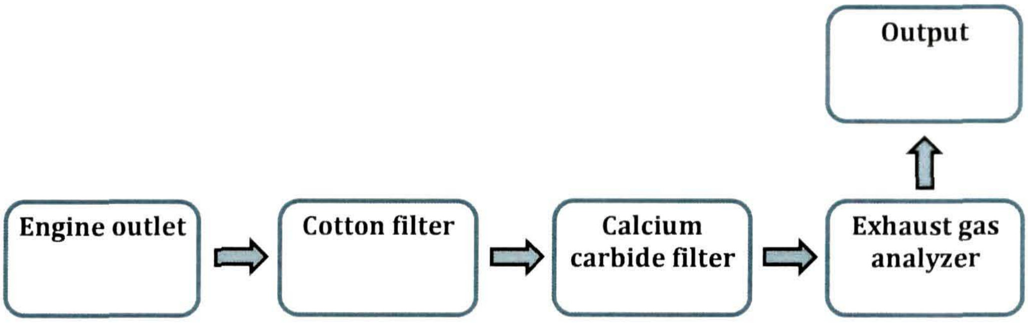


Fig 3.14 Arrangement for exhaust gas analysis

CHAPTER 4

RESULTS AND DISCUSSIONS

CHAPTER 4
RESULTS AND DISCUSSIONS

Prospects of two locally available oil seeds (obtained from forest trees) as feedstocks for biodiesel production are investigated in the present study.

The results of the present investigation *viz.*, (i) Characterization of vegetable oils (Part I) (ii) Production and characterization of biodiesels (Part II) (iii) Oxidation, storage stability of biodiesels and efficacy of antioxidants for enhancing IP (Part III) and (iv) Engine performance and emission characteristics of biodiesel blends (Part IV) are presented in this chapter. Brief introduction of the presentation is highlighted below.

Part I: Properties of *Terminalia belerica* and *Sapindus mukorossi* seed oil

Based on the properties of *Terminalia belerica* and *Sapindus mukorossi* oils suitability of these two oils as raw materials for biodiesel production is discussed. Further, biodiesel feedstock characteristics of similar oilseeds are also compared.

Part II: Production of biodiesels from *Terminalia belerica* and *Sapindus mukorossi* oil and their characterization

Results of transesterification of *Terminalia belerica* and *Sapindus mukorossi* vegetable oils, pertaining to determination of optimum process parameters are discussed. Further, fuel characteristics of both the biodiesels are presented with a comprehensive review of the biodiesels obtained from similar feedstocks reported earlier.

Part III: Oxidation and storage stability of biodiesel obtained from *Terminalia belerica* oil and *Sapindus mukorossi* oil

Oxidation and storage stability is one of the major areas of present investigation. Oxidation stability assessed through measurement of Induction periods (IPs) are presented in this part. Efficacies of some antioxidant additives on storage stability are also studied. Based on the results of efficacy of antioxidants, the most effective additive and concentration is identified.

Part IV: Engine performance and emission characteristics of blends obtained from *Terminalia belerica* and *Sapindus mukorossi* biodiesel and petroleum diesel

Terminalia belerica and *Sapindus mukorossi* neat biodiesel blended with petrodiesel are used for testing engine performance. The results of engine performance including emission results are discussed in this part.

Part I

Properties of *Terminalia belerica* and *Sapindus mukorossi* seed oil

Feedstocks characteristics in terms of oil content, fatty acid profile and other properties of *Terminalia belerica* and *Sapindus mukorossi* are presented and discussed in this part. Further, results pertaining to *Terminalia belerica* and *Sapindus mukorossi* oils compared with oils obtained from similar feedstocks are also presented.

4.1 Characterization of vegetable oils

The morphological features of *Terminalia belerica* and *Sapindus mukorossi* fruits are discussed in Chapter 3.

Terminalia belerica seed consists of 9% kernel, 30% mesocarp and 61% endocarp. The oil content of kernel has experimentally been determined and found as 43% (w/w). With the available information of *Terminalia belerica* seed production and present findings on oil content, it is estimated that, about 1.05 tonne of *Terminalia belerica* seed oil will be available from one hectare of *Terminalia belerica* forest land.

Sapindus mukorossi seed consists of 15% kernel, 29% mesocarp and 56% endocarp. The oil content of kernel has experimentally been determined and found as 39% (w/w). With the available information of *Sapindus mukorossi* seed production and present findings on oil content, it is estimated that, about 0.70 tonne of *Sapindus mukorossi* seed oil will be available from one hectare of *Sapindus mukorossi* forest land.

Further, the oils are characterized in terms of fatty acid profile and other properties (*viz.*, density, viscosity, calorific value, acid value, flash point, cloud and pour point, ash content and carbon residue) which are presented and discussed below.

4.1.1 Fatty acid composition of *Terminalia belerica* and *Sapindus mukorossi* seed oil

Fatty acid profile of *Terminalia belerica, Sapindus mukorossi* and oils of similar feedstocks are presented in Table 4.1.

Terminalia belerica oil contains 39.5% saturated and 60.5% unsaturated fatty acid, whereas *Sapindus mukorossi* contains 16.5% saturated and 81.6% unsaturated fatty acid. Amongst the saturated fatty acid of *Terminalia belerica,* palmitic (32.8%) and stearic (6.4%) are the major constituents. Trace amount of arachidic acid (0.3%) is also present. Dominancy of arachidic (7.5%) and palmitic (5.5%) acid are observed in *Sapindus mukorossi* oil in the domain of saturated fatty acid. Moreover stearic (2.3%), behenic (1%) and lignoceric (0.2%) acid are also present in *Sapindus mukorossi* oil. Amongst the unsaturated fatty acid, major share is contributed by oleic acid in both *Terminalia belerica* (31.3%) and *Sapindus mukorossi* (58.4%) oils. Linoleic (28.8%) and palmitoloic (0.5%) are other unsaturated fatty acid present in *Terminalia belerica* oil, whereas linolenic (17.1%) and linoleic acid (5.4%), erucic (0.4%) and palmitoleic (0.3%) are the other unsaturated fatty acids present in *Sapindus mukorossi* oil.

4.1.2 Comparison of fatty acid profile of *Terminalia belerica* and *Sapindus mukorossi* seed oil with similar forest tree seed oils

Fatty acid profiles of *Terminalia belerica* and *Sapindus mukorossi* oil are also reported elsewhere[214,215,216]. While comparing the results of the present study of *Terminalia belerica* with the previous two studies (Table 4.1), some compositional differences are noticed. Firstly, the minor components of palmitoloic and arachidic acid obtain in present study were not reported by earlier two studies. Secondly, palmitic, oleic and linoleic were the major components obtain in the present study with almost equal contribution of each of these. However, the earlier two studies reported the dominancy of oleic acid with highest share. Moreover, the study conducted by Molla *et al.* (2007)[214] reported the presence of myristic acid instead of linoleic acid in *Terminalia belerica* oil (Table 4.1). The results of present study of *Sapindus mukorossi* is also compared with the study reported by Sengupta *et al.* (1975)[216]. The minor

Table 4.1 Fatty acid profile of *Terminalia belerica*, *Sapindus mukorossi* and comparison with similar oil bearing tree species

Fatty acid	Molecular formula	% by weight								
		Terminalia belerica[a]	*Terminalia belerica*[b]	*Terminalia belerica*[c]	*Sapindus mukorossi*[d]	*Sapindus mukorossi*[e]	*Madhuca indica**	*Pongamia glabra*	*Mesua ferrea*	*Hevea brasiliensis*
Myristic acid	$C_{14}H28O_2$	0	0	17 7	0	0	0	0	0	0
Palmitic acid	$C_{16}H_{32}O_2$	32 8	18 2	21 67	5 5	4	16 00-28 20 **(-48.42)** **(-75.11)**	11 3 **(-190.27)** **(-51.33)**	15 9 **(-106.29)** **(-65.41)**	10 2 **(-221.57)** **(-46.08)**
Palmitoleic acid	$C_{16}H_{30}O_2$	0 5			0 3	0	0	0	0	0
Stearic acid	$C_{18}H_{36}O_2$	6 4	8 2	14 93	2 3	0 2	20 00-25 10 **(-71.62)** **(-89.8)**	9 8 **(-34.69)** **(-76.53)**	9 5 **(-32.63)** **(-75.79)**	8 7 **(-26.44)** **(-73.56)**
Oleic acid	$C_{18}H_{34}O_2$	31 3	50 2	45 67	58 4	62 8	41 00-51 00 **(-31.96)** **(-26.96)**	45 25 **(-30.83)** **(-29.06)**	50 3 **(-37.77)** **(-16.10)**	24 7 **(-26.72)** **(-136.44)**
Linoleic acid	$C_{18}H_{32}O_2$	28 8	10 8	0	5 4	4 6	8 90-13 70 **(-154.87)** **(-52.21)**	24 75 **(-16.36)** **(-78.18)**	0	39 6 **(-27.27)** **(-86.36)**
Arachidic acid	$C_{20}H_{40}O_2$	0 3	0	0	7 5	4 4	0 00-3 30 **(-90.91)** **(-127.27)**	0	0	0
Linolenic acid	$C_{18}H_{30}O_2$	0	0	0	17 1	1 6	0	2 9	21 3	16 3
Behenic acid	$C_{22}H_{44}O_2$	0	0	0	1	22 4	0	3 2	0	0
Erucic acid	$C_{22}H_{42}O_2$	0	0	0	0 4	0	0	0	0	0
Lignoceric acid	$C_{24}H_{48}O_2$	0	0	0	0 2	0	0	0	0	0
Unidentified	-	0	0	0	1 9	0	0	0	0	0
Saturated fatty acids	-	**39.5**	**26.4**	**54.3**	**16.5**	**31**	**47.95**	**24.3**	**25.4**	**18.9**
Unsaturated fatty acids		**60.5**	**61**	**45.67**	**81.6**	**69**	**57.3**	**72.9**	**71.6**	**80.6**

[a]- *Terminalia belerica* in present study, [b]-*Terminalia belerica* reported by Bera *et al.*[215] [c]-*Terminalia belerica* reported by Molla *et al.*[214], [d]-*Sapindus mukorossi* in present study,[e]-*Sapindus mukorossi* by Sengupta *et al.*[216],* values are reported in range, Figures within parenthesis represent percentage change in values w.r.t *Terminalia belerica* (first row) and *Sapindus mukorossi* (second row)

palmitoleic, behenic, erucic and lignoceric acid obtain in the present study were not reported in the earlier study. Oleic acid is the dominant fatty acid in both studies. Presence of eicosenoic acid is reported in the study by Sengupta *et al.*, however, is found absent in the present case. The varietal difference of the plants might be the reason of compositional variation which requires further investigation. Overall, all these results indicate the dominancy of total unsaturated fatty acid in both the vegetable oils considered for the present study.

The fatty acid profiles of *Terminalia belerica* and *Sapindus mukorossi* are also compared with oils obtained from similar non-edible feedstocks which are reported earlier. The oils considered for comparison here are madhuca (*Madhuca indica*)[50], pongamia (*Pongamia glabra*)[48], hevea (*Hevea brasiliensis*)[59], and mesua (*Mesua ferrea*)[53].

The fatty acid profile of *Terminalia belerica* oil differs from that of other four types of oil. *Terminalia belerica* oil is richer in palmitic acid while poorer in stearic acid compared to the other four varieties of oils considered in this study. Like madhuca, *Terminalia belerica* oil also contains small amount of arachidic acid, which remains absent in other three varieties of oil. *Sapindus mukorossi* oil is richer in arachidic acid while poorer in stearic acid as compared to the other four varieties of oils considered in this study. Like pongamia, small amount of behenic acid is present in *Sapindus mukorossi*, and also contain lignoceric acid which is absent in all the oils considered for the study.

Amongst the unsaturated fatty acids, oleic and linoleic are the major components in *Terminalia belerica* oil. Share of oleic in *Terminalia belerica* is lesser than that of madhuca, pongamia and mesua, whereas, it is higher than that of hevea seed oil. On the other hand, linoleic compound in *Terminalia belerica* is higher than that of madhuca and pongamia and lower than that of hevea seed oil. It is further noted that as in madhuca seed oil, linolenic acid is absent in *Terminalia belerica* oil. Amongst the unsaturated fatty acids, oleic and linolenic are the major components in *Sapindus mukorossi* oil. Share of oleic is the highest in *Sapindus mukorossi* than all the oils considered in the present study. On the other hand, linolenic percentage in *Sapindus mukorossi* is higher than that of pongamia and hevea, but lower than that of mesua seed oil. It is further noted that a small amount of erucic acid is present in *Sapindus mukorossi*, which is found absent in all other cases.

It is also seen that the total unsaturated fatty acid of *Terminalia belerica* and *Sapindus mukorossi* oil is marginally lower than the pongamia and mesua, but higher than that of some species of madhuca seed oil. It is found that saturated fatty acid in *Terminalia belerica* is less than that of madhuca by about 17% and more than that of pongamia and mesua by about 38% and 35%, respectively. Similarly, saturated fatty acid present in *Sapindus mukorossi* is less than that of madhuca, pongamia and mesua by 66%, 32% and 35%, respectively. These varieties of forest based seeds are reported as potential source of biodiesel feedstock in India.

Thus, considering the comparison results of fatty acid profile of *Terminalia belerica* and *Sapindus mukorossi* seed oil with similar feedstocks, both of these found locally available raw materials could be suitable for biodiesel production in the northeastern region of India.

4.1.3 Characterization of oils obtained from *Terminalia belerica* and *Sapindus mukorossi*

Different properties (*viz*., density, viscosity, calorific value, acid value, flash point, cloud and pour point, ash content and carbon residue) of *Terminalia belerica* and *Sapindus mukorossi* oil have been evaluated using standard ASTM techniques, details of which are discussed in Chapter 3. The results are presented in Table 4.2 and discussed below.

Density

The densities of *Terminalia belerica* and *Sapindus mukorossi* oils at 15^{0}C are 910 kg/m^3 and 923 kg/m^3, respectively (Table 4.1). Density of *Terminalia belerica* oil is lower than that of pongamia, mesua and madhuca by 2.26%, 2.67% and 5.21%,

Table 4.2 Properties of *Terminalia belerica*, *Sapindus mukorossi* and comparison with similar oil bearing tree species

Properties	Units	*Terminalia belerica*	*Sapindus mukorossi*	*Madhuca indica*	*Mesua ferrea*	*Pongamia glabra*	*Hevea brasiliensis*
Density at 15°C	kg/m^3	910	923	960	935	931	910
				(5.21)	**(2.67)**	**(2.26)**	**(0.00)**
				(3.85)	**(1.28)**	**(0.86)**	**(-1.43)**
Viscosity at 40°C	mm^2/s	25 60	32 10	24 58	26 00	26 06	66 20
				(-4.15)	**(1.54)**	**(1.77)**	**61.33**
				(-30.59)	**(-23.46)**	**(-23.18)**	**51.51**
Calorific value	MJ/kg	37 50	38 00	36 10	39 84	40 51	37 50
				(-3.88)	**(5.87)**	**(7.43)**	**(0.00)**
				(-5.26)	**(4.62)**	**(6.20)**	**(-1.33)**
Acid value	mgKOH/g	8 01	15 60	38 00	16 40	1 21	34 00
				(77.63)	**(48.17)**	**(-602.48)**	**(75.00)**
				(59.00)	**(5.00)**	**(-1187.60)**	**(54.18)**
Flash point	°C	102	159	232	NA	NA	198
				(61.21)	-	-	**(54.55)**
				(31.47)	-	-	**(19.70)**
Cloud point	°C	9	8	NA	NA	NA	NA
Pour point	°C	6	6	15	0	0	NA
				(60.00)	-	-	-
				(60.00)	-	-	-
Ash content	wt%	0 0012	0 02	0 90	0 02	0 00	NA
				(99.89)	**(95.00)**	-	-
				(98.33)	**(25.00)**	-	-
Carbon residue	wt%	1 06	1 10	3 70	1 60	1 21	NA
				(71.41)	**(33.88)**	**(12.20)**	-
				(70.22)	**(31.13)**	**(8.55)**	-

Figures within parenthesis represent percentage change in values w.r.t Terminalia belerica (first row) and Sapindus mukorossi (second row); NA-Not avilable

Though heavier than *Terminalia belerica* oil, *Sapindus mukorossi* oil is lighter than pongamia, mesua and madhuca by 0.86%, 1.28% and 3.85%.

Viscosity

The viscosity of *Terminalia belerica* oil is 25.6 mm^2/s, which is comparable with madhuca (-4.15%), mesua (1.54%) and pongamia (1.77%), but much lesser than hevea (61.33%). On the other hand, viscosity of *Sapindus mukorossi* oil is 32.1 mm^2/s, which is higher than *Terminalia belerica*, madhuca, mesua and pongamia by 20.25%, 30.59%, 23.43% and 23.18%, respectively. Viscosity of hevea is 51.51% more than *Sapindus mukorossi* oil.

Calorific value

Calorific value of *Terminalia belerica* and *Sapindus mukorossi* oil is found to be 37.5 MJ/kg and 38 MJ/kg, respectively, which is higher than madhuca (3.88% and 5.26%), but lower than mesua (5.87% and 4.62%) and pongamia (7.43% and 6.20%).

Acid value

The acid value of *Terminalia belerica* oil is 8.01 mgKOH/g, which is higher than pongamia, but lower than that of madhuca (38 mgKOH/g), mesua (16.40 mgKOH/g) and hevea (34 mgKOH/g). Again, the acid value of *Sapindus mukorossi* (15.6 mgKOH/g) is more than *Terminalia belerica* and pongamia (1.21 mgKOH/g), but lower than that of that of mesua, madhuca and hevea.

Acid value mainly depends on the harvesting and storage condition of the seed. For the present study, *Terminalia belerica* seeds have been purchased from local vendor in the month of January. According to the information, the seeds were freshly harvested, as the harvesting time is during November-December. The harvesting time for *Sapindus mukorossi* is during November. But the seeds have been collected from nursery, which were stored for about 6 months after harvesting. This might be the reason of higher acid value of *Sapindus mukorossi* oil as compared to *Terminalia belerica* oil. After collection, without further delay, both the oil seeds were first dried in Sun and then de-shelled and milled to get the vegetable oil.

Flash point

Flash point of *Terminalia belerica* is 102^{0}C, which is lower than madhuca (232^{0}C) and hevea (198^{0}C). Whereas flash point of *Sapindus mukorossi* oil is 159^{0}C, which is higher than *Terminalia belerica*, but lower as compared to madhuca (232^{0}C) and hevea (198^{0}C).

Cloud and pour point

The cloud point and pour points of *Terminalia belerica* oil are found as 9^{0}C and 6^{0}C, respectively, whereas the cloud point and pour point of *Sapindus mukorossi* are found as 8^{0}C and 6^{0}C, respectively. Only pour point data of madhuca (15^{0}C), mesua (0^{0}C) and pongamia (0^{0}C) could be compared. Thus it is found that cold flow property of *Sapindus mukorossi* oil is better than *Terminalia belerica* oil.

Ash content

Ash content of *Terminalia belerica* oil is found to be as 0.0012 wt%. It is lower than madhuca (0.9 wt%) and mesua (0.02 wt%). The ash content of *Sapindus mukorossi* oil (0.02 wt%) is much higher than *Terminalia belerica* oil and comparable with mesua (0.02 wt%), but lower than that of madhuca (0.9 wt%).

Carbon residue

Carbon residue of *Terminalia belerica* is found as 1.06 wt%, which less than pongamia, mesua and madhuca by 12.20%, 33.88% and 71.41% respectively. Again, carbon residue value for *Sapindus mukorossi* oil is 1.10 wt%, which is also lower than pongamia (8.55%), mesua (31.13%) and madhuca (70.22%), but comparable with *Terminalia belerica* (1.06 wt%).

4.1.4 Summary

From the results of the properties, it has been observed that the fatty acid profiles of both the new varieties of oil are found suitable for biodiesel production. It is observed that *Sapindus mukorossi* oil is heavier and more viscous compared to *Terminalia belerica* oil. Calorific value of *Terminalia belerica* oil is marginally lower than the calorific value of *Sapindus mukorossi* oil. *Sapindus mukorossi* oil is safer to handle with its higher flash point as compared to *Terminalia belerica.* The differences in characteristics of these two oils are expected to reflect in varying fuel properties of the resultant biodiesel. Moreover, the transesterification requirement would also vary between *Terminalia belerica* and *Sapindus mukorossi*, as they have varying level of acid values. Comprehensively, results of vegetable oil characterization show that both of these seed oils as prospective feedstock for biodiesel production.

Part II

Production of biodiesels from *Terminalia belerica* and *Sapindus mukorossi* oil and their characterization

4.2 Production of *Terminalia belerica* and *Sapindus mukorossi* biodiesel

Transesterification of vegetable oil for biodiesel production is achieved through a series of unit operations. Alcohol to oil molar ratio, catalyst type and amount, temperature and reaction time are generally operational variables. It has been earlier reported that alcohol to oil molar ratio, temperatures, type and amount of catalyst and reaction time are the variable parameters which affect the transesterification process of a given vegetable oil. Mostly these parameters are identified through optimization procedure based on experimental results. The detail of the transesterification process is presented in Chapter 3 (Section 3.4). Results pertaining to the optimization process are presented and discussed below.

4.2.1 Optimization of parameters for production of *Terminalia belerica* biodiesel

Single stage alkaline transesterification reaction is the technique employed for production of biodiesel from *Terminalia belerica* oil with varying alcohol to oil molar ratio and catalyst amount. The reaction yield is monitored at different time interval, keeping temperature and rotation speed of reaction vessel constant throughout the experiments.

The methanol/oil molar ratio (4:1, 6:1, 8:1, 10:1 and 12:1) is varied to find the effect of varying amount of methanol on biodiesel production. In all the five experiments, 600 rpm rate of agitation, 65^0C reaction temperature and 1.00 wt% $NaOCH_3$ are employed. The optimum yield (93%) of *Terminalia belerica* biodiesel is gained at methanol/ oil molar ratio of 10:1 (Fig 4.1(a)). Higher quantities (beyond 10:1) of methanol had an adverse effect on *Terminalia belerica* biodiesel production. This is evident by steadily lowering yields with increasing molar ratio from 10:1 to 12:1 (Fig

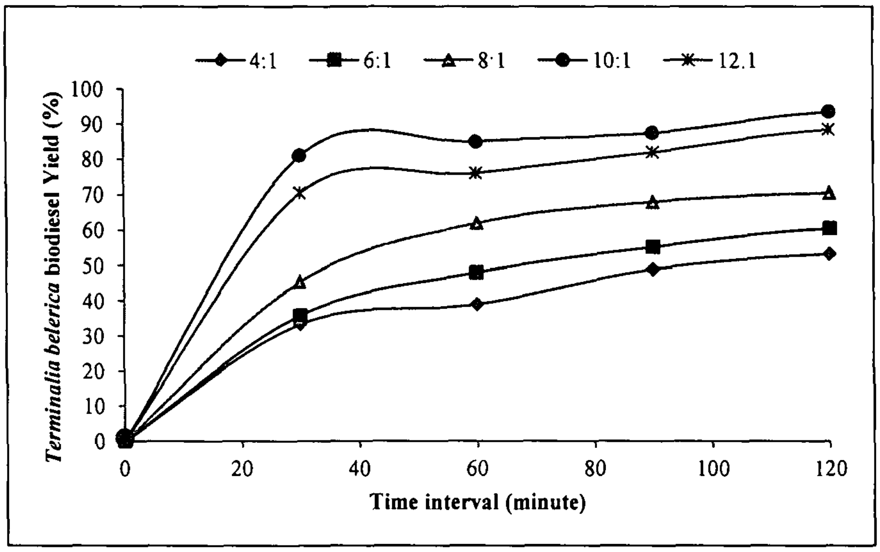


Fig 4.1(a) Yield of *Terminalia belerica* biodiesel by varying the alcohol to oil molar ratio with reaction time

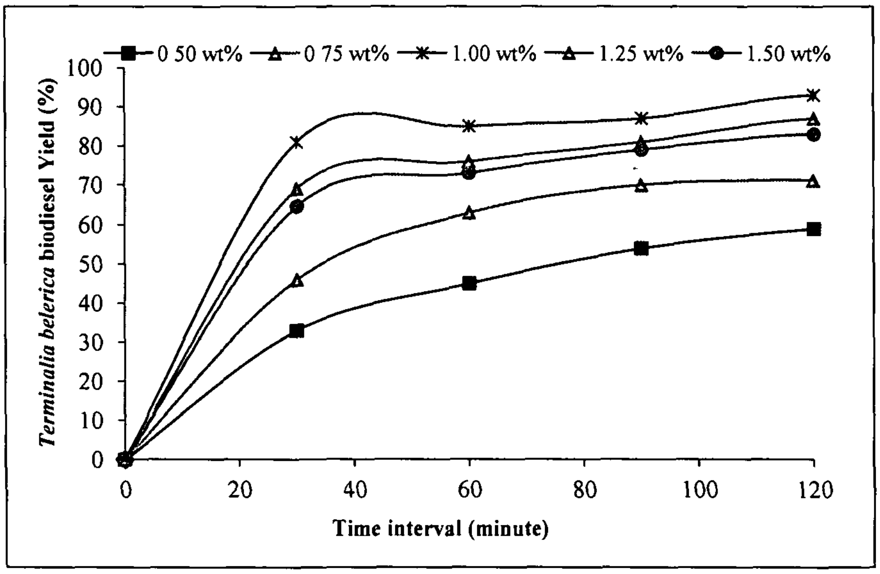


Fig 4.1(b) Yield of *Terminalia belerica* biodiesel by varying the catalyst concentration with reaction time

4.1(a)). At methanol to oil molar ratios greater than 10:1, separation of esters from glycerol was difficult. The unreacted methanol, when present, can suppress the gravity decantation so that the apparent yield of biodiesel decreases because traces of glycerol may remain in the biodiesel phase. Similar results are also obtained by Kafuku and Mbarawa (2010)[92] and Anwara et al. (2010)[167] while transesterifying *Moringa oleifera* and *Hibiscus esculentus* oils, respectively.

While studying the effect of catalyst amount on biodiesel yield, different sets of experiments are carried out with varying the amount of catalyst, keeping molar ratio 10:1 and temperature 65^{0}C and stirring speed at 600 rpm as constant (Fig 4.1(b)). The effect of sodium methoxide ($NaOCH_3$) concentration on the transesterification of the oil is observed with its concentration varying from 0.5 to 1.5 wt %. Experimental results show changes in ester yield with different catalyst concentration. As the sodium hydroxide concentration increases, the yield of ester content also increases. Insufficient amounts of $NaOCH_3$ resulted in incomplete conversion of triglycerides into the esters, as indicated, from its lower ester yield. The ester content reached an optimal value as the $NaOCH_3$ concentration reached 1 wt%, and further increases in catalyst concentration caused decrease in ester production (Fig 4.1(b)). A large amount of soap is observed while adding excess amount of sodium methoxide (1.5 wt%). This observation is explained by earlier researchers[72,92,94,167] due to increased saponification due to the addition of excess alkaline catalyst.

4.2.2 Optimized process parameters for production of *Sapindus mukorossi* biodiesel

Since the acid value of *Sapindus mukorossi* oil is found to be 15.6 mgKOH/g, a pretreatment stage is required prior to alkaline transesterification for successful production *Sapindus mukorossi* biodiesel.

It is experimentally observed that molar ratio of 6:1 with 1 wt% of H_2SO_4, give the maximum reduction in acid value (acid value 1.89 mgKOH/g) within 60 minutes and yield high amount of methyl ester in the next stage. It is also observed that with the addition of 1 wt% of H_2SO_4, the product did not seem much darker. For this experiment, temperature is kept constant at 55^0 C.

Alkaline catalytic transesterification

The formation of biodiesel (methyl ester) is affected by the amount of oil to alcohol ratio. Experiments are also performed with varying molar ratios *viz.*, 4:1, 6:1, 8:1, 10:1, 12:1, keeping temperature (65^{0}C) catalyst amount (1 wt%) as constant. Molar ratio of 8:1 gives the optimum yield (92.5%) as compared to others, as observed from Fig 4.2(a). Further increase in molar ratio result in decrease in yield, because high methanol amount interfere with the separation of glycerol because of its high solubility [159,165,167].

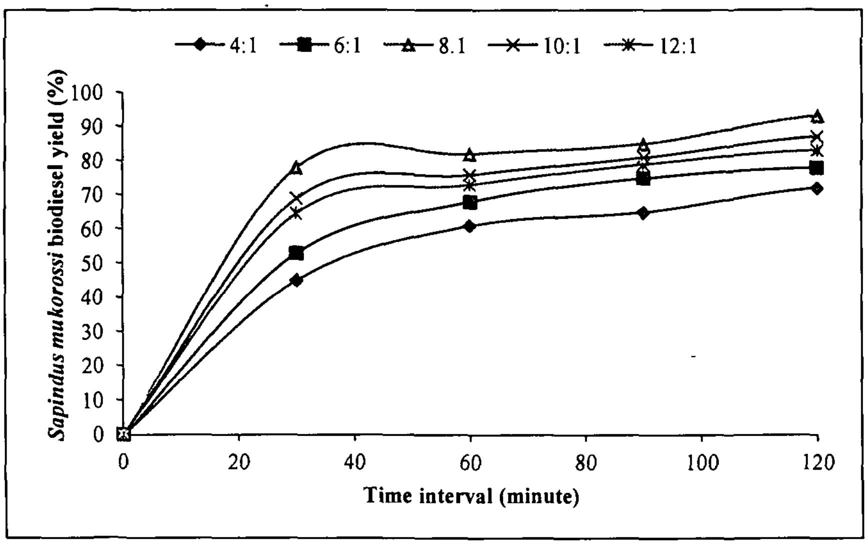


Fig 4.2(a) Yield of *Sapindus mukorossi* biodiesel by varying the methanol to oil with reaction time

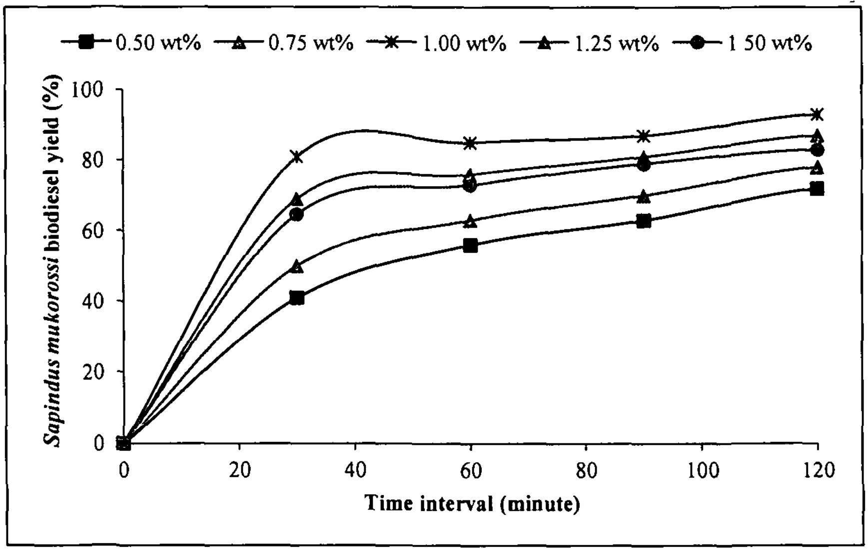


Fig 4.2(b) Yield of *Sapindus mukorossi* biodiesel by varying the catalyst concentration with reaction time

The unreacted methanol also creates problem in phase separation, resulting in apparent decrease in methyl ester yield. Fig 4.2(b) shows the effect of different amount of catalyst on biodiesel yield in different time intervals. 1 wt% of $NaOCH_3$ is found to be the optimum quantity as on addition of more amount of catalyst results in a decrease in the yield of methyl ester. This is attributed to the fact of soap formation, which in turn decreases the methyl ester yield. Anwara *et al.* (2010)[167] and Sinha *et al.* (2008)[36] found the same observation while transesterifying *Hibiscus esculentus* and rice bran oil.

4.2.3 Analysis of biodiesel samples through NMR spectroscopy

The product (biodiesel) formation is analyzed by the peaks appeared in ^1H NMR and ^{13}C NMR for *Terminalia belerica* and *Sapindus mukorossi* biodiesel is as shown in Fig 4.3((a)-(b)) and Fig 4.4((a)-(b)), respectively. The details of the peaks for both the biodiesel samples are discussed in Table 4.3.

Table 4.3 Analysis of the NMR peaks of *Terminalia belerica* and *Sapindus mukorossi*

^1H NMR		^{13}C NMR	
Peaks	**Corresponding bonding**	**Peaks**	**Corresponding bonding**
δ 5.33	olefinic proton (-CH=CH-)	δ 173.95	carbonyl carbon
3.64	methoxy proton ($-CO_2CH_3$)],	129.57& 128.01	olefinic carbon
2.76	bis-allylic protons ($-C=C-CH_2-C=C-$)	51.2	methoxy carbon
2.28	α-methylene to ester ($-CH_2-CO_2Me$)],	33.98-14.03	methylene and methyl carbons
2.01	α-methylene to double bond ($-CH_2-C=C-$)		
1.61	β-methylene to ester (CH_2-C-CO_2Me)		
1.30 and 1.25	backbones methylens ($-(CH_2)n-$)		

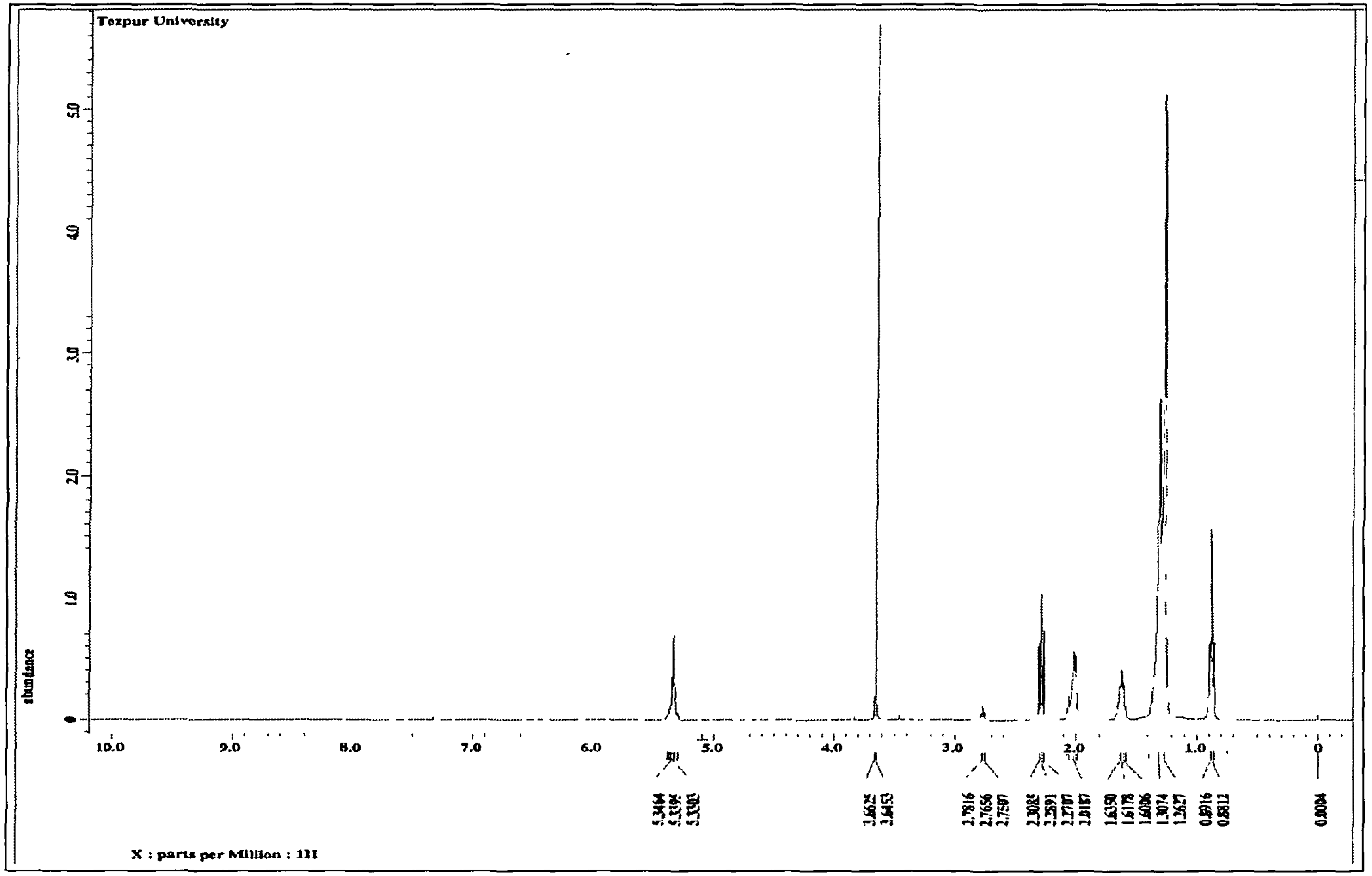


Fig 4.3 (a) ^{1}H NMR spectra of *Terminalia belerica* biodiesel

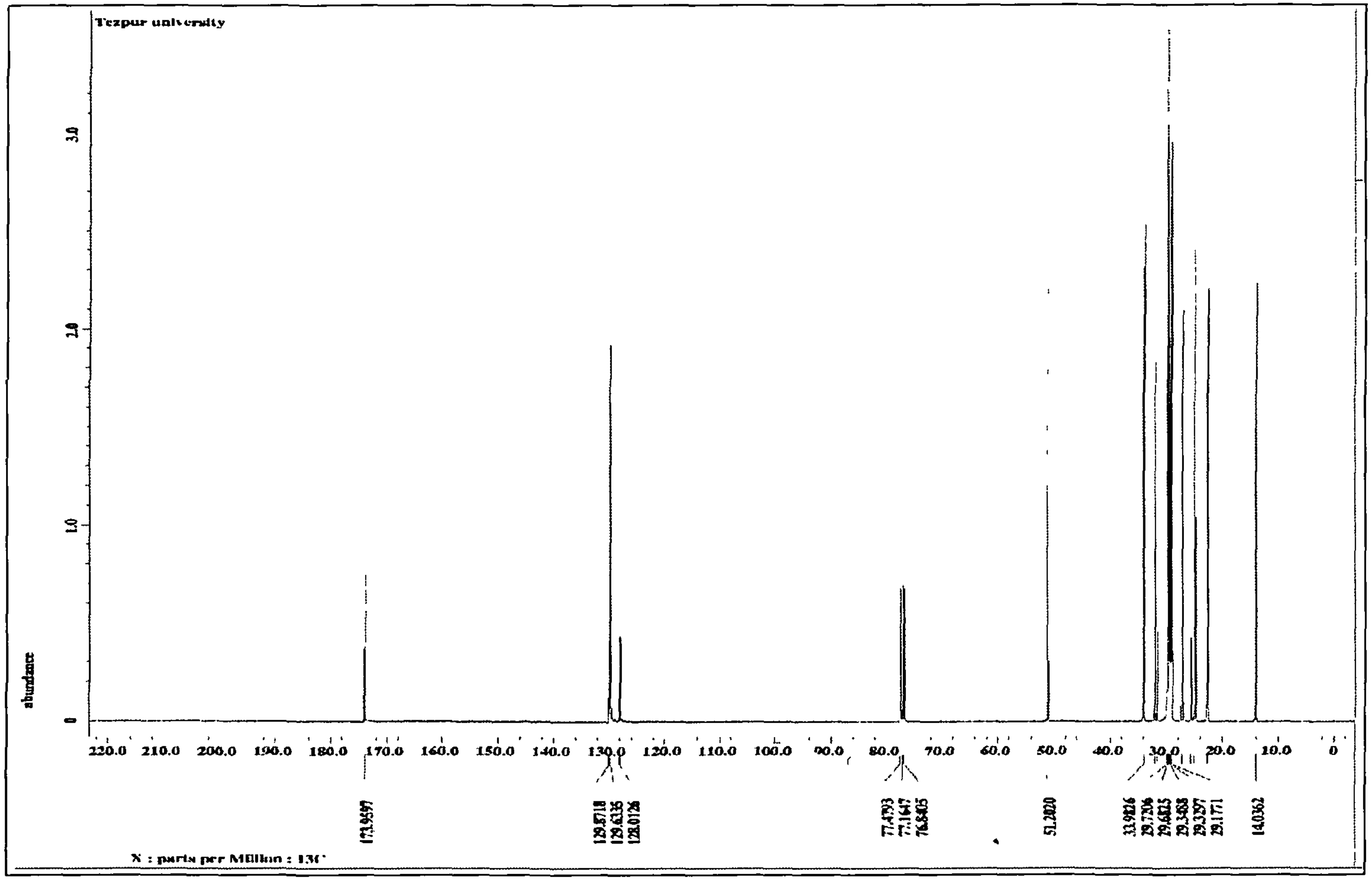


Fig 4.3 (b) ^{13}C NMR spectra of *Terminalia belerica* biodiesel

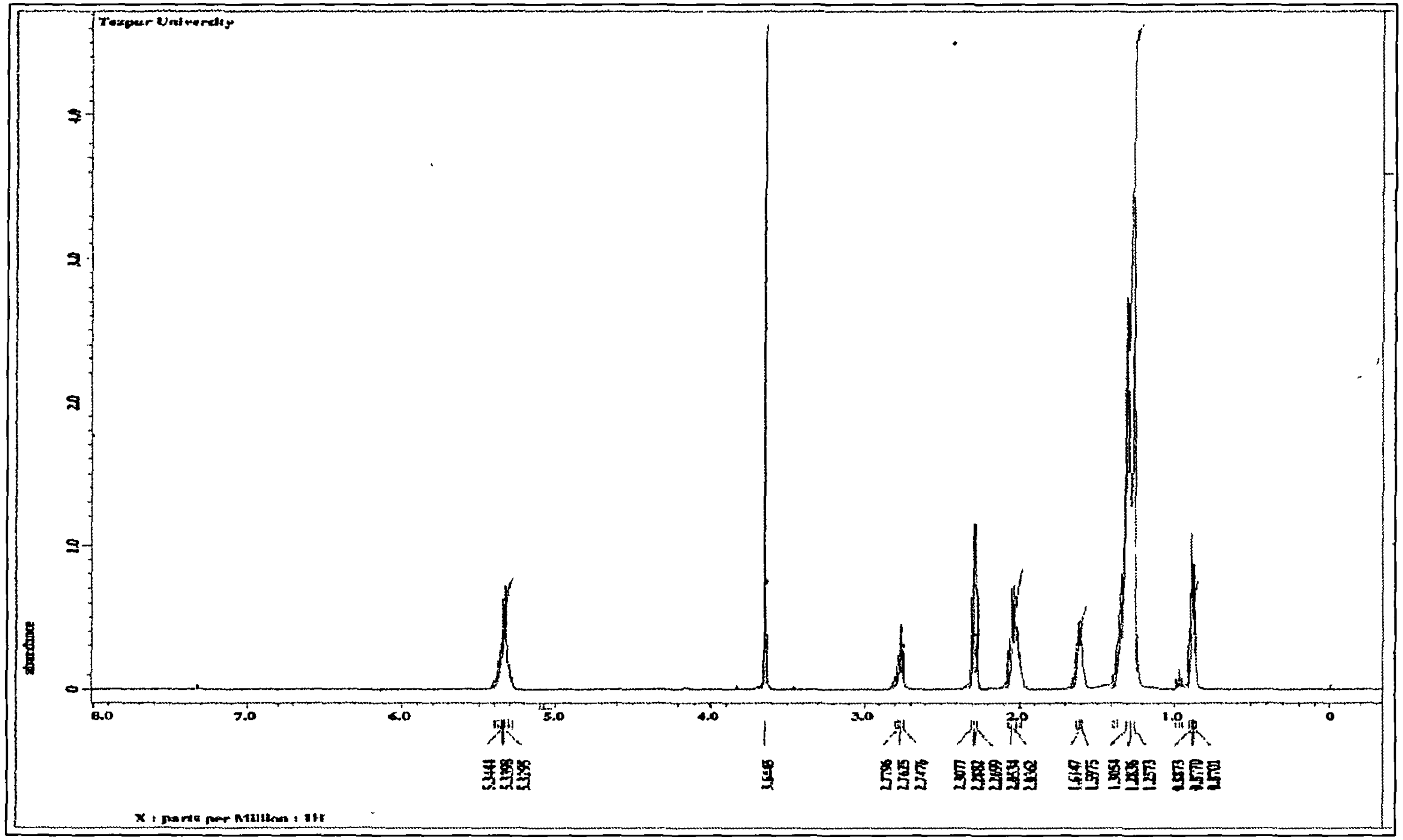


Fig 4.4 (a) ^{1}H NMR spectra of *Sapindus mukorossi* biodiesel

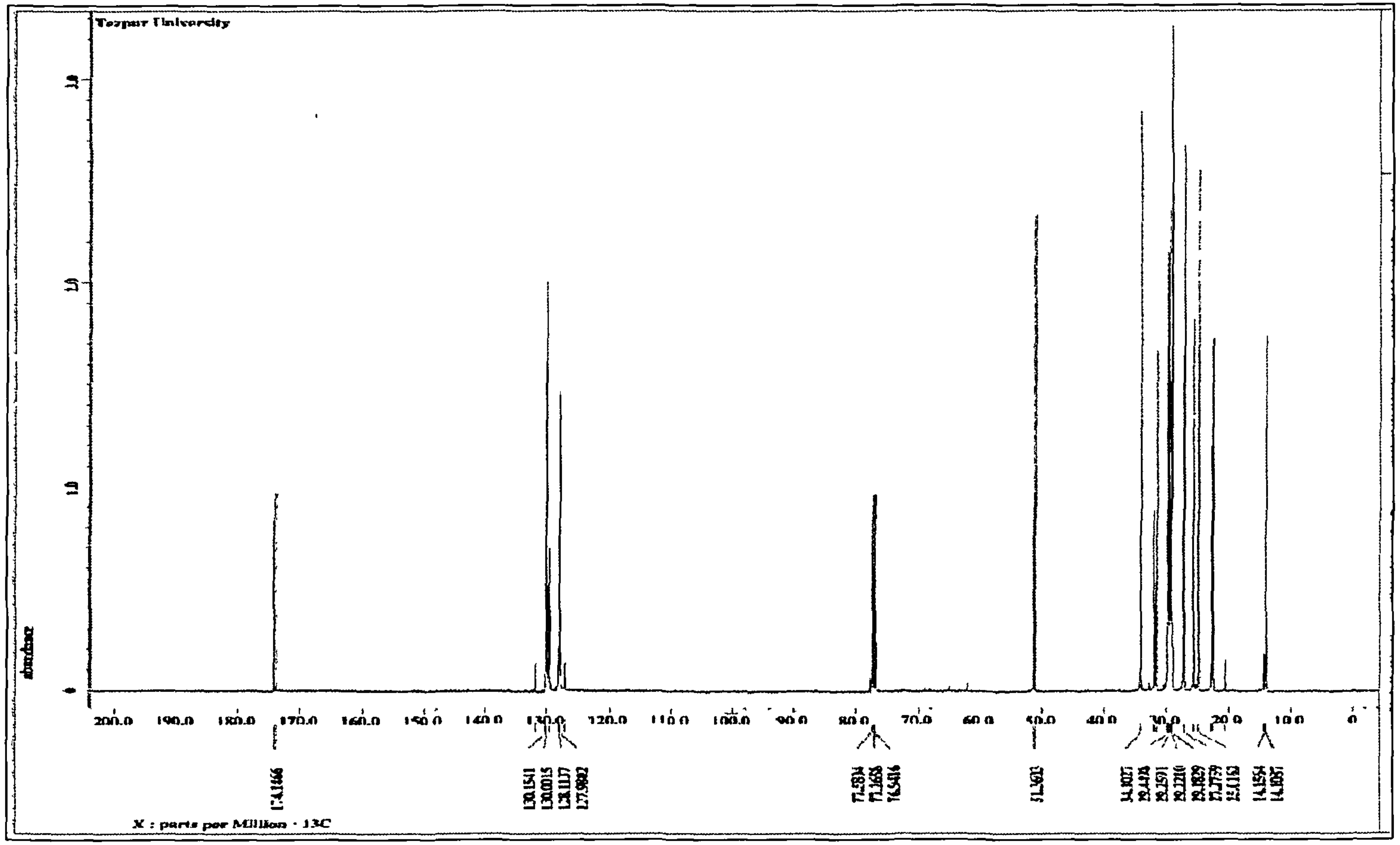


Fig 4.4 (b) ^{13}C NMR spectra of *Sapindus mukorossi* biodiesel

The appearance of singlet signals at δ3.64 in ^{1}H NMR and δ51.20 in ^{13}C NMR represents methoxy protons and methoxy carbon of the ester functionality which ensures conversion of oil to methyl ester. The NMR spectra also conform that the biodiesel is free from glycerol as no signal corresponding to glycerol moiety appears in ^{1}H NMR and ^{13}C NMR spectra for *Terminalia belerica* and *Sapindus mukorossi* biodiesel. Proton and carbon NMR spectra obtained in this study is comparable with *Thevetia peruviana* methyl ester as reported in literature[133].

4.2.4 Characterization of *Terminalia belerica* and *Sapindus mukorossi* biodiesel

Engine performance studies of biodiesel produced from different feedstocks produces highly variable results. In most of the cases the quality and purity of the biodiesel is considered as the major reason for such variable results. There are some specific quality parameters, details of which are discussed in Chapter 3 (section 3.6). After successful transesterification of *Terminalia belerica* and *Sapindus mukorossi* oil into biodiesel, it is then attempted to investigate the fuel quality parameters of both the biodiesel samples. The detail of the assessment procedure is discussed in Chapter 3, and results are presented (Table 4.4) and discussed below.

Density

The densities of both the oils are reduced with transesterification as seen from Table 4.4. The densities of *Terminalia belerica* and *Sapindus mukorossi* biodiesels at 15^{0}C are 882 kg/m^{3} and 876 kg/m^{3} respectively, which are marginally higher than the density of diesel, and within the prescribed limit of European (EN 14214-07) standard specification.

Viscosity

The viscosities of *Terminalia belerica* and *Sapindus mukorossi* biodiesels are 5.17 mm^{2}/s and 4.63 mm^{2}/s, respectively, which is much higher than petro-diesel. The viscosity of *Sapindus mukorossi* lies within the limit of both EN 14214-07 and ASTM D6751-07. However, viscosity of *Terminalia belerica* biodiesel lies only within the limit of ASTM D6751-07 (Table 4.4).

Calorific value

The calorific values of *Terminalia belerica* (39.22 MJ/kg) and *Sapindus mukorossi* (40.00 MJ/kg) biodiesels are less as compared to petroleum diesel (45 MJ/kg).

Acid value

The acid values of *Terminalia belerica* (0.23 mgKOH/g) and *Sapindus mukorossi* (0.14 mgKOH/g) biodiesels are higher than diesel (0.104 mgKOH/g). The acid value of freshly prepared biodiesel should be within 0.50 mgKOH/g as per EN 14214-07 (Table 4.4). Thus, the acid value of both the biodiesels conforms to the required norm.

Flash point

Flash points of *Terminalia belerica* and *Sapindus mukorossi* biodiesel are found to be 90^0C and 140^0C respectively. Both the biodiesels show higher flash point than that of petrodiesel (49^0C). The flash point of *Sapindus mukorossi* lies within the prescribed limit of EN 14214-07. A fuel with 90^0C or greater flash point is considered as non-hazardous from storage point of view. In this regard, *Sapindus mukorossi* biodiesel is safer as compared to *Terminalia belerica* biodiesel and petro-diesel.

Cloud point and pour point

The cloud and pour point of *Terminalia belerica* biodiesel are found as 6^0C and 3^0C, respectively; whereas for *Sapindus mukorossi* biodiesel, these are -1^0C and -4^0C, respectively. Cloud and pour point of diesel (-12^0C, -15^0C) are much lower than those of both the biodiesels samples. However, both the biodiesels satisfy EN 14214-07 specification in terms of cloud and pour point.

Sulphated ash content

The ash content of biodiesels of *Terminalia belerica* and *Sapindus mukorossi* are found to be as 0.0005 wt% and 0.003 wt%, respectively. Both the biodiesels are superior to diesel (0.01 wt%) in terms of ash content, and well within the limit of EN 14214-07 and ASTM D6751-07 specification.

Carbon residue

Carbon residue of *Terminalia belerica* biodiesel (0.0085 wt%) is much lower than the petro-diesel (0.10 wt%) and *Sapindus mukorossi* biodiesel (0.12 wt%). According to EN 14214-07, carbon residue value should be within 0.05 wt%, and *Sapindus mukorossi* biodiesel does not conform to this norm.

Copper strip corrosion

Copper strip corrosion of both the biodiesels and diesel are found to be as 1a (Class 1), which is within the prescribed limit of EN14214-07.

Distillation characteristics

Petroleum diesel has wider boiling range of 139^{0}C to 370^{0}C relative to *Terminalia belerica* (130^{0}C- 347^{0}C) and *Sapindus mukorossi* (193^{0}C to 383^{0}C) biodiesel. According to ASTM standards specification, the maximum temperature should not exceed 360^{0}C for 90% distillation fraction of the fuel. Thus, *Terminalia belerica* has favourable distillation characteristics considering the standards prescribed by ASTM D6751-07.

Sulphur content

Sulphur contents of *Terminalia belerica* (96 ppm) and *Sapindus mukorossi* (102 ppm) biodiesel is lower than diesel considered for the present study (250 ppm). However, sulphur content of both the biodiesels does not conform to the norm of EN 14214-07.

Sulphuric acid is used as catalyst in the esterification stage for producing *Sapindus mukorossi* biodiesel and may be some remain as residue. This could cause to the higher level of sulphur content in *Sapindus mukorossi* biodiesel as compared to *Terminalia belerica* biodiesel. Sulphur contents of both the biodiesels are above EN

14214-07 limit. Therefore, so hydro-treating or distillation of the biodiesels before use is recommended.

Cetane number

Cetane number (CN) of *Terminalia belerica* (53) and *Sapindus mukorossi* (56) biodiesels are greater than that of petroleum diesel (46). Moreover, CNs of both the biodiesels are within the limit of both EN 14214-07 and ASTM D6751-07 specification (Table 4.4).

Water content

Water content of *Terminalia belerica* and *Sapindus mukorossi* biodiesel are 126 mg/kg and 86 mg/kg, respectively and found to conform to the limit of EN 14214-07 standard specification.

Lubricity

Biodiesel shows better lubricating property as compared to petro-diesel. Lubricity is measured in terms of wear scar diameter, which is found as 0.193 mm for *Terminalia belerica* and 0.181 mm for *Sapindus mukorossi* biodiesel, much less than that of diesel (0.450 mm).

Oxidation stability

Oxidation stability is measured in terms of Induction period, which is found to be 3.76 h for *Terminalia belerica*, and 1.20 h for *Sapindus mukorossi* biodiesel, which are well below the standard norm as per EN 14214.

Elemental analysis

Terminalia belerica biodiesel contain 75.2 wt% Carbon, 13.5 wt% Hydrogen and 10.1 wt% Oxygen, whereas *Sapindus mukorossi* biodiesel contain 74.1 wt% Carbon, 14.1 wt% Hydrogen and 10.6 wt% Oxygen.

4.2.5 Reflection of fatty acid profile on biodiesel properties

It is explained elsewhere that viscosity, cetane number and calorific value of fuel increases with increase in chain length, and decrease with increase in unsaturation. The degree of unsaturation (DU) for *Terminalia belerica* and *Sapindus mukorossi* oils are 89.4 and 103.4, respectively. DU is calculated using the procedure reported elsewhere[105]. Positive correlation between viscosity and DU was reported earlier and supports the higher viscosity of *Terminalia belerica* biodiesel than that of *Sapindus mukorossi* biodiesel.

The major fatty acid components of *Terminalia belerica* oil are oleic, linoleic, palmitic and stearic acid. Viscosities of the corresponding methyl esters at 40^0C are reported previously as 4.51 mm^2/s, 3.65 mm^2/s, 4.38 mm^2/s and 5.51 mm^2/s, respectively[101]. Thus, viscosity of *Terminalia belerica* (5.17 mm^2/s) could be the weighted average values of the components. The major fatty acid components present in *Sapindus mukorossi* oil are oleic, linolenic, palmitic and arachidic acid, with relatively lower viscosity values of corresponding methyl esters at 40^0C as 4.51 mm^2/s (oleic acid), 3.14 mm^2/s (linolenic acid) and 4.38 mm^2/s (palmitic acid) respectively.

As mentioned earlier, the molecular weight, carbon number and density of the constituent fatty acids govern the calorific value of a fuel[17]. The calorific value and cetane number of *Sapindus mukorossi* biodiesel is more than *Terminalia belerica* biodiesel. This is probably due to the presence of long chain fatty acid present in *Sapindus mukorossi* biodiesel as compared to *Terminalia belerica* biodiesel.

Cloud and pour point of biodiesel samples decrease with increase in unsaturation as reported in several literature[17,105]. *Sapindus mukorossi* shows better fuel properties in terms of cloud and pour point, probably because of the presence of more amount of unsaturated fatty acid. It is also reported that unsaturated fatty acids exhibit better lubricity than saturated one[217]. In this context, better lubricating property of *Sapindus mukorossi* is well explained. As it is already reported that fuel containing substantial amount of oleic, linoleic, linolenic acids have strong influence on oxidative stability. DU of *Sapindus mukorossi* biodiesel is more than *Terminalia belerica* biodiesel. Lower oxidation stability of *Sapindus mukorossi* might be due to higher degree of unsaturation compared to DU of parent material of *Terminalia belerica.*

Table 4.4 Properties of *Terminalia belerica* and *Sapindus mukorossi* biodiesel

Properties	*Terminalia belerica*	*Sapindus mukorossi*	Diesel	Europe (EN 14214-07)	USA(ASTM D6751-07)
Density at 15^{0}C (kg/m^3)	882	876	852	860-900	NA
Viscosity at 40^{0}C (mm^2/s)	5.17	4.63	2.781	3.5-5.0	1.9-6.0
Calorific value (MJ/kg)	39.22	40	45	35(calculated)	NA
Acid value (mgKOH/g)	0.23	0.14	0.104	0.5	NA
Flash point (^{0}C)	90	140	49	>101	130
Cloud point (^{0}C)	6	-1	-12	-3 to 12	NA
Pour point (^{0}C)	3	-4	-15	-15 to 10	NA
Sulphated ash content (wt%)	0.0005	0.003	0.01	0.02 max	0.02 max
Carbon residue (wt%)	0.0085	0.12	0.1	0.05	NA
Copper strip corrosion	1a	1a	1a	1a	1c
IBP/FBP(^{0}C)	130/347	193/383	139/370	NA	360^{0}C, 90% distillation
Sulphur content (ppm)	96	102	250	10 (max)	NA
Cetane number	53	56	46	51(min)	47(min)
Water (mg/kg)	126	86		150	NA
Lubricity (WSD, mm)	0.193	0.181	0.45	NA	NA
Oxidation stability (h)	3.76	1.20	NA	6	3
Elemental analysis (wt%)					
Carbon	75.2	74.1			
Hydrogen	13.5	14.1			
Oxygen	10.1	10.6			

NA- Not available

4.2.6 Comparison of properties of *Terminalia belerica* and *Sapindus mukorossi* biodiesel with the biodiesels obtained from similar feedstocks

The properties of biodiesel obtained from four different tree seed vegetable oils are compared with *Terminalia belerica* biodiesel (Table 4.5) and *Sapindus mukorossi* biodiesel (Table 4.6).

The densities of *Terminalia belerica* and *Sapindus mukorossi* are higher than that of madhuca and hevea by 1.01% and 0.23%, respectively (Table 4.5 & Table 4.6). However, *Terminalia belerica* and *Sapindus mukorossi* biodiesels are lighter than mesua and pongamia. It is also observed that the percentage decrease in density during esterification (estimated from the values of vegetable oil and respective biodiesel) is the highest in madhuca which is 8.96%, followed by *Sapindus mukorossi* (5.09%) mesua (3.96%), pongamia (3.01%) and *Terminalia belerica* (2.99%). Thus, a variation of decrease in density has been observed with minimum change shown by *Terminalia belerica*. The composition of fatty acid in the resultant biodiesel might be the reason of such variation in percentage change.

Viscosities of *Terminalia belerica* and *Sapindus mukorossi* biodiesels are higher than madhuca but less than mesua, pongamia and hevea (Table 4.5 & 4.6). The percentage reduction of viscosity with transesterification is found to be the highest in seed oils of hevea (91.22%) followed by that of *Sapindus mukorossi* (85.57%), madhuca (83.81%), *Terminalia belerica* (79.80%), pongamia (76.48%) and mesua (76.15%).

Calorific values of *Terminalia belerica* and *Sapindus mukorossi* biodiesels are more than that of madhuca (36.80 MJ/kg) and hevea (36.50 MJ/kg) but less as compared to pongamia (43.42 MJ/kg) and mesua (42.23 MJ/kg) (Table 4.6). The higher level of water content might be the reason of lower calorific values of *Terminalia belerica* in comparison with mesua and pongamia.

Cetane number of *Terminalia belerica* and *Sapindus mukorossi* biodiesels are comparable with the biodiesels. Flash point of *Sapindus mukorossi* biodiesel is higher than *Terminalia belerica*, mesua, pongamia and hevea, but lower than that of madhuca. The pour point of *Terminalia belerica* is higher than mesua and pongamia but that of *Sapindus mukorossi* biodiesel is higher than hevea, but lower than all the four biodiesels considered for the study. The distillation characteristics of *Terminalia belerica* and *Sapindus mukorossi* biodiesel are almost similar to that of madhuca (126^0C - 350^0C) and mesua (210^0C - 375^0C). Sulphur content of *Terminalia belerica* and *Sapindus mukorossi* biodiesels are higher than that of the biodiesels of mesua (70 ppm) and pongamia (50 ppm) but much lower than madhuca (164.8 ppm). Wear scar diameter of pongamia is found highest (0.200 mm), followed by *Terminalia belerica* (0.193 mm), *Sapindus mukorossi* (0.181 mm) and madhuca (0.171 mm).

4.2.7 Fuel characteristics of the blends of biodiesel obtained from *Terminalia belerica* and *Sapindus mukorossi* seed oils with petroleum diesel

The fuel characteristics of the biodiesels obtained from *Terminalia belerica* and *Sapindus mukorossi* oils (Table 4.3) it has been observed that they do not meet all the required specifications to be used as diesel engine fuels as per ASTM standards or European standards for biodiesels.

Density, cetane number, ash content, acid value and copper strip corrosion test of both the biodiesels were found to be within the acceptable limits, whereas viscosity, carbon residue, flash point are not within the acceptable limits. Moreover, both the biodiesels showed narrow boiling ranges as compared to petro-diesel. Calorific values of the biodiesels were also found to be significantly lower than that of petro-diesel.

Considering the above, blends of each of the biodiesels with petroleum diesel were prepared (B5, B10, B20 and B30) and the fuel characteristics of each of the blends were determined, and presented in Tables 4.7.

Table 4.5 Comparison of *Terminalia belerica* biodiesel with similar forest seed biodiesels

Properties	Diesel	*Terminalia belerica*	*Sapindus mukorossi*	*Madhuca indica*	*Mesua ferrea*	*Pongamia glabra*	*Hevea brasiliensis*	EN 14214-07	ASTM D6751-07
Density at 15^{0}C (kg/m^3)	852	882.8	876	874	898	903	874	860-900	NA
				(-1.01)	**(-1.69)**	**(-2.24)**	**(-1.01)**		
				(-0.23)	**(-2.45)**	**(-2.99)**	**(-0.23)**		
Viscosity at 40^{0}C (mm^2/s)	2.781	5.17	4.63	3.98	6.2	6.13	5.81	3.5-5.0	1.9-6.0
				(-29.90)	**(-16.61)**	**(-15.66)**	**(-11.02)**		
				(-16.33)	**(-25.32)**	**(-24.47)**	**(-20.31)**		
Calorific value (MJ/kg)	45.01	39.22	40.02	36.8	42.23	43.42	36.5	NA	NA
				(-6.58)	**(-7.13)**	**(-9.67)**	**(-7.45)**		
				(-8.70)	**(-5.28)**	**(-7.88)**	**(-9.59)**		
Acid value (mg KOH/g)	0.104	0.23	0.14	0.41	0.01	0	NA	0.5	NA
				(-43.90)	**(-2200.00)**				
				(-65.85)	**(-1300.00)**				
Flash point (^{0}C)	49	90	140	208	112	95	138	>101	130
				(-56.73)	**(-19.64)**	**(-5.26)**	**(-34.78)**		
				(-32.69)	**(-25.00)**	**(-47.37)**	**(-1.45)**		
Cloud point (^{0}C)	-12	6	-1	NA	NA	NA	NA	-3 to 12	NA
Pour point (^{0}C)	-15	3	-4	6	3	3	-8	-15 to 10	NA
				(-50)	**(0.00)**	**(0.00)**	**(-1.37)**		
				(0.00)	**(-233.33)**	**(-233.33)**	**(-50)**		
Ash content (wt%)	0.01	0.0005	0.003	0.01	0.01	0.001	NA	0.02 (max)	0.02 (max)
				(-95.00)	**(-95.00)**	**(-50.00)**			
				(0.00)	**(-70.00)**	**(-70.00)**	**(-200.00)**		
Carbon residue (wt%)	0.1	0.0085	0.12	0.02	0.25	0.781	NA	0.05	NA
				(-57.50)	**(-96.60)**	**(-98.91)**			
				(-500.00)	**(-52.00)**	**(-84.64)**			

Copper strip corrosion	1a	1a	1a	1a	NA	NA	1a	1a	1c
IBP/FBP(^{0}C)	139/370	130/347	193/383	126/350	210/375	219/430	NA	NA	360^{0}C, 90%
Water content (mg/kg)	55	126	102	NA	35	3	NA	150	NA
					(-260.00)	**(-320.00)**			
Sulphur content (ppm)	250	96		164 8	70	50	NA	10 (max)	NA
			56	**(-41.75)**	**(-37.14)**	**(-92.00)**			
				(-38.11)	**(-45.71)**	**(-104.00)**			
Cetane Number	46	53	0 181	65	54	55	NA	51 (min)	47 (min)
				(-18.46)	**(-1.85)**	**(-3.64)**			
				(-13.85)	**(-3.70)**	**(-1.82)**			
Lubricity (WSD, mm)	0 45	0 193		0 171	NA	0 2	NA	NA	NA
				(-12.86)		**(-3.50)**			
				(-5.85)		**(-9.50)**			

Figures in the parenthesis represent percentage change in property values w.r.t *Terminalia belerica* and *Sapindus mukorossi*; NA-Not available

The kinematic viscosity of the blends at 40^0C was found to increase gradually with the increase of percentage of biodiesel in the blends. When biodiesel of *Terminalia belerica* was blended with petrodiesel, the viscosities of B5 and B10 blends became 2.9 mm^2/s and 3.45 mm^2/s, respectively. Similarly B5 and B10 of *Sapindus mukorossi* became 2.5 mm^2/s and 3.81 mm^2/s, respectively. However, higher level of viscosity increase is noticed with increase in blending level for both the biodiesels. The viscosities of the blends containing up to 20% by volume of biodiesel from *Terminalia belerica* seed oil most likely meets the requirement as per ASTM D 7467 standard for biodiesel blends. Similar to viscosity, marginal change of densities of B5 and B10 are noticed for both *Terminalia belerica* and *Sapindus mukorossi* biodiesel.

Gradual increase in densities is observed while increasing the percentage of biodiesel in blends. On blending the biodiesel with petroleum diesel, the carbon residue values of both *Terminalia belerica* and *Sapindus mukorossi* blends gradually increases with the increase of percentage of biodiesel in the blends. The carbon residues of all the blends of *Sapindus mukorossi* are more than petro-diesel. All these values are within the acceptable limit of ASTM D7467. On blending the cetane numbers of the blends were found to increase with the increase of concentration of biodiesel in them. All these values are within the acceptable limit of ASTM D7467.

4.2.8 Summary

Alkaline catalytic transesterification process is chosen for production of biodiesel from *Terminalia belerica* oil. The molar ratio (10:1) and catalyst concentration (1 wt%) could be ascertained for *Terminalia belerica*, which ensure the highest possible yield (93%) of biodiesel amongst the series of experiments. Similar attempts are also made to identify the process parameters for conversion of *Sapindus mukorossi* oil to biodiesel. The molar ratio and catalyst concentration for conversion of *Sapindus mukorossi* oil at 65^0C for 120 minutes are found as 8:1 and 1 wt%, with a yield of 92.5%. The process parameters are corresponding to reaction time of 120 minutes at 65^0C.

Table 4.6 Properties of *Terminalia belerica* and *Sapindus mukorossi* biodiesel blends

Property	Units	*Terminalia belerica* Biodiesel/Diesel blend				*Sapindus mukorossi* Biodiesel/Diesel blend				Diesel	ASTM D7467
		B5	B10	B20	B30	B5	B10	B20	B30		
Density	kg/m^3	837	842	852	856	835	836	842	853	835	NA
Viscosity	mm^2/s	2 9	3 45	4 12	4 23	2 5	3 31	3 59	3 81	2 781	1 9-4 1
Calorific Value	MJ/kg	44	42 1	41 8	41	44 32	43 1	42 7	41 18	45 01	NA
Acid Value	mgKOH/g	0	0 02	0 5	0 7	0	0 04	0 05	0 18	0 104	NA
Peroxide Value	meq/kg	4 56	5 1	5 78	6 2	6 1	6 5	8 23	8 9	NA	NA
Flash point	^{0}C	59	63	67	71	64	67	73	89	49	52
Pour point	^{0}C	-6	-4	0	0	-8	-4	-2	0	0	Country specific
Carbon residue	wt%	0 012	0 023	0 028	0 037	0 12	0 26	0 28	0 33	0 1	0 35
Sulphur content	ppm	54	62	70	73	54	62	70	73	42	NA
Cetane Number	-	47	49	49	50	49	49	50	51	45	40
IBP/FBP	^{0}C	132/377	148/377	152/372	156/348	146/369	149/371	156/375	162/377	139/370	345^0,T90

While obtaining the properties of both the biodiesel, it was observed that *Sapindus mukorossi* biodiesel is less viscous and denser than *Terminalia belerica* biodiesel. Calorific value of *Sapindus mukorossi* biodiesel is marginally higher than *Terminalia belerica* biodiesel. Moreover, *Sapindus mukorossi* biodiesel shows better fuel handling properties considering flash point as compared to *Terminalia belerica* biodiesel. *Sapindus mukorossi* biodiesel also exhibits better cold flow properties compared to *Terminalia belerica* biodiesel. However, both the biodiesels fail to meet the EN 14214-07 specification, as far as oxidation stability is concerned.

Overall, the fuel characterizations of both the new varieties of biodiesels are found comparable with the similar biodiesel varieties reported earlier. Overall, density, viscosity, cetane number, ash content, carbon residue, flash point, pour point, acid value, copper strip corrosion, IBP/FBP for both the biodiesels are found to conform the existing biodiesel norms. Two aspects of both the types of biodiesels, namely, sulphur content and oxidation stability would require further attention.

Part III
Oxidation and storage stability of biodiesels obtained from *Terminalia belerica* and *Sapindus mukorossi* oil

4.3 Oxidation and storage stability

Biodiesel has lower oxidation stability as compared with petroleum diesel because of its high content of unsaturated methyl esters, especially poly-unsaturated methyl esters such as methyl linoleate (C18:2) and methyl linolenate (C18:3), which can easily be oxidized to form acids, aldehydes, esters, ketones, peroxides and alcohols. These products not only affect the properties of biodiesel, but also create problems of engine operation. As a result, the European Committee for Standardization established a standard (EN 14214) for biodiesel in 2007, which requires that biodiesel must reach a minimum induction period of 6 h as tested by Rancimat method at 110^0C.

This part deals with the oxidation stability of neat biodiesel and blends (B5, B10, B20 and B30) and improvement of stability with the addition of antioxidants by adding in different concentration. The methodology is presented in Chapter 3 and results are presented and discussed below.

4.3.1. Changes of fuel properties of *Terminalia belerica* and *Sapindus mukorossi* biodiesel and their blends on storage

Degradation of fuel quality during storage due the oxidation could be estimated through the changes in viscosity, acid value and peroxide value[218]. Biodiesel obtained from *Terminalia belerica* and *Sapindus mukorossi* oil is stored in borosilicate glass bottle as described in Chapter 3, Section 3.7.2. Viscosity, acid value and peroxide values for the both the stored samples are determined in 2 weeks interval. The detail of which is presented in Chapter 3.

Quality deterioration pertaining to these three specific parameters up to 12 weeks of storage are presented in Fig 4.5(a)-(b), Fig 4.6(a)-(b), Fig 4.7(a)-(b) and discussed below.

Viscosity

The changes in viscosity with storage time are presented in Fig 4.5(a) and Fig 4.5(b) for all the five samples (B5, B10, B20, B30 and B100) of both *Terminalia belerica*

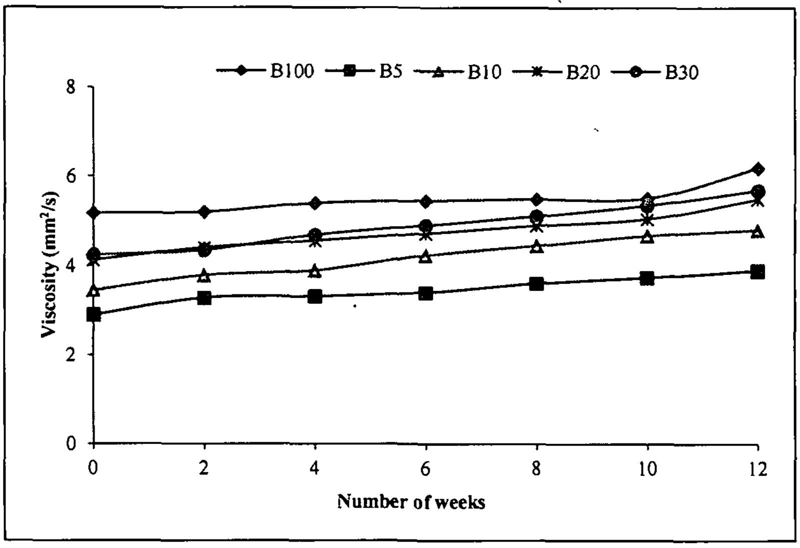


Fig 4.5(a) Variation of viscosity of *Terminalia belerica* biodiesel (B100) and blends during storage (B5, B10, B20 and B30)

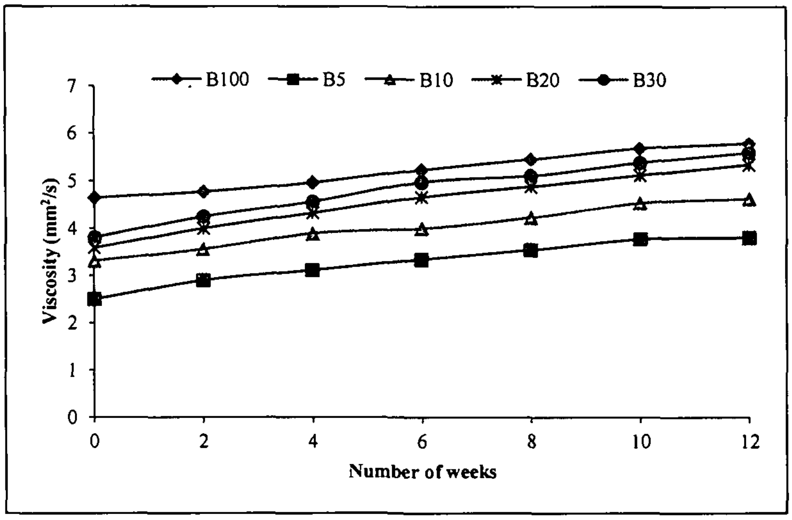


Fig 4.5(b) Variation of viscosity of *Sapindus mukorossi* biodiesel (B100) and blends during storage (B5, B10, B20 and B30)

and *Sapindus mukorossi* biodiesel. In general, viscosity values of all the samples are found to increase with time of storage and this might be attributed to the oxidation process. Further, it is also noticed from Fig 4.5(a) that except the 12th week old *Terminalia belerica* B100 sample, viscosity values of all other samples remain within the limit of ASTM D6751 (6 mm^2/s). The rates of increase in viscosity during storage up to 12 weeks are found to vary amongst the samples. Neat biodiesel (B100), with an increase from 5.17 mm^2/s to 6.2 mm^2/s during the 12 weeks, exhibits lesser rate of increase as compared to blended samples.

Again, 12th week old samples of *Sapindus mukorossi* (B5, B10, B20, B30 and B100), viscosity values of all the samples remain within the limit of ASTM D6751 (6 mm^2/s) (Fig 4.5(b)). The viscosity of neat biodiesel of *Sapindus mukorossi* increases from 4.63 mm^2/s to 5.78 mm^2/s during 12 weeks. Here also the increase in viscosity amongst the samples found to vary at different rate. Evidence of formation of insoluble products due to interaction of biodiesel and petro-diesel is reported elsewhere[219]. Possible chemical reaction and formation of products during interaction of biodiesel and petro-diesel might be the reason of varying rates of increase in viscosity amongst the samples in the present study.

Peroxide value

Peroxide value (meq/kg) is another significant indicator of oxidative degradation and measures the extent of lipid peroxidation[106]. A higher peroxide value implies greater formation of hydroperoxide through the peroxide chain mechanism. Although value for this parameter is not specified in biodiesel fuel standard, yet it is reported to influence CN, a parameter influencing ignition behavior of biodiesel. Increases in peroxide value of all the five samples of both *Terminalia belerica* and *Sapindus mukorossi* during 12th weeks of storage are presented in Fig 4.6(a) and Fig 4.6(b).

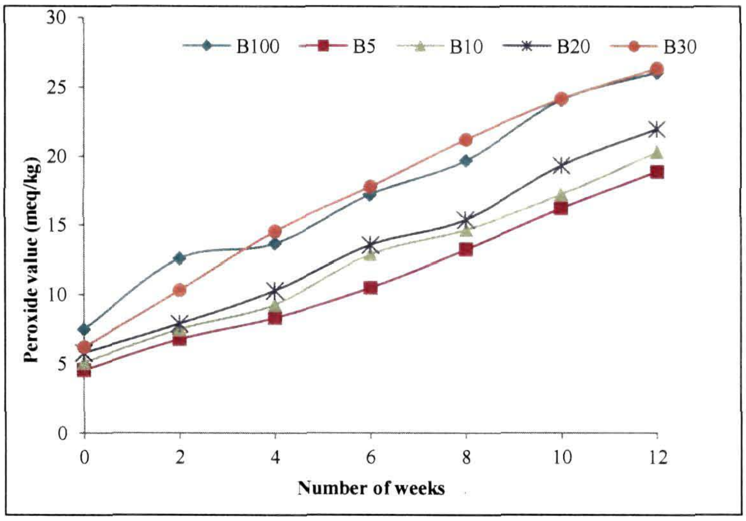


Fig 4.6(a) Variation of peroxide value of *Terminalia belerica* biodiesel (B100) and blends during storage (B5, B10, B20 and B30)

Peroxide value of neat biodiesel (B100) of *Terminalia belerica* changes from 7.5 meq/kg to 26.1 meq/kg during 12th weeks of storage. Rate of increase in peroxide value of two samples *viz*., B30 and B100 are different than the remaining three samples.

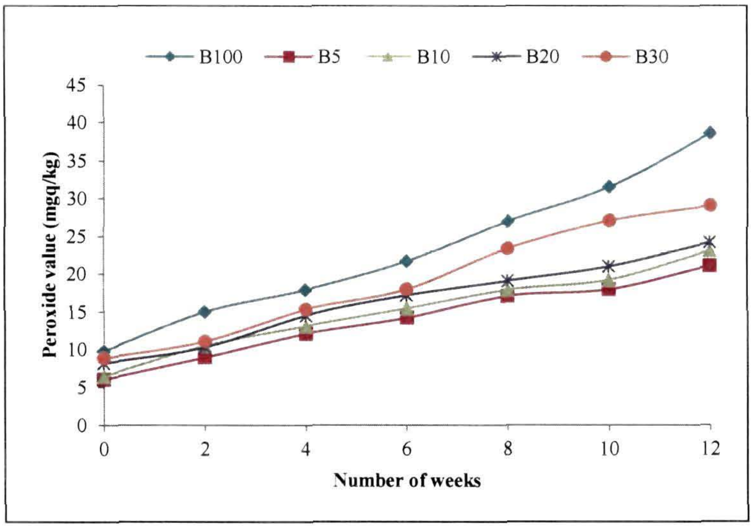


Fig 4.6(b) Variation of peroxide value of *Sapindus mukorossi* biodiesel (B100) and blends during storage (B5, B10, B20 and B30)

Peroxide value of neat biodiesel (B100) of *Sapindus mukorossi* changes from 9.8 meq/kg to 38.59 meq/kg during 12th week of storage. Rate of increase of samples B5, B10 and B20 are uniform during 12th week of storage. Like *Terminalia belerica,* samples B100 and B30 of *Sapindus mukorossi* also show higher rate of increase in peroxide value as compared to other blends. This might be due to formation of varying amount of hydroperoxide resulted due to blend dependent reaction.

Acid value

Degradation of biodiesel quality is also reflected by change in acid value (mgKOH/g) of biodiesel. The changes of acid value of all the five samples of *Terminalia belerica* and *Sapindus mukorossi* during 12 weeks of storage are presented in Fig. 4.7(a) and Fig 4.7(b).

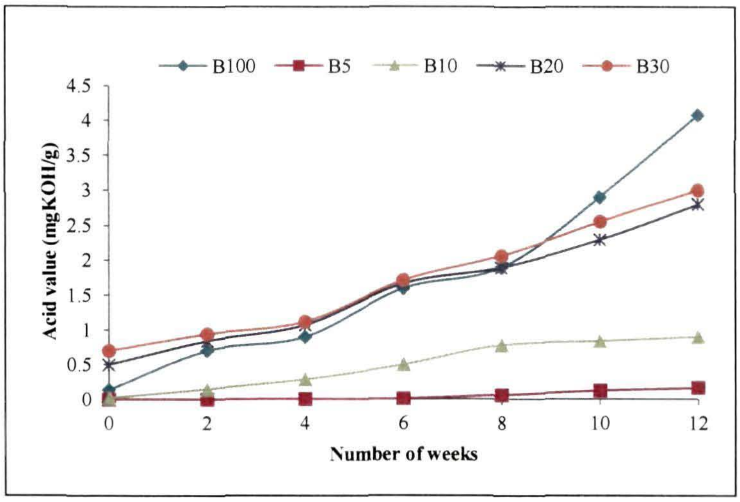


Fig 4.7(a) Variation of acid value of *Terminalia belerica* biodiesel (B100) and blends during storage (B5, B10, B20 and B30)

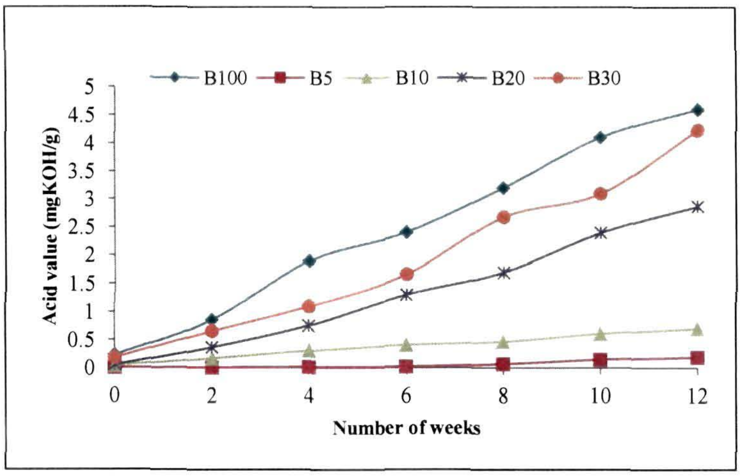


Fig 4.7(b) Variation of acid value of *Sapindus mukorossi* biodiesel (B100) and blends during storage (B5, B10, B20 and B30)

Identical rate of increase in acid value is observed in case of three samples of *Terminalia belerica viz.*, B100, B30 and B20 up to 8th week of storage. Rate of increase in acid value of neat *Terminalia belerica* biodiesel (B100) accelerates after 8th week of storage. However, *Sapindus mukorossi* shows uniform rate of increase throughout the storage period. The rates of increase in acid value of B5 and B10 during storage are lesser than remaining three samples. This is true for both the samples Fig 4.7(a) and Fig 4.7(b).

During storage, the esters are first oxidized to form peroxides, which then undergo complex reaction including a split into more reactive aldehydes which further oxidize into acids, and thus increase in the acid value[106]. However, hydrolysis of ester into alcohol and acids by the traces of water present in samples are also thought to increase acid value[213]. The higher acid value exhibited by the blends (B20 and B30) could be attributed to differences in magnitude of hydrolysis reaction due to the presence of higher concentration of biodiesel in diesel[220].

4.3.2. Oxidation stability of neat biodiesel (B100) of *Terminalia belerica* and *Sapindus mukorossi* with and without antioxidants

Induction period (IP) of freshly prepared biodiesel samples of *Terminalia belerica* and *Sapindus mukorossi* without antioxidant are found as 3.76 h and 1.20 h, respectively, which fail to conform to EN 14214. Six antioxidants *viz.*, PY, PG, TBHQ, BHT, BHA and α-tocopherol are added in varying concentration from 100 ppm to 1500 ppm for testing their efficacy. It is observed that both the type and concentration of antioxidants are found to influence the oxidation stability (IP).

Effect of six different antioxidants on oxidation stability of freshly prepared B100 of *Terminalia belerica* and *Sapindus mukorossi* samples are shown in Fig 4.8(a) and Fig 4.8(b).

Two antioxidants namely PG and PY are found to enhance IP of *Terminalia belerica* to satisfy the existing norm even with the lowest level of concentration. On the other hand, TBHQ and BHT could enhance IP up to the desired level above the concentration of 500 and 1000 ppm, respectively. On the other hand, remaining two antioxidants *viz.*, α-tocopherol and BHA are not effective even with 1500 ppm of loading concentration.

In case of *Sapindus mukorossi* biodiesel, the efficacy of antioxidant is found a different trend than that of *Terminalia belerica* biodiesel. PY and BHT become effective only at 500 ppm, to enhance IP to the level of EN 14214. Moreover, TBHQ above the concentration of 1000 ppm and BHA above 1500 ppm are also effective to increase the IP above EN 14214 level. Only PG at its minimum concentration (100 ppm) is effective.

Overall, the activity of antioxidants for *Terminalia belerica* biodiesel are summarized as, PG>PY>TBHQ>BHT>BHA>α-tocopherol and that of *Sapindus mukorossi* biodiesel are PG>PY>BHT>TBHQ>BHA> α-tocopherol. The different degree of activities possessed by antioxidants in both the biodiesels may be explained by the presence of the active hydroxyl group in aromatic ring of antioxidant (Table 3.3). It is noteworthy to mention that as the oxidation mechanism is initiated by the formation of free radical, the addition of antioxidant helps to restrain the formation of these free radicals by providing protons, donated by the hydroxyl group. So, more the number of protons donated by the antioxidants more are the termination of free radical reactions, which in turn helps in the improvement of IP[119,171].

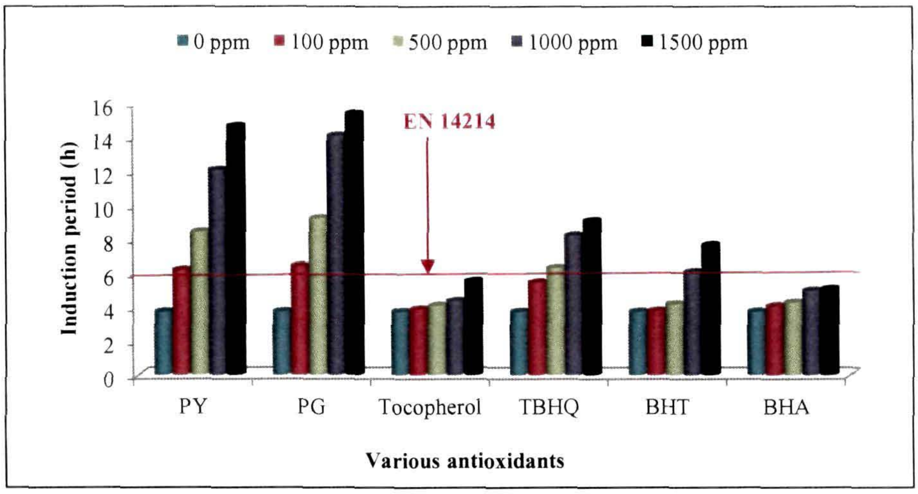


Fig 4.8(a) Effect of six different antioxidants on IP of *Terminalia belerica* biodiesel

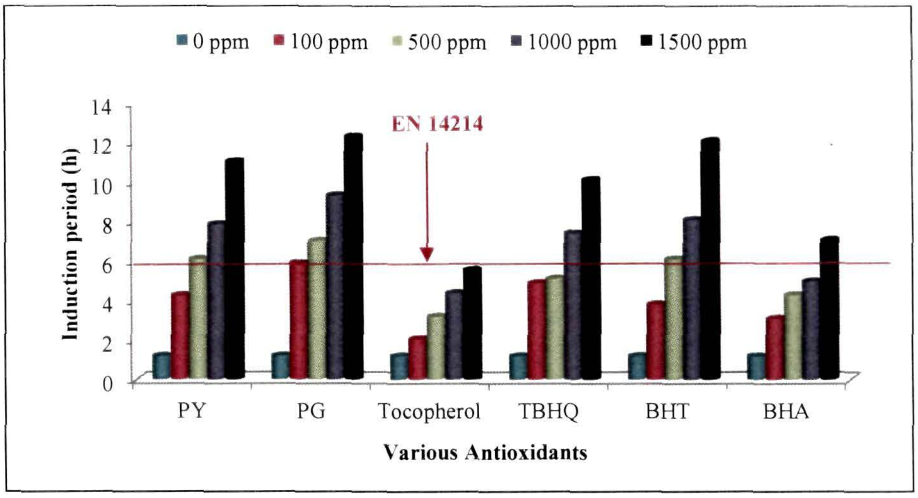


Fig 4.8(b) Effect of six different antioxidants on IP of *Sapindus mukorossi* biodiesel

It is a well established fact that BHT acts as the most effective synthetic antioxidant for hydrocarbon materials[119]. In the present study, the activity of BHT in *Terminalia belerica* is lesser as compared to *Sapindus mukorossi*, even after higher level of antioxidant loading. Generally, activities of BHT and BHA in fatty oils and esters have been reported as less effective. This may be due the different structure of fatty oils, compared to non-polar hydrocarbons, and may interact with the highly hindered polar phenol group of BHT to reduce its antioxidant capability. Moreover, it is also reported that BHT is comparatively more volatile, and might be lost during the early stage of the reaction, when added in small amount[221].

4.3.3. Oxidation stability of biodiesel blends of *Terminalia belerica* and *Sapindus mukorossi* with and without antioxidants

The efficacy of antioxidants on neat biodiesel has been explained in previous section. The efficacies of three selected antioxidants namely, PG, TBHQ and BHT at 1000 ppm concentration are also tested on blended biodiesel through observation of IP. The results are presented in Fig 4.9(a) for *Terminalia belerica* and Fig 4.9(b) for *Sapindus mukorossi* biodiesel and discussed below.

In general, IP decreases with increase in concentration of biodiesel in blends. According to EN 14214, the minimum induction period requirement for blended biodiesel is 20 h. Therefore, except untreated sample of B30 of both the biodiesels, all other samples conform to IP standard for EN 14214. PG treated samples of both the biodiesel blends increase the IP value to a greater extent, followed by BHT. Performance of TBHQ is better in neat *Terminalia belerica* biodiesel as compared to BHT while in case of blends; BHT shows greater activity as compared to TBHQ. But the activity of BHT is found better both in biodiesel and blends of *Sapindus mukorossi*.

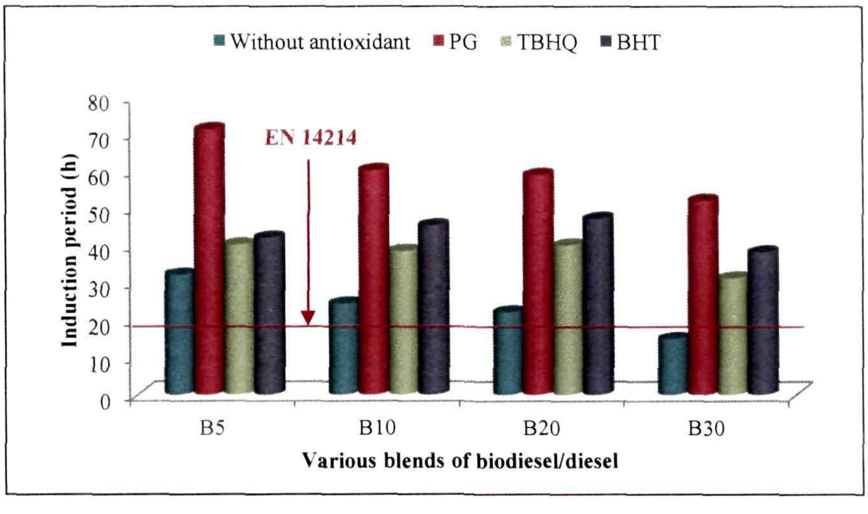


Fig 4.9(a) Effect of three selected antioxidants on IP of *Terminalia belerica* biodiesel blends (B5, B10, B20 and B30)

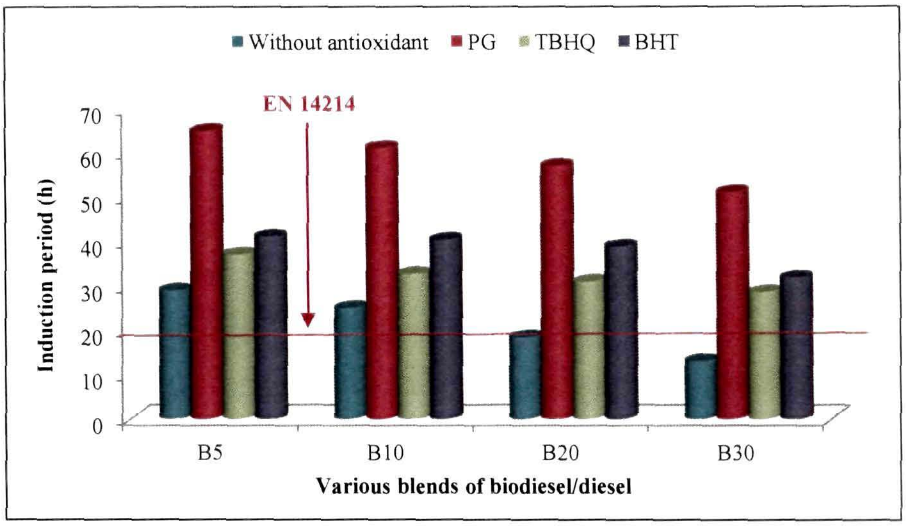


Fig 4.9(b) Effect of three selected antioxidants on IP of *Sapindus mukorossi* biodiesel blends (B5, B10, B20 and B30)

Overall, the activity of antioxidants on freshly prepared biodiesel blends is summarized as, PG>BHT>TBHQ.

4.3.4. Effects of antioxidant additives on storage of *Terminalia belerica* and *Sapindus mukorossi* biodiesel and blends

Relative influences of the selected antioxidants on five different samples (B100, B30, B20, B10 and B5) of both *Terminalia belerica* and *Sapindus mukorossi* during 12 weeks of storage are presented in Fig 4.10(a)-Fig 4.10(e) and Fig 4.11(a)-Fig 4.11(e).

Overall, IP decreases for all the samples with storage duration. However, addition of antioxidant enhances the IP of all the samples of *Terminalia belerica.* Apparently, it is observed that PG, which initially enhances the IP value up to the highest level, reduces at faster rate during storage as compared to TBHQ and BHT for all the samples of *Terminalia belerica.*

Further, after 6 weeks of storage, IP of TBHQ treated B100 (1000 ppm) fails to meet the minimum required limit of EN 14214. PG treated *Terminalia belerica* biodiesel can be safely stored up to 12 weeks (Fig 4.10(a)). Again, without antioxidant, B5 and B10 can be stored safely up to 11 weeks and 4.5 weeks, respectively (Fig 4.10(b)-(c)).

The IP of untreated B30 sample is below the minimum IP limit as per the EN 14214 standard (Fig 4.10(d)-(e)). With addition of antioxidants, IPs of the samples (B5, B10, B20 and B30) lie well above the minimum limit, even after 12 weeks of storage.

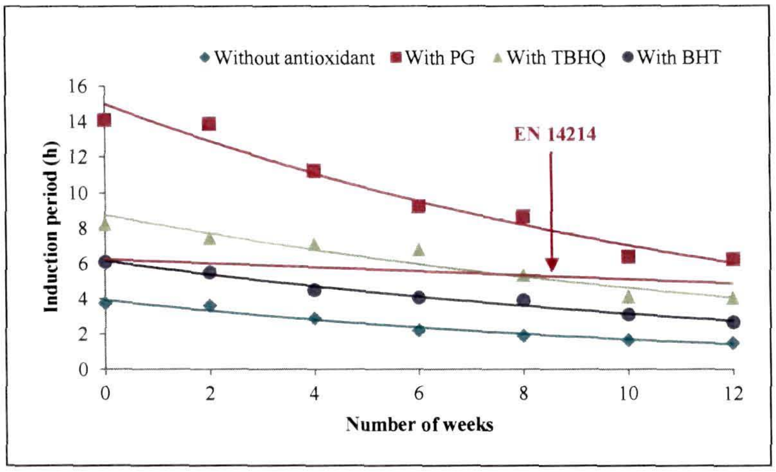


Fig 4.10(a) Effect of antioxidants on IP of *Terminalia belerica* biodiesel during storage

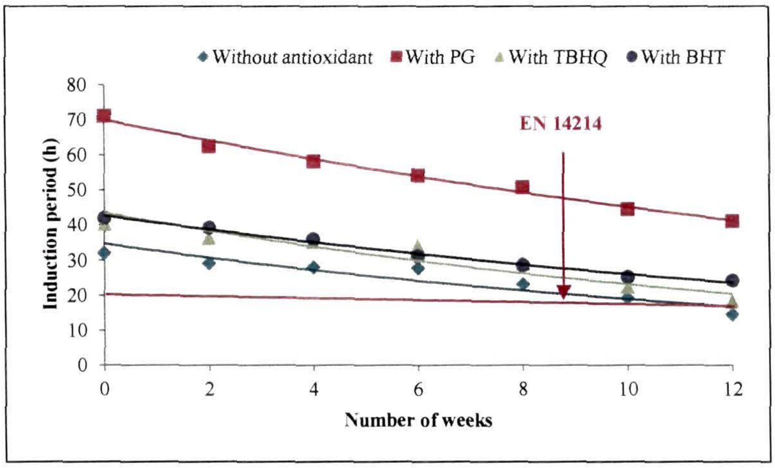


Fig 4.10(b) Effect of antioxidants on IP of *Terminalia belerica*/diesel blend (B5) during storage

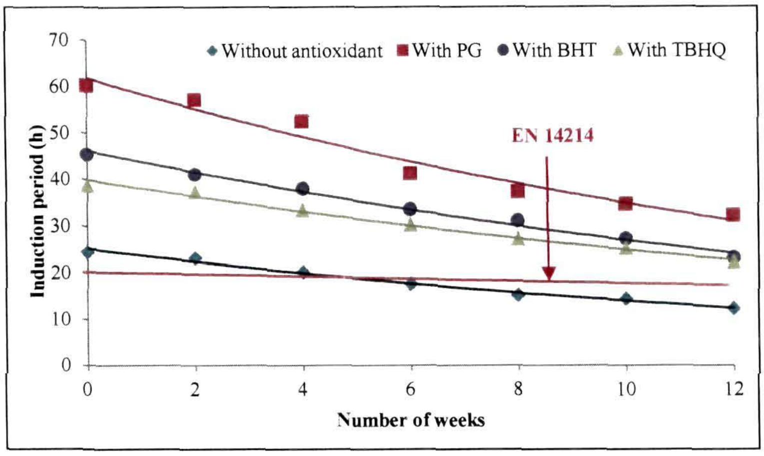


Fig 4.10(c) Effect of antioxidant on IP of *Terminalia belerica*/diesel blend (B10) during storage

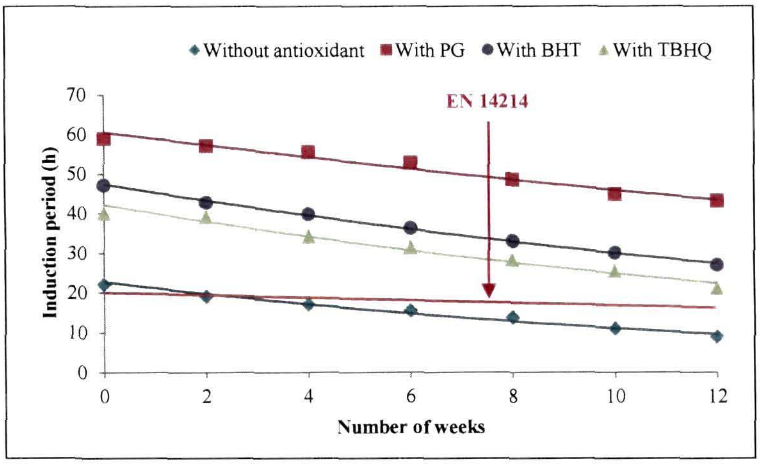


Fig 4.10(d) Effect of antioxidants on IP of *Terminalia belerica*/diesel blend (B20) during storage

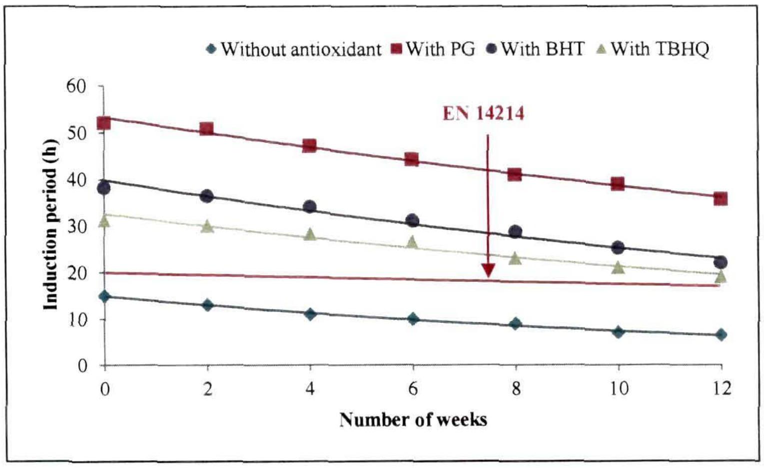


Fig 4.10(e) Effect of antioxidants on IP of *Terminalia belerica*/diesel blend (B30) during storage

For *Sapindus mukorossi* biodiesel, it is observed that amongst the three antioxidants, the antioxidant activity of PG decrease at faster rate, as compared to TBHQ and BHT during storage. Further, after 6 weeks of storage, IP of PG and BHT treated B100 (1000 ppm) fail to meet the minimum required limit of EN 14214. The safe storage periods for PG, BHT and TBHQ treated *Sapindus mukorossi* (B100) are 6 weeks (for both PG and BHT) and 3 weeks, respectively (Fig 4.11(a)). Again, without antioxidant, B5 and B10 can be stored safely up to 7 weeks and 4 weeks, respectively (Fig 4.11(b)-(c)). The IPs of untreated B20 and B30 samples are below the minimum IP limit as per the EN 14214 standard (Fig 4.11(d)-(e)). With addition of antioxidants, IPs of the samples lie well above the minimum limit, even after 12 weeks of storage.

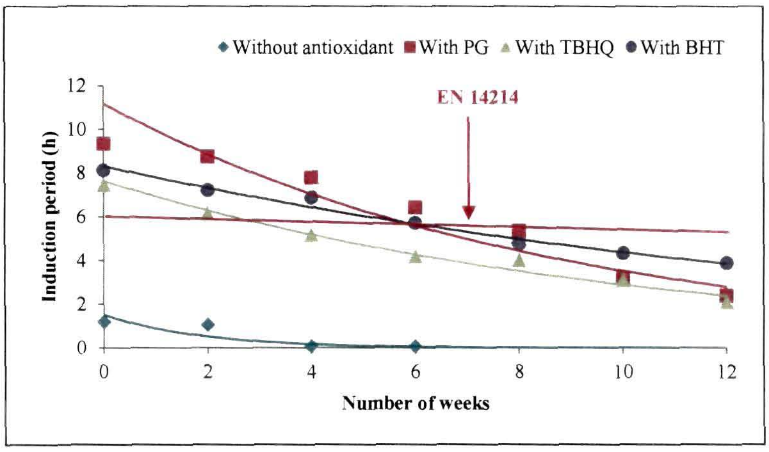


Fig 4.11(a) Effect of antioxidants on IP of *Sapindus mukorossi* biodiesel during storage

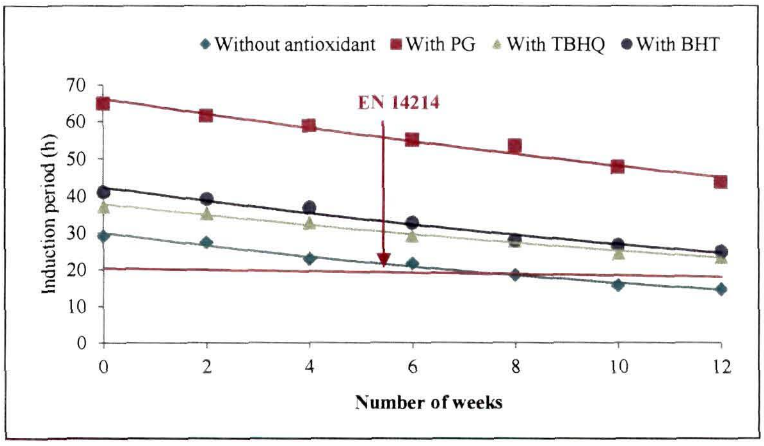


Fig 4.11(b) Effect of antioxidants on IP of *Sapindus mukorossi*/diesel blend (B5) during storage

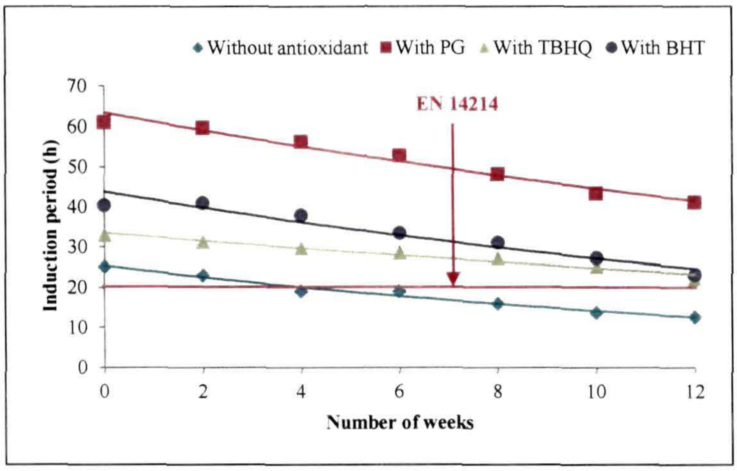


Fig 4.11(c) Effect of antioxidants on IP of *Sapindus mukorossi*/diesel blend (B10) during storage

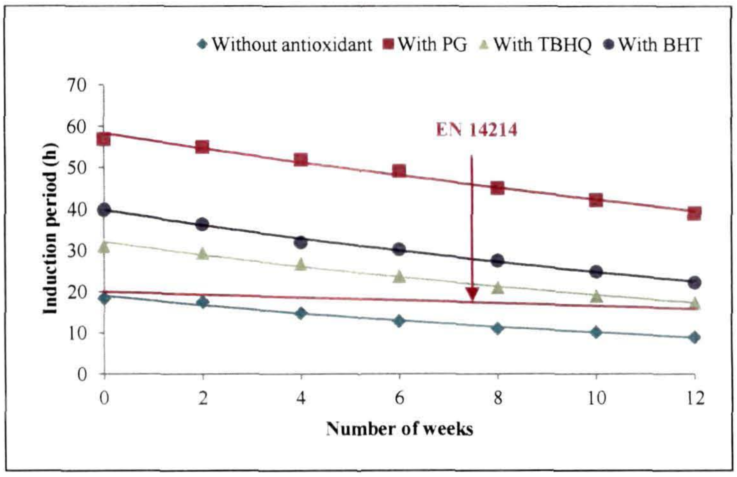


Fig 4.11(d) Effect of antioxidants on IP of *Sapindus mukorossi*/diesel blend (B20) during storage

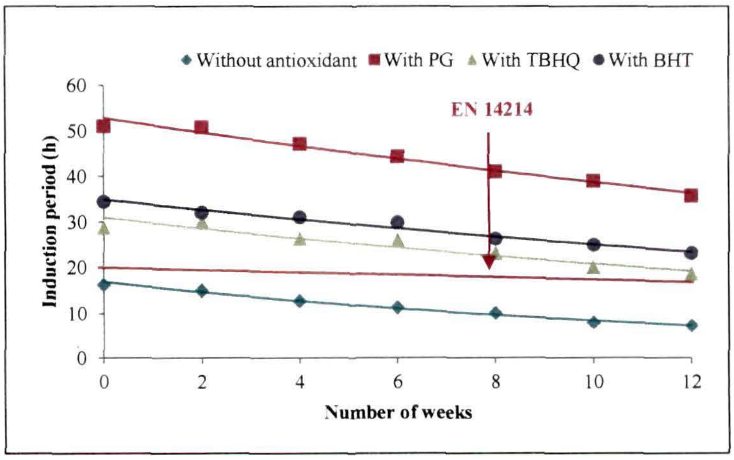


Fig 4.11(e) Effect of antioxidants on IP of *Sapindus mukorossi*/diesel blend (B30) during storage

4.3.5. Summary

Induction period (IP) is considered as an index for evaluation of oxidation stability of biodiesel in the present investigation. IPs are determined following EN 14112 (Rancimat method) for pure biodiesels (B100). Since IP for both the biodiesels found very low, antioxidant additives are added in different proportions. The highest antioxidant concentration provides the highest IP, and this is true for both the biodiesels. Overall, the efficacy of antioxidants are summarized as, PG>PY>TBHQ>BHT>BHA>α-tocopherol for *Terminalia belerica* biodiesel and PG>PY>BHT>TBHQ>BHA>α-tocopherol for *Sapindus mukorossi* biodiesel.

While assessing the IPs of *Terminalia belerica* biodiesel (B100) and its different blends (B5, B10, B20, B30), with PG, TBHQ and BHT, IP of TBHQ treated B100 (1000 ppm) fails to meet the minimum required limit of EN 14214, after 6 weeks of storage. It was also found that without antioxidants, B5 and B10 can be stored only up to 11 weeks and 4.5 weeks, respectively. However, safe storage period for PG, TBHQ and BHT treated *Sapindus mukorossi* biodiesel 6 weeks, 3 weeks and 6 weeks, respectively. Moreover, without antioxidant, B5 and B10 of *Sapindus mukorossi* can be stored safely up to 7 weeks and 4 weeks, respectively.

Part IV

Engine performance and emission characteristics of blends obtained from *Terminalia belerica* and *Sapindus mukorossi* biodiesel and petroleum diesel

4.4 Engine performance and emission characteristics

A number of researchers have investigated the use of vegetable oils and biodiesel blends in diesel engine[177-180]. Most of them have concluded that biodiesel blends starting from B5 to B100 can be used in diesel engine without engine modification. There has been almost a general consensus that with the increase of biodiesel percentage in the blends (exceeding 20% v/v), engine efficiency parameters decreases (resulting increase in specific fuel consumption) and NO_x emission increases. In the present investigation fuel blends (B5, B10 and B20 blends) are prepared separately for both the biodiesel samples (*Terminalia belerica* and *Sapindus mukorossi*) and characterized. As discussed earlier (sec 4.2.4) most of the fuel characteristics were found to be within the acceptable limits of ASTM as well as EN 14214-07 standards for biodiesel. Engine performance testing and emission testing are done using the selected blends under identical experimental conditions. The detail methodology is presented in Chapter 3 (Sec 3.7) and results are presented and discussed below.

4.4.1 Engine performance characteristics of *Terminalia belerica* and *Sapindus mukorossi* biodiesel blends

As discussed earlier, performance of a 39 kW CI type of engine has been tested for a limited range of loading conditions (randomly chosen) for blends of both the biodiesel samples (*Terminalia belerica* and *Sapindus mukorossi* biodiesel). Brake power, brake specific fuel consumption and brake thermal efficiency values as obtained from the computerized engine test rig are presented in Table 4.8. The results are discussed below.

Comprehensively the test results are analyzed at three relative loading conditions *viz.*, low load (~5%), medium load (~25%) and high load (~80%). The variation in engine performance at low load is not noticeable amongst the fuel samples used for testing the performance. This may be attributed to limitation of the test set up and associated measuring devices rather than the fuel characteristics. At medium load condition, biodiesel sample of *Sapindus mukorossi* perform better compared to the biodiesel samples of *Terminalia belerica.* The Brake thermal efficiency (BTE) of the engine fuel with B10 sample of *Sapindus mukorossi* was 27.1% (at 29% load), whereas B10 sample of *Terminalia belerica* at relatively low load (at 22% load) was 16.76%. The similar trend of variation of BTE was also observed at higher level of engine loading. The BTE of around 32% was recorded for B10 *Sapindus mukorossi* biodiesel at around 71% of engine loading, whereas at a similar level of blending and loading condition, about 20% BTE was recorded using biodiesel of *Terminalia belerica.*

The calorific value of B10 *Sapindus mukorossi* is 2.32% higher than *Terminalia belerica.* Moreover, the viscosity of B10 *Sapindus mukorossi* is 4.22% lighter than that of *Terminalia belerica.* Moreover, cetane number of *Sapindus mukorossi* 2% higher than that of Terminalia belerica. Higher cetane number, calorific value and lower viscosity may be attributed to the relatively better performance of *Sapindus mukorossi* as compared to *Terminalia belerica* biodiesel.

Diesel (B0) was also used as one of the treatment of engine performance. At medium loading condition, performance of biodiesel blend was found better than diesel as exhibited relatively higher BTE. Similar results of lower BTE of diesel fuel compared to biodiesel blends were also reported earlier[50,125]. The engine performance results using biodiesel blends cited elsewhere have been compared with the results of present investigation. Raheman and Phadatate[125] reported that the maximum brake thermal efficiencies (BTE) as 26.79% and 26.19% for B20 and B40 of karanja biodiesel, respectively, which were higher than that of diesel (24.62%). Raheman and Ghadge[50] also reported the maximum BTE as 25 % and 24 % for B20 and B40 of *Madhuca indica* biodiesel, respectively, as compared to 24% for diesel. The better heat release associated with better combustion due to the presence of biodiesel might be the reason of better performance of biodiesel blends as compared to diesel.

The values of the brake specific fuel consumption (BSFC) are also provided in Table 4.8. The lowest BSFC was exhibited by the blends of *Sapindus mukorossi* (B5 and B10) as observed from Table 4.8. However, engine performance of *Sapindus mukorossi* was found to deteriorate with reduction of BTE and associated increase of BSFC.

The results of the present investigation on engine performance could only be considered as an indication. Because only limited number of test has been performed. To understand the behavior under varying load condition, extensive testing will be required.

4.4.2 Emission characteristics of *Terminalia belerica* and *Sapindus mukorossi* biodiesel blends

The exhaust gas of engine was analyzed corresponding to specific test condition, the details of which are presented in Chapter 3. The results pertaining to the emission of carbon monoxide (CO), nitrous oxide (NO_x) and unburnt hydrocarbon (HC) are presented and discussed below.

Carbon monoxide (CO) emission

Among the various pollutants of air, carbon monoxide (CO) is considered as the most harmful one. Emissions from incomplete combustion of fuels in automobile engines are considered as the source of carbon monoxide present in air[123]. The combustion phenomenon is a function of both combustion chamber design and fuel characteristics. The incomplete combustion is not desirable from both emission and performance points of view. Undesirable CO emission and power loss are resulted by incomplete combustion [50,123]. It is also revealed that engine load and corresponding air to fuel ratio might affect the combustion phenomenon, hence, the CO emission.

Emission of CO for diesel, B5, B10 and B20 of *Terminalia belerica* and *Sapindus mukorossi* biodiesel blends at different engine load, are presented in Table 4.9. In general, with increase in biodiesel percentage, CO emission level decreases. No definite trend could be observed for CO emission vs. engine loading while considering the entire set of results. However, overall emission of CO in biodiesel blended fuel is less than that

Table 4.7 Engine performances of *Terminalia belerica*, *Sapindus mukorossi* biodiesel blends and diesel

Fuel	Blending level	% of full load	Brake Power, kW	Speed, rpm	Brake Thermal Efficiency, %	Brake specific fuel consumption, kg/kWh
Diesel	B0	5.08	1.98	5001	2.26	3.79
		22.82	8.90	5003	11.75	0.73
		80.82	31.52	4620	21.89	0.39
Terminalia belerica	B5	4.85	1.89	5034	2.78	3.09
		23.10	9.01	4972	14.58	0.59
		73.85	28.80	3695	26.44	0.32
		83.00	32.37	4667	23.16	0.37
	B10	4.03	1.57	4957	2.09	4.10
		21.67	8.45	4840	16.76	0.51
		70.15	27.36	4163	19.93	0.43
	B20	0.97	0.38	931	4.20	2.04
		6.41	2.50	5055	3.70	2.32
		73.64	28.72	4121	19.53	0.44
Sapindus mukorossi	B5	4.26	1.66	5043	2.23	4.14
		54.69	21.33	2622	31.75	0.29
		80.85	31.53	4458	22.25	0.42
	B10	4.79	1.87	5071	2.92	3.16
		29.00	11.31	2541	27.10	0.49
		71.41	27.85	3993	32.35	0.29
	B20	4.90	1.91	4928	2.56	3.60
		26.51	10.34	1363	21.12	0.44
		68.05	26.54	3939	25.24	0.37

Table 4.8 Emission characteristics of *Terminalia belerica* and *Sapindus mukorossi* biodiesel blends and diesel

Fuel	Blending level	% of full load	Speed, rpm	Carbon monoxide (%)	Nitrous Oxide (ppm)	Unburnt hydrocarbon (ppm)
Diesel	B0	5.08	5001	0.130	6	60
		22.82	5003	0.120	68	49
		80.82	4620	0.159	282	11
Terminalia belerica	B5	4.85	5034	0.112	38	54
		23.1	4972	0.092	70	35
		83	4667	0.145	299	8
	B10	4.03	4957	0.100	30	27
		21.67	4840	0.081	128	15
		70.15	4163	0.137	305	5
	B20	0.97	931	0.090	26	21
		6.41	5055	0.078	168	12
		73.64	4121	0.127	334	2
Sapindus mukorossi	B5	4.26	5043	0.121	45	50
		54.69	2622	0.1	90	32
		80.85	4458	0.151	340	10.4
	B10	4.79	5071	0.115	55	25
		29	2541	0.091	102	16
		71.41	3993	0.141	354	5
	B20	4.9	4928	0.105	61	20
		26.51	1363	0.082	160	14
		68.05	3939	0.134	367	4

of diesel. This is true for both *Terminalia belerica* and *Sapindus mukorossi.* The estimated CO reductions at high load were found as 9.65%, 16.05% and 25.19% for B5, B10 and B20 of *Terminalia belerica* compared to B0. Similarly, for *Sapindus mukorossi,* the reductions of CO emission are 5.29% (B5), 12.76% (B10) and 18.75% (B20) as compared to diesel. Overall, the CO emission of *Sapindus mukorossi* for all the load condition is higher than the *Terminalia belerica* biodiesel.

Similar pattern of CO emission was also reported earlier while investigating emission performance of biodiesel blends[50,125,185]. Similar types of results are shown by *Pongamia pinnata* biodiesel while testing in a single cylinder 4-stroke diesel engine. Maximum reduction in CO was 94%, as compared to diesel[125]. Reduction of CO was also observed in *Madhuca indica* biodiesel, while using in diesel engine, maximum and minimum reduction being 81% and 12%, respectively[50]. The presence of O_2 in biodiesel fuel is considered as a factor for favouring the combustion chemistry. There is also another view, higher cetane number of biodiesel which favour better combustion results in reduction of CO[177,221].

Nitrous oxide (NO_x) emission

NO_x emission of biodiesel fuel has been a major concern of investigation. The measured NO_x emission corresponding to the specific test conditions are presented in Table 4.9. In general, higher levels of NO_x emissions are observed in biodiesel as compared to diesel.

The maximum emission of NO_x for diesel is 282 ppm, which is lower than B5 (299 ppm), B10 (305 ppm), B20 (334 ppm) of *Terminalia belerica* biodiesel, and B5 (340 ppm), B10 (354 ppm) and B20 (367 ppm) of *Sapindus mukorossi* respectively. Overall, NOx emission of *Sapindus mukorossi* biodiesel is higher than that of *Terminalia belerica* biodiesel.

There are some arguments which explain higher NO_x emission of biodiesel fuel compared to diesel fuel. Higher peak flame temperature is considered as a reason of NO_x

formation[50,222]. In addition, it is also reported that the NO_x formation is enhanced and became significant in the presence of the chemically bound oxygen content in the biodiesel, thus resulting in higher level of NO_x emissions in biodiesel blends as compared to diesel. This might be due to slightly higher cetane number of *Sapindus mukorossi* as compared to *Terminalia belerica* biodiesel.

Hydrocarbon (HC) emission

Unburnt hydrocarbon in exhaust gas is an indication of energy loss. It is reported that improper combustion causes unburnt hydrocarbon emission. The reason of appearing HCs during combustion is due to disability to reach the ignition temperature or disability of fuel to be oxidized because of lack of oxygen[123]. The reduction in HC emission in biodiesel fuels is mainly attributed to the oxygen present in such fuel, which is sufficient for fuel oxidation, producing a rich air-fuel mixture.

The unburnt hydrocarbon measured in present investigation in specific test conditions are presented in Table 4.9. The hydrocarbon (HC) emission resulted from *Terminalia belerica* and *Sapindus mukorossi* biodiesel blends are quite low as compared to diesel. As the biodiesel percentage in blends increases, overall HC emission decreases. The maximum emission of HC in diesel (B0) is 60 ppm, whereas the emissions of *Terminalia belerica* corresponding to B5, B10 and B20 are 54 ppm, 27 ppm and 21 ppm, respectively. Again, the emissions of *Sapindus mukorossi* corresponding to B5, B10 and B20 are 50 ppm, 25 ppm and 20 ppm, respectively. Total unburnt hydrocarbon is higher in *Terminalia belerica* as compared to *Sapindus mukorossi*. This may be due to the presence of slightly higher percentage of O_2 in *Sapindus mukorossi* as compared to *Terminalia belerica*.

The reason for the decrease HC for biodiesel blends is that biodiesel blends might be attributed to improve combustion due to the presence of O_2. It is also reported earlier that about 35% reduction in HC is observed while using *Madhuca indica* biodiesel, as compared to diesel[50,125].

4.4.3 Summary

At medium load condition, biodiesel sample of *Sapindus mukorossi* perform better compared to the biodiesel samples of *Terminalia belerica*. The Brake thermal efficiency (BTE) of the engine fuel with B10 sample of *Sapindus mukorossi* was 27.1% whereas B10 sample of *Terminalia belerica* at relatively lower load was 16.76%. The similar trend of variation of BTE was also observed at higher level of engine loading. At medium loading condition, performance of biodiesel blend was found better than diesel as exhibited relatively higher BTE.

In general, with increase in biodiesel percentage, CO emission level decreases. No definite trend could be observed for CO emission vs. engine loading while considering the entire set of results. However, overall emission of CO in biodiesel blended fuel is less than that of diesel. This is true for both *Terminalia belerica* and *Sapindus mukorossi*. In general, higher levels of NO_x emissions are observed in biodiesel as compared to diesel. The maximum emission of NO_x for diesel is 282 ppm, which is lower than B5, B10, B20 of both *Terminalia belerica* and *Sapindus mukorossi* biodiesel blends, respectively. The hydrocarbon (HC) emission resulted from *Terminalia belerica* and *Sapindus mukorossi* biodiesel blends are quite low as compared to diesel. As the biodiesel percentage in blends increases, overall HC emission decreases.

CHAPTER 5

SUMMARY AND CONCLUSIONS

CHAPTER 5

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Northeast India has adequate forest land and the prospect of some of its tree species as source of biodiesel feedstock could favourably complement the growth of both forestry and biodiesel as entrepreneur activities in this region. The present research work is carried out to investigate the prospect of non-edible seed oils from tree species available in forests of northeast India. The findings of the present investigation are summarized below.

5.1 Feedstock: description of the trees

Two forest origin oilseeds of *Terminalia belerica* R. and *Sapindus mukorossi* G. trees could be identified as a prospective source of biodiesel feedstock. *Terminalia belerica* is a large deciduous tree available in the forests of North-eastern region of India. It attains up to the height of 40 m, with a girth and clear bole of about 3 to 9 m, respectively. The fruit pulp of *Terminalia belerica* is traditionally used as medicinal ingredient for many ailments in India which includes dyspepsia, chronic diarrhea, dysentery, intestinal parasites, fever, sore throat, cough etc. *Sapindus mukorossi* is also a fairly large, deciduous tree, usually of height of up to 20 m tall with about 1.8 m girth. *Sapindus mukorossi* seed has high saponin content, therefore traditionally used as cleaning agent like soap. The pulp of *Sapindus mukorossi* also has medicinal usage. Thus, fruits of both the trees have existing utilities, and seeds remain as by-product. The total available forest area of Assam is 27,826 km^2. Part of this area, including the area needing replanting, could be considered for growing *Terminalia belerica* and *Sapindus mukorossi* tree so as to increase the biodiesel feedstock. However, appropriate planning will be required for extending the area for oil bearing trees in order to increase feedstock supply. The research effort of this present work is only to identify the potential tree species.

5.2 Oil contents and fatty acid profile of vegetable oils

Oil content (w/w% of kernels) of *Terminalia belerica* and *Sapindus mukorossi* are found as 43% and 39%, respectively. Fatty acid profile of vegetable oil is an important consideration as it influences the properties of oil and hence the biodiesel. *Terminalia belerica* oil composes of 39.5% saturated fatty acid and 60.5% unsaturated fatty acid. Palmitic (32.8%), oleic (31.3%) and linoleic (28.8%) acids are dominant in *Terminalia belerica* oil. On the other hand, *Sapindus mukorossi* oil composes of 16.5% saturated and 83.5% unsaturated fatty acids. Oleic (58.4%), linolenic (17.1%) and arachidic (7.5%) acids, are the major constituents of *Sapindus mukorossi* oil. Variations in fatty acid profile are observed amongst the new variety of oils and oils reported earlier. Overall, fatty acid profiles of both the new varieties of oil are suitable for biodiesel production.

5.3 Characterization of vegetable oils

Sapindus mukorossi oil is heavier (923 kg/m^3) and more viscous (32.10 mm^2/s) compared to *Terminalia belerica* (910 kg/m^3, 25.60 mm^2/s) oil. Densities of both the oils are lighter than some of the earlier reported tree seed oils such as *Pongamia glabra* (931 kg/m^3), *Mesua ferrea* (935 kg/m^3) and *Madhuca indica* (960 kg/m^3). However, viscosities of both the oils are comparable with similar tree seed oils reported earlier. Calorific value of *Terminalia belerica* oil (37.5 MJ/kg) is marginally lower than the calorific value of *Sapindus mukorossi* oil (38 MJ/kg), and comparable with similar tree born oils reported earlier. Acid value of *Terminalia belerica* oil is found as 8.01 mgKOH/g, which is less than *Sapindus mukorossi* (15.6 mgKOH/g) oil, and comparable with similar tree born seed oils reported earlier. *Sapindus mukorossi* oil is relatively safer to handle with flash point of 159^{0}C, compared to *Terminalia belerica* oil, which has flash point of 102^{0}C. *Terminalia belerica* has less carbon and ash content as compared to *Sapindus mukorossi*. Comprehensively, results of vegetable oil characterization show both of these seed oils as prospective feedstock for biodiesel production.

5.4 Conversion of oil to biodiesel

Alkaline catalytic transesterification process is chosen for production of biodiesel from *Terminalia belerica* oil. Repeated experiments are conducted with varying molar ratio (methanol: oil) and catalyst ($NaOCH_3$) concentration through standard transesterification procedure, maintaining 65^0C temperature for 120 minutes. The optimum molar ratio (10:1) and catalyst concentration (1 wt%) could be ascertained for *Terminalia belerica*, which ensure the highest possible yield (93%) of biodiesel amongst the series of experiments.

Two step transesterification is followed for *Sapindus mukorossi* as the acid value of *Sapindus mukorossi* oil is higher. In the first step, oil is reacted with H_2SO_4 (1 wt%), at 55^0C, with 6:1 (alcohol to oil) molar ratio for 90 minutes. After removing the unreacted methanol and free fatty acid from the first stage reaction product, the remaining part is subjected to alkaline transesterification. The molar ratio and catalyst concentration for conversion of *Sapindus mukorossi* oil are 8:1 and 1 wt%, respectively, at 65^0C for 120 minutes with a yield of 92.5%. The production of biodiesel is confirmed through ^1H NMR and ^{13}C NMR spectral analysis.

5.5 Fuel quality

Although *Sapindus mukorossi* oil is heavier than *Terminalia belerica* oil, more reduction in density is observed in *Sapindus mukorossi* biodiesel (876 kg/m^3), as compared to *Terminalia belerica* (882 kg/m^3) biodiesel. Moreover, density of both the biodiesels conform to EN 14214-07 standard specification. *Sapindus mukorossi* biodiesel is less viscous (4.63 mm^2/s) than *Terminalia belerica* biodiesel (5.17 mm^2/s). The viscosity values obtained for both the biodiesels are similar to some other biodiesels reported earlier and also conform to ASTM D6751-07 specification. Calorific value of *Sapindus mukorossi* biodiesel (40.00 MJ/kg) is marginally higher than *Terminalia belerica* biodiesel (39.22 MJ/kg), and is comparable with some other biodiesels obtained from tree seed oils. Acid values of both the oils are reduced after transesterification to 0.23 mgKOH/g and 0.14 mgKOH/g for *Terminalia belerica* and *Sapindus mukorossi* biodiesel, respectively. *Sapindus mukorossi* biodiesel shows better fuel handling properties with higher flash point (140^{0}C) as compared to *Terminalia belerica* biodiesel (90^{0}C). *Sapindus mukorossi* biodiesel also exhibits better cold flow properties compared to *Terminalia belerica* biodiesel. Cloud points of *Terminalia belerica* and *Sapindus mukorossi* biodiesels are 6^{0}C and -1^{0}C, respectively, whereas pour points are 3^{0}C for *Terminalia belerica* and -4^{0}C for *Sapindus mukorossi*. Both the biodiesels are within the specific cloud point and pour point limits of EN 14214-07. In terms of ash and carbon residue contents, *Terminalia belerica* biodiesel (0.0005 wt% ash, 0.0085 wt% carbon residue) is found superior than *Sapindus mukorossi* (0.003 wt% ash, 0.12 wt% carbon residue) biodiesel. Similarly, oxidation stability of *Terminalia belerica* biodiesel (3.76 h) is relatively higher than *Sapindus mukorossi* (1.2 h) biodiesel. However, both the biodiesels fail to meet the EN 14214-07 specification, as far as oxidation stability is concerned. Lubricating property is also accessed using standard index (wear scar diameter). Lubricity of *Sapindus mukorossi* (0.181 mm) biodiesel is marginally better than *Terminalia belerica* (0.193 mm) biodiesel and comparable with similar biodiesels, reported earlier. Cetane number of *Terminalia belerica* (53) and *Sapindus mukorossi* (56) biodiesels are also found satisfactory to ensure proper ignition behavior. The distillation characteristic of *Terminalia belerica* (130^{0}C - 347^{0}C) and *Sapindus mukorossi* (193^{0}C - 383^{0}C) biodiesel are comparable with similar biodiesels and also satisfies the ASTM D6751-07 standard specification. Sulphur content of *Sapindus mukorossi* biodiesel is 102 ppm which is more than *Terminalia belerica* biodiesel (96 ppm).

Overall, density, viscosity, cetane number, ash content, carbon residue, flash point, pour point, acid value, copper strip corrosion, IBP/FBP for both the biodiesels are found to conform the existing biodiesel norms. However, two aspects of both the types of biodiesels, namely, sulphur content and oxidation stability would require further attention.

5.6 Storage behavior of biodiesel and identification of additives

Biodiesels obtained from *Terminalia belerica* and *Sapindus mukorossi* oils and their blends with petro-diesel (B5, B10, B20 and B30) are stored in borosilicate glass bottle in normal laboratory condition for 12 weeks. Viscosity, acid value and peroxide value are found to increase while measuring at 2 week interval. Viscosities of all the stored samples lie within the limit of ASTM D6751, except for 12th week old *Terminalia belerica* biodiesel.

Efficacy of six phenolic antioxidants *viz.*, vitamin E (α-tocopherol), butylated hydroxyanisole (BHA), pyrogallol (PY), propyl gallate (PG), tert-butylhydroxytoluene (BHT) and tert-butylhydroxyquinone (TBHQ) and their concentrations (*viz.*, 100 ppm, 500 ppm, 1000 ppm, and 1500 ppm) are investigated for freshly prepared samples of neat biodiesels on the basis of Induction period. PG treated biodiesel (B100) exhibited the highest IP amongst all the antioxidants for both *Terminalia belerica* and *Sapindus mukorossi* considered for present investigation. The higher the antioxidant concentration more is the IP, and this is true for both the biodiesels. Results show that treating with PG could enhance IP from 3.76 h to 14.67 h in *Terminalia belerica*, whereas in *Sapindus mukorossi* biodiesel, the increase in IP is from 1.2 h to 11.03 h. Overall, the efficacy of antioxidants are summarized as, PG>PY>TBHQ>BHT>BHA>α-tocopherol for *Terminalia belerica* biodiesel and PG>PY>BHT>TBHQ>BHA>α-tocopherol for *Sapindus mukorossi* biodiesel.

Oxidation stability of biodiesel (B100) and its different blends (B5, B10, B20, B30) are also assessed with and without antioxidant additives up to a storage period of 12 weeks considering three specific antioxidants *viz.*, PG, TBHQ and BHT, with a concentration of 1000 ppm. For freshly prepared biodiesel blends, the activities of antioxidants are in the order of, PG>BHT>TBHQ for both the biodiesels. After 6 weeks of storage, IP of TBHQ treated B100 (1000 ppm) fails to meet the minimum required limit of EN 14214. Also, without antioxidants, B5 and B10 can be stored only up to 11 weeks and 4.5 weeks respectively. With addition of antioxidants, IPs of all blended samples lie well above the minimum limit, even after 12 weeks of storage. However, safe storage period for PG, TBHQ and BHT treated *Sapindus mukorossi* biodiesel are 6 weeks, 3 weeks and 6 weeks, respectively. Moreover, without antioxidant, B5 and B10 of *Sapindus mukorossi* can be stored safely only up to 7 weeks and 4 weeks, respectively.

5.7 Assessments of engine performance characteristics

The blended biodiesel (B5, B10 and B20) of both the types are tested in a 39 kW test engine and compared with the performance results of petrodiesel. The experiments are conducted at randomly varying loads with all levels of blending. Increase in brake thermal efficiency associated with decrease in specific fuel consumption by the increase in engine load has been the characteristics feature for all the biodiesel blends, as well as for petrodiesel. Overall, acceptable performances are observed for both the types of biodiesel (*Terminalia belerica* and *Sapindus mukorossi*) up to 20% blending.

At medium load condition, biodiesel sample of *Sapindus mukorossi* perform better compared to the biodiesel samples of *Terminalia belerica*. The Brake thermal efficiency (BTE) of the engine with B10 sample of *Sapindus mukorossi* was 27.1% whereas B10 sample of *Terminalia belerica* at relatively lighter load was 16.76%. The similar trend of variation of BTE was also observed at higher level of engine loading. At medium loading condition, performance of biodiesel blend was better than diesel as exhibited by relatively higher BTE.

In general, with increase in biodiesel percentage, CO emission level decreases. No definite trend could be observed for CO emission vs. engine loading while considering the entire set of results. However, overall emission of CO in biodiesel blended fuel is less than that of diesel. This is true for both *Terminalia belerica* and *Sapindus mukorossi*. In general, higher levels of NO_x emissions were observed in biodiesel as compared to diesel. The maximum emission of NO_x for diesel is 282 ppm, which is lower than B5, B10, B20 of both *Terminalia belerica* and *Sapindus mukorossi* biodiesel blends, respectively. The hydrocarbon (HC) emission resulted from *Terminalia belerica* and *Sapindus mukorossi* biodiesel blends are quite low as compared to diesel. As the biodiesel percentage in blends increases, overall HC emission decreases.

5.8 Conclusions

From the study the following conclusions are drawn.

i. Tree seed oils have potential for biodiesel production. Proper R & D intervention is required for promotion of biodiesel using these tree oils.

ii. Properties of biodiesels are the reflection of the fatty acid profile of the parent material. This is true for both *Terminalia belerica* and *Sapindus mukorossi* seed oils. Both the types of oils have distinguishing fatty acid profile, and can be converted into biodiesel. *Terminalia belerica* requires single stage alkaline transesterification whereas *Sapindus mukorossi* requires two stage transesterification (acid followed by alkaline).

iii. Alcohol to oil molar ratio required for *Terminalia belerica* oil (10:1) to result the highest yield (93%) was different than the molar ratio for *Sapindus mukorossi* (8:1) with a yield of (92.5%). However, for both the transesterification process require 1wt% catalyst ($NaOCH_3$) concentration.

iv. Most of the fuel properties of *Terminalia belerica* and *Sapindus mukorossi* conform to the ASTM and European standard specifications. However, oxidation stability and sulphur content do not conform to the norms.

v. Biodiesel produced from both the oils require additives to enhance oxidation stability (Induction Period). Specific phenolic antioxidants additives are identified for both the biodiesels.

vi. Short duration engine testing with blended biodiesels of both the oil seeds result satisfactory performances both in terms of efficiency and emissions. However, there are some differences between *Terminalia belerica* and *Sapindus mukorossi* biodiesel, which might be due to the differences in fuel characteristics of these biodiesel.

5.9 Suggestions for future works

i. Optimization of process parameters (*viz.*, temperature, alcohol to oil molar ratio, catalyst type and concentration and reaction time) are important while transesterifying vegetable oil to biodiesel. In this study, limited numbers of parameters (alcohol to oil molar ratio and catalyst concentration) are varied for maximum yield of biodiesel. Future study is recommended to optimize the process parameters incorporating all possible variable combinations of treatments and formulate a suitable mathematical model for better understanding.

ii. The results of the storage stability test of the present investigation are pertaining to 12 weeks of storage period with a few specific storage conditions. Future study is recommended for storing the sample for extended period of time, incorporating all possible storage conditions.

    The remedy for higher sulphur level is not investigated in the present work and suggested as research for future work

iii. Long duration engine performance testing at different load conditions including the impact on engine health is recommended, for future work both *Terminalia belerica* and *Sapindus mukorossi* biodiesel.

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APPENDIX I

APPENDIX I

Sample: *Terminalia belerica* **Year**: 2009

Data reported by the weather station: **424150**

	January				**February**				**March**				**April**			
	Temperature (°C)			**Humidity (%)**	**Temperature (°C)**			**Humidity (%)**	**Temperature (°C)**			**Humidity (%)**	**Temperature (°C)**			**Humidity (%)**
Day	**Mean**	**Max**	**Min**	**Mean**	**Mean**	**Max**	**Min**	**Mean**	**Mean**	**Max**	**Min**	**Mean**	**Mean**	**Max**	**Min**	**Mean**
1	-	-	-	-	19 7	25 4	16	75	22 2	28	17	48	20 2	23 7	18 2	85
2	-	-	-	-	19 1	26	13 4	74	-	-	-	-	23 5	30 6	16 7	64
3	-	-	-	-	18 4	28	11 8	73	22 2	32 4	13 6	50	22 8	27	19 4	76
4	-	-	-	-	18 9	27 7	12	73	22 2	30 8	14 9	57	20 4	22 4	19 4	91
5	-	-	-	-	19 4	28 4	12 1	73	24 4	30 7	17 2	51	22 6	24 9	19 4	81
6	-	-	-	-	21 3	29 7	12 8	63	21 1	23 5	18 7	69	24 1	29 6	19 9	82
7	-	-	-	-	21 9	30	12 5	61	24 6	31 2	18 6	60	24 5	31 2	20 6	76
8	-	-	-	-	20 4	30	13 8	69	24	30 5	20	59	23 6	28	20 1	72
9	-	-	-	-	21 3	30 1	13 9	68	25 1	32 6	18 9	60	25 5	33	20 1	66
10	-	-	-	-	20 9	30 5	13 9	69	25 4	33 5	19 2	57	25 8	31 4	20 2	67
11	-	-	-	-	21 7	31 6	13 5	65	25 2	33	17 6	37	23 9	29 5	19 2	68
12	-	-	-	-	20 7	28 2	15	71	23 6	33 5	17 3	43	27	33 5	21 2	60
13	-	-	-	-	20 7	27	15 5	73	22 8	34	17 4	51	27 2	34 8	21 9	62
14	-	-	-	-	20 7	29 1	14 4	66	25 6	35	14 9	42	-	-	-	-
15	-	-	-	-	20 9	29	15	73	24 6	34 7	16	44	-	-	-	-
16	-	-	-	-	21 9	31	15 4	72	22 2	29 2	16 7	58	-	-	-	-
17	-	-	-	-	22 6	31	15 6	69	23	32	15 1	55	-	-	-	-
18	-	-	-	-	22 5	30 8	15 5	66	22 7	31 3	16 7	58	-	-	-	-
19	18 8	26 4	13	79	22 2	31	16 4	70	25 1	32 8	17 7	50	-	-	-	-
20	19 8	25 5	15 4	81	21 8	30 6	15 8	70	24 9	32 5	19 8	49	-	-	-	-
21	18 7	26 4	15 4	85	22	29 6	14 9	61	24 7	33 4	18 7	52	-	-	-	-
22	18 7	25 8	14 2	83	22 2	29 2	16 5	56	24 9	31 7	18 5	58	-	-	-	-
23	18	24 2	13 9	84	21 7	28 6	16 1	58	25 2	33 6	18 5	61	-	-	-	-
24	16 8	24 1	13 6	94	21 4	27 2	16 2	57	26 2	35	18 1	50	-	-	-	-
25	19 6	24 7	15 4	87	20 3	27 7	15 2	71	26 2	35 1	18 7	50	-	-	-	-
26	20 2	23 5	17 4	86	21 9	29 7	16 5	68	24 2	35 1	17 6	58	-	-	-	-
27	20 2	23 8	18 2	86	21 9	29 7	16 4	58	21 8	28 2	16 9	66	-	-	-	-
28	20 6	23	17 2	78	21 9	30 1	16 5	51	24 9	31	16 1	55	-	-	-	-
29	19 5	26	15 6	79					22 1	25 2	18 5	75	-	-	-	-
30	18 9	26 5	13 7	81					19 8	23 1	17 8	89	-	-	-	-
31	19 9	26 8	13 9	81					20 4	25 5	17 3	86	-	-	-	-
Monthly Means																
	17.9	**25.7**	**12.2**	**78.4**	**21.1**	**29.2**	**14.7**	**66.9**	**23.7**	**31.3**	**17.5**	**56.6**	**25.5**	**30.5**	**21.2**	**73.8**

Sample: *Sapindus mukorossi* **Year:** 2010

Data reported by the weather station: **424150**

	March				April				May				June			
	Temperature (°C)			Humidity (%)	Temperature (°C)			Humidity (%)	Temperature (°C)			Humidity (%)	Temperature (°C)			Humidity (%)
Day	**Mean**	**Max**	**Min**	**Mean**	**Mean**	**Max**	**Min**	**Mean**	**Mean**	**Max**	**Min**	**Mean**	**Mean**	**Max**	**Min**	**Mean**
1	-	-	-	-	22.3	27.9	17.9	81	27.7	33	21.6	74	26.1	31.7	22.8	88
2	-	-	-	-	24.3	30.5	18.9	76	25.2	28.1	22.9	90	25.6	29.5	22.3	88
3	-	-	-	-	24.2	30	19.8	79	28	32.8	22.9	78	-	-	-	-
4	-	-	-	-	24.4	29.1	20.9	74	26.3	32.9	22.8	78	-	-	-	-
5	-	-	-	-	24.6	30.1	20.4	78	26.8	32.2	20.9	82	-	-	-	-
6	-	-	-	-	26.3	32.6	21.4	74	27.7	34.4	23.7	78	-	-	-	-
7	-	-	-	-	25.3	30.3	22.3	70	26.3	29.8	24	85	-	-	-	-
8	-	-	-	-	27.3	33.8	20.5	69	25.9	27	23.5	88	-	-	-	-
9	-	-	-	-	25.7	28.9	23.1	72	24.6	27.6	22.5	89	-	-	-	-
10	23.5	32.3	17.7	66	26.2	30	21.5	68	22.2	23.2	21.4	92	-	-	-	-
11	23.3	31	16.8	67	-	-	-	-	24.4	28.4	21.4	90	-	-	-	-
12	23.2	31.7	16.8	63	25.1	29.2	21	79	26.2	32.3	22	83	-	-	-	-
13	22.3	30.1	13.2	68	26.1	31.4	22	78	25.9	29.4	21.9	84	-	-	-	-
14	23.9	31	16.4	62	25.7	31.4	21.9	75	24.7	30.4	21.4	85	-	-	-	-
15	22.8	31.5	16.8	60	27	32.7	20.9	68	26.6	31.5	20.9	79	-	-	-	-
16	24	32.6	17.5	54	26.8	33.1	20.7	69	23.4	27.5	20.9	86	-	-	-	-
17	25.1	34.5	17.2	56	23.6	25	22.4	91	25.5	29.2	21.4	76	-	-	-	-
18	25.5	35	17.4	55	24.7	29.4	21.2	85	27.6	33	21.9	79	-	-	-	-
19	26.1	36.4	17.6	54	22.3	24	20.9	95	25.5	28	23.4	88	-	-	-	-
20	27	36.5	18.7	55	21.7	23.8	20.2	96	25.2	27.5	22.4	93	-	-	-	-
21	27.8	36.5	19.1	59	23.7	28.5	20.9	89	25.9	28.5	23.6	87	-	-	-	-
22	24.3	29.6	21.1	70	25.3	30.4	21	85	26.3	30.3	22.6	88	-	-	-	-
23	21.6	23.5	20.6	85	25.6	31.8	21.7	84	27.6	32	24.4	85	-	-	-	-
24	23.1	27.9	19.9	79	24.2	30	20.2	89	27.1	32.6	23.6	86	-	-	-	-
25	23	28	19.6	80	22.2	25.5	19.8	89	26.9	31.8	23.2	84	-	-	-	-
26	23.3	29	19.3	79	20.3	23.2	18.8	95	28	32.9	23.1	80	-	-	-	-
27	21.6	27.7	18	84	22.7	26.9	18.4	87	26.7	28	24.9	86	-	-	-	-
28	19.5	21.9	18.4	93	25.8	31.4	19.7	76	27.8	32.2	21.8	80	-	-	-	-
29	18.6	19.4	16.8	93	22.6	25	21.2	90	29.4	34	25.1	75	-	-	-	-
30	20.8	24.1	18	87	24.6	29.1	20.4	82	28.1	31.9	25.5	80	-	-	-	-
31	20.2	25.6	18.4	91					28.1	32	23.9	82				
Monthly Means																
	22.9	**29.5**	**17.6**	**70.2**	**24.5**	**29.1**	**20.7**	**80.8**	**26.4**	**30.5**	**22.8**	**83.5**	**27.2**	**30.8**	**24.1**	**88.7**

LIST OF PUBLICATIONS

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List of Publications

Journal Publications

1. **Chakraborty, M.,** Baruah, D.C. Investigation of oxidation stability of *Terminalia belerica* biodiesel and its blends with petrodiesel, *Fuel Proces. Technol.* **98**, 51-58 (2012)
2. **Chakraborty, M.,** Baruah, D.C., Konwer, D. Investigation of terminalia (*Terminalia belerica*) seed oil as prospective biodiesel source of North east India, *Fuel Proces. Technol.* **90**,1435-1441 (2009)

Conference Publications

1. Bhowmik, R., **Chakraborty, M.,** Baruah, D. C. Studies of *Mesua Ferrea* L.: Biodiesel Production and Characterization, Proceedings of International Congress of Renewable Energy (ICORE-2011), Tezpur University, 2-4 November, 2011
2. **Chakraborty, M.,** Baruah, D.C. Improvement of oxidation stability of biodiesel prepared from forest origin non-edible oil, Proceedings of Renewable Energy Technology: Issues and Prospects (RETIP), NERIST, 2-3 September, 2011
3. **Chakraborty, M.,** Baruah, D.C., Konwer, D. *Sapindus mukorossi* seed oil as potential biodiesel source of North-East India, Proceedings of International conference on Renewable energy (ICRE 2011), University of Rajasthan, Jaipur, 17-21 January, 2011
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