BIODIESEL PRODUCTION FROM *MESUA FERREA* L. (NAHAR) AND *PONGAMIA GLABRA* VENT. (KOROCH) SEED OIL

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CERTIFICATE BY THE SUPERVISOR

This is to certify that the matter embodied in the thesis entitled ‘Biodiesel Production from *Mesua ferrea* L. (Nahar) and *Pongamia glabra* Vent. (Koroch) seed oil ’ submitted by Sri Anil Kumar Sarma for the award of degree of Doctor of Philosophy of Tezpur University is a record of bonafide research work carried out by him 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.

DKonwer

Date: 4.4.06

D. Konwer

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CHAPTER I

INTRODUCTION

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Chapter I
Introduction

With the rapid depletion of world petroleum reserves and increased demand of petroleum products, especially of transportation fuels, it has become necessary for all the nations to search for alternative liquid fuels. A number studies have shown that triglycerides hold promise as alternative diesel engine fuels (Adams *et al.,* 1983; Srivastava and Prasad, 2000; Shay, 1993; Ma and Hanna, 1999; Engler *et al.,*1983; Strayer *et al.,*1983). All naturally occurring oils and fats are tri-esters of the tri-alcohol, glycerol. These are known as triglycerides or triacylglycerides. However, the direct use of vegetable oils and/or blends is generally considered to be unsatisfactory for diesel engine. The high viscosity and free fatty acid content of such oils as well as gum formation due to oxidation and polymerization during storage and combustion, carbon deposits and lubricating oil thickening are some of the obvious problems (Harwood, 1984; Ma and Hanna, 1999; Srivastava and Prasad, 2000). To overcome these drawbacks considerable effort has gone into developing vegetable oil derivatives that approximate the properties and performance of petroleum based diesel fuels.

Three main processes that have been investigated in attempts to allow vegetable oils and oil waste to be utilized as viable alternative fuels: Pyrolysis, micro-emulsification and transesterification.

Pyrolysis

Pyrolysis is the conversion of one substance into one or more products by means of heat or by heat with the aid of a catalyst in the absence of air or oxygen. It involves the cleavage of chemical bonds to yield small molecules (Weisz *et al.*, 1979). Many investigators have studied the pyrolysis of triglycerides with the aim of obtaining suitable fuel for diesel engine.

Pyrolysis chemistry is difficult to characterize because of the variety of reaction paths and the variety of reaction products that may be obtained from the reactions that occur.

The pyrolysis of fats and vegetable oils has been investigated for more than 100 years, especially in those countries that lack deposits of petroleum (Sonntag, 1979b). Pyrolysis of triglycerides produces compounds of several classes, including alkanes, alkenes, alkadienes, aromatics and carboxylic acids. The mechanism of thermal decomposition of triglycerides is shown in Fig.1 (Schwab *et al.*, 1988).

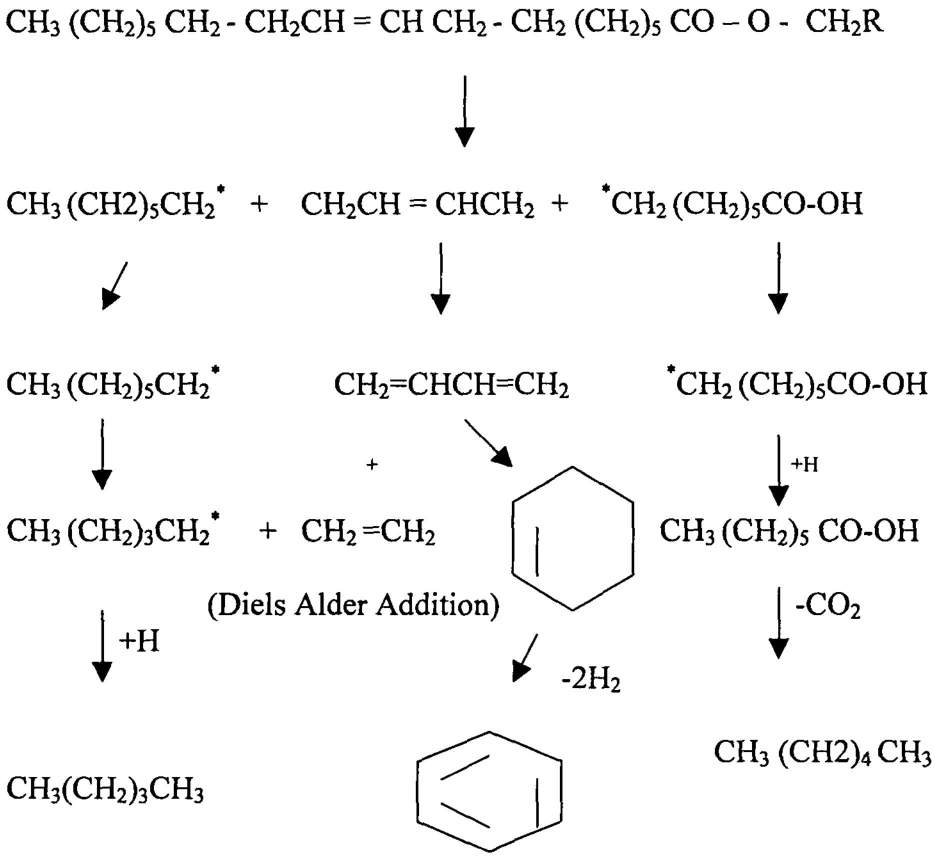


Fig. 1 Mechanism of thermal decomposition of triglycerides.

Different types of vegetable oils show large differences in composition when they are pyrolyzed. The other properties such as viscosity, cetane number, pour point, heating value etc of the pyrolytic oils change significantly from those of the pure vegetable oils.

In 1947, Chang and Wan, (1947) carried out thermal cracking of tung oil calcium soaps. Tung oil was first saponified with lime and then thermally cracked to yield a crude oil which was fractionated to produce diesel and small amount of gasoline and kerosene. Soybean oil was thermally cracked and distilled with a standard ASTM distillation apparatus (Niehaus *et al.,* 1986; Schwab *et al.,* 1988). The total identified hydrocarbons obtained from distillation of cracked soybean oil were 73-77 %.

Konwer and Baruah (1984) produced biocrude oil by cracking of *Mesua ferrea* L. seed oil in the presence of 1% wt of solid sodium carbonate. The properties of the biocrude oil thus obtained were almost similar to those of the typical high wax Assam crude oil (Konwer, 2004). The fraction of the biocrude oil distilling between 37^0-140 ^{0}C could be used as the substitute of gasoline while the fraction distilling between 140^0– 300 ^{0}C and140^0 – 370 ^{0}C could be used as the substitute of kerosene and diesel oil respectively (Konwer and Baruah, 1985). From hydrocarbon type analysis Konwer *et al.* (1989) reported that the fractions of the biocrude oil distilling between 60^0 – 320 ^{0}C yielded 31.8 % wt. of saturates, 46.9 % wt. olefins and 21.3% wt. of aromatics.

Pioch *et al.* (1993) studied the catalytic cracking of vegetable oils to produce biofuels. Copra oil and palm oil stearin were cracked over SiO_2/ Al_2O_3 catalyst at 450 ^{0}C to produce gaseous, liquid and solid products. The condensed organic phase was fractionated to produce biogasoline and diesel fuels.

Recently Twaiq *et al.* (2003) produced liquid hydrocarbon fuels from palm oil by catalytic cracking over aluminosilicate mesoporous catalyst with various Si /Al ratios. Raphael *et al.* (1997) studied the catalytic conversion of canola oils to fuels and chemicals.

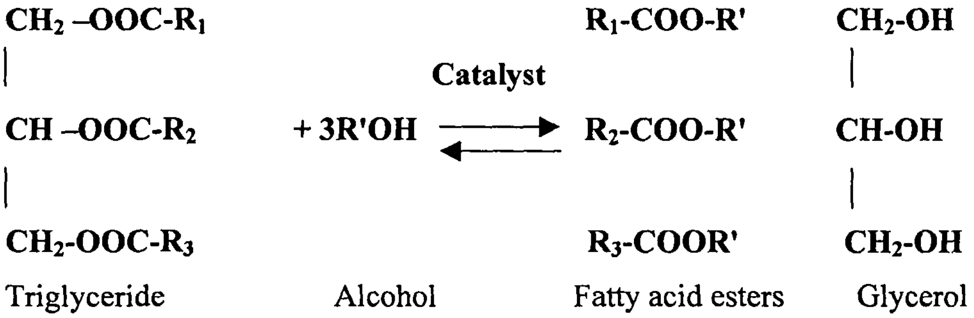
Microemulsion

To solve the problem of high viscosity of the vegetable oils the use of microemulsion with the solvents such as methanol, ethanol and 1-butanol has been studied by many researchers. A microemulsion is defined as a colloidal thermodynamically stable dispersion of oil, water, a surfactant and often a small amphiphilic molecule called a cosurfactant (Schwab *et al.*, 1987). They can improve spray characteristics by explosive vaporization of the low boiling constituents of the micelles (Pryde, 1984).

Ziejewski *et al.* (1984) prepared an emulsion of 53% (v/v) alkali refined and winterized sunflower oil, 13.3% (v/v) 190- proof ethanol and 33.4% (v/v) 1-butanol. This emulsion had a viscosity of 6.31 cSt at 40 ^{0}C, a cetane number of 25, a sulphur content of 0.01% wt., free fatty acids of 0.01% wt. and an ash content of less than 0.01% wt. Lower viscosity values and better spray patterns were obtained by increasing the amount of 1-butanol. Schwab *et al.* (1987) observed that 2- octanol was an effective amphiphillic in the micellar solubilization of methanol in triolein and soybean oil.

Transesterification

Transesterification, also called alcoholysis, is the reaction of an oil or fat with an alcohol to form esters and glycerol. The reaction is shown in Fig 2.



$$\begin{array}{llll}
\mathbf{CH_2{-}OOC{-}R_1} & & \mathbf{R_1{-}COO{-}R'} & \mathbf{CH_2{-}OH} \\
| & \quad\mathbf{Catalyst} & & | \\
\mathbf{CH{-}OOC{-}R_2} & \mathbf{+\,3R'OH} \ \rightleftarrows & \mathbf{R_2{-}COO{-}R'} & \mathbf{CH{-}OH} \\
| & & & | \\
\mathbf{CH_2{-}OOC{-}R_3} & & \mathbf{R_3{-}COOR'} & \mathbf{CH_2{-}OH} \\
\text{Triglyceride} & \text{Alcohol} & \text{Fatty acid esters} & \text{Glycerol}
\end{array}$$

Fig. 2. Transesterification of triglycerides with alcohol.

Stoichiometric material balance yields the following simplified equation:

Fat or Oil	+ 3 Methanol	→	3 Methyl Ester	+ Glycerol
1000 kg	107.5 kg		1004.5 kg	103 kg

The mass flows in the equation are for the case of complete conversion of stearic acid triglyceride.

The alcohols that can be used in the transesterification process are methanol, ethanol, propanol, butanol and amyl alcohol. Among all these alcohols methanol and ethanol are used most frequently, especially methanol because of its low cost, polar nature and shortest chain length. It can quickly react with triglycerides and sodium hydroxide easily dissolves in it.

The transesterification reaction can be catalyzed by alkalis, acids or enzymes. The alkalis include sodium hydroxide, potassium hydroxide, carbonates and corresponding sodium and potassium alkoxides. The acid catalysts include sulphuric acid, sulphonic acids, hydrochloric acids etc. Lipases can be used as biocatalysts.

Mechanism and kinetics of transesterification

Transesterification of triglyceride oils with alcohol represented by the general equation shown in Fig. 2 consists of a number of consecutive reversible reactions (Freedman *et al.*, 1986: schwab *et al.*, 1987) as shown in Fig. 3.

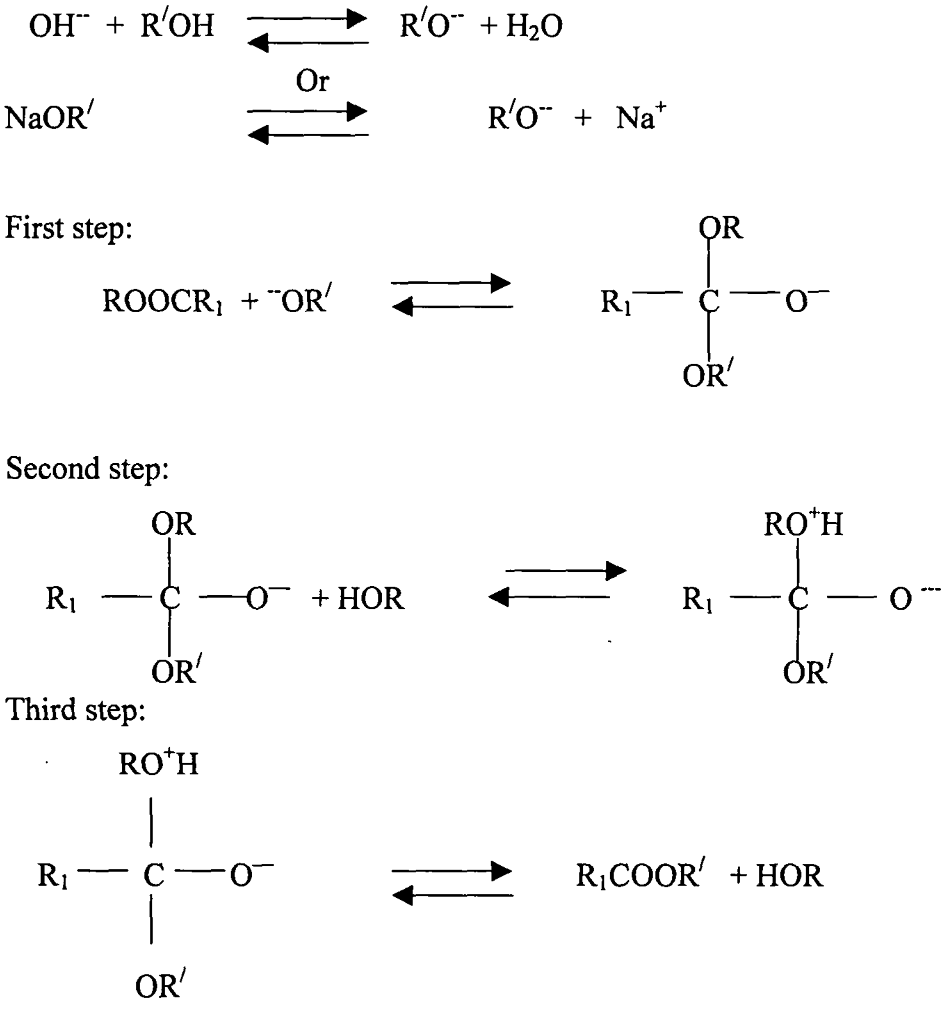
$$\text{i) Triglyceride (TG)} + R'OH \underset{k_4}{\overset{k_1}{\rightleftharpoons}} \text{Diglyceride (DG)} + R'COOR_1$$

$$\text{ii) Diglyceride (DG)} + R'OH \underset{k_5}{\overset{k_2}{\rightleftharpoons}} \text{Monoglyceride (MG)} + R'COOR_2$$

$$\text{iii) Monoglyceride (MG)} + R'OH \underset{k_6}{\overset{k_3}{\rightleftharpoons}} \text{Glycerol (GL)} + R'COOR_3$$

Fig. 3. The transesterification reactions of triglyceride (oil) with alcohol to esters and glycerol.

The reaction mechanism for alkali catalyzed transesterification was shown by Eckey (1956) as the three step reactions. The first step is an attack on the carbonyl carbon atom of the triglyceride molecule by the anion of the alcohol (methoxide ion) to form a tetrahedral intermediate. In the second step the tetrahedral intermediate reacts with an alcohol (methanol) to regenerate a methoxide ion. In the third step, rearrangement of tetrahedral intermediate results in the formation of a fatty acid ester and a diglyceride. Fig. 4 summarizes the mechanism of alkali catalyzed transesterification reactions.



$$OH^{-} + R'OH \rightleftharpoons R'O^{-} + H_2O$$

Or

$$NaOR' \rightleftharpoons R'O^{-} + Na^{+}$$

First step:

$$ROOCR_1 + {}^{-}OR' \rightleftharpoons R_1-\overset{OR}{\underset{OR'}{C}}-O^{-}$$

Second step:

$$R_1-\overset{OR}{\underset{OR'}{C}}-O^{-} + HOR \rightleftharpoons R_1-\overset{RO^{+}H}{\underset{OR'}{C}}-O^{-}$$

Third step:

$$R_1-\overset{RO^{+}H}{\underset{OR'}{C}}-O^{-} \rightleftharpoons R_1COOR' + HOR$$

Where R-OH: diglyceride

R_1: long chain alkyl group and

R': short alkyl group

Fig. 4. The mechanism of alkali catalyzed transesterification of triglyceride with alcohol (Eckey, 1956; Sridharan and Mathai, 1974).

Effect of moisture and free fatty acids

For alkali catalyzed transesterification, the triglycerides and alcohol must be substantially anhydrous because water causes a partial reaction change to saponification which produces soap (Wright *et al.*, 1944). The soap reduces the efficiency of the catalyst and increases the viscosity by formation of gels which causes problems in separation of glycerol. Normally the free fatty acid content of the refined oil should be below 0.5% (Ma *et al.*, 1998).

Effect of molar ratio

An important variable affecting the ester yield is the molar ratio of alcohol to vegetable oil. Freedman *et al.* (1984) studied the effect of molar ratios ranging from 1:1 to 6:1 on ester conversion with vegetable oils and highest conversion was achieved at a molar ratio of 6:1. Normally a molar ratio of 6:1 is used in industrial processes to obtained methyl ester yield higher than 98% on weight basis.

Effect of reaction temperature

Temperature is another variable that has the influence on the reaction rate and yield of esters. Esterification can occur at different temperatures depending on the oil used. Smith (1949) observed that in methanolysis of castor oil to ricinoleate, the reaction proceeded most satisfactorily at 20^0- 30 ^{0}C with a molar ratio of 6:1 – 12:1 using sodium hydroxide catalyst. In esterification of refined soybean oil with a molar ratio of 6:1 using 1% sodium hydroxide catalyst highest yield of ester was obtained at a reaction temperature of 60 ^{0}C (Freedman *et al.*,1984).

Effect of reaction time

The ester conversion rate increases with reaction time. When peanut, cottonseed, sunflower and soybean oils were esterified with methanol at molar ratio of 6:1, 0.5% sodium methoxide catalyst and 60 ^{0}C, Freedman *et al.* (1984) found that an approximately 80% of yield of esters after 1min. for soybean and sunflower oil. After 1 h, the conversions were almost the same for all the four oils (93 – 98%).

Other types of transesterification

Although chemical esterification using an alkali-catalysis process gives high yield of esters in short reaction times, the reaction has several drawbacks: it is energy intensive, recovery of glycerol is difficult, the catalyst has to be removed from the product, free fatty acids and moisture interfere with the reaction, and alkaline waste water requires treatment before discharging to the environment.

Enzymatic transesterification methods can overcome the problems mentioned above. Both extracellular and intacellular lipases are able to effectively catalyze the transesterification of triglycerides in either aqueous or non-aqueous systems. Enzymatic transesterification reactions using various types of alcohols and lipases are given in Table-1.

Table-1: Enzymatic transesterification reactions using various types of alcohols and lipases.

Oil	Alcohol	Solvent	Lipase	Conversion % wt	Ref.
Rapeseed	2-ethyl-1-hexanol	None	C. rugosa	97	Linko *et al.* (1998)
Sunflower	Ethanol	None	M. meihei(Lypozyme)	83	Selmi and Thomas (1998)
	Methanol	Petroleum ether	P. fluorescens	79	Mittelbach(1990)
Palm kernels	Methanol	None	P. cepacia (Lipase PS-30)	15	Abigor *et al.*(2000)
	Ethanol	None	P. cepacia (Lipase PS-30)	72	
Fish	Ethanol	None	C Antarctica	100	Breivik *et al.*(1997)
Recycle Resturant grease	Ethanol	Nine	P. cepacia (Lipase PS-30) +C. Antarctica (Lipase SP-435)	85.4	Wu *et al.* (1999)

Transesterification using supercritical fluids

Very recently there has been growing interest in the transesterification of triglycerides using supercritical fluids. Saka and Kusdiana (2001) reported that preheating to a temperature of 350 ^{0}C and treatment for 240 sec. in supercritical methanol were sufficient to convert rapeseed oil to methyl esters. A reaction temperature of 350 ^{0}C and a molar ratio of methanol to rapeseed oil of 42:1 to be the best conditions (Kusdiana and Saka, 2001). They further reported that free fatty acids contained in oils and fats could also be converted efficiently to methyl esters in supercritical methanol.

Chemical composition and properties of biodiesel

The chemical composition of fat and oil esters is dependent upon the length and degree of unsaturation of the fatty acid alkyl chains. The most important compositional differences between petroleum diesel and biodiesel are oxygen content. Biodiesels contain 10-12 %wt oxygen, which lowers energy density and hence lowers the particulate emission.

Table2 shows the chemical structure of the fatty acid chains found in the most common biodiesel source materials.

Table:- 2. Chemical structure of the fatty acid chains found in the most common biodiesel source materials.

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	$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOH$

Acids may be saturated or unsaturated (contain one or more double bonds). Depending on the nature of the fatty acids present in the source, the fuel properties of the biodiesels may differ to different extent.

Specific gravity

Biodiesel specific gravity is reported to vary between 0.86 and 0.90 and is typically 0.88. Therefore volumetric metering of biodiesel results in the delivery of a slightly greater mass of fuel. Biodiesels have a lower energy content on both volumetric and mass basis.

Iodine number

Iodine number is a measure of the degree of unsaturation of the fuel. Unsaturation can lead to deposit formation and storage stability problems with fuels. Shafer (1994) suggested that fuel with iodine number greater than 115 was not acceptable because of excessive carbon deposit. Ryan *et al.* (1984) addressed soybean, sunflower and cottonseed oil use in engine and suggested that the maximum iodine number should be limited to 135.

Cetane number

The cetane number of a fuel as specified by ASTM D-613, is a measure of its ignition delay. A higher cetane number indicates shorter time between the initiation of fuel injection and ignition, a desirable property in diesel engine fuel. The cetane number of biodiesels depends on the parent oil sources. Reported cetane numbers for soybean oil methylesters ranges from 45.8 to 56.9 and that of rapeseed oil methylesters ranges from 48 to 61.8. Highly saturated esters such as those prepared from tallow and used frying oil have the highest cetane numbers. Cetane increases with chain length, decreases with the number of double bonds, and decreases as double bonds and carbonyl groups move towards the centre of the chain. Increasing cetane number of biodiesel has been shown to reduce nitrogen oxides (NO_x) emissions (Ullman *et al.,* 1990).

Flash Point

Flash point as specified by ASTM D-93 is a measure of the temperature to which a fuel must be heated such that the mixture of vapor and air above the fuel can be ignited. The flash point of the neat biodiesels are always higher than those of petroleum diesel fuels, typically greater than 90^0C and thus neat biodiesel is much safer than diesel from a storage and fire-hazard point of view. However, because of the oxidative instability flash point of biodiesel prepared from unsaturated fatty acids may change during storage.

Distillation Temperature

Fats and oil ester fuels have a narrow boiling point range relative to petroleum diesel and exhibit average boiling points ranging between about 325^0 and 350^0C(Graboski and McCormick, 1998).

Flow properties

Cloud point and pour point are the key flow properties for fuels in winter use. Cloud point, ASTM D-2500, is the temperature at which wax formation occurs to plug the fuel filter. It is measure as the temperature of first formation of wax when the fuel is cooled.

All biodiesel fuels exhibit poor cold flow properties with cloud and pour point 20^0 - 25^0C, higher than those of petroleum diesel. The structural properties of biodiesel that affect freezing point are degree of unsaturation, chain length and degree of branching. Highly saturated tallow esters are poorer in freezing point than soybean and rapeseed esters.

Viscosity and surface tension:

According to ASTM D-445 specification, the maximum viscosity of diesel fuel is 4.1 cSt at 40^0C. Viscosity values for esters of rapeseed oil and tallow exceed this value significantly. High viscosity leads to poorer atomization of the fuel spray and less accurate operation of the injectors. Moreover, the viscosity of neat biodiesel and biodiesel blends increases more rapidly as temperature is decreased (EMA, 1995). Van Gerpen *et al.*(1997) reported that monoglyceride impurities significantly increased the viscosity of methyl soyesters.

Surface tension of a fuel affects its spray atomization, droplet size and other important properties of the diesel spray. Only very limited data on the surface tension of neat biodiesel are available. Stotler and Human (1995) reported a value of 34.9 dyne/cm at 60^0C for neat soybean oil methylester and Recce and Peterson (1993) reported 25.4 dyne/cm at 100^0C for rapeseed oil methylester.

Storage and Stability

Stability includes thermal stability under both hot and cold conditions, resistance to oxidation, polymerization and microbial activity during storage and absorption of water. The main source of instability in biodiesel fuels is unsaturation in the fatty acids chain. If two or more double bonds are present in the fatty acid chain, they have a mutually activating effect. The metals and elastomers, in contact with biodiesel during storage can also impact stability. Oxidation leads to the formation of hydro peroxide, which can polymerize to form insoluble gum.

Water present in biodiesel fuels can cause the formation of rust. Water is also a necessary ingredient for microbial growth.

Oxidative Stability

Oxidation products formed in biodiesels affect fuel storage life and contribute to deposit formation in tanks, fuel systems and filters. Gum number is a measure of deposit formation. Unsaturated fatty acid esters posses high gum numbers.

Earlier workers determined the gum numbers of the methyl- and ethylesters of soybean oil were reported to be 16,400 and 19,200 respectively which were much higher than the gum number of petroleum diesel oil (Graboski and Mc Cormick, 1998).

Recently biodiesel has become more attractive because of its environmental benefits and the fact that it is made from renewable resources. The major challenges of biodiesel are its cost and limited availability of fat and oil resources. The cost of raw materials accounts for 60 to 75% of the total cost of biodiesel fuel (Krawczyk, 1996).

Moreover with the increase of human population, more land may be needed to produce food for human consumption rather than to produce oilseeds for biodiesel production.

In India where fossil fuel resources are limited, the production and use of biodiesel from vegetable oils and fats may be a viable solution to supplement the growing demand of fuel for diesel engine in the country. However while selecting the sources of triglycerides for biodiesel production special attention should be given to utilize the indigenous non-edible oils and used cooking oils. In the forests of India especially of north-east India, a variety of oilseeds bearing tree and shrub species grow well in their natural habitats. The seeds of some of such trees are normally not used for any productive purpose. While searching for oilseed bearing indigenous tree and shrub species we were attracted by two promising indigenous tree species of north-east India namely Nahar (M*esua ferrea* L) and Koroch (a variety of *Pongamia glabra*) which produce significant amounts of oil seeds per plant.

With a view to utilize the seeds of these two trees, we made an attempt to convert the seed oils to biodiesels and to examine the feasibility of using them as fuels for diesel engine.

The objectives of the study are-

(i) to determine the properties of *Mesua ferrea* seed oil and *Pongamia glabra* seed oil;

(ii) to produce biodiesel from these two seed oils by transesterification using suitable process and to determine the fuel characteristics of the biodiesels (methylesters) produced;

(iii) to prepare various blends of each of the biodiesels with a typical petroleum diesel and determine their fuel characteristics so as to select the most suitable blends which may be used as fuels for diesel engine and

(iv) to conduct the engine performance tests and emission characteristics with the selected blends of each of the two biodiesels.

Such a study may be helpful in evaluating the feasibility of using these two oils as the source of biodiesels that can be used in neat form or in blends.

CHAPTER II

REVIEW OF LITERATURE

(15-29)

Chapter II
Review of Literature

Rudolf Diesel, the inventor of diesel engine, was the first to test vegetable oil as fuel for his engine (Shay, 1993). But it was immediately recognized that the use of whole vegetable oils was not acceptable in diesel engines. In the 1930s and 1940s vegetable oils were used as diesel fuels from time to time but only in emergency situations (Ma *et al.* 1999). Walton (1938) reported on pioneering work with vegetable oils as diesel fuel and suggested an early concept for biodiesel. He examined three different vegetable oils soybean oil, palm oil and cottonseed oil in a diesel engine and observed that when whole oils were used in diesel engines, they formed carbon deposits and exhibited poor pour point problems. Because of these difficulties experienced, he suggested splitting of the triglycerides and using the resulting fatty acids as fuel.

Since the beginning of 1980s, there has been growing interest worldwide on the use of biodiesel fuels. The first international conference on plant and vegetable oils as fuels was held in Fargo, North Dakota, in August 1982. The primary concerns discussed in this conference were the cost of the fuels, the effect of vegetable oil fuels on engine performance and durability, fuel preparation, specifications and additives and extraction (ASAE, 1982).

Bruwer and co-workers (1980) reported that using an ester of sunflower oil seemed to resolve the problems associated with the whole oil and in fact produced less carbon deposits in a test engine than petroleum derived diesel fuel. They also reported that smoke opacity was also lower with the ester than with petroleum diesel. Bacon and co-workers (1981) reported that coking and polymerization of vegetable oils could be minimized by transesterfication. Fort and Blumberg (1982) performed engine-testing studies of cottonseed oil methyl ester and observed that performance was comparable to diesel with no change in power output over a 200-hour endurance test.

There are numerous transesterfication citations in the scientific and patent leteratures (Trent, 1945, Tanaka *et al.* 1981; Allen *et al.* 1945; Freedman *et al.* 1984; Ali 1995; Bradshaw and Meuly 1944; Ma *et al.* 1998 a; Ma *et al.* 1998 b).

Reed *et al.* (1992) reported one method for producing esters from waste cooking oils containing significant quantities of tree fatty acids liberated during the cooking process. They suggested that additional caustic must be added to the waste cooking oils to neutralize the free fatty acids by converting them to soap prior to transesterification.

Freedman *et al.*(1984) compared both crude and refined vegetable oils as feedstocks of transesterfication and found that the methyl esters was reduced from 93% to 98% for refined oil to 67% to 86% for crude vegetable oils. This was attributed to the presence of free fatty acids in the crude oil. Van Gerpen and Dvorak (2002) studied the effect of phospholipids on biodiesel production and found that phosphorus compounds in the oil did not carry over into the methyl esters while the yield of esters was reduced by 3% - 5%for phosphorus levels above 50 ppm.

Though almost all commercial biodiesel producers use an alkali-catalyzed process for the transesterification other approaches have also been tried including acid catalysis (Canakci and Van Gerpen, 1999) and enzyme catalysis (Nelson et al.,1996; Shimada et al.,1999; Watanbe et al.,2000; Wu et al.,1999).

The alkali catalysts include NaOH, KOH, carbonates and corresponding sodium and potassium alkoxide such as sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide. The acid catalysts usually include sulphuric acids, sulphonic acids and hydrochloric acids. Wright *et al.* (1944) reported that for an alkali-catalyzed transesterfication the glycerides and alcohol must be substantially anhydrous, because water makes the reaction partially change to saponification. If more water and free fatty acids are in the triglycerides, acid catalysed transesterification can be used (Keim, 1945). Bradshaw and Meuly (1944) and Feuge and Grose (1949) also stressed the importance of oils being dry and free of fatty acids. Ma *et al.*(1998a) 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.

Various workers investigated the effect of catalysts on transesterification. Freedman et al. (1984) reported that alkali-catalysed transesterification was much faster than acid-catalysed transesterification. However, if a glyceride has a higher free fatty acid content and more water content, acid-catalyzed transesterification is more suitable. They also observed that sodium methoxide was a more effective catalyst than sodium hydroxide. Recently an immobilized lipase was employed to catalyze the methanolysis of corn oil in flowing superficial carbondioxide with an ester conversion of more than 98% (Jackson and King, 1996).

The effect of alcohol to oil ratio on the yield of the ester was studied by several workers. Bradshaw and Meuly (1944) reported that the practical range of molar ratio was from 3.3 to 5.25:1 of methanol to vegetable oil. Higher molar ratios result in greater ester conversion in a short time. In the ethanolysis of peanut oil, a 6:1 molar ratio liberated more glycerin than did a 3:1 molar ratio (Feuge and Grose, 1949). Nye and Southwell,(1983) methanolysed rapeseed oil using 1% NaOH or KOH and found that a molar ratio of 6:1 of methanol to oil gave the best conversion. Sprules and Price (1950) 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. Freedman *et al.* (1984) applied a molar ratio of 6:1 of alcohol to oil in transesterification of soybean, sunflower, peanut and cottonseed oils and achieved highest conversion (93-98%). Ali (1995) and Zhang (1994) also used a molar ratio of 6:1 for beef tallow transesterification.

Earlier workers reported that with the increase of reaction time the conversion rate of triglyceride to ester was found to increase significantly. Ma *et al.* (1998a) studied the effect of reaction time on transesterification of beef tallow with methanol and observed that reaction was very slow during the first minute. However, it was observed that from 1to 5 minutes, the reaction proceeded very fast. Freedman *et al.* (1984) transesterified peanut, cottonseed, soybean and sunflower oils under the condition of methanol to oil ratio of 6:1, 0.5% NaOMe catalyst and 60 ^{0}C. The achieved 80% of yield of ester after 1 minute, for soybean and sunflower oil, but after1-h the conversions were observed to be 93-98% for all the oils.

Freedman *et al.*(1984) transesterified refined soybean oil with methanol using 1% NaOH catalyst at three different temperatures namely 60 ^{0}C, 45 ^{0}C, 32 ^{0}C and after 1 h ester yields were found to be 94%, 87% and 64% respectively.

Bradshaw and Meuly (1944) patented a two step process for making soap from vegetable oils or fats. In the first step fatty acid esters were formed from oils and then soap was produced from the esters. Trent (1945) patented a continuous transesterification process. Sprules and Price (1950) used an alkali and then acid-catalyzed transesterification process for high acid value oils. Tanaka et al. (1981) developed a novel method for preparation of lower alkyl in methyl esters of fatty acids glycerides. Zhang (1994) transesterified beef tallow with a free fatty acids content of 0.27%. In this process the tallow was heated to remove moisture under vacuum, then kept at 60 ^{0}C. The transesterification reaction was conducted using 6:1 molar ratio of methanol to tallow and 1% (by the weight of tallow) NaOH dissolved in the methanol and 60 ^{0}C for about 30 minutes. After separation of glycerol, the ester layer was transesterified again using 0.2% NaOH and 20% methanol at 60 ^{0}C for about 1h. The mixture was washed with water until the wash water was clear. The purified ester was then heated to 70 ^{0}C under vacuum to remove moisture. The yield of ester was 80 %.

Wimmer (1992b) prepared methyl esters by etsreification of glycerides with C 1-5 alkanols C 2-5 alkoxy alkanols in the presence of basic catalysts. In this process after the reaction was finished, 0.5-10 % acid or water was added to neutralize the catalyst. Distillation of the ester phase after treatment with fuller's earth or silica gel was optimal.

Stern *et al.* (1995) patented a method for making fatty acid esters from acid oils. In his method the free fatty acids in the oil were recovered by transferring them with glycerol to form glycerides. After transesterification, a large portion of the glycerol was mixed with the ester wash water and then neutralised with acid. The salt was separated by filtration and alcohol evaporated. The separated free fatty acids reacted with the non-neutralized glycerol phase at about 200 ^{0}C. The triglycerides from the reaction were added to the next alcoholysis step.

Boocock (2001) and Zhou *et al.* (2003) have developed a novel technique for accelerating the transesterfication reaction rate. This technique is applicable for use with various simple alcohols and acid catalysed pretreatment of high free fatty acid feedstocks.

Hass *et al.* (2002, 2003) have shown that acid-catalyzed esterification can be used to produce biodiesel from low-grade by-products of the oil refining industries such as soapstock. Soapstock is a mixture of water, soap and oil, was dried, saponified and then esterified with methanol or some other simple alcohol using an inorganic acid as catalyst.

Zhang *et al.* (2003, 2003) reviewed the commonly used procedures for producing biodiesel, including a process simulation using the commercial software package HYSYS. They reported that use of waste cooking oil feedstocks provided a higher rate of return than refined vegetable oils even after including the additional capital and operating costs of acid catalyzed pretreatment.

The impact of contaminants and impurities on the cold flow properties of methyl soyesters was studied by Van Gerpen *et al.* (1997) and showed that unsaponifiable matter (sterols, tocopherols and other hydrocarbons) had no effect on cold flow properties up to the 2% level.

The viscosity of biodiesel and biodiesel blends increases more rapidly as temperature is decreased than that of Number 2 diesel (EMA, 1995). Monoglyceride impurities have also been shown to increase the viscosity of methyl soyesters (Van Gerpen *et al*, 1997).

EMA (1995) reported that compared to Number 2 diesel, methyl esters of tallow and soy were far more prone to oxidation. Number 2 diesel consume 5% of the available oxygen, tallow methyl ester consumed 60% and soymethyl ester consumed 90%. Van Gerpen *et al.*(1997) observed that certain minor components of biodiesel such as tocopherol, acted as natural antioxidants and that these are removed if the biodiesel is purified by distillation. Oxidation products formed in biodiesel are known to affect fuel storage life and contribute to deposit formation in tanks, fuel systems and filters. Gum number is measure of deposit formation. Fuel with high iodine numbers may posses high gum numbers. Clark *et al.*(1984) determined gum numbers for methyl ester and ethyl esters of soybean oil and found 16400 and 19200 respectively, while the gum numbers for Number 2 diesel was found to be 6-7 only.

Recently various workers have studied enzymatic transesterification by lipase. Both intracellular and extracellular lipases are able to effectively catalyze the transesterification of triglyceride in either aqueous or non-aqueous systems. In such systems the biproduct glycerol can be easily recovered without any complex process and also that free fatty acids contained in waste oils and fats can be completely converted to methyl esters.

Linko *et al.* (1998) demonstrated the production of a variety of esters and polyesters with lipase as the biocatalyst. In the transesterification of rapeseed oil with

2-ethyl-1-hexanol 97% conversion of esters was obtained using *candida rugosa* lipase powder.

Kaieda *et al.* (2001, 1999) investigated the methanolysis of soybean oil with both non-regiospecific and 1(3)-regiospecific lipases in a water containing system without an organic solvent.

The *R. Oryzae lipase* which exhibits 1(3)- regiospecificity was also formed to be effective for the methanolysis of soybean oil (Okumura *et. al.*,1976; Macrae, 1983; Matori *et. al.*,1991).

Abigor *et. al.*(2000) found that in the conversion of Palm oil to alkyl esters using P. cepacia lipase, ethanol gave the conversion of 72% while only 15% methyl esters was obtained with methanol. Lipases are known to have a propensity to act on long-chain fatty alcohols better than short-chain ones (Shimada *et. al.*, 1999).

The transesterification by using supercritical fluids is a subject of current interest. Saka and Kusdiana (2001) made fundamental study of biodiesel production in supercritical methanol. They demonstrated that preheating to temperature of 350^0C and treatment for 240s in supercritical methanol were sufficient to convert rapeseed oil to methyl esters. A reaction temperature of 350^0C and a molar ratio of methanol to rapeseed oil of 42 to 1 were considered to the best condition (Kusdiana and Saka, 2001). Free fatty acids contained in crude oils and fats could also be converted efficiently to methyl esters in supercritical methanol, with increased yield of methyl esters from used oil (Kusdiana and Saka, 2001)

Ikwuagwu *et al.* (2000) reported the production of methyl ester using rubberseed oil and sodium hydroxide as catalyst. They found that the viscosity was substantially reduced from 37.85 to 6.29 cSt while calculated cetane index increased from 34.00 to 44.81.

Alcantara *et al.* (2000) describe the catalytic production of biodiesel from soybean oil, used frying oil and tallow by transesterification and amidation reactions with methanol and diethylamine respectively. The ignition properties of these types of biodiesel were evaluated calculating the cetane index of the transesterification products and the blending cetane number of the amide biodiesel blended with conventional diesel. Amide biodiesel enhances the ignition properties of the petrochemical diesel fuel and it could account for the 5% market share that should be secured to biofuels by 2005.

Pizarro *et al.* (2002) reported the lipase-catalyzed production of biodiesel fuel from vegetable oils derived from the waste bleaching earth's of crude vegetable oil. Low valued oils (40%) are potential substrates for biodiesel fuel production. The waste bleaching oil extracted with organic solvents was identified as soybean, palm and rapeseed oil. Methanolysis was efficiently catalyzed by lipase in the presence of high water content and by a single addition of methanol. The highest conversion yield reached 55% (w/w) with palm oil after 96 hours of reaction. Adverse viscosity condition might have influenced methanolysis of extracted soybean and rapeseed oil in spite of high water and methanol concentration.

Kalligeros *et al.* (2003) investigated the application of biodiesel / marine diesel blends and tested the performance of a stationary single cylinder diesel engine. The engine was fuelled with pure marine diesel fuel and blends containing two types of biodiesel, at proportion up to 50%. They reported that the two types of biodiesel appeared to have equal performance and irrespective of the raw materials used for their production, their addition to the marine diesel fuel improved the particulate matter, unburned hydrocarbon, and nitrogen oxide and carbon monoxide emission.

Kalam and Masjuki (2002) carried out experiments to evaluate the effect of anticorrosion additive in palm oil biodiesel on diesel engines, performance, and emissions and wear characteristics. They concluded that the physicochemical properties of palm oil biodiesel meet the requirement of diesel engine combustion and were comparable with other biodiesels such as soybean and rapeseed oil biodiesels.

Raneses *et al.* (1999) reported about the potential biodiesel markets and their economic effects on the agricultural sector of the United States. They estimated the potential US biodiesel demand in three specific markets that the US biodiesel industry had identified as likely candidates for commercialization: federal fleets, mining and marine/estuary areas. They stated that if a 20% biodiesel blend becomes a competitive alternative fuel in the future, these markets could demand as much as 379Ml of biodiesel. The food and agricultural policy simulator, an econometric model of US agriculture, was used to estimates the impacts of 76, 189 and 379 Ml of soybean oil based biodiesel production on the agricultural sector of the united states. Their results indicated that the increased demand of the soybean oil would increase US soybean oil price by as much as 14.1%. Corresponding to this price change, US soybean price would rise 2.0% and soybean meal price would fall by 3.3%. US net farm income would be increased by as much as 0.3%.

Van Dyne *et al.* (1996) reported the macroeconomic effect of community-based biodiesel production systems. They found that Net permanent job creation in rural communities was found to be slight with the operation of a single 500,000-gallon community based biodiesel plant; however temporary jobs were increased due to plant construction. Overall community based biodiesel plants were reported to be beneficial to the local economies, in terms of increased wages, increased tax base and the value added to the soybean.

Antolin *et al.* (2002) studied about the optimization of biodiesel production by sunflower oil transesterification. They reported that Taguchi's methodology could be well adopted for the optimization of most important variables (temperature condition, reactants proportion, and methods of purification) with the purpose of obtaining a high quality biodiesel that fulfil the European pre-legislation with the maximum process yield. Finally they characterized sunflower oil methyl ester's properties such as viscosity, flash point, cold filter plugging and acid value to test in diesel engine and they reported that biodiesel obtained in optimum conditions is an excellent substitute for fossil fuels.

Machacon *et al.* (2001) reported the performance and emission characteristics of a diesel engine fuelled with coconut oil-diesel fuel blend. They reported that operation of the test engine with pure coconut oil and coconut oil diesel fuel blends for a wide range of engine load condition was shown to be successful even without engine modification. It was also reported that increasing the amount of coconut oil diesel fuel blend resulted in lower smoke and NOx emission; however that resulted an increased in BSFC. This was attributed to lower heating value of the neat coconut oil to that of diesel.

Review of literature in India context:

Though India has high potential for biodiesel production, very little work has been done so far.

De and Bhattacharya (1999) reported the preliminary investigation on the production of biodiesel from vegetable like Nahar oil and Karanja oil. From their experimental report the specific values of density, viscosity, flash point, pour point and cetane index (calculated value 54 and 56 for Nahar oil and Karanja oil respectively) had been known for the methylester.

Ashok Kumar and Aithal Arvind (2003) reported the production of fuel esters from palm oil and *pongamia* oil (Karanja oil) and their performance evaluation by using these in a stationary diesel engine. They found that about 1.2 liters of *pongamia* oil diesel could produce the same energy as that produced by a liter of petroleum diesel. Use of sponge iron ores as a catalytic package brought down vegetable oil emission to half that of diesel emission. On account of lack of sulfur content in the esters, oxides of nitrogen a responsible constituent for smog and ozone formation could be kept in the limit unlike the petrodiesel. The vegetable oil in general or pongamia oil ester in particular could save annually about 3000 liters of diesel on an average of eight hours daily engine operation and curtail atmospheric pollution by 20 to 25 %.

Senthil Kumar *et al.* (2003) reported a comparative study of the different methods to improve the engine performance while using *Jatropha* oil as the primary fuel in a compression ignition engine. Neat *Jatropha* oil resulted in slightly reduced thermal efficiency, higher smoke emissions and increased hydrocarbon and carbon monoxide emissions. Brake thermal efficiency was 27.3% with neat *Jatropha* oil and 30.3% with diesel. That was improved to 28.5% with 30% methanol blend and 28.3% with 20% orange oil blend by volume. Performance and emissions were considerably improved by the methyl ester of Jatrapha oil. Duel fuel operation with methanol induction and Jatropha oil injection also showed higher brake thermal efficiency at peak power. There was an increase to 29.4% and 29.3% at 31% orange oil and 18% hydrogen energy shares respectively. Smoke was significantly reduced from 4.4 BSU with neat Jatropha oil to 2.6 BSU with methanol induction. Methanol and orange oil induction reduced the NO emission and increased hydrocarbon and carbon monoxide emission. With hydrogen induction, hydrocarbon and carbon monoxide emissions were significantly reduced.

Ramdhas *et al.*(2003)reported the experimental investigations with rubber seed oil as an alternative fuel for C.I. Engines. The blends of varying proportion of rubber seed oil and diesel were prepared and their properties were analyzed. The performance of the engine using various rubber seed oil diesel blends was evaluated in a single cylinder compression ignition engine. Noticeable improvement in engine performance was reported to observe in duel fuel operation as compared to that of pure diesel.

Shasidhara *et al.* (2003) reported the preparation, C.I. Engine operation and energy conservation with methyl esters of sunflower oil and castor oil as fuels. It had been reported that about 1.12, 1.18 and 1.27 liters of sunflower oil, MESO and MECO respectively were required to produce the same energy as that generated by a liter of diesel. However the engine exhibited the similar smoke density level for both pure diesel and MESO modes of operation.

Shrivastava and Prasad (2000) highlighted the possibilities and potential in the field of biodiesel production in India and worldwide. In this review article, the disadvantages and problems that could arise from the direct use of biodiesel and the advantages due to its renewable nature and environmental benefits are clearly highlighted.

Barnwal and Sharma, (2005) had reported an attempt has been made to review the work done on biodiesel production and utilization, resources available, process(es) developed/being developed, performance in existing engines, environmental considerations, the economic aspect, and advantages in and barriers to the use of biodiesel. They highlighted in a conclusive statement that the initiative taken by the Ministry of Non-conventional Energy Sources (MNES), India, for expansion of biodiesel production from nonedible oilseeds like *Jatrapha Curcas*, *Karanja oil* etc. can fulfill the demand in near future.

Ramdhas *et al.* (2003) reported an alkali catalyzed two step processes for the production of biodiesel from high free fatty acid containing rubber seed oil. The sample oil after pretreatment was stored for overnight before final transeterification. They claimed for 98% conversion of the triglycerides to the corresponding methyl ester. The two-step esterification procedure converts rubber seed oil to its methyl esters. The viscosity of biodiesel oil is nearer to that of diesel and the calorific value is about 14% less than that of diesel.

Ghadge and Raheman (2005) reported a technique to produce biodiesel from mahua oil (*Madhuca indica*) having high free fatty acids (19% FFA) has been developed. The high FFA level of mahua oil was reduced to less than 1% by a two-step pretreatment process. Each step was carried out with 0.30–0.35 v/v methanol-to-oil ratio in the presence of 1% v/v H_2SO_4 as an acid catalyst in 1-hour reaction at 60°C. After the reaction, the mixture was allowed to settle for an hour and methanol–water mixture that separated at the top was removed. The second step product at the bottom was transesterified using 0.25 v/v methanol and 0.7% w/v KOH as alkaline catalyst to produce biodiesel. The fuel properties of mahua biodiesel were found to be comparable to those of diesel and conforming to both the American and European standards.

Subramanian *et al.* (2005) reported the feasibility of liquid bio-fuel utilization (biodiesel and ethanol) in automotive diesel engine. In their paper they dealt with the policy and planning issues for utilization of ethanol and biodiesel in automotive diesel engines in Indian context in view of environmental benefits, energy self-sufficiency and boosting of the rural economy as well as measures related to implementation and barriers. The main focus of this paper was on transport and refinery scenario, land availability for production of biodiesel and potential sources for biodiesel and ethanol. The availability of ethanol and estimations for its consumption as transport fuel were made and necessary remedial measures to increase the availability of ethanol in the country in future were suggested.

Shah *et al.* (2004) reported a lipase catalyzed tranesterification procedure for *Jatrapha Curcus* oil. In their work three different lipases (*Chromo bacterium viscosum*, *Candida rugosa,* and *porcine pancreas*) were screened for a transesterification reaction of *Jatropha* oil in a solvent-free system to produce biodiesel; only lipase from *Chromo bacterium viscosum* was found to give appreciable yield. Immobilization of lipase (*Chromo bacterium viscosum*) on Celite-545 enhanced the biodiesel yield to 71% from 62% yield obtained by using free tuned enzyme preparation with a process time of 8 h at 40 °C. Further addition of water to the free (1%, w v-1) and immobilized (0.5%, w v-1) enzyme preparations enhanced the yields to 73 and 92%, respectively. Immobilized *Chromo bacterium viscosum* lipase can be used for ethanolysis of oil. It was seen that immobilization of lipases and optimization of transesterification conditions resulted in adequate yield of biodiesel in the case of the enzyme-based process.

Apart from these many Universities and Institutes of India are now actively participating in the biodiesel production research and investigation. Ministry of Non Conventional Energy Sources, Govt of India is funding for many such projects (Tiwari B K, 2003).

In recent times some interest has been shown on the conversion of vegetable oils and fats to liquid fuels and feedstocks for petrochemical industries through their catalytic cracking (Raphael *et al.*, 1997). It is a well-established fact that the triglycerides derived from the plant seed oil, animal fats, waste cooking oil etc can be transformed into cracked oil, which is similar in properties to petroleum crude oil (Ma F and Hanna AM, 1999; Meher L C *et al.*,2004; Twaig F A *et al.*,2003; Reed T B *et al.*,1992; Ikwuagwu O E *et al.*, 2000; Idem R O *et al.*, 1997; Billaud F *et al.*,1995, 2003).

Konwer and Baruah (1984,1985), Konwer *et al.* (1989) reported a simple method of conversion of *Mesua ferrea* seed oil to biocrude oil, which was similar to mineral crude oil. From the studies of the fuel characteristics of different fractions of the biocrude oil they have shown that the fraction distilling between 37^0 C to 140^0 C can be used as the substitute of gasoline while the fractions distilling between 140^0 – 300^0 C and 140^0 C- 370^0 C could be used as kerosene and diesel oil respectively. From the biocrude oil about 55-60 % of diesel oil can easily be obtained. Recently, Konwer (2004) suggested that conversion of high acid value oil like *Mesua ferrea* seed oil may be first converted to biocrude oil and then fractionated to obtain gasoline, kerosene and diesel oil. Such diesel oil can be used directly in diesel engine without blending with petroleum diesel and also without engine modification. In a recent publication (Sarma and Konwer, 2005) it was shown that the biocrude obtained by catalytic cracking can easily be mixed with petroleum crude oil for fractional distillation in a conventional petroleum refinery. However, to improve the quality of the fuel fractions of the biocude obtained by catalytic cracking hydrogenation, isomerization and alkylation processes may be tried.

CHAPTER III

MATERIALS AND METHODS

(30-39)

Chapter III
Materials and Methods

3.1 Study Site

The site selected for collecting the oil seeds were the forests of the state of Assam, located in the north-east India. The state is located between $24^0 8'$ to $28^0 9'$ N latitude and $89^0 42'$ to $95^0 16'$ E longitude. It experiences a humid subtropical climate with an average rainfall ranging from slightly below 1400mm to slightly above 3000mm. The mean maximum temperature goes upto 37^0 C in summer and mean minimum temperature comes down to10^0 C in winter. Soils of the state are slightly acidic in nature.

3.2 Selection of the oil seeds

In the forests of north-east India a variety of indigenous oil seeds bearing plants grow well in their natural habitats. For the present study we selected the oil seeds of *Mesua ferrea* L. and *Pongamia glabra* Vent. trees. These two trees are found in abundance in this region and their seeds contain high percentages of oil which are nonedible. At present the seeds of these trees are not utilized for any productive purpose.

3.3 Characteristics of the tree species

Characteristics of *Mesua ferrea* and *Pongamia glabra* on the basis of their botanical description, wood quality, availability etc. are described elsewhere (Hooker, 1875; Dutta, 1985).

Mesua ferrea

Botanical Name	: *Mesua ferrea* L.
English Name	: Iron wood tree

Vernacular Name : Nahar (Assamese); Nageswar (Hindi).

Family : guttiferae

It is a middle-size tree that grows mostly in the mountains of the Eastern Himalayas, Eastern Bengal, Eastern and Western Peninsulas and Andamand

Fig. 5. A juvenile *Mesua ferrea* tree

Fig. 6. *Mesua ferrea* flower

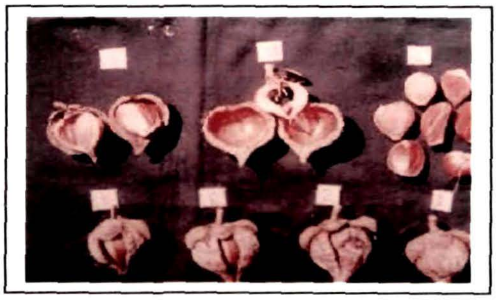


Fig. 7. *Mesua ferrea* seeds and their seed coats

Islands. In Assam it is found particularly in upper Assam, lower Nagaland, Darrang district and the North Cashar Hills. Its seeds contain 75% percent of oil on the basis of shelled kernel weight. Flowering starts in April-May and seeds become mature in August-October. A fully mature tree yields 30-60 kg of seeds annually. *Mesua ferrea* is one of the hardest trees of north-east India. Its timbers are used in railway sleepers, construction of houses, furniture and cart wheels etc. In early days when kerosene and electricity were not available the rural people of this region used its seeds for illumination at night. Flowers and leaves have snake repellent properties.

Pongamia glabra

Botanical Name	: *Pongamia glabra* Vent.
English Name	: Indian Beech, Pongam, Hongay.
Vernacular Name	: Koroch (Assamese), Papar (Hindi).
Family	: Leguminosae

Fig. 8. *Pongamia glabra* Vent. tree

Fig. 9. *Pongamia glabra* seeds and their kernels

It is a middle-size evergreen tree with spreading branches. In north-east India it is normally found in Lakhimpur, Sibsagar, Dibrugarh, Darrang, Kamrup and Nowgong districts of Assam, lower Nagaland and Meghalaya. Wood of *Pongamia glabra* is hard and heavy and yellowish in colour. A fully mature tree yields 20-50 kg of seeds yearly. The oil content of the seeds varies from 30-35 %. The oil is used in treatment of skin disease and fresh bark is used as medicine in the treatment of piles.

3.4 Extraction of oils:

About 100 kg of *Mesua ferrea* seeds were collected from mature trees grown in the forests of Assam in October 2004 and dried at 50^0 C for 24h in a hot air oven. The dried seeds were shelled and milled. The oil was extracted from the milled kernels with petroleum ether (40-60 ^{0}C) using the Soxhlet extraction method (Raheman and Phadatare, 2004). The solvent was removed from the extract and the oil content was found to be 75% by weight of the milled kernel. About 10 litres of the oil were extracted and kept over anhydrous sodium sulphate for three 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.

About 100kg of the *Pongamia glabra* seeds were collected from the forest of Assam in March 2004 and dried at 50^0 C for 24h. The dried seeds were shelled and milled. About 10 lit of the oil were extracted from the milled kernels through a similar procedure used for extraction of oil from *Mesua ferrea* seeds. The oil content was found to be 33.6% by weight of the milled kernel. The extracted oil was kept over anhydrous sodium sulphate for three days and then filtered through glass wool. The filtered oil was then stored in glass bottles for further experiments.

3.5 Determination of the properties of the oils:

Various properties such as density, pour point, kinematic viscosity, acid value, ash content, carbon residue, calorific value etc. of *Mesua ferrea* seed oil and *Pongamia glabra* seed oil were determined by different standard methods.

Density was determined by ASTM D287 method.

Pour point was determined by ASTM D97 method.

Kinematic viscosity at 40^0 C was determined by ASTM D445 method.

Acid value was determined by ASTM D874 method.

Carbon residue was determined by ASTM D4530 method.

Calorific value was determined by using a bomb calorimeter.

All the tests were carried out in triplicate and average values are presented in Tables 4 & 5.

3.6 Determination of fatty acid composition of the oils:

Fatty acid composition of *Mesua ferrea* seed oil and *Pongamia glabra* seed oil were determined by using a GC as per AOCS official method 1998, Ce 1-62 and Ce 2-26. GC analysis was carried out in triplicate and the average values are presented in Table 4 & 5.

3.7 Production of Biodiesel from *Pongamia glabra* seed oil:

The production of biodiesel (methyl ester) of *Pongamia glabra* seed oil was carried out in a 2lit. capacity glass vessel equipped with a mechanical stirrer, a funnel and a condenser placed in water bath having a proportional integral derivative temperature control device. *Pongamia glabra* seed oil (500ml) and 150 ml of methanol (98% pure) were mixed (1:6 molar ratio) and the mixture was placed inside the reactor. The temperature of the reactor was raised to 60^0 C, and the mixer was stirred at 600rpm. When the mixture temperature reached 60^0 C, 4.5g of freshly prepared sodium methoxide was added to it. Thus the reaction was continued for 1h, an optimum reaction time, as determined from three sets of experiments conducted initially for 0.5, 1, and 1.5 h duration. As soon as the reaction time was over, the mixture was placed in a separating funnel and allowed to cool for 2h. Two distinct layers were found to form, the upper layer being the mixture of methyl ester and unreacted methanol and the lower layer was a mixture of glycerol and water. A rotary vacuum evaporator was used to recover the unreacted alcohol from the ester layer. The unreactd alcohol recovered was found to be 30ml. The ester was then washed twice with distilled water. The emulsified water was removed through rotary vacuum evaporator method. Biodiesel (488ml) and

32 ml of glycerol were recovered by this method. A small quantity of the esters thus produced was kept separately for Sim-Dis distillation in a gas chromatograph. The remaining esters were then refined by distilling under reduced pressure. Following the same procedure a 10 lit. of biodiesel from *Pongamia glabra* seed oil was produced and kept over anhydrous sodium sulphate for further experiments.

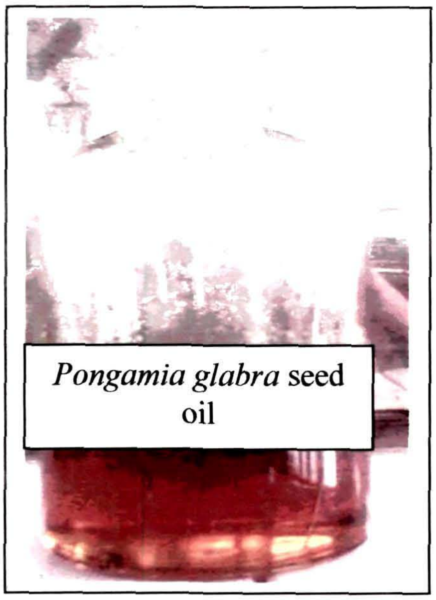


Fig. 10. *Pongamia glabra* seed oil

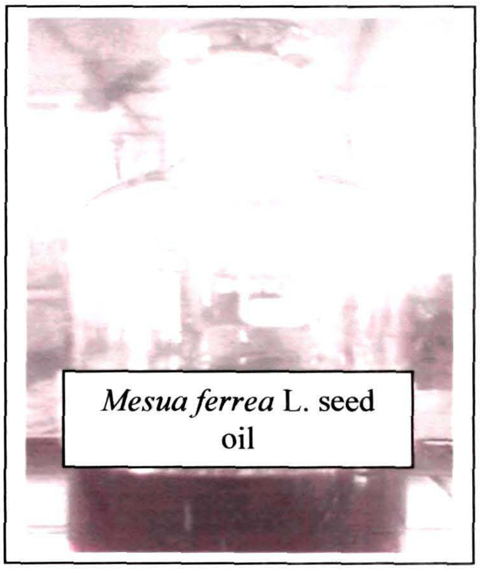


Fig. 11. *Mesua ferrea* L seed oil

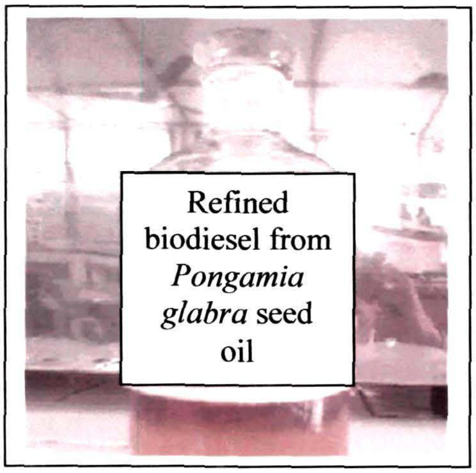


Fig. 12. Refined biodiesel from *Pongamia glabra* seed oil.

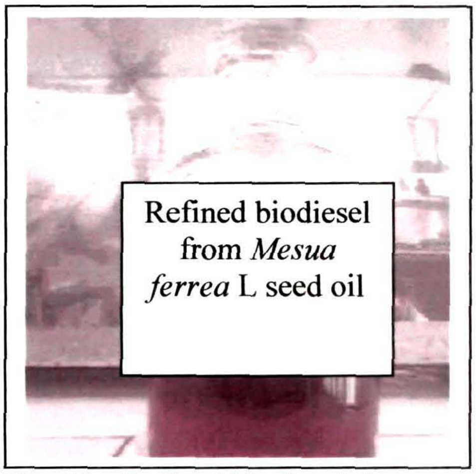


Fig. 13. Refined biodiesel from *Mesua ferrea* seed oil.

3.8 Production of Biodiesel from *Mesua ferrea* seed oil:

Following the same procedure and the same reactor as used in the production of biodiesel from *Pongamia glabra* seed oil and using sodium methoxide catalyst, we attempted to produce biodiesel from *Mesua ferrea* seed oil using sodium methoxide catalyst. It was observed that the yield of biodiesel was quite low (< 85%) and the separation of the ester layer from glycerol layer was found to be very difficult. Canakci and Van Gerpen (1999) has suggested that special processes are required for transesterification of oil or fat containing significant amount of free fatty acids (FFAs). They reported that pretreatment processes using strong acid catalyst have been shown to provide good conversion yields and high quality final products. Hence for production of biodiesel from *Mesua ferrea* seed oil which contains higher amounts of free fatty acids (Acid value, 16.4mg KOH/g), we attempted to produce biodiesel through a two step process. In the first step esterification of the free fatty acids to methyl esters was carried out using sulphuric acid catalyst. In the second step low free fatty acids pretreated oil was esterified with alkali catalyst to convert to methyl esters. Keim (1945) used this method to convert palm oil containing 50.8% of free fatty acids to methyl esters.

Experimental procedure

A 500 ml of *Mesua ferrea* seed oil and 150ml of methanol (98% pure) were mixed (1:6 molar ratio) and the mixture was placed inside a 2lit capacity glass reactor. A 5ml of conc. sulphuric acid was then added to the mixture. The temperature of the reactor was raised to 60^0 C and the mixture was stirred at 600 rpm for 1.5 h. As soon as the reaction was over, the mixture was placed in a separating funnel. After cooling, the upper layer being the mixture of esters, unreacted triglycerids and unreacted methanol was separated from the lower layer. After neutralization of this mixture with KOH solution, 1.25% sodium methoxide was added, and the mixture was stirred for an additional 1h at 60^0 C. The mixture was then placed in a separating funnel where two distinct layers were found to form. The upper layer was the mixture of esters and the unreacted methanol while the lower layer consisted of salt, water and glycerol. The esters were then separated from methanol through rotary vacuum evaporation method. A small quantity of the esters thus produced was kept separately for Sim-Dis distillation in a gas chromatograph. The remaining esters were then refined by distilling under reduced pressure. The yield of esters thus produced was 94%. Thus about 10 lit. of biodiesel were prepared and stored in glass bottles for further experiments.

3.9 Determination of Properties of the Biodiesels

Various properties of the biodiesels thus obtained from *Mesua ferrea* seed oil and *Pongamia glabra* seed oil were determined by different standard test methods.

Density was determined by ASTM D 287 methods.

Ash content was determined by ASTM D 874 method.

Carbon residue was determined by ASTM D 4530 method.

Pour point was determined by ASTM D 97 method.

Flash point was determined by ASTM D 93 method.

Water content was determined by ASTM D 2709 method.

Kinematic Viscosity at 40^0 C was determined by ASTM D 445 method.

Cetane number was determined by ASTM 613 method (in CFR cetane).

Acid value was determined by ASTM D 664 method.

Sulphur content was determined by ASTM D 5453 method.

Oxidation stability test was done by ASTM D 2274 method.

Initial boiling point (IBP) and final boiling point (FBP) were determined by Sim-Dis GC distillation (ASTM D 2887 and D86 correlation).

Calorific values were determined by using an Adiabatic Bomb calorimeter.

All the tests were carried out in triplicate and the average values are reported in Tables-7 & 8.

3.10 Preparation of biodiesel blends with petroleum diesel

A 100 lit. petroleum diesel used in blending with the biodiesel was obtained from Numaligarh Refinery Limited, Assam. Specifications of the petroleum diesel are given in Table 9.

Five different blends of biodiesel from *Mesua ferrea* seed oil with petroleum diesel were prepared in the following compositions.

B5 : 5% (vol.) of biodiesel + 95% (vol.) of petroleum diesel.
B10 : 10% (vol.) of biodiesel + 90% (vol.) of petroleum diesel.
B15 : 15%(vol.) of biodiesel + 85% (vol.) of petroleum diesel.
B20 : 20% (vol.) of biodiesel + 80% (vol.) of petroleum diesel.
B25 : 25%(vol.) of biodiesel + 75% (vol.) of petroleum diesel.

Similarly, five different blends of biodiesel from *Pongamia glabra* seed oil with petroleum diesel were prepared in the following compositions

B10: 10% (vol.) of biodiesel + 90% (vol.) of petroleum diesel.
B20: 20% (vol.) of biodiesel + 80% (vol.) of petroleum diesel.
B30: 30% (vol.) of biodiesel + 70% (vol.) of petroleum diesel.
B40: 40% (vol.) of biodiesel + 60% (vol.) of petroleum diesel.
B50: 50% (vol.) of biodiesel + 50% (vol.) of petroleum diesel.

Since the viscosity of *Pongamia glabra* biodiesel was found to be lower than *Mesua ferrea* biodiesel, we prepared the blends of *Pongamia glabra* biodiesel starting from 10% (vol.) of it.

3.11 Determination of properties of the biodiesel blends with petroleum diesel

Various properties of the blends of biodiesel from *Mesua ferrea* seed oil with petroleum diesel and biodiesel from *Pongamia glabra* seed oil with petroleum diesel, thus prepared were determined by using different standard methods as used in the case of neat biodiesel of *Mesua ferrea* seed oil and *Pongamia glabra* seed oil. All the tests were carried out in triplicate and the average values are reported in Tables 13 & 14.

3.12 Diesel engine performance and emission tests

Diesel engine performance tests and emission characteristics of two selected biodiesel blends namely B5 and B20 and also the typical petroleum diesel were carried out in a Bajaj-Tempo, direct injection, 4 cylinder, 4 stroke, vertical, water cooled computer-based Test IC diesel engine. Technical details of the diesel engine are given in Table 3.

Table. 3:- Technnical details of the diesel engine.

Type of engine	Bajaj-Tempo, direct injection, 4-cylinder, 4-stroke,vertical, water-cooled, computer-based Test IC diesel engine
Rated output	34kW at 3800 RPM
Bore	78mm
Stroke	94mm
Compression ratio	19.8 : 1
Capacity	1797 cm^3
Throttle opening	100 %
Maximum cylinder volume	450 cm^3
RPM, Dynamometer load (kg)	3500 ± 10, 39 ± 0.15; 3000 ± 10, 43 ± 0.15; 2500±10; 44 ± 0.15.

For each of the fuels under test, the engine was set for 0.5h, without applying load and then load was applied at 2500, 3000 and 3500 rpm engine speed. All the required data were recorded automatically in a computer coupled with both the engine system and the dynamometer.

Emission characteristics of CO and NOx were measured with the help of a smokemeter and a portable NUCON series 400 toxic gas analyzer.

Sim-Dis GC distillations of the biodiesels and the petroleum diesel were carried out at Numaligarh Refinery Laboratory.

CHAPTER IV

RESULTS AND DISCUSSION

(40-82)

Chapter IV
Results and Discussion

The results of the present study are presented and discussed in four parts.

Part 1

In this part various properties of *Mesua ferrea* seed oil and *Pongamia glabra* seed oil are presented and based on them the suitability of these two oils as raw materials for biodiesel production is discussed.

Part 2

In this part fuel characteristics of the biodiesels produced from *Mesua ferrea* seed oil and *Pongamia glabra* seed oil are discussed and compared with those of a typical petroleum diesel obtained from Numaligarh Refinery Ltd., Assam.

Part 3

In this part the fuel characteristics of different blends of biodiesel from *Mesua ferrea* seed oil with petroleum diesel and biodiesel from *Pongamia glabra* seed oil with petroleum diesel are presented and discussed. From their fuel characteristics an attempt is made to find out the most suitable compositions of the blends for each of the two biodiesels to be tested in diesel engine.

Part 4

In this part the results of the engine performance tests and gas emission characteristics from the typical petroleum diesel and the blends of selected compositions of the biodiesels with petroleum diesel are presented and discussed.

Part 1

Properties of *Mesua ferrea* seed oil and *Pongamia glabra* seed oil

Chemically common vegetable oils and fats are assortment of saturated and unsaturated triglycerides present in varying proportions. Oils of different types of plants differ in their compositions. Even for the same plant species, grown in different agroclimatic conditions the proportions of different triglycerides may show marked differences (Barnwal and Sharma, 2005). With few exceptions, the carboxylic acids (fatty acids) from which fats and oils are derived are all straight chain compounds varying in size from 3 to 18 carbons. Table 6 shows the chemical structure of the fatty acids chains found in the most common biodiesel source materials (Graboski and McCormick, 1998). Acids may be saturated (contain only single bond) or unsaturated (contain one or more double bonds).

The saturated fatty acids exhibit higher freezing points than the unsaturated fatty acids. The boiling points of the fatty acids, on the other hand are dependent on the length of the carbon chain but merely independent of the degree of unsaturation of the acids (Graboski and McCormick, 1998).

Triglycerides, except triacetin, others containing ten or more carbon atoms in their chains are virtually insoluble in water. In general at temperatures above their melting points, all members of these classes of compounds are completely miscible with a wide variety of organic solvents such as hydrocarbons, ethers, ketones and esters.

Various properties of *Mesua ferrea* seed oil and *Pongamia glabra* seed oil are presented in Tables 4 & 5 respectively.

Density, viscosity, ash content, calorific value etc. of both *Mesua ferrea* seed oil and *Pongamia glabra* seed oil are more or less similar to other vegetable oils which are used as feedstocks for biodiesel production.

The pour point of both the oils is zero, which indicates their liquid states at ambient temperature, and therefore it will be easy for processing these materials in industrial level.

Table- 4 : Major properties of *Mesua ferrea* seed oil

Property	
Density at 15^0 C g/ cm^3	0.935
Pour point ^{0} C	0
Kinematic viscosity at 40^0 C cSt.	26.00
Ash %wt of dried kernels	0.02
Acid value mgKOH/g	16.4
Ramsbottom carbon residue %wt.	1.6
Calorific value (gross) kJ/g	39.84
Fatty acids composition	
Acid	% wt.
Saturated	
Palmitic (hexadecanoic)	15.9
Stearic (octadecanoic)	9.5
Unsaturated	
Oleic (9 – octadecenoic)	50.3
Linoleic (9, 12 – octadecenoic)	21.3

Table- 5: Major properties of *Pongamia glabra* seed oil.

Property	
Density at 15^0 C g/ cm^3	0.931
Pour point ^{0} C	0
Kinematic viscosity at 40^0 C cSt.	26.06
Ash %wt of dried kernels	0.001
Acid value mgKOH/g	1.21
Ramsbottom carbon residue %wt.	1.205
Calorific value (gross) kJ/g	40.51

Fatty acids compositions

Acid	% wt.
Saturated	
Palmitic (hexadecanoic)	11.90
Stearic (octadecanoic)	9.80
Srachidic (eicosanoic)	1.75
Behenic (docosanoic)	3.20
Unsaturated	
Oleic (9 – octadecenoic)	45.21
Linoleic (9, 12 – octadecenoic)	24.75
Linolenic (9, 12, 15-octadecenoic)	2.90
Unidentified	1.05

Table- 6: % wt. of fatty acids in some commonly used biodiesel feedstock and *Mesua ferrea* seed and *Pongamia glabra* seed.

Oil	Carbon No	Saturated							Monounsaturated				Diunsaturated	Triunsaturated
		8	10	12	14	16	18	>18	<16	16	18	>18		
Sunflower						6	4.2	1.4			18.7		69.3	0.3
Soybean					0.3	7-11	3-6	5-10		0-1	22-34		50-60	2-10
Rapeseed						2-5	1-2	0.9		0.2	10-15	50-60	10-20	5-10
Linseed					0.2	5-9	0-1				9-29		8-29	45-67
Cottonseed					0-3	17-23	1-3				23-41	2-3	34-55	
Mesua ferrea seed						15.9	9.5				50.3		21.3	
Pongamia glabra seed						11.9	9.8				45.21	1.95	24.75	2.9

Source: Graboski and McCormick, 1998; and Tables 4 & 5.

The acid value of *Mesua ferrea* seed oil was found to be 16.4 mgKOH/g while that of *Pongamia glabra* seed oil was 1.21 mgKOH/g. Because of the low acid value of *Pongamia glabra* seed oil, it can easily be transesterified simply by using a base catalyst, whereas high acid value of *Mesua ferrea* seed oil indicates the requirement of special processes for its transesterification. Recently, Van Gerpen (2005) has also suggested the requirement of special processes for transesterification of oil containing higher amount of free fatty acids.

Fatty acid composition of the feedstock is an important factor for biodiesel production. Fatty acid compositions of some commonly used biodiesel feedstocks and *Mesua ferrea* seed oil and *Pongamia glabra* seed oil are given in Table 6. Fatty acid compositions of both *Mesua ferrea* seed oil and *Pongamia glabra* seed oil are almost similar to those of sunflower oil, soybean oil, rapeseed oil, linseed oil and cottonseed oil with little variation. The lowest carbon number in the fatty acids is 16 in both the oils. In *Mesua ferrea* seed oil 25.4% fatty acids are saturated and 71.6% are unsaturated fatty acids. Similarly in *Pongamia glabra* seed oil 26.7% are saturated fatty acids and 72.86% are unsaturated fatty acids. Because of the presence of higher percentages of unsaturated fatty acids in both the oils, their esters will exhibit lower freezing point and pour points than the esters of saturated fatty acids.

Presence of higher carbon numbers in the fatty acids chains of the oils make them insoluble in water, but completely miscible with organic solvents like petroleum ether or other nonpolar hydrocarbons and such behaviour will facilitate the separation of the biodiesel phase from water and glycerol mixture. However these unsaturated fatty acids will enhance the oxidative instability of the biodiesels derived from them.

From the analysis of the properties of *Mesua ferrea* seed oil and *Pongamia glabra* seed oil, it is evident that both the oils can be used as feedstocks for the production of biodiesels by using transesterification process. In the case of *Pongamia glabra* seed oil the production of biodiesel can be achieved simply by its transesterification with alcohol using a base catalyst, which is the most common practice in commercial biodiesel production. However, in the case of *Mesua ferrea* seed oil with high acid value (16.4 mg KOH/g) a two-step transesterification process will be required which may increase the cost of biodiesel production from it.

Part 2

Fuel characteristics of the refined biodiesels from *Mesua ferrea* seed oil and *Pongamia glabra* seed oil and a typical petroleum diesel obtained from Numaligarh Refinery Ltd., Assam

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Engine and vehicle studies of biodiesel have produced highly variable results. In most cases this can be traced to the quality and purity of the biodiesel. To control the quality and purity of biodiesel produced by various biodiesel manufacturers certain standard specifications have been recommended. Among the various standards, ASTM standards for biodiesels and their blends, International standards for biodiesel and En 14214-2003 standards for biodiesel are commonly followed by biodiesel production industries for quality control of biodiesels.

Almost all the test methods used in evaluating petroleum diesels are used to evaluate biodiesels and their blends.

In the present study the major fuel characteristics such as density, viscosity, pour point, cetane number, flash point, Ramsbottom carbon, water content, sulphur content, copper strip corrosion, calorific value, distillation characteristics etc. of the refined biodiesels from *Mesua ferrea* seed oil and *Pongamia glabra* seed oil were determined separately to examine the feasibility of using them in diesel engine either in pure form or in the form of their blends with petroleum diesel.

Density:

Densities of neat *Mesua ferrea* seed oil and *Pongamia glabra* seed oil were 0.935 and 0.931 respectively (Tables 4 & 5) which are almost similar to that of canola oil (Raphael *et al.*,1997). After esterification followed by distillation their density values changed to 0.898 and 0.887 (Tables 7 & 8) which are within the proposed fuel property standard for biodiesels from soybean oil methylester (0.86-0.90) and rapeseed oil methylester (0.875-0.900) (Engine Manufacturers Association, 1995). Lforgia and Ardito (1995) have also reported density value of 0.883 for some biodiesel.

Viscosity

Viscosity is a very important flow property of fuel. High viscosity of fuel leads to poorer atomization of the fuel spray and less accurate operation of the fuel injectors. In general the viscosity of neat biodiesels is higher than that of petroleum diesel.

From Tables 4 & 7 it can be seen that the kinematic viscosity at 40^0 C of *Mesua ferrea* seed oil was 26 cSt and after esterification, the kinematic viscosity reduced to 6.2 cSt which is still slightly higher than the acceptable limit for biodiesel as per ASTM standard (Table10). Similarly kinematic viscosity of *Pongamia glabra* seed oil was 26.06 cSt and after esterification its kinematic viscosity reduced to 5.8 cSt (Tables 5 & 8). The average kinematic viscosity values (at 40^0 C) of soybean oil methylester, rapeseed oil methylester and tallow methylester were reported to be 4.08, 4.83 and 4.80 cSt respectively (Graboski and McCormick,1998).

Pour point

Pour point (ASTM-97) is a measure of the fuel gelling. It is the lowest temperature, expressed as a multiple of 5^0 F (or 3^0 C) at which the fuel is observed to flow when cooled and examined under prescribed conditions.

All biodiesel fuels exhibit poor cold flow properties with pour points 20-25^0 C higher than that of Number 2 diesel. The structural properties of biodiesel that affect freezing points are degree of unsaturation, chain length and degree of branching. Highly saturated tallow esters are poorer in cold flow properties than soybean oil and rapeseed oil methylesters. Methylesters of soybean oil and rapeseed oil were reported to exhibit average pour points about -4^0 C and -15^0 C respectively (Marshall, 1994; Peterson et al., 1996).

Table- 7: Fuel characteristics of the refined biodiesel obtained from *Mesua ferrea* seed oil.

Property	
Density at 15^{0}C g/cm^3	0.898
Kinematic viscosity at 40^0 C cSt	6.2
Water content % vol	0.035
Ramsbottom carbon residue %wt.	0.250
Pour Point ^{0}C	+3
Flash point ^{0}C	112
Cetane number	54
Sulphur content %wt.	0.007
Ash content %wt.	0.01
Acid value mg KOH/g	0.01
Oxidation stability g/100ml	0.120
Copper strip corrosion	1a
Calorific value(gross) kJ/g	42.232
IBP/FBP ^{0}C	210/375

Table-8: Fuel characteristics of the refined biodiesel obtained from P*ongamia glabra* seed oil.

Property	
Density at 15^{0}C g/cm^3	0.887
Kinematic viscosity at 40^0 C cSt	5.80
Water content % vol	0.03
Ramsbottom carbon residue %wt.	0.267
Pour Point ^{0}C	+3
Flash point ^{0}C	95
Cetane number	55
Sulphur content %wt.	0.005
Ash content %wt.	0.001
Acid value mg KOH/g	0.01
Oxidation stability g/100ml	0.15
Copper strip corrosion	1a
Calorific value(gross) kJ/g	42.822
IBP/FBP ^{0}C	219/372

From Tables 4 & 5 it is seen that the pour point of both *Mesua ferrea* seed oil and *Pongamia glabra* seed oil was zero. But after esterification of these two oils, the biodiesels (methylesters) produced showed poorer pour points. The pour points were found to be $+3^0$ C for both the biodiesels indicating their poorer cold flow property than that of soybean oil and rapeseed oil biodiesels.

Cetane number

The cetane number of a fuel is a measure of its ignition delay with higher cetane number indicating shorter time between the initiation of fuel injection and ignition, a desirable property of diesel engine fuel. The cetane number of biodiesel depends on the parent oil source, but in general it is higher than that of petroleum diesel. It has been reported that highly saturated esters such as those prepared from tallow and used frying oil have the highest cetane numbers (Graboski and McCormick, 1998). For example palmitic acid methylester and stearic acid methylester have the cetane numbers 74.5 and 86.9 respectively (Klopfenstein, 1983). Further it was reported that the cetane number increases with chain length, decreases with the number of double bonds and decreases as double bonds and carbonyl groups move toward the centre of the chain (Graboski and McCormick, 1998).

From the results of the present study (Tables 7 & 8) it is seen that the biodiesels from *Mesua ferrea* seed oil and *Pongamia glabra* seed oil have cetane number 54 and 55 respecively, which are higher than that of petroleum diesel. Earlier workers have reported the cetane number of soybean oil methylester ranging from 45.8 to 56.9 (Manicom *et al.,* 1993; Stotler and Human, 1995) and for rapeseed oil methylesters it ranges from 48 to 61.8 (Rantanen *et al.*, 1993; Peterson *et al.*, 1996). Kalligerous *et al.*,(2003) also reported the cetane number of sunflower oil methylester as 58 and that of olive oil methylester as 61. Since in the biodiesels of *Mesua ferrea* seed oil and *Pongamia glabra* seed oil percentages of unsaturated fatty acids are more than the saturated fatty acids, the cetane numbers are low as compared to those of methylesters of stearic and palmitic acids.

Flash point

Flash point is a measure of the temperature to which a fuel must be heated such that the mixture of vapour and air above the fuel can be ignited. The flash point of neat biodiesels is typically greater than 90^0 C. A fuel with 90^0 C or greater flash point is considered as non-hazardous from storage point of view. Neat biodiesel is thus much safer than petroleum diesel.

Flash points of neat biodiesels from *Mesua ferrea* seed oil and *Pongamia glabra* seed oil were found to be 112^0 C and 95^0 C respectively. Flash point of biodiesel from *Mesua ferrea* seed oil is close to that of soybean oil methylester (110^0 C) as reported in the literaure (Final Report No. NSDB 4F15, 1994) while the flash point of biodiesel from *Pongamia glabra* seed oil is close to that of tallow methylester (96^0 C) (Ali *et al*, 1995). Flash points of the biodiesels are almost similar to that of sunflower oil methylester (110^0 C) and olive oil methylester (< 110^0 C) (Kalligeros *et al.*, 2003). Thus from storage and fire –hazard point of view both these two biodiesels are safer than petroleum diesel.

Carbon residue

The carbon residue of a fuel serves as rough approximation of the tendency of the fuel to form deposits in the combustion chamber. Lower is the value of carbon residue better is the fuel.

Ramsbottom carbon residue of the biodiesels from *Mesua ferrea* seed oil and *Pongamia glabra* seed oil were found to be 0.250 % and 0.267 % by wt. respectively (Tables 7 & 8). These values are slightly higher than that of petroleum diesel obtained from Numaligarh Refinery Ltd. (Table 9). Kalligeros et al.,(2003) also reported higher carbon residue for sunflower oil methylester (0.98% wt) and olive oil methylester (0.22% by wt.).

Water content

Water present in fuel can cause the formation of rust and in the presence of acids and hydroperoxides formed by fuel oxidation, leads to engine corrosion. Water may also enhance the microbial growth, which can occur at the interface between the fuel and any free water phase. Growth of algae in fuel storage tanks was observed in a biodiesel transit bus demonstration program (Report to Iowa Soybean Promotion Board, 1995).

Table- 9: Fuel characteristics of a typical petroleum diesel obtained from Numaligarh Refinery Ltd.

Property	
Density at 15^{0}C g/cm^3	0.852
Kinematic viscosity at 40^0 C cSt	2.781
Water content % vol	0.055
Ramsbottom carbon residue %wt.	0.10
Pour Point ^{0}C	0
Flash point ^{0}C	49
Cetane number	46
Sulphur content %wt.	0.0165
Ash content %wt.	0.010
Acid value mg KOH/g	0.104
Oxidation stability g/100ml	0.01
Copper strip corrosion	1a
Calorific value(gross) kJ/g	45.013
IBP/FBP ^{0}C	139/370

Table- 10: ASTM standards for biodiesels and their blends.

Property	Test Method	Limit for acceptance
Density at 15 °C g/cm^3	ASTM D 287	Not available
Kinematic viscosity at 40 °C cSt	ASTM D 445	1.9 - 6.0
Water content % vol.	ASTM D 2709	0.050 max.
Flash Point ^{0}C	ASTM D 93	130 min
Pour point ^{0}C	ASTM D-97	Not available
Ash % wt	ASTM D 874	0.020 max.
Carbon residue % wt	ASTM D 4530	0.050 max.
Cetane number	ASTM D 613	47 min
Copper strip corrosion at 50 ^{0}C	ASTM D 130, 3-hours	1c min.
Acid number mg KOH/g	ASTM D 664	0.80 max
Distillation	SIM DIS GC distillation	90% recovery, at 360 °C max and at atmospheric pressure.
Sulfur %wt	ASTM D 5453	0.05 max
Oxidation stability g/100ml	ASTM D2274	Not available
Calorific value kJ/g	Adiabatic bomb calorimeter	Not available
IBP/FBP ^{0}C	SIM DIS GC distillation	Not available

Reference: Biodiesel, The Official Site of National Biodiesel Board, USA. (www.biodiesel.org/resources/fuelfactsheet, standatds_and_warranties.shtm

From the present investigation it was found that the water content in the biodiesels from *Mesua ferrea* seed oil and *Pongamia glabra* seed oil were 0.035 and 0.03 % vol. respectively (Tables 7 & 8). These values are less than that of petroleum diesel fuel (0.05 % vol. max.) proposed by Engine Manufacturers Association (1995).

Oxidation stability

Oxidation stability of a fuel is one of the major properties and is measured by ASTM D 2274. All biodiesel fuels exhibit a dramatic increase in the formation of gum deposits. The main source of instability in biodiesel fuels is unsaturation in the fatty acid chain. The metals and elastomers in contact with biodiesel during storage can also impact stability. Oxidation leads to the formation of hydroperoxides, which may polymerize to form insoluble gums. Oxidation products formed in biodiesels may affect fuel storage life and contribute to deposit formation in tanks, fuel systems and filters. Fuel with high iodine number may posses high gum numbers.

Oxidation stability values of the biodiesel from *Mesua ferrea* seed oil and *Pongamia glabra* seed oil were found to be 0.120 g/100ml and 0.150g/100ml respectively (Tables 7 & 8). These values are slightly higher than that of the typical petroleum diesel obtained from Numaligarh Refinery Ltd. (Table 9). As more of unsaturated fatty acids are present in both the oils, their oxidation stability values are higher than that of petroleum diesel.

Ash content

As per ASTM standards for biodiesels and their blends (Table10) the acceptable ash content of diesel fuel should be maximum of 0.05% by wt.

In the present investigation ash content of the biodiesel from *Mesua ferrea* seed oil was 0.01% by wt. whereas that of *Pongamia glabra* seed oil was 0.001% by wt. Both the values of ash content are within the acceptable limit.

Acid value

According to the Engine Manufacturers Association (1995) the maximum acceptable limit of acid value of rapeseed oil methylester is 0.5% mg KOH/g and as per ASTM Standards for biodiesels and their blends the maximum acceptable limit of acid value is 0.8mgKOH/g (Table 10). The acid values of biodiesels from both *Mesua ferrea* seed oil and *Pongamia glabra* seed oil was 0.01% which is within the acceptable limit.

Sulphur content

The presence of sulphur compounds in fuel often produces harmful effects. Sulphur compounds are believed to promote corrosion of engine parts especially when water containing sulphur dioxide from the combustion may accumulate in the crankcase.

In diesel fuels, sulphur compounds increase wear and can contribute to the formation of engine deposits (Speight, 1998).

According to the ASTM Standards for biodiesel and their blends, the maximum limit of sulphur content for acceptance is 0.05% by wt. (Table 10). From Tables 7 & 8 it is seen that the sulphur content of the neat biodiesels obtained from *Mesua ferrea* seed oil and *Pongamia glabra* seed oil were found to be 0.007% and 0.005% by wt. respectively, which are much below the maximum limit and from corrosion and environmental point of view, these biodiesel should be better than petroleum diesel. Kalligeros *et al.*(2003) have also reported very low values of sulphur content in sunflower methylester (0.0007 %wt.) and olive oil methylester (0.001% wt.).

Copper strip corrosion

Copper strip corrosion test is intended for detection of corrosive substances in the fuel. From this test it was found that the refined biodiesels obtained from both *Mesua ferrea* seed oil and *Pongamia glabra* seed oil were free from corrosive substances (Tables 7 & 8).

Calorific value

The gross calorific value of a fuel at constant volume is the number of heat units measured as being liberated at 25^0 C when unit weight of the fuel is burned in oxygen saturated with water vapor in a bomb under standard conditions.

From Tables 4 & 5 it is seen that the calorific values of *Mesua ferrea* seed oil and *Pongamia glabra* seed oil were 39.84 and 42.51 kJ/g respectively. After esterification the calorific values of the methyl esters were found to increase. Calorific value of methylester of *Mesua ferrea* was 42.232 kJ/g whereas that of *Pongamia glabra* seed oil was 42.822 kJ/g (Tables 7 & 8). However the calorific values of the methylesters of these two seed oil were lower than that of petroleum diesel. Earlier workers have also reported almost similar calorific values for some other neat biodiesel (Raheman and Phadatare, 2004)

Table- 11: International standards for biodiesel.

{PRIVATE}			**AUSTRIA**	**FRANCE**	**GERMANY**	**ITALY**	**SWEDEN**	**USA**	**MBTI**
Standard/ Specifications	**Test Value**	**Unit**	**ON C1191**	**Journal Official**	**DIN E 51606**	**UNI 10635**	**SS 15 54 36**	**D-6751~02**	
Date			1 July 1997	14 Sep 1997	Sep 1997	21 April 1997	27 Nov 1996	10Jan 2002	August 03
Application			FAME**	VOME**	FAME**	VOME**	VOME**	FAME**	FAME**
Density	15°C	g/cm^3	0.85 - 0.89	0.87 - 0.90	0.875 - 0.90	0.86 - 0.90	0.87 - 0.90	-	-
Viscosity	40°C	mm^2/s	3.5 - 5.0	3.5 - 5.0	3.5 - 5.0	3.5 - 5.0	3.5 - 5.0	1.9 - 6.0	4.473
Distillation	I.B.P.	°C	-	-	-	>300	-	-	339
Distillation	95%	°C	-	<360	-	<360	-	-	357
Flashpoint		°C	>100	>100	>110	>100	>100	>130	162
CFPP		°C	<0/-15	-	<0/-10/-20	<0/-15	<-5	-	-
Pourpoint	summer	°C	-	<10	-	-	-	-	-
Total Sulphur		% Mass	<0.02	-	<0.01	<0.01	<0.001	-	0.0004
CCR	100%	% Mass	<0.05	-	<0.05	-	-	0.050	0.04
CCR	10%	% Mass	-	<0.3	-	<0.5	-	-	-
Sulphate ash		% Mass	<0.02	-	<0.03	-	-	<0.02	-
(Oxide) Ash		% Mass	-	-	-	<0.01	<0.01	-	-
Water content		mg/kg	-	<200	<300	<700	<300	<300	0
Impurities total		mg/kg	-	-	<20	-	<20	-	0
Cetane No.		-	>49	>49	>49	-	>48	>47	52.9
Neutral No.		mgKOH/g	<0.8	<0.3	<0.5	<0.5	<0.6	<0.80	0.23
Methanol content		% Mass	<0.20	<0.1	<0.3	<0.2	<0.2	-	-
Ester content		% Mass	-	>96.5	-	>98	>98	-	-
Monoglycides		% Mass	-	<0.8	<0.8	<0.8	<0.8	-	-
Diglyceride		% Mass	-	<0.2	<0.4	<0.2	<0.1	-	-
Triglyceride		% Mass	-	<0.2	<0.4	<0.1	<0.1	-	-
Free glycerol		% Mass	<0.02	<0.02	<0.02	<0.05	<0.02	0.020	0.003
Total glycerol		% Mass	<0.24	<0.25	<0.25	-	-	0.240	0.146
Iodine No.		-	<120	<115	<115	-	<125	-	<120
Phosphor		mg/kg	<20	<10	<10	<10	<10	<10	<10
Alcaline met.	NA/K	mg/kg	-	<5/5	<5	-	<10/10	-	-

**FAME: Fatty Acid Methyl Ester **VOME: Vegetable Oil Methyl Ester

Source: http://www.svlele.com/biodiesel_astm_std.htm

Table- 12: En 14214 - 2003 standards for biodiesel.

{PRIVATE}Property	Unit	Minimum	Maximum	Test Method
Ester Content	% (m/m)	96.5		prEN 14103
Density @ 15 °C	Kg/m^2	860	900	EN ISO 3675 EN ISO 12185
Viscosity @ 40 °C	Mm^2	3.5	5.0	EN ISO 310
Flash Point	°C	Above 101		ISO / CD 3679
Sulfur Content	Mg/Kg		10	
Carbon Residue (10% Bottoms)	% (m/m)		0.3	EN ISO 10370
Cetane Number		51.0		EN ISO 5165
Sulphated Ash Content	% (m/m)		0.02	ISO 3987
Water Content	Mg/Kg		500	EN ISO 12937
Total Contamination	Mg/Kg		24	EN 12662
Copper Strip Corrosion (3hr @ 50 °C)	Rating	Class 1	Class 1	EN ISO 2160
Thermal Stability				
Oxidation Stability, 110 °C	Hours	6		pr EN 14112
Acid Value	mg KOH/g		0.5	pr EN 14104
Iodine Value			120	pr EN 14111
Linolenic acid methyl ester	% (m/m)		12	pr EN 14103
Polyunsaturated (>= 4 double bonds) methyl esters	% (m/m)		1	
Methanol Content	% (m/m)		0.2	pr EN 14110
Monoglyceride Content	% (m/m)		0.8	pr EN 14105
Diglyceride Content	% (m/m)		0.2	pr EN 14105
Triglyceride Content	% (m/m)		0.2	pr EN 14105
Free Gylcerol	% (m/m)		0.02	pr EN 14105 pr EN 14106
Total Gylcerol	% (m/m)		0.25	pr EN 14105
Alkaline Metals (Na + K)	Mg/Kg		5	pr EN 14108 pr EN 14109
Phosphorus Content	Mg/Kg		10	pr EN 14107

Source: http://www.svlele.com/biodiesel_astm_std.htm

Distillation characteristics:

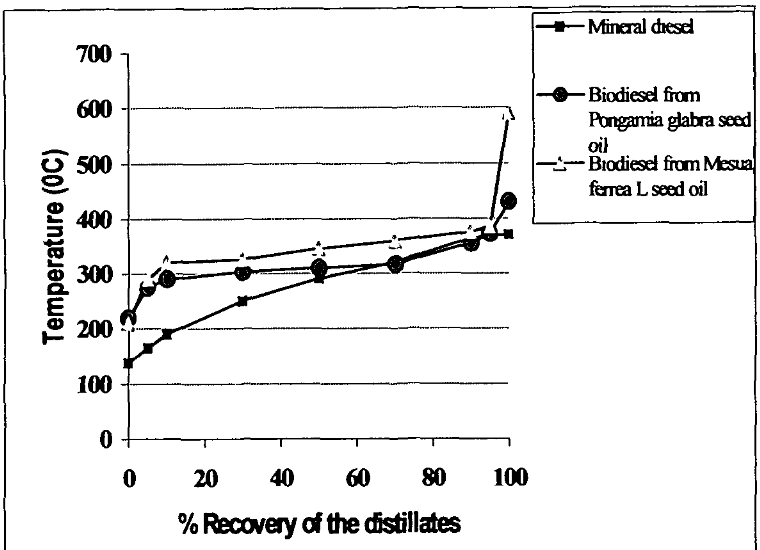

Fig. 14. Sim-Dis GC distillation analysis of Mesua ferrea L biodiesel, Pongamia glabra biodiesel and Petroleum diesel.

The distillation (volatility) characteristics of hydrocarbon have immense implication on the engine performance and safety. Volatility is the major determinant of the tendency of a liquid fuel to produce potentially explosive vapour and proper air fuel mixture. The presence of high boiling point components can significantly affect the degree of formation of solid combustion deposits (Sarma *et al.*, 2005).

Fat and oil esters have a narrow boiling range relative to petroleum diesel and exhibit boiling points ranging between about 325^{0} and 350^{0} C. Average initial boiling point (IBP) and final boiling point (FBP) of soybean oil methylester were reported to be 299^{0} and 346^{0} C respectively and for rapeseed oil these values were 326^{0} and 366^{0} C (Graboski and Mc Cormick,1998).

The Sim-Dis GC distillation characteristics of the unrefined biodiesels from *Mesua ferrea* seed oil and *Pongamia glabra* seed oil, and petroleum diesel from Numaligarh Refinery Ltd. are presented in Fig 14. It is seen that the biodiesel from *Mesua ferrea* seed oil had a narrow boiling range 210-520^{0} C, 94 % of which was distilled off between 210 and 375^0 C. Similarly, the biodiesel from *Pongamia glabra* seed oil had the boiling range of 219-430^0 C, 95% of which was distilled off between 210 and 370 ^{0}C, while petroleum diesel had a uniform boiling range of 139-370^0 C. The IBP value of petroleum diesel was 139^0 C, while those for biodiesels from *Mesua ferrea* seed oil and *Pongamia glabra* seed oil were 210^0 C and 219^0 C respectively. This implies that there was shortage of about 25% lower boiling point hydrocarbons (below 220^0 C) in both the biodiesel. Similarly the steeply rising portion from about 350 to 370^0 C indicates the shortage of about 10% long chain hydrocarbons in both the biodiesels to achieve similar distillation properties such as petroleum diesel.

When the undistilled biodiesels obtained from *Mesua ferrea* seed oil and *Pongamia glabra* seed oil were further refined by distillation under reduced pressure, their final boiling points (FBP) changed to 375^0 C and 372^0 C respectively which are almost similar to IBP of the petroleum diesel (Table 10). Thus, to achieve the distillation characteristics of both the biodiesels similar to that of petroleum diesel, they should be blended with petroleum diesel.

From the fuel characteristics of the biodiesels from *Mesua ferrea* seed oil and *Pongamia grabra* seed oil (Table 7 & 8) it is seen that the density values of both the neat biodiesels are within the acceptable limit as per the standards of Engine Manufacturers Association (1995). Similarly cetane number, flash point, water content, ash content and sulphur content values of both the biodiesels are within the acceptable limits. Acid values and copper strip corrosion tests show their non-corrosive nature. But the kinematic viscosity of the biodiesel from *Mesua ferrea* seed oil at 40^0 C is slightly higher than the maximum acceptable limit of ASTM standard for biodiesel and their blends (Table 10). Though the kinematic viscosity of the biodiesel from *Pongamia glabra* seed oil is within the acceptable limit, it is almost close to the maximum acceptable limit (6 cSt) of ASTM standard. Pour points of both the biodiesels are higher than that of the petroleum diesel. Ramsbottom carbon residue values of the biodiesels are higher than that of the petroleum diesel. Comparatively higher oxidation stability values of both the biodiesels indicate their poor stability toward oxidation. High initial boiling points (IBP s) of the biodiesels may reduce their tendency to promote potentially explosive vapour and proper air-fuel mixture.

Considering the above mentioned points, it can be concluded that neat biodiesels of both *Mesua ferrea* seed oil and *Pongamia glabra* seed oil may not be suitable to use as fuels in diesel engine. Hence to meet the required specifications of a diesel fuel each of the biodiesels should be blended with petroleum diesel and to determine the fuel characteristics of the blends to find out the optimum blending composition.

Part 3

Fuel characteristics of the blends of refined biodiesel from *Mesua ferrea* seed oil and *Pongamia glabra* seed oil with petroleum diesel

From the fuel characteristics of the refined biodiesels obtained from *Mesua ferrea* seed oil and *Pongamia glabra* seed oil (Table 8 & 9) it has been observed that they do not meet all the required specifications to be used as diesel engine fuels as per ASTM standards (Table 10) or International standards for biodiesels (Table 11).

Water content, flash point, cetane number, sulphur content, ash content, acid value and copper strip corrosion test of both the biodiesels were found to be within the acceptable limits whereas viscosity, Ramsbottom carbon residue, pour point, oxidation stability and density values were not within the acceptable limits. Apart from these, both the biodiesels showed narrow boiling ranges as compared to petroleum diesel. As the IBPs of both the biodiesels were much higher than that of petroleum diesel, it might affect their tendency to produce potentially explosive vapour and proper air-fuel mixture. Calorific values of the biodiesels were also found to be significantly lower than that of petroleum diesel.

Considering the above mentioned points, blends of each of the biodielels with petroleum diesel in various proportions were prepared separately and the fuel characteristics of each of the blends were determined, and presented in Tables13& 14.

Since the biodielel obtained from *Mesua ferrea* seed oil showed comparatively highter density and kinematic viscosity values than petroleum diesel, its blends with petroleum diesel were prepared as 5%(B5), 10%(B10), 15%(B15), 20%(B20) and 25%(B25). On the other hand as the density and kinematic viscosity values of the neat biodiesel obtained from *Pongamia glabra* seed oil were found to be comparatively lower than those of the biodiesel obtained from *Mesua ferrea* seed oil, therefore its blends with petroleum diesel were prepared as 10%(B10), 20%(B20), 30%(B30), 40%(B40) and 50%(B50).

Fuel characteristics of the blends of biodiesel from *Mesua ferrea* seed oil with petroleum diesel:

From Table 13 it is seen that the density values of B5 and B10 blends of biodiesel from *Mesua ferrea* seed oil with petroleum diesel were almost similar to the density of the petroleum diesel. However, with the increase of percentages of biodiesel in the blends, the density was found to increase in a gradual manner.

The kinematic viscosity at 40^0 C of the petroleum diesel used in the blends was 2.781 cSt (Table 9). On blending the biodiesel with it, the viscosity was found to increase. The effect of biodiesel content on the viscosity of blends is shown in Fig. 15 .The curve in this figure suggests that the blend viscosity was lower than would be predicted from a linear combination model, which may be because of the fact that dissolution of the biodiesel in the petroleum diesel minimizes intra-molecular interactions responsible for this property (Graboski and McCormick, 1998). Based on the curve in Fig 15 the viscosity of blends containing upto 20% by vol. of biodiesel from *Mesua ferrea* seed oil will most likely meet the standards for petroleum diesel.

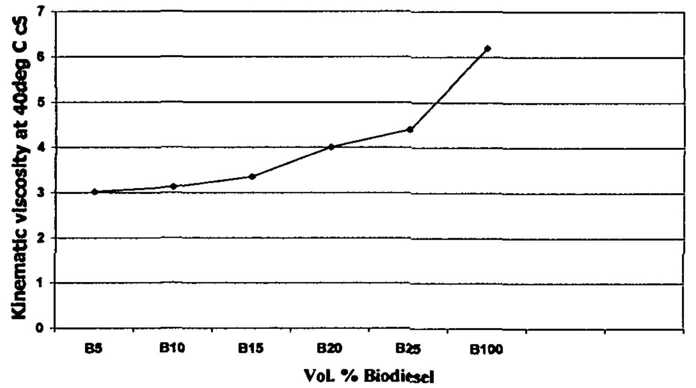

Fig. 15. Effect of blending *Mesua ferrea* seed oil biodiesel on fuel viscosity

Water content of the biodiesel from *Mesua ferrea* seed oil was found to be 0.035% by vol. (Table 7) and that of the petroleum diesel used in blending was 0.055 % by vol. (Table 9). As per ASTM standards for biodiesel and their blends the maximum limit of water content for acceptance is 0.050 % by vol. (Table 10). However, with the increase of percentage of biodiesel in the blends, the water content gradually decreased.

Ramsbottom carbon residue of the biodiesel from *Mesua ferrea* seed oil was found to be 0.250 % by wt. which is much higher than that of the petroleum diesel obtained from Numaligarh Refinery Ltd. (0.1% by wt.). On blending the biodiesel with petroleum diesel, the carbon residue values of the blends gradually increased with the increase of percentage of biodiesel in the blends. All these values are within the acceptable limit proposed for fuel property standard for biodiesels (Engine Manufacturers Association, 1995).

Pour point of the biodiesel from *Mesua ferrea* seed oil was found to be $+3^0$ C and that of the petroleum diesel was 0^0 C. On blending this biodiesel with petroleum diesel, it was found that upto a concentration of 20% by vol. of biodiesel in the blends, there was no effect on the pour points. Only at a concentration above 20% by vol. the effect was prominent.

Flash point of the petroleum diesel was 49^0 C while that of neat biodiesel was 112^0 C. With the increase of concentration of biodiesel in the blends their flash points increased gradually. Higher values of flash points of the blends indicate that they are much safer from the fire-hazard point of view.

In general the cetane numbers of biodiesels are always higher than that of petroleum diesel. Cetane number of neat biodiesel from *Mesua ferrea* seed oil was found to be 54, while that of petroleum diesel used in the blend was 46. On blending the cetane numbers of the blends were found to increase with the increase of concentration of biodiesel in them (Table 13).

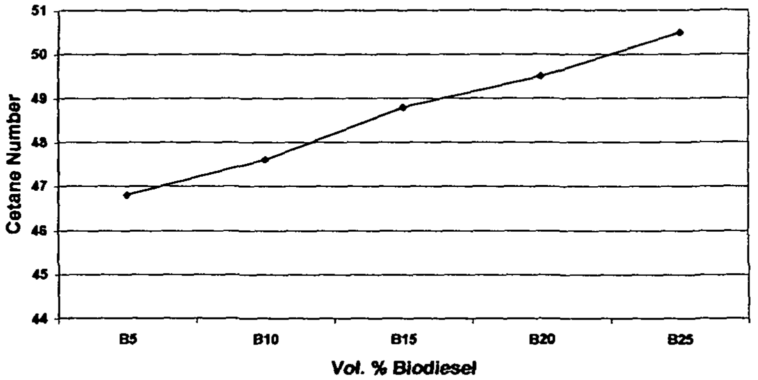

Fig. 16 Cetane number for blends of *Mesua ferrea* seed oil biodiesel with petroleum diesel

From Fig 16 it is evident that the effect of blending this biodiesel on cetane number is near linear for mixtures of various compositions. Earlier workers have also observed linear relationship between cetane numbers of neat esters and diesel fuel blends. (Graboski *et al.* 1996; Midwest Biofuels Inc, 1993).

Oxidation stability of neat biodiesel from *Mesua ferrea* seed oil was 0.012 g/100ml (Table 7) and that of petroleum diesel was 0.012g/100ml (Table 9). On blending the biodiesel with petroleum diesel the oxidation stability values increased gradually with the increase of concentration of biodiesel. This increase of oxidation stability value is due to the increase of methylester of unsaturated fatty acids present in the biodiesel.

Sulphur content of neat biodiesel from *Mesua ferrea* seed oil was very low (0.007% wt.) (Table 7) and that of the petroleum diesel were 0.0165% wt. (Table 9).

Therefore on blending the biodiesel with petroleum diesel, the sulphur content of the blends were found to decrease with the increase of biodiesel concentration in them. As per ASTM Standards for biodiesels and their blends, the maximum acceptable limit of sulphur content is 0.05% wt (Table 10). Hence, the sulphur content of all the blends (B5, B10, B15, B20 and B25) are within the acceptable limits.

Copper strip corrosion test of all the blends indicates their non-corrosive nature.

Table-13: Fuel characteristics of various blends of biodiesel from *Mesua ferrea* seed oil with petroleum diesel.

Property	Blends % vol.				
	B5	B10	B15	B20	B25
Density at 15^0C g/cm^3	0.8561	0.8589	0.8621	0.8682	0.8750
Kinematic viscosity at 40^0 C cSt	3.02	3.13	3.35	4.01	4.39
Water content % vol.	0.053	0.044	0.036	0.029	0.025
Ramsbottom carbon residue %wt	0.115	0.116	0.118	0.122	0.125
Pour Point ^{0}C	0	0	0	0	+3
Flash point ^{0}C	55	58	66	70	72
Cetane number	46.8	47.6	48.8	49.5	50.5
Oxidation stability g/100ml	0.014	0.017	0.018	0.035	0.068
Sulphur content %wt.	0.014	0.012	0.01	0.009	0.007
Copper strip corrosion	1a	1a	1a	1a	1a
Ash content %wt.	0.01	0.01	0.01	0.011	0.011
Acid value mg KOH/g	0.101	0.094	0.087	0.0802	0.076
Calorific value(gross) kJ/g	44.67	43.92	43.67	43.23	43.15
IBP/FBP ^{0}C	139/371	140/369	140/370	140/370	141/370

Ash content of neat biodiesel from *Mesua ferrea* seed oil was found to be 0.01%wt. (Table 7) and that of the petroleum diesel was also 0.01%wt.(Table 9). Therefore on blending the biodiesel with the pertoleum diesel, there was no change of ash content of the blends. Ash content of all the blends are below the maximum acceptable limit (Table 10).

Acid value of *Mesua ferrea* seed oil was 16.4 mg KOH/g (Table 4) and after transesterification the acid value of the biodiesel (methylester) was found to be 0.01 mgKOH/g, which is much less than that of the petroleum diesel (0.104 mgKOH/g). On blending the biodiesel with the petroleum diesel, the acid value decreased gradually with the increase of biodiesel concentration in the blends. Acid values of all the blends are within the acceptance limit (Table 10).

Calorific value (gross) of the biodiesel obtained from *Mesua ferrea* seed oil was 42.232 kJ/g (Table 7) and that of petroleum diesel was 45.013 kJ/g (Table 9). When blended the biodiesel with the petroleum diesel, the calorific value was found to decrease with the increase of biodiesel concentration in the blends. The calorific value of B5 blend is closed to that of the petroleum diesel (Table 13).

The initial boiling point (IBP) and final boiling point (FBP) of the biodiesels obtained from *Mesua ferrea* seed oil and those of the petroleum diesel were determined from the SIM-DIS GC distillation.

For the biodiesel IBP/FBP were 210^0 /375^0 C (Table 13) whereas those of the petroleum diesels were 139^0/370^0C (Table 9). When blended the biodiesel with the petroleum diesel, the IBP/FBP values were found to be almost similar to those of petroleum diesel. Slight increase of IBP at higher concentration of biodiesels in the blends may be due to the interaction among the petroleum diesel molecules and the biodiesel molecules.

Fuel characterstics of the blends of biodiesel obtained from *Pongamia glabra* seed oil with petroleum diesel:

Density values of B10 and B20 blends of biodiesel from *Pongamia glabra* seed oil with petroleum diesel (Table 14) were almost similar to the density of petroleum diesel (Table 9). However it is seen that with the increase of percentage of biodiesel in the blends, the density increased gradually.

The kinematic viscosity at 40^0 C of the blends was found to increase gradually with the increase of percentage of biodiesel in the blends. The effect of biodiesel content on viscosity in the blends is shown in Fig 17. The viscosity of petroleum diesel was 2.781 cSt and when biodiesel was blended with it, the viscosity of B10 and B20 blends changed to 3.01 cSt and 3.20 cSt respectively. But for B30, B40 and B50 blends, the viscosity values changed significantly. Based on the curve in Fig 17, the viscosity of the blends containing upto 20% by vol. of biodiesel from *Pongamia glabra* seed oil most likely meets the requirement as per ASTM standard for biodiesels and their blends.

From the Table 14 it is seen that the water content of the blends decreased with the increase percentage of biodiesel in the blends and this is because of the fact that the biodiesel from *Pongamia glabra* seed oil contain lower percentage of water (0.03% wt) than the petroleum diesel (0.055% wt).

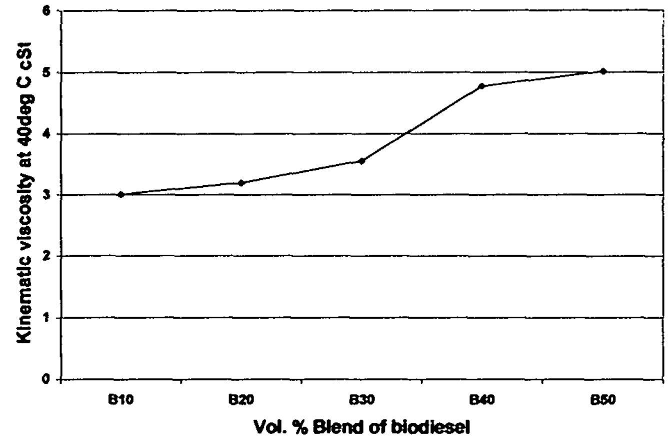

Fig. 17. Effect of Pongamia glabra seed oil Biodiesel on fuel viscosity

Carbon residue of the neat biodiesel obtained from *Pongamia glabra* seed oil was 0.267 %wt, which is much higher than that of the petroleum diesel (0.1% wt). When the biodiesel was blended with the petroleum diesel, the carbon residue of the blends increased with the increase of percentage of the biodiesel (Table 14). The carbon residues of B10 and B20 blends were quite close to that of the petroleum diesel.

The pour point of the petroleum diesel used in the blends was 0^0 C. When the biodiesel was blended with it, there was no change of the pour point upto a concentration 40% by vol. of the biodiesel in the blends (Table 14). Only for B50 blend, the pour point became equal to that of the neat biodiesel.

Flash points of the blends were found to be higher than that of the petroleum diesel and found to increase with the increase of biodiesel concentration in the blends.

When the biodiesel from *Pongamia glabra* seed oil was blended with the petroleum diesel, the cetane numbers of the blends were found to increase with the increase of percentages of biodiesel in them (Table 14). From Fig 18 it is seen that the effect of blending the biodiesel on cetane number is near linear for mixtures of the biodiesel and the petroleum diesel.

Table-14: Fuel characteristics of various blends of biodiesel from *Pongamia glabra* seed oil with petroleum diesel.

Property	Blends % vol.				
	B10	B20	B30	B40	B50
Density at 15^{0}C g/cm^3	0.853	0.860	0.870	0.874	0.878
Kinematic viscosity at 40^0 C cSt	3.01	3.20	3.56	4.78	5.02
Water content % vol.	0.050	0.047	0.042	0.039	0.036
Ramsbottom carbon residue %wt	0.124	0.130	0.158	0.172	0.184
Pour Point ^{0}C	0	0	0	0	+3
Flash point ^{0}C	59	68	72	73	78
Cetane number	46.8	47.6	48.8	49.5	50.5
Oxidation stability g/100ml	0.01	0.012	0.013	0.013	0.014
Sulphur content %wt.	0.01	0.008	0.008	0.007	0.007
Copper strip corrosion	1a	1a	1a	1a	1a
Ash content %wt.	0.01	0.009	0.009	0.008	0.005
Acid value mg KOH/g	0.102	0.098	0.086	0.081	0.078
Calorific value(gross) kJ/g	44.77	44.12	43.78	43.70	43.68
IBP/FBP ^{0}C	139/371	139/369	140/370	141/369	142/369

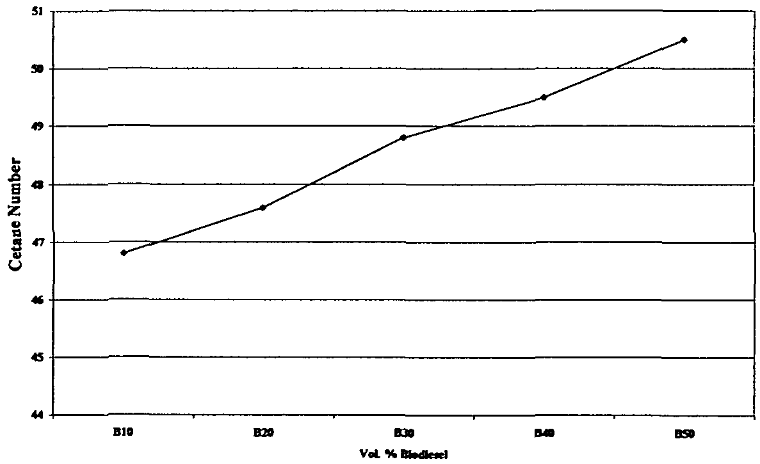

Fig. 18 -Cetane number for blends of *Pongamia glabra* seed oil biodiesel with petroleum diesel

The oxidation stability value of the petroleum diesel was 0.01 g/100ml (Table 9) and that of the neat biodiesel from *Pongamia glabra* seed oil was 0.15 g/100ml (Table 8). When this biodiesel was blended with the petroleum diesel, the oxidation stability values of the blends increased with the increase of biodiesel concentration.

Sulphur content of the neat biodiesel was 0.005% wt (Table 8) and that of petroleum diesel was 0.0165% wt. When the biodiesel was blended with the petroleum diesel, the sulphur content of the blends decreased gradually with the increase of percentages of biodiesel. Sulphur content values of all the blends were within the acceptable limits for biodiesel and their blends (Table 14).

Copper strip corrosion test of the blends indicates that they are non-corrosive in nature.

Ash content of the neat biodiesel from *Pongamia glabra* seed oil was significantly low (0.001 %wt) while that of the petroleum diesel was 0.01%wt. According to the ASTM standards for biodiesels and their blends the maximum limit acceptable limit of ash content is 0.05% wt. (Table 10). When the biodiesel was blended with the petroleum diesel, the ash content was found to decrease gradually with the increase of biodiesel concentration in the blends (Table 14). Ash contents of B10, B20, B30, B40 and B50 blends were much below the maximum acceptable limit.

The acid value of petroleum diesel was much higher (0.104-mg KOH/g) than that of the neat biodiesel from *Pongamia glabra* seed oil (0.01mg KOH/g). Hence the acid values of the blends gradually decreased with the increase of biodiesel concentration. The acid values of all the blends were found to be much below the maximum acceptable limit as per ASTM standards for biodiesels and their blends (Table 10).

The gross calorific value of neat biodiesel from *Pongamia glabra* seed oil was 42.822 kJ/g (Table 8) whereas that of the petroleum diesel was 45.013 kJ/g (Table 9). When the biodiesel was blended with the petroleum diesel, the calorific values decreased with the increase of percentages of biodiesel in the blends (Table 14). However, the calorific values of B10 and B20 blends were close to that of the petroleum diesel.

IBP/FBP values for B10, B20, B30, B40 and B50 blends were found to be 139/371^0 C, 139/369^0 C, 140/370^0 C, 141/369^0 C and 142/369^0 C respectively. The higher IBP values at higher concentration of biodiesel in the blends may be due to the molecular interaction among the petroleum diesel molecules and biodiesel molecules.

From the analysis of the fuel characteristics of the various blends of the biodiesels from *Mesua ferrea* seed oil and *Pongamia glabra* seed oil with petroleum diesel, it is evident that both B5 and B10 blends of the biodiesel from *Mesua ferrea* seed oil with petroleum diesel can be used as fuels for diesel engine without any engine modification. However, in the case of B10 blend the calorific value was found to be 2.42% lower than that of the petroleum diesel. Hence, B5 blend may be considered to be the most suitable one to be used as a fuel for diesel engine.

On the other hand B10 and B20 blends of the biodiesel from *Pongamia glabra* seed oil with petroleum diesel meet all the required specifications as a diesel engine fuel.

Part 4

Diesel engine performance and emission characteristics of B5 and B20 blends and the petroleum diesel

A number of researchers have investigated the use of vegetable oils and biodiesel blends in diesel engine (Nye, 1984; Pramanik, 2003; Raheman and Phadatare, 2004; Centikaya and Karaosmaboglu,2005; Monyem and Van Gerpen, 2004; Laforgia and Ardito,1995). Most of them have concluded that biodiesel blends starting from B5 to B100 can be used in diesel engine without engine modification. But with the increase of biodiesel percentage in the blends of biodiesel and petroleum diesel (exceeding 20% by vol. of biodiesel), engine efficiency parameters decreases whereas specific fuel consumption as well as NOx emission increases.

Selection of the blends

For diesel engine performance tests and emission characteristics studies we selected the B5 blend of biodiesel from *Mesua ferrea* seed oil and the B20 blend of biodiesel from *Pongamia glab*ra seed oil, as these two blends showed similar fuel characteristics, especilaly the density, viscosity and calorific values (Tables 13 & 14) with those of the typical petroleum diesel (Table 9). Moreover, most of their fuel characteristics were found to be within the acceptable limits of ASTM standards for biodiesel and their blends (Table 10), International standards for biodiesel (Table 11) and En-14214-2003 standards for biodiesel (Table 12). For comparison of the results with those of the petroleum diesel, engine performance and gas emission characteristics of the petroleum diesel was also tested under identical experimental conditions using the same diesel engine.

For testing the engine performance and emission characteristics of fuels i.e. B5, B20 and the petroleum diesel a Bajaj- Tempo, direct injection, 4-cylinder, 4 stroke, vertical, water-cooled computer-base Test IC diesel engine was used. The technical details and operation conditions of the diesel engine are given in Chapter III (Table 3).

For each of the tested fuels the engine was set for half-an-hour without applying load and then load was applied at 2500rpm, 3000rpm and 3500rpm. All the required data were recorded in a computer coupled with the engine systems and the dynamometer. Emission characteristics of CO and NOx were measured with the help of a smokemeter and a portable NUCON series 400 toxic gas analyzer.

Brake Specific fuel consumption characteristics of B5, B20 and petroleum diesel

From Fig. 19 it is seen that the Brake Specific fuel consumption of the three fuels under test decreased from 0.35kg/kWh at 2500 rpm to 0.3 kg/kWh at 3000 rpm and then increased to1.0 kg/kWh at 3500 rpm. This indicates that all the three fuels have *shown identical Brake Specific fuel consumption under the test conditions which may* be attributed to the fact that the gross calorific values of B5 and B20 blends (Table 13 &14) are almost equal to that of the petroleum diesel (Table 9). Moreover, the viscosity and density values of these two blends are also almost equal to those of the petroleum diesel. However, Cetinkaya and Karaosmanoglu (2005) observed slightly higher values of brake specific fuel consumption for 20% and 100% blends of used cooking oil originated biodiesel with petroleum diesel within 1800 rpm to 3000 rpm.

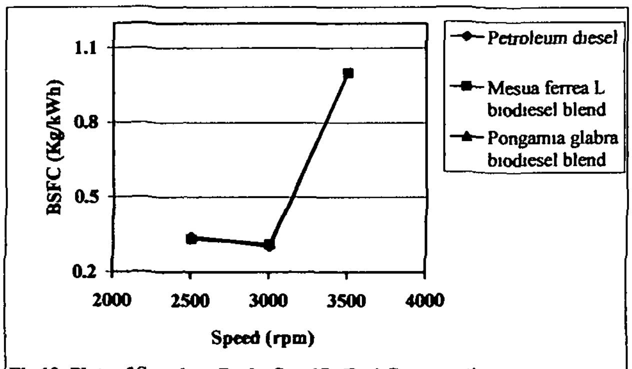

Fig.19. Plots of Speed vs. Brake Specific Fuel Consumption (BSFC)

Indicated Horse Power (IHP) Generation for B5, B20 and petroleum diesel

The Indicated horsepower increased linearly with the increase of engine speed from 2500 rpm to 3500 rpm for all the tested fuels (Fig.20). No significant difference was observed among the fuels so far as indicated horsepower is concerned indicating that almost equal amount of power was developed at a particular engine speed.

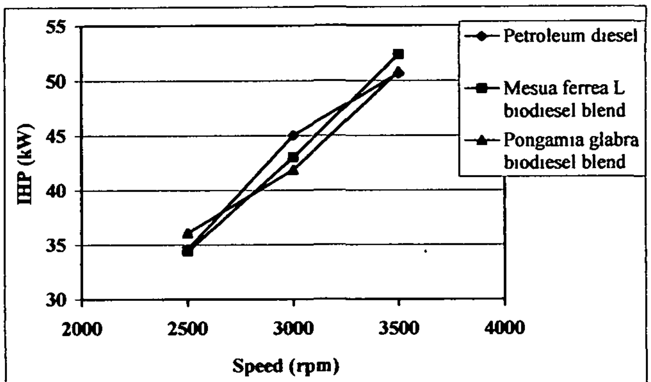

Fig: 20 Plots of Speed vs. Indicated Horse Power (IHP)

Brake Horse Power (BHP) generation results for B5, B20 and petroleum diesel

Brake horsepower was found to increase with the increase of speed from 2500 rpm to 3500 rpm in the cases of all the fuels under tests (Fig.21). At 2500 rpm B20 blend showed the highest brake horsepower generation (24.2kW) while at 3500 rpm, B5 blend showed maximum power generation (29.55kW) and minimum power was generated by B20 blend. At 3000 rpm equal power (27.2kW) was generated by all the three fuels indicating that all these three fuels can be used conveniently at around 3000 rpm.

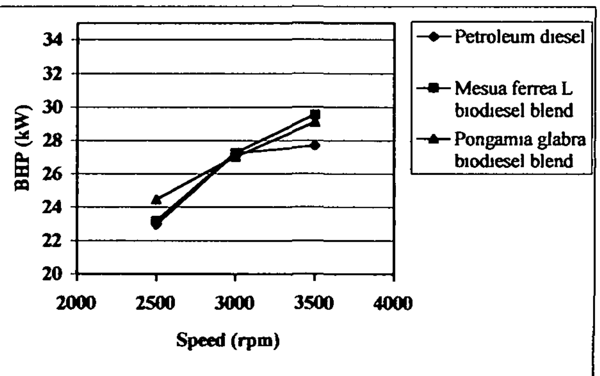

Fig.21. Plots of Speed vs. Brake Horse Power (BHP)

Other workers (Cetinkaya and Karaosmanoglu, 2005; Laforgia and Ardito, 1995) also observed similar increasing trend of brake horsepower with the increase of engine speed for other neat biodiesel and biodiesel blends.

Frictional Horse Power (FHP) generation results for B5, B20 and petroleum diesel

Frictional horsepower was found to increase with the increase of rpm for all the three tested fuels (Fig 22). At 2500 rpm, the frictional horsepower values for all the fuels were equal and at 3000 rpm, petroleum diesel showed the highest frictional horsepower and B20 blend showed the lowest of it. Again at 3500 rpm, the lowest value of frictional horsepower was shown B20 blend. The lowest frictional horsepower shown by B20 blend may be attributed to the fact that with the increase of percentage of biodiesel in the blend, the lubricity of the fuel increased (Knothe & Steidley, 2005).

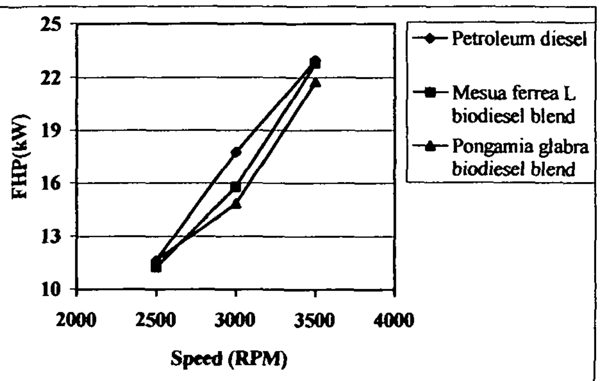

Fig. 22 Plots of Speed vs. Frictional Horse Power (FHP)

Mechanical Efficiency

Mechanical efficiency is the ratio of brake horsepower to indicated horsepower. Since Indicated horsepower is the sum of brake horsepower and frictional horsepower, therefore,

$$\text{Mechanical efficiency} = \frac{\text{BHP}}{\text{BHP} + \text{FHP}}$$

Mechanical efficiency of an engine varies with load. The other factors affecting the mechanical efficiency of an engine are – engine design, speed, cooling conditions, quality and quantity of lubrication, fitting and alignments of various parts and manufacturing accuracy (Gupta, 1998).

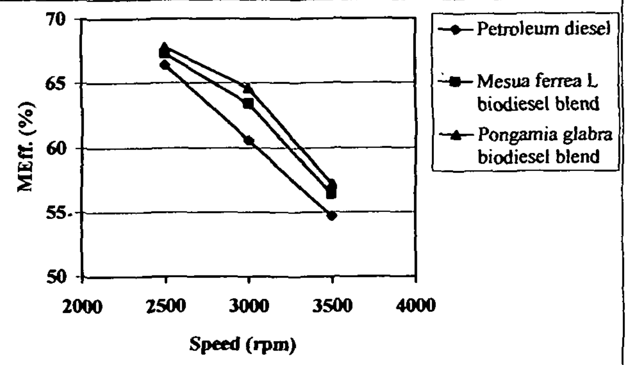

Figure:23 Plots of Speed vs. Mechanical Efficiency (MEff.)

From the experimental results of the present study (Fig 23) it has been observed that the mechanical efficiency of the engine decreased with the increase of rpm for all the three tested fuels. With B20 and B5 blends, the engine showed higher mechanical efficiency as compared to that shown by petroleum diesel. Highest mechanical efficiency was shown by B20 blend followed by B5 blend indicating that presence of biodiesel in blends enhances its lubricity and thereby reducing the frictional horsepower (Knothe & Steidley, 2005).

Indicated Thermal efficiency

Fig 24 shows the variation of indicated thermal efficiency of the engine for the three tested fuels. Indicated thermal efficiency was found to decrease gradually with the increase of rpm from 2500 to 3500 rpm for petroleum diesel whereas in case of B20 blend it increased with the increase of rpm. In the case of B5 blend, indicated thermal efficiency was found to decrease slightly from 2500rpm to 3000rpm and then increased. However, lowest indicated thermal efficiency was observed for B20 blend at all the engine speeds, while highest of it was found for petroleum diesel. At 3500 rpm, the indicated thermal efficiency for petroleum diesel and B5 blend were almost equal.

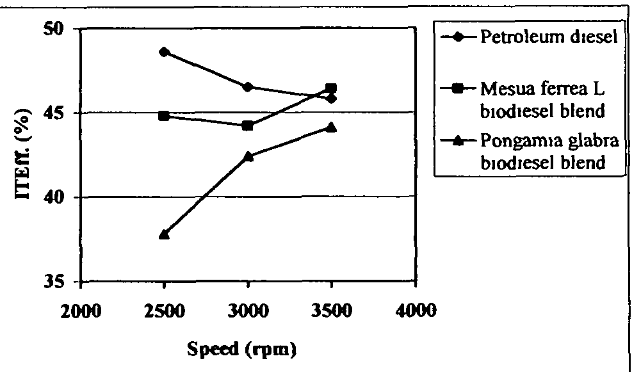

Figure:24 Plots of Speed vs. Indicated Thermal Efficiency (ITEff.)

Brake Thermal Efficiency

The brake thermal efficiency with both the petroleum diesel and B5 blend decreased with the increase of rpm while with B20 blend it increased from 2500 rpm to 3000 rpm and then decreased.

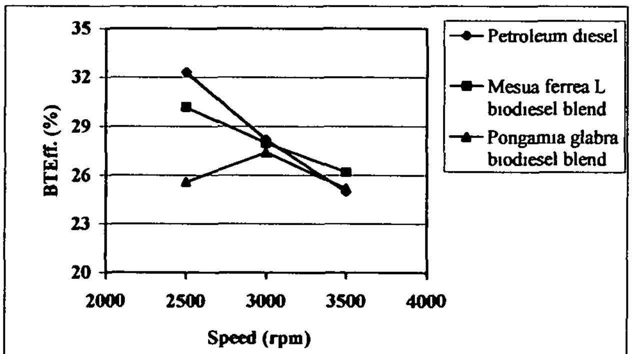

Figure:25 Plots of Speed vs. Brake Thermal Efficiency (BTEff.)

In the case of B20 blend, the brake thermal efficiency increased when the engine speed was increased from 2500 rpm to 3000 rpm and then decreased (Fig 25). At 3000 rpm, the brake thermal efficiency percentages of all the tested fuels were found to be almost similar.

Volumetric efficiency

The volume of the fuel-air mixture drawn into the cylinder at atmospheric pressure during the intake stroke compared to the volume of the cylinder gives the volumetric efficiency of an engine.

Some of the important factors determining the volumetric efficiency of engine are carburetor design, valve timing, throttle-opening etc. The higher the volumetric efficiency the more power the piston will develop when the mixture is burned. The volumetric efficiency of an engine running at fairly high speed should be around 80% (Gupta, 1998).

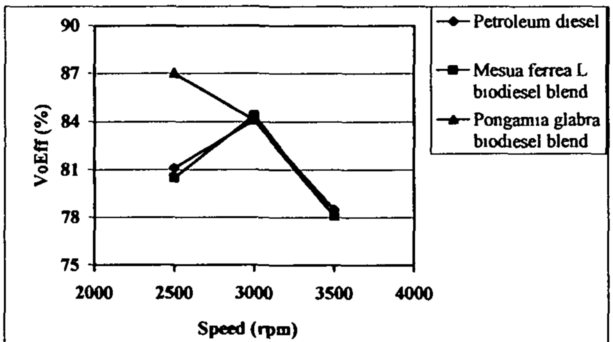

Fig. 26 Plots of Speed vs.Volumetric efficiency (VoEff)

From the Fig 26 it is seen that the maximum volumetric efficiency at 2500 rpm was obtained for B20 blend (87%), which then dropped to 78.1% at 3500 rpm. The other two tested fuels namely the petroleum diesel and B5 blend showed maximum volumetric efficiency (about 81%) at 3000 rpm. At 3500 rpm, all the fuels showed similar volumetric efficiencies (78.5% for petroleum diesel; 78.1% for B5 blend and 78.1% for B20 blend). These volumetric efficiencies are almost similar to that of an engine running at fairly high speed.

Torque

The engine torque values for B5, B20 and petroleum diesel at 2500, 3000 and 3500 rpm are shown in Fig 27. With the increase of engine speed from 2500 rpm to 3500 rpm, the torque was found to decrease for all the three tested fuels. From 2500 rpm to 3000 rpm, the decrease of torque was gradual and from 3000 rpm to 4000rpm, the decrease was sharp. However with petroleum diesel, the decrease of torque between 3000 rpm to 4000 rpm was significantly high. Since the change of torque between 2000 rpm and 3000 rpm speed is not significant, 3000 rpm may be considered as the optimum speed limit for moderate power output. Laforgia and Ardito (1995) also observed similar decreasing trend of torque values of the petroleum diesel and biodiesel with increase of engine speed from 2000 rpm to 4000 rpm.

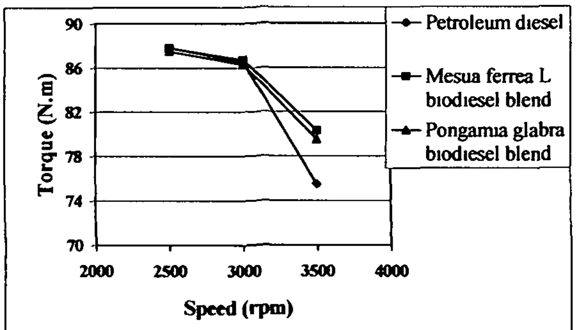

Fig.27 Plots of Speed vs. Torque

Heat balance

The heat produced inside the engine cylinder is not fully utilized to do the external work. A part of the heat is carried away by the engine cooling system, exhaust gases and radiation. About 10% of the total heat produced are consumed by friction. These heat losses reduce the thermal efficiency of the engine. During a specified period (usually a minute) the total heat produced inside the cylinder must be equal to the sum of the various heat losses and that utilized for useful work. All these items when recorded in a tabular form constitute what is called a heat balance sheet.

Table15 present the heat balance sheet for the three tested fuels at 2500 rpm, 3000 rpm and 3500 rpm.

From Table15 it is seen that at 2500 rpm, petroleum diesel provided the highest amount of useful heat (32%) whereas B5 blend and B20 blend provided 30% and 25% of useful heat respectively. When the engine speed was increased from 2500 rpm to 3000 rpm the useful heat produced by the petroleum diesel decreased to 30% while B5 blend produced the same amount of useful heat (28%) as it provided at 2500 rpm. On the otherhand, the useful heat provided by B20 at 3000 rpm increased to 27%. At 3500 rpm, the useful heat provided by the petroleum diesel, B5 blend and B20 blend were 25%, 26% and 25% respectively.

Table- 15: Energy balance sheet for petroleum diesel, B5 and B20 blends.

Types of Energy	Petroleum diesel			B5 *Mesua ferrea* L biodiesel			B20 *Pongamia glabra* biodiesel		
	Speed (rpm)			Speed (rpm)			Speed (rpm)		
	2500	3000	3500	2500	3000	3500	2500	3000	3500
Useful Energy (%)	32	28	25	30	28	26	25	27	25
Energy to coolant (%)	30	29	27	32	29	27	34	34	33
Energy to Exhaust (%)	35	34	33	34	34	33	32	33	33
Radiation and Unaccounted heat (%)	3	9	15	4	9	14	15	12	16
Total	100	100	100	100	100	100	100	100	100

At 2500 rpm, 3000 rpm and 3500 rpm the highest energy was utilized from B20 blend for the engine cooling systems whereas petroleum diesel utilized the lowest percentage of heat energy for the same at 2500 rpm. Percentages of heat energy carried away by exhaust gases were found to be almost identical for all the three tested fuels at 2500 rpm, 3000 rpm and 3500 rpm engine speeds.

At 2500 rpm the heat lost due to radiation and unaccountable reason for petroleum diesel was very low as compared to B5 and B20 blends (Table 15). As compared to the petroleum diesel the heat lost by radiation etc. was found to be higher in case of both the biodiesel blends in B5 and B20.

Emission characteristics of the fuels

Carbon monoxide (CO) emission

Among the various pollutants of air carbon monoxide is considered as the most harmful one. A substantial percentage of carbon monoxide present in air is due to its emission from incomplete combustion of fossil fuels in vehicles.

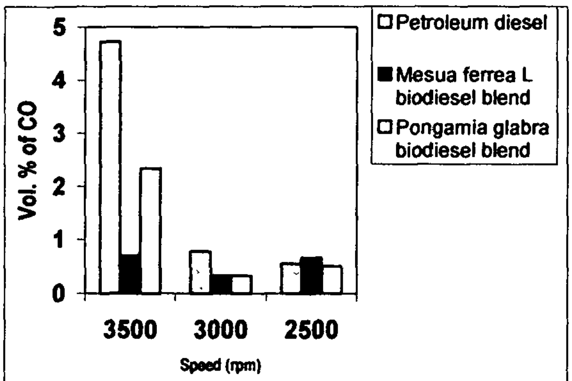

Fig. 28 Chart for variation of CO emission with rpm

Emission characteristics of the petroleum diesel, B5 and B20 blends are shown in Fig 28. From the figure it is seen that at 2500 rpm, all the three tested fuels emitted less than 0.6% of CO. Similarly at 3000 rpm, B5 and B20 blends emitted about 0.2% of CO, whereas petroleum diesel emitted about 0.7% of it. When the engine speed was increased to 3500 rpm, maximum percentage of CO was emitted by the petroleum diesel (4.7%) while B5 and B20 blends emitted only 0.7% and 2.4% of CO respectively. From environmental pollution point of view, both B5 and B20 blends were found to be much superior than the petroleum diesel.

NOx emission

NOx emission by B5 and B20 blends were found to be slightly higher than that of the petroleum diesel, which may be attributed to the presence of more oxygen content in the biodiesel blends. Earlier workers (Montagne, 1996; Graboski *et al.*, 1996) have also observed higher NOx emission from neat biodiesel or biodiesel blends. The possible causes for increased NOx during biodiesel and diesel oxygenates combustion have been discussed elsewhere (Parker, 1996).

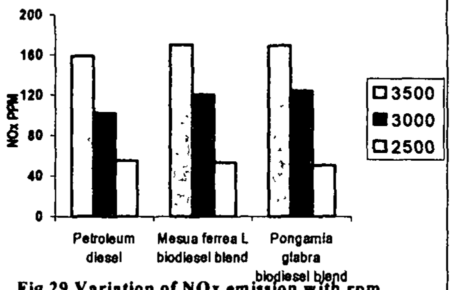

Fig.29 Variation of NOx emission with rpm for the tested fuels.

Further NOx emission from all the tested fuels was found to increase with the increase of engine speed. From their studies Graboski and McCormick (1998) concluded that the NOx emission was dependent upon engine speed and load.

Exhaust gas temperature:

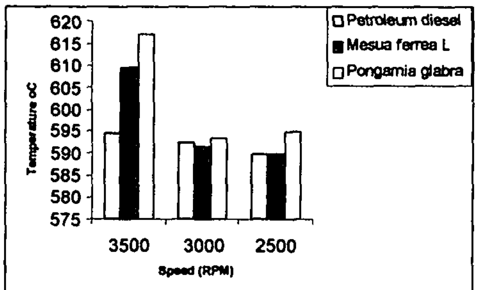

Fig. 30 Chart for exhaust gas temperature.

The temperature of the exhaust gases from the tested fuels (Fig 30) was found to increase with the increase of engine rpm. For B20 blend, the exhaust gas temperature was maximum (616 ^{0}C) at 3500 rpm, which may be due to poor and delayed combustion characteristics of biodiesel present in the blend. At 3000 rpm and 2500 rpm, the exhaust gas temperature of all the fuels were found to be almost similar.

CHAPTER V

SUMMARY AND CONCLUSION

(83-89)

Chapter V
Summary and Conclusion

Recently there has been growing interest all over the world on the use of biodiesel as an alternative fuel for diesel engine that is produced by chemically reacting a vegetable oil or animal fat with an alcohol such as methanol. As its primary feedstock is a vegetable oil or animal fat, biodiesel is generally considered to be renewable. Non-edible oilseeds are getting more attention for biodiesel production.

In India where fossil fuel reserves are limited, the use of biodiesel may be a viable solution to supplement the growing demand of diesel engine fuel in the country. In the forests of North-East India a variety of oil seeds bearing tree and shrub species grow well in their natural habitats. Among the oilseeds of such indigenous tree and shrub species oil seeds of *Mesua ferrea* L. (Nahar) and *Pongamia glabra* Vent. (Koroch) seem to have high potentiality as the source of feedstocks for biodiesel production.

Mesua ferrea is a middle-size tree that grows mostly in the mountains of the Eastern Himalayas, Eastern Bengal, Eastern and Western Peninsulas and North-East India. Its seeds contain about 75% of oil on the basis of shelled kernel weight. A fully mature tree yields 20-70kg of seeds annually.

Pongamia glabra is also a middle-size tree that grows well in the North-East India. Its seeds contain 30-35% of oil on the basis of kernel weight. A mature tree yields 20-50 kg of seeds annually.

At present the seeds of both *Mesua ferrea* and *Pongamia glabra* trees are not utilized for any productive purpose. With a view to utilize the seed oils of these two trees an attempt was made to convert them to biodsiesels by transesterification and to examine the feasibility of using these biodiesels as fuels for diesel engine.

The objectives of the study are-

(i) to determine the properties of *Mesua ferrea* seed oil and *Pongamia glabra* seed oil;

(ii) to produce biodiesel from these two seed oils by transesterification using suitable process and to determine the fuel characteristics of the biodiesels (methylesters) produced;

(iii) to prepare various blends of each of the biodiesels with a typical petroleum diesel and determine their fuel characteristics so as to select the most suitable blends which may be used as fuels for diesel engine and

(iv) to conduct the engine performance tests and emission characteristics with the selected blends of each of the two biodiesels.

The study was conducted in the laboratory conditions.

Before transesterification of *Mesua ferrea* seed oil and *Pongamia glabra* seed oil, their fatty acids compositions and other important properties were determined by following different standard methods. *Mesua ferrea* seed oil was found to contain 25.4 % of saturated fatty acids and 71.6% of unsaturated fatty acids while *Pongamia glabra* seed oil was found to contain 21.9% of saturated fatty acids and 74.81% of unsaturated fatty acids. The lowest carbon number in the fatty acids of both the oils was 16. From the results of their proximate analysis and fatty acid compositions it was found that both the oils are suitable as feedstocks for production of biodiesels by transesterification process.

In the case of *Pongamia glabra* seed oil with low acid value (1.21 mgKOH/g), the production of biodiesel was achieved simply by its transesterification with methanol using a base catalyst (NaOMe) which is the most common practice in commercial biodiesel production. However, in the case *of Mesua ferrea* seed oil with high acid value (16.4 mgKOH/g) a two-step transesterification process was required to produce biodiesel from it. Biodiesels thus produced were further refined by distillation under reduced pressure.

Various fuel characteristics such as density, viscosity, ash content, acid value, cetane number, water content, pour point, flash point, sulphur content, carbon residue, oxidation stability, calorific value, copper strip corrosion, IBP/ FBP etc. of both the refined biodiesels were determined by standard methods and compared with those of a typical petroleum diesel obtained from Numaligarh Refinery Ltd., Assam.

Density, cetane number, flash point, water content, ash content and sulphur content of both the neat biodiesels were found to be within the acceptable limits as per ASTM standards for biodiesels and their blends, standards of Engine Manufacturers Association, International standards for biodiesel, En 14214-2003 standards for biodiesel etc. Acid values and copper strip corrosion tests of the biodiesels indicated their non-corrosive nature.

The kinematic viscosity of the neat biodiesel from *Mesua ferrea* seed oil at 40^0 C was found to be slightly higher (6.2 cSt) than that of the maximum acceptable limit (6 cSt) as per ASTM standard. On the other hand, though the kinematic viscosity of the neat biodiesel from *Pongamia glabra* seed oil was found to be within the acceptable limit (5.8 cSt) it was quite close to the maximum limit of acceptance. Pour points of both the biodiesels were higher than that of the typical petroleum diesel. Carbon residue values were also higher than that of the petroleum diesel. Higher IBPs of both the biodiesels (210^0 C for biodiesel from *Mesua ferrea* seed oil and 219^0 C for biodiesel from *Pongamia glabra* seed oil) indicate the shortage of about 20-25% of lower boiling point hydrocarbons (below 220^0 C) in them.

Considering the above mentioned points, it can be concluded that the neat biodiesels of both *Mesua ferrea* seed oil and *Pongamia glabra* seed oil may not be suitable to use as fuels in diesel engine. Hence to meet the required specifications as diesel fuels each of the neat biodiesels needs to be blended with petroleum diesel.

Since the biodiesel from *Mesua ferrea* seed oil showed comparatively higher density and kinematic viscosity values than the petroleum diesel, its blends with petroleum diesel were prepared as 5% (B5), 10% (B10), 15% (B15), 20% (B20) and 25% (B25). On the other hand as the kinematic viscosity of the biodiesel from *Pongamia glabra* seed oil was found to be lower than that of the biodiesel from *Mesua ferrea* seed oil, its blends with petroleum diesel were prepared as 10% (B10), 20% (B20), 30% (B30), 40% (B40) and 50% (B50). Various fuel characteristics of all the blends, thus prepared were determined by standards methods.

From the analysis of the fuel characteristics of various blends of the biodiesel from *Mesua ferrea* seed oil and *Pongamia glabra* seed oil, it was found that both B5 and B10 blends of the biodiesel from *Mesua ferrea* seed oil could be used as fuel for diesel engine. The calorific value of the B10 blend was found to be 2.42% lower than that of the petroleum diesel while that of the B5 blend was quite close to the calorific value of the petroleum diesel. Hence among all the blends B5 blend may be considered as the most suitable one to be used as fuel for diesel engine. In the case of blends of biodiesel from *Pongamia glabra* seed oil both B10 and B20 blends were found to meet all the required specifications as per ASTM standards for biodiesel and their blends.

As a matter of interest we conducted the engine performance test and emission characteristics studies of B5 blend of biodiesel from *Mesua ferrea* seed oil with petroleum diesel and B20 blend of the biodiesel from Pongamia glabra seed oil with the same petroleum diesel and the petroleum diesel alone using a Bajaj-Tempo, direct injection, 4-cylinder, 4-stroke, vertical, water-cooled, computer-base Test IC diesel engine. The technical details of the engine are as follows:

Technical details of the diesel engine

Rated output	34kW at 3800 RPM
Bore	78mm
Stroke	94mm
Compression ratio	19.8 : 1
Capacity	1797 cm^3
Throttle opening	100 %
Maximum cylinder volume	450 cm^3
RPM, Dynamometer load (kg)	3500 ± 10, 39 ± 0.15; 3000 ± 10, 43 ± 0.15; 2500±10; 44 ± 0.15.

From engine performance tests and emission characteristics studies of the fuels namely B5, B20, blends and the petroleum diesel, it was observed that the brake specific fuel consumption of all the three fuels under the test conditions were almost identical at engine speeds of 2500 rpm to 3000 rpm and 3500 rpm which may be attributed to the fact that the gross calorific value, density and viscosity of B5 and B20 blends were almost equal to those of the petroleum diesel.

The indicated horse power generation increased linearly with the increase of engine speed from 2500 rpm to 3500 rpm for all the tested fuels.

Similarly, brake horse power generation was found to increase with the increase of engine speed for all the fuels. At 2500 rpm B20 blend showed the highest horse power generation whereas B5 blend showed the maximum of it at 3500 rpm.

Frictional horse power generation increased with the increase of engine speed from 2500 rpm to 3500 rpm. At 3000 rpm the petroleum diesel showed higher frictional horse power than the blends. Lower frictional horse power generation by the biodiesel blend may be attributed to the fact that with the increase of biodiesel percentage in blends the lubricity increases.

Mechanical efficiency of the engine decreased with the increase of speed from 2500 rpm to 3500 rpm for all the three fuels.

Indicated thermal efficiency decreased gradually with the increase of speed from 2500 rpm to 3500 rpm for the petroleum diesel, while in the case of B5 blend it was observed to decrease from 2500 rpm to 3000 rpm and then increase at 3500 rpm. In the case of B20 blend it increased with the increase of engine speed from 2500 rpm to 3500 rpm.

Volumetric efficiency with B5 blend and the petroleum diesel increased with the increase of engine speed from 2500 rpm to 3000 rpm and then started decreasing whereas with B20 blend it started decreasing from 2500 rpm to 3500 rpm.

The torque was found to decrease with the increase of engine speed from 2500 rpm to 3500 rpm for all the tested fuels.

From heat balance results it was observed that at 2500 rpm engine speed petroleum diesel provided the highest amount of useful heat (32%), whereas B5 and B20 blend provided 30% and 25% of it respectively. When the engine speed was increased from 2500 rpm to 3000 rpm, the useful heat produced by the petroleum diesel decreased to 30% while B5 blend produced the same amount of heat (28%) as it provided at 2500 rpm. Lowest useful heat was produced by B20 blends in all the engine speeds. The highest energy was utilised by B20 blend for engine cooling, whereas B5 blend and the petroleum diesel utilised almost identical energy for the same. Percentages of heat energy carried away by exhaust gases were found to be almost identical for all the tested fuels at all the engine speeds. As compared to the petroleum diesel, the heat lost by radiation and other unaccountable reasons was found to be higher for both the biodiesel blends.

From the emission characteristics studies of the fuels it was found that biodiesel blends produced less percentages of CO than the petroleum diesel.

NOx emission was found to be slightly higher with both B5 and B20 blends than that of the petroleum diesel which may be attributed to the presence of more oxygen content in the biodiesel blends. Further NOx emission from all the fuels was found to increase with the increase of engine speed.

At 2500 rpm, 3000 rpm the temperature of the exhaust gases for all the tested fuels were found to be almost equal while at 3500 rpm biodiesel blends showed higher gas temperatures than the petroleum diesel.

From the results of the present study, it is evident that the seed oils of both *Mesua ferrea* and *Pongamia glabra* trees can be used as the source of feed stocks for biodiesel production. The neat biodiesels produced from both the oils by transesterification process followed by distillation do not meet all the required fuel characteristics as per ASTM standards for biodiesels and their blends. Hence each of these two biodiesels needs to be blended with petroleum diesel to achieve the required specifications.

From the analysis of the fuel characteristics of various blends of each of the biodiesels with petroleum diesel it is seen that B5 blend of the biodiesel from *Mesua ferrea* seed oil and B20 blend of the biodiesel from *Pongamia glabra* seed oil are the most suitable blends which may be used as fuels for diesel engine. Further the engine performance and emission characteristics studies for these two blends confirm their suitability as diesel engine fuels.

For commercial production of biodiesels from these two seed oils, large-scale plantation of *Mesua ferrea* tree and *Pongamia glabra* tree in wasteland and roadsides should be taken up. Moreover, R & D efforts should be made to increase the yield of seeds per plant of these two tree species through agronomic practice or by genetic manipulation. Such a programme will not only produce the feedstocks for biodiesels, but also provide ample opportunity for employment generation among the rural people of the region.

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