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Production of Neem Oil Methyl Ester and Its Blends with Diesel with Cost Analysis and Theoretically Evaluated the Properties

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ABSTRACT: *The aim of producing the Neem oil methyl ester can be used as a substitute for Diesel fuel in transportation, stationary engine and agricultural engines. It can also been used in DI compression Ignition engine without any engine modifications. The emissions of the engine such as carbon dioxide, carbon monoxide, un burnt hydrocarbons and smoke density are reduced when compared to Diesel fuel except oxides of nitrogen. Because of the increase in edible oil prices, it is not viable to produce bio-diesel from edible oils. Low cost abundantly found non-edible oil such as Neem oil could be the better option for bio-diesel processing. Neem oil could not be easily converted into bio-diesel prior to its refining, because of its higher moisture and Free Fatty Acids(FFA) content. In this study a soil to oil level study has been done to overcome the problems associated with bio-diesel production from Neem oil. Oil extraction, refining of raw oils, optimization of process variables of transesterification as has been evaluated. The parameters of NOME have been evaluated theoretically. The properties of Neem oil have been measured experimentally. An estimation of cost analysis of Neem oil methyl ester is evaluated.*

Keywords : *Transesterification, Free Fatty Acids, NOME,*

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1. INTRODUCTION

1.1 Need for alternative fuels

Alternative fuels for automobiles are currently a topic of growing interest and importance. An alternative fuel vehicle may be defined as a vehicle that is powered by any fuel other than the conventional petroleum fuels (diesel or petrol). It also indicates any technology of engine powering that does not entail solely petroleum (such as solar powered, electric car or hybrid electric vehicles). Such a vehicle is therefore “cleaner” and safer for the environment. A green vehicle (also known as an environmentally friendly vehicle) is a motor vehicle for the road that produces less environmental impacts than comparable traditional internal combustion engine vehicles that are powered by diesel or gasoline, or one that utilizes specific alternative fuels. The essential points for the need for alternative fuels are listed below:

- Fossil fuels are in limited supply
- Global consumption of fossil fuels is increasing, and much of that increase is from the transportation sector.
- Fossil fuel combustion releases large amounts of greenhouse gases, the most significant being carbon dioxide.
- Greenhouse gases trap heat in the earth's atmosphere.
- The average temperature of the earth is increasing.
- Increased concentration of carbon dioxide in the atmosphere contribute to global warming, which is receiving world-wide attention as significant environmental problem.

1.2 Benefits of Alternative fuels

- Low environmental impact
- Ease of handling
- Leads to savings in a foreign exchange
- Improves energy security of the nation
- Provides employment to the rural masses
- Produce sustainable and relatively in expensive fuel

- Start propagating the concept with village population to supplement their income with existing tree population
- Possibility of use in the existing Diesel engines without any major modifications.
- Protect against global warming
- Reduction of pollution such as CO_2, CO, UBHC and smoke
- Wastage can be reused.
- Can be produced domestically
- Fuel economy

1.3 Types of alternative fuels

The different type of alternative fuels are Solar, Air engine, Battery/electric, Biofuels, hydrogen, propane, Natural gas, hybrid and flexible fuels. In the present work Bio-fuel have been taken for production to be used in Diesel engines.

1.4 Vegetable oils

Around the world and particularly in India, Diesel engine dominates the field of commercial transportation and agricultural machinery on account of its superior fuel efficiency. The increasing cost of petroleum and uncertainties in its supply have accelerated the tendency to depend heavily on Diesel engines. The consumption of Diesel oil in India is seven times higher than petrol. Due to shortage of Diesel fuel and its increasing cost, an alternate source of fuel for Diesel is very much needed.

The search for suitable oil source is necessary for the development of bio-Diesel industry especially in heavily populated and food-deficient countries. Some of the plant-based oils suitable for generation of bio-diesel are rapeseed/mustard, peanut, coconut, soybean, sunflower, palm, corn, rice bran, neem, mahua, jatropha, cotton seed, linseed and karanja / pungam oil. For developing countries like India with a large population, there is an increasing demand for edible oil for human consumption. Therefore, production of bio-diesel from edible oil is not an affordable solution for India. Instead non-edible oil and animal fat can be considered as good options. The major advantage of vegetable oils as fuel is that it is a non-exhaustible type and can be cropped in a cyclic order. Neem oil methyl ester (NOME) is one of the best options in non-edible category.

Different types of vegetable oils can be used in different countries based on the availability. Interest in vegetable oils as alternative Diesel engine fuels goes back to several decades. Dr. Rudolf Diesel was the first one to use vegetable oil in a C.I engine. During Second World War, attempts were made to use vegetable oil as Diesel engine fuel. However, due to their viscosity, poor volatility and high cost, vegetable oils were not accepted as Diesel engine fuels for a long time.

The cetane number and calorific value of vegetable oils are comparable with those of Diesel oil and they are also compatible with the materials used in distribution and vehicle fuel system. The main disadvantage is high viscosity resulting in difficulties with fuel injection and with cold flow pumping. The unsaturated oils are less chemically stable, which affect storage and promotes deposits on injector components and pistons.

There are also problems of incompatibility with engine lubricants. Difficulties with physical properties may be overcome by simple chemical processing like esterification. Irrespective of all the difficulties mentioned above, vegetable oils may prove an alternative option as Diesel fuel in some countries in future. India being an agro based country; it will not be an issue for cultivating crops for vegetable oils.

Vegetable oils can be classified as edible and non-edible oils. Only non-edible vegetable oils can be considered as Diesel engine fuel, as edible oils are in great demand and are too expensive to be used as fuel. Different oil crops can be cultivated in different areas depending on the climatic conditions and can be met with rural demands for Diesel during crisis.

The importance of bio-diesel as a renewable and economically viable alternative to fossil Diesel for application in compression ignition (CI) engines has led to intense research in the field over the last two decades. This is predominately due to depletion of petroleum resources and increasing awareness of environmental and health impacts from the combustion of fossil Diesel. Bio-diesel is favoured over other bio-fuels because of its compatibility with present day CI engines, with no further adjustments required to the core engine configurations when used in either neat or blended forms. Studies conducted on various CI engines fuel with varying bio-diesel types and blends under numerous test cycles have shown the key tail pipe pollutants, such as carbon monoxide, aromatics, sulphur oxides, unburnt hydrocarbon and particulate matters are potentially reduced. The effect of bio-diesel on nitrogen oxides emission requires further test and validation. The improvement in most of the Diesel emission species comes with a reduction of brake power and increase in fuel consumption. Bio-diesel's lubricating properties are generally better than those of its fossil Diesel counterpart, which result in an increased engine life. These substantial differences in engine-output responses between bio-diesel and fossil Diesel combustion are mainly attributed to the physical properties and chemical composition of the fuels. Despite the purported benefits, wide spread adoption of bio-diesel usage in CI engines is hindered by formidable technical challenges, such as low temperature inoperability, storage instabilities, in-cylinder carbon deposition and fuel line corrosion.

Vegetable oils from crops such as soybeans, peanut, sunflower, rap, coconut, karanja, neem, cotton, mustard, jetropha, linseed and castor have been evaluated in many parts of the world, which lack petroleum resource as fuels for compression ignition engine. The results show that because of the long chain hydrocarbon structure, vegetable oils have good ignition characteristics.

Unlike Diesel fuel, vegetable oils are triglycerides consisting of glycerol ester fatty acids. Vegetable oils have different chemical structure. Upto three fatty acids are linked to a glycerine molecule with ester linkages. The fatty acids vary in carbon chain length and in number of double bonds. Table 1 summarises the structure of fatty acids that are commonly found in vegetable oils.

Table 1 Fatty acids and their structure in vegetable oils

Fatty acid	Structure*
Myristic	14:0
Palmitic	16:0
Stearic	18:0
Arachidic	20:0
Behenic	22:0
Lignoceric	24:0
Oleic	18:1
Ricinoleic	18:1
Erucic	22:1
Linileic	18:2
Linolenic	18:3

*xx:y indicates xx carbon in the fatty acid chain with y double bonds. Source: Babu et al. (2003)

The major differences between vegetable oils and Diesel fuel are:

- The viscosities of vegetable oils are significantly higher (an order of magnitude higher) while the densities are only moderately higher.
- Vegetable oils have lower heating values.
- Vegetable oils increase the stoichiometric fuel/air ratio due to the presence of molecular oxygen.
- Vegetable oils may experience thermal cracking at the temperatures encountered by the fuel spray in naturally aspirated Diesel engines (Babu et al. 2003).

The vegetable oils are found to be suitable in engines due to the following reasons:

- Cetane numbers generally are in the range suitable for or close to that of Diesel fuel.
- Heat contents of various vegetable oils are nearly 90% as that of Diesel fuel.
- Presence of long chain saturated, un-branched hydrocarbons in the fatty acids (Babu et al. 2003).

The problems associated with the use of vegetable oils are:

- The fresh vegetable oil has a chain of about 18 carbons when compared to Diesel fuel that has a chain of 11-13 carbons. To burn in an engine the chain needs to be broken down to be similar in length to Diesel.
- Highly viscous and are poly-unsaturated in nature
- Incomplete combustion due to coking, engine deposits, lubricating oil dilution, ring sticking, scuffing of the cylinder liners, injection nozzle failure, and lubricant failure due to polymerisation of the vegetable oil.
- Poor durability and thermal efficiency
- Due to higher cloud and pour points of esters compared to Diesel fuel they cause problems during cold weather (Babu et al. 2003).

2. RAW NEEM OIL

Neem is scattered all over the country except at high altitudes and in thick forests. It grows in utter Pradesh, Tamil Nadu, Andhra Pradesh, Madhya Pradesh and Delhi. Neem oil is non-edible oil available in huge surplus quantities in south Asia. Annual production of Neem oil in India is estimated to be 30,000 tons. Traditionally, it has been used as fuel in lamps for lighting purpose in rural areas and is used on an industrial scale for manufacturing of soap, cosmetics, pharmaceuticals and other non-edible products. India has shortage of edible oils so its bio-diesel program is centred on non-edible vegetable oils like Neem. For feed stock diversification and utilization of currently available local resources, non-edible sources like Neem, karanja etc. should be scientifically investigated for efficient bio-diesel production and engine utilization. Keeping this background in consideration, production of bio-diesel from high free fatty acids Neem oil and its utilization as a potential alternative fuel for Diesel engine has been investigated. 50 kg of fruit yields 30 kg of seed, which gives 6 kg of oil and 24 kg of seed cake. The raw Neem oil is obtained of 20% from the neem seed. Mechanical press method is the one used since antiquity. Neem seed kernels are placed into a tub and either a screw or some form of press is used to squeeze the kernels under pressure until the oil is pressed out and collected.

2.1 PRODUCTION OF RAW NEEM OIL

2.1.1 Cleaning, Drying and Preparation of the seeds/beans

- The seed is cleaned and dried as a first step. Foreign material (like stones, glass and metal) is taken out by sieving and magnets and disposed of safely.
- Drying is performed by avoiding contact with combustion gasses unless natural gas is used.

2.1.2 Crushing

- Seeds with a high oil content, are usually mechanically pressed in expellers after a preheating step in indirectly heated conditioners.
- The expeller cake (or pressed cake) will then be further treated in the extractor, since it might still content up to 10 per cent of oil.
- The expeller works as follows: the oil bearing material is fed into one end of a cylinder within which a power-driven worm conveyor forces the material to the other end of the cylinder and out against resistance. The pressure exerted in the process squeezes out the oil.

2.1.3 Degumming

- Crude oils having relatively high levels of phosphatides may be degummed prior to refining to remove the majority of those phospholipid compounds.
- During the degumming process the crude oil is treated with a limited amount of water in order to hydrate the phosphatides and then separate them by centrifugation. After the degumming process, the crude oil is dried.

2.1.4 Pressed crude oil

- The resulting pressed crude oil can be consumed as such or be further refined.

2.1.5 Solvent extraction

- Solvent extraction is used to separate oil from seeds/beans where the principle is to employ a volatile liquid in which the oil is freely soluble.
- The common solvent used by crushers is hexane. The pre-processed seeds/beans are treated in a multistage counter-current process with solvent until the remaining oil content is reduced to the lowest possible level.

2.1.6 Removing of solvent by distillation

- A mixture of oil and solvent, is separated by distillation into two components, oil and solvent. The solvent is recycled into the extraction process.

2.1.7 Extracted crude oil

- Crude oils obtained by pressing and/or extraction are refined in a multistage process.

The flow diagram of the extracted raw neem oil is shown in fig. 1. A simple process flow diagram of the extracted neem oil with concerned equipments is shown in fig.2

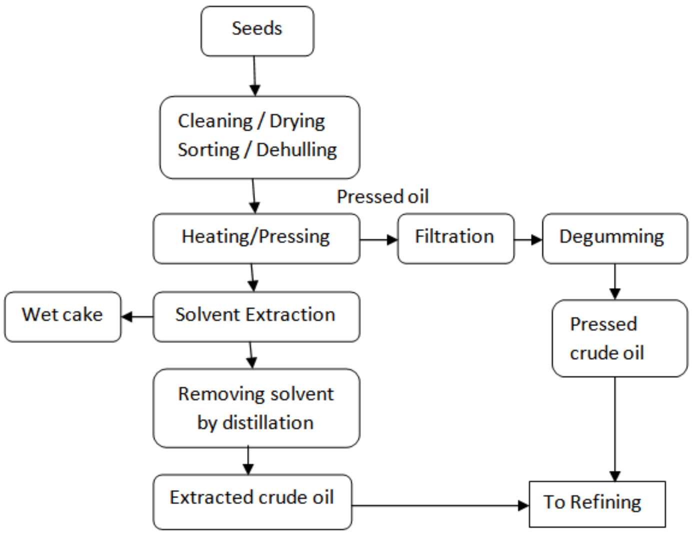


Fig.1 Flow diagram of oil seed crushing

Fig.2 Process flow diagram of raw neem oil.

2.2 Viscosity reduction

Pre heating, pyrolyis, micro emulsification, blending and transesterification are the different methods used to reduce the viscosity of vegetable oils. The transesterification process is one of the best method for reducing viscosity of the vegetable oils moreover it is cost effective and very simple process.

2.3 Transesterification of raw neem oil into Neem Oil Methyl Ester (NOME)

Transesterification is the process of using an alcohol (e.g. methanol or ethanol) in the presence of catalyst, such as Sodium Hydroxide (NaOH) or Sodium Methoxide (NaOMe) or Potassium Hydroxide (KOH) to chemically break the molecule of the raw renewable Neem oil into Neem oil methyl ester (NOME) with glycerol as a byproduct.

2.4 The chemistry of Bio-diesel production

The Chemistry of transesterification process is shown in fig. 3

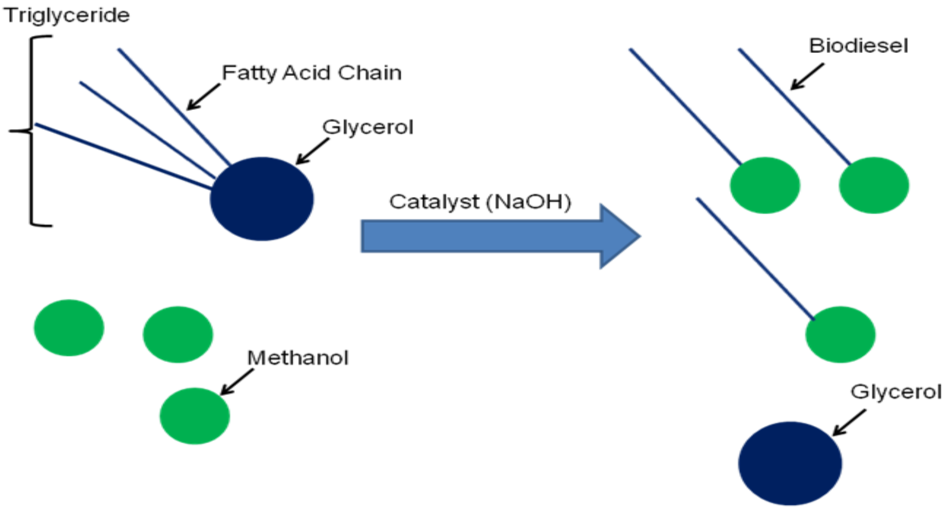


Fig.3 Transesterification process of Bio-diesel

Source : http://www.chemistryland.com/CHM107Lab/Exp04_biodiesel/BiodieselLab/Exp4Biodiesel.html

3. NEEM OIL METHYL ESTER (BIODIESEL) PREPARATION

Biodiesel is a diesel fuel that is made by reacting vegetable oil with other common chemicals. Bio-diesel may be used in any diesel automotive engine in its pure form or Blended with petroleum based diesel. No modifications are required and the result is less expensive, renewable and clean burning fuel.

3.1 Experimental setup

- The setup in which the methyl ester of neem oil was prepared consists of the following components.
- ➢ Conical bottle flask
- ➢ Condenser
- ➢ Silicon oil Bath
- ➢ Magnetic stirrer/Paddle
- ➢ Dimmer start
- ➢ Thermometer
- ➢ Weighing Machine
- ➢ Measuring Jar
- ➢ Separating Funnel
- Openings are provided in the round bottom flask for connecting condenser and temperature sensor.
- The heater coil surrounds the reactor vessel and it provides uniform heating all round the flask.
- The magnetic stirrer enables proper mixing of the neem oil and methanol. The speed of the stirrer is adjusted.
- Dimmer start is used to maintain constant temperature.
- Condenser is used to condense if any alcohol vaporizes from the mixture.
- Separating funnel helps to separate Bio diesel from glycerol.

3.2 Materials Used

- Raw Neem Oil
- Methanol
- Sodium Hydroxide
- Acetone
- Acetic acid

3.3 Making Biodiesel and B25

- First methanol (CH3OH) and accurately weighed sodium hydroxide (NaOH) (Catalyst) were mixed vigorously for 10-15 minutes.
- The sodium methoxide formed was mixed with the moisture free neem oil in round bottom flask.
- The magnetic stirrer and heaters were switched on.
- The speed of the magnetic stirrer is maintained at constant value.
- The temperature of the reactant is maintained at the required reaction Temperature.
- The dimmer start should be properly adjusted to control the voltage and thereby maintaining the temperature at 55-60°C
- Once the reaction time is over, the contents were emptied into a separating funnel.
- If the reaction is complete, two layers will be formed within few minutes.
- For proper separation, it should be allowed to settle for two to four hours.
- A thick red high viscous glycerol layer at the lower phase of the funnel. And the methyl ester of neem oil will be at the upper part of the funnel as shown in Fig 4.
- The methyl ester was washed with water, acetic acid and neutralized with water.
- Translucent Methyl Ester of Neem Oil is named as Bio Diesel.
- Taking 25 % of Neem Oil Methyl Ester and 75% of Diesel fuel.
- Blending both of them properly and this combination are called B25.

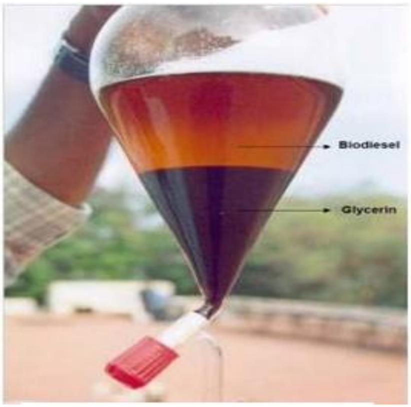


Fig. 4 Separation of Bio-diesel and Glycerin

3.4 Flow diagram of biodiesel production (NOME and B25)

A flow diagram of biodiesel production is shown in Fig. 5

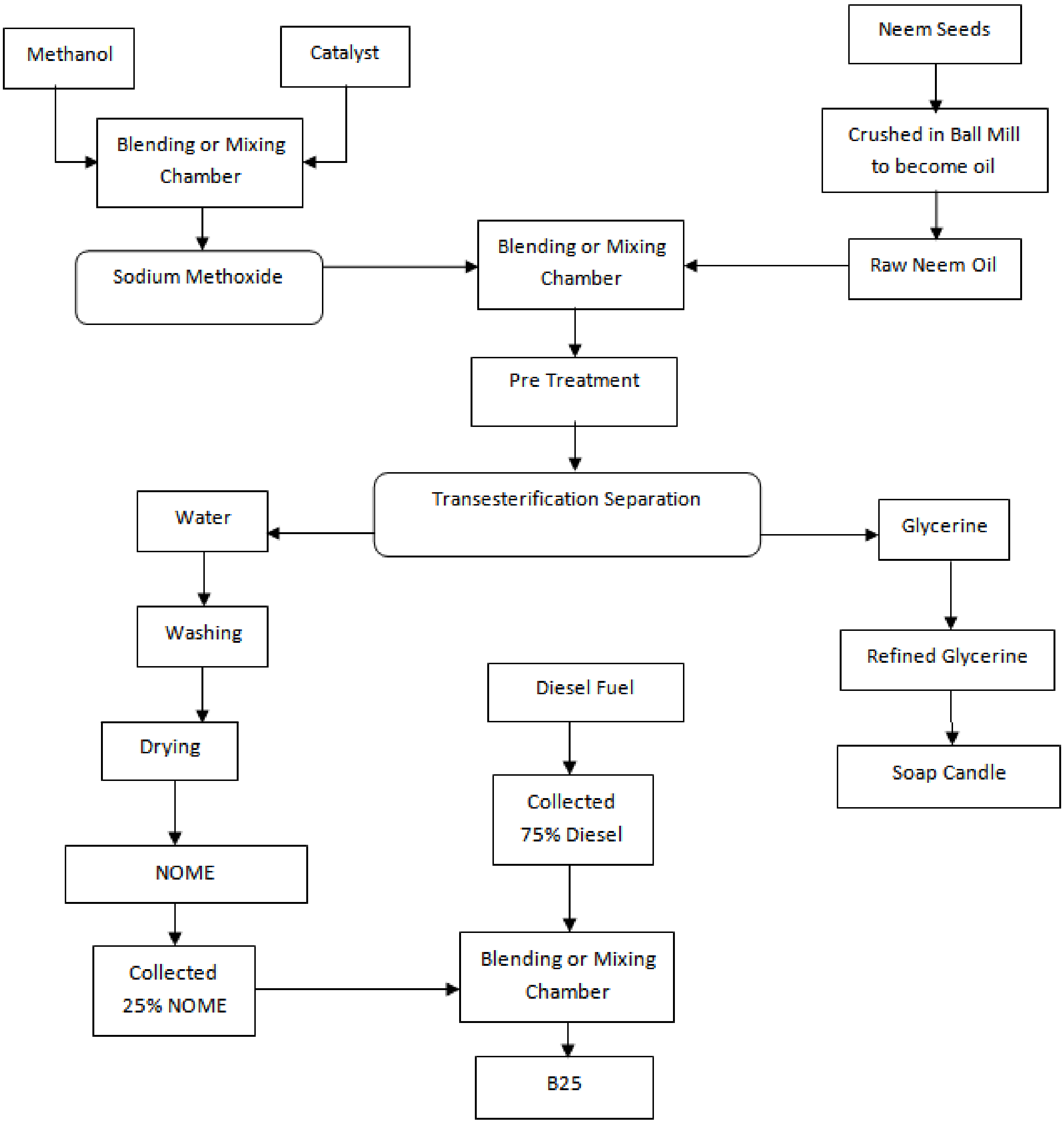


Fig. 5 Bio-diesel production (NOME and B25)

3.5 Fatty acids

Fatty acids are long carbon chains with a methyl group at one end of the molecule and a carboxyl group at the other end. The chain is typically straight linear and usually contains an even number of carbons. The chain length of carbons varies from 4 to 30. The most common range is 12 to 24. The general chemical formula is used as $\mathbf{C_nH_{2n+1}\ COOH\ or\ CH_3\ (CH_2)_n\ COOH}$ where n is the number of carbon atoms. The structure of Fatty acid is shown in Fig.6.

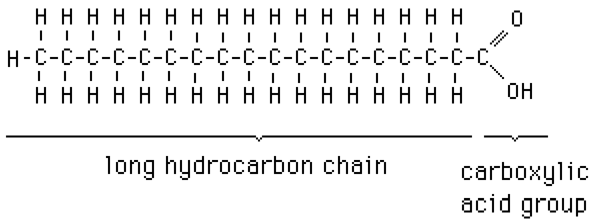


Fig.6 Structure of fatty acid

3.6 Classification of Fatty Acids

The classification of fatty acids are shown in Fig.7

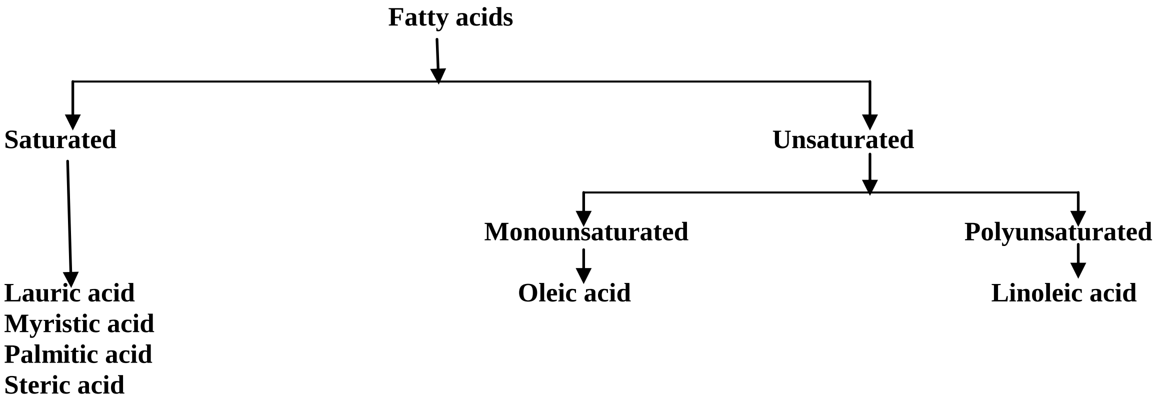


Fig.7 Classification of fatty acids

The fatty acids have been classified as saturated and unsaturated. The unsaturated is further classified into two groups namely monounsaturated and polyunsaturated.

3.6.1 Saturated fatty acids

Saturated fatty acids are "filled" (saturated) with hydrogen. Most saturated fatty acids of straight hydrocarbon chain with an even number of carbon atoms. In saturated fatty acid there is no double bond. Lauric acid, Myristic acid, palmetic acid and streric acid are belongs to saturated fatty acids. An example for 0 (zero) double bond is shown in Fig.8

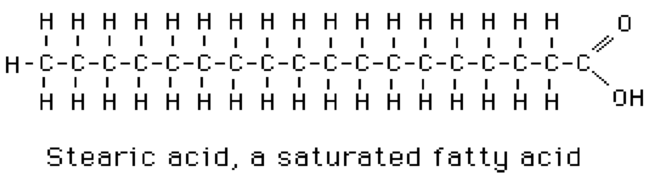


Fig.8 Stearic acid structural formula

3.6.2 Mono unsaturated fatty acids

The monounsaturated fatty acids have one single double bond. Olelic acid is a monounsaturated fatty acid and it is shown in Fig. 9.

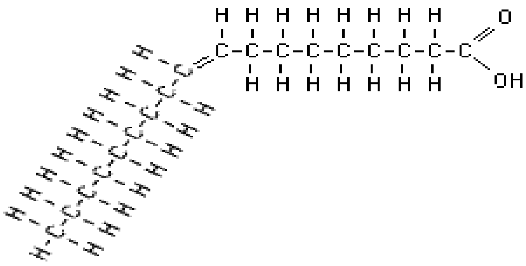


Fig.9 Oleic acid Structural formula

3.6.3 Polyunsaturated fatty acids.

The polyunsaturated fatty acid have two are more double bonds. An example for double bond polyunsaturated fatty acid is Linoleic acid and is shown in Fig.10

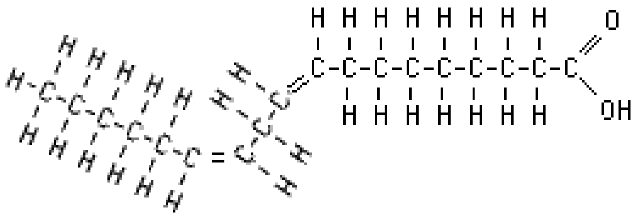


Fig.10 Linoleic acid structural formula

The chemical structures of fatty acids of Neem oil is shown in Table 2.

Table 2 Chemical structures of fatty acids of neem oil

Fatty acids	Structure	S/US	Formula	Structure	Molecular Weight	% by volume in the oil	Type of fatty acid
Palmitic	C16:0	S	$C_{16} H_{32} O_2$	$CH_3(CH_2)_{14}COOH$	256	10	
Stearic	C18:0	S	$C_{18} H_{36} O_2$	$CH_3(CH_2)_{16}COOH$	284	11	Saturated fatty acids
Myristic	C3:0	S	$C_3 H_6 O_2$	$CH_3(CH_2)_1COOH$	74	7	
Oleic	C18:1	US	$C_{18} H_{34} O_2$	$CH_3(CH_2)_7CH=CH$ $(CH_2)_7COOH$	282	30	Mono-unsaturated fatty acids
Linoleic	C18:2	US	$C_{18} H_{32} O_2$	$CH_3(CH_2)_4CH=CH$ CH_2 $CH=CH$ $(CH_2)_7COOH$	280	42	Poly-unsaturated fatty acids

Note : S- Saturated and US- Unsaturated

4. DERIVATION OF MOLECULAR AND STRUCTURAL FORMULA FOR NOME

The molecular and structural formula for NOME is derived from the composition of carbon, hydrogen and oxygen present in the fuel. The derivation is given below.

4.1 Chemical Reaction Method

Fatty acid

The main acids present in raw neem oil are

PALMITIC $\rightarrow C_{14}H_{28}O_2$

STEARIC $\rightarrow C_{17} H_{34} O_2$

LINOLEIC $\rightarrow C_{10} H_{20} O_2$

By taking into consideration of the raw neem oil composition, a general formula is arrived at as $C_{18}H_{35}O_2$ $\rightarrow$ fatty acid. To show it is in the form of an acid the structural formula with functional group is shown as $C_{17} H_{34} COOH$. COOH is a functional group to indicate carboxylic acid.

Glycerol

$CH_2OH - CHOH - CH_2OH$

Triglyceride

Neem oil is triglycerides of fatty acids that are composed of glycerol in combination of fatty acids. Since glycerol is having 3OH groups, three molecules of fatty acid are always associated with one molecule of glycerol. The formula for glyceride ester is $(C_{17}H_{34}COO)_3\ C_3H_5$

Methyl ester

The conversion of glyceride ester into methyl ester by the addition of methanol in the presence of catalyst sodium hydroxide (NaOH) can be written as

1. $(C_{17}H_{34}COO)_3C_3H_5 + 3NaOH \rightarrow 3C_{17}H_{34}\ COONa$
2. $3C_{17}H_{34}COONa + 3CH_3OH \rightarrow 3C_{17}H_{34}COOCH_3 + 3NaOH$
3. $C_{17}H_{34}COONa + CH_3\ OH \rightarrow C_{17}H_{34}\ COOCH_3 + NaOH$

The structural formula for NOME is $C_{17}H_{34}\ COOCH_3$.

4.2 Analytical method

The following are the percentage of combustion of a NOME

Carbon	: 76.76%
Hydrogen	: 12.10%
Oxygen	: 11.15%

The general chemical formula for any vegetable oil is $C_nH_mO_r$

The percentage of Carbon	$= C_n/(C_nH_mO_r)$	
0.7676	= 12n/(12n + m + 16r)	

Since it is an oxygenated fuel r can be taken as 2.

0.7676	= 12n/(12n + m +32)	
12n	= 0.7676 (12n + m +32)	
12n	= 9.2112n + 0.7676m +24.5692	
12n-9.2112n	= 0.7676m + 24.5692	
2.7888n – 0.7676m	= 24.5672	
n – 0.27524m	= 8.0995	(1)
The percentage of Hydrogen	$= H_m / (C_nH_mO_r)$	
0.121	= m/(12n+m+32)	
m	= 0.121 (12n +m +32)	
m	= 1.452n +0.121 m + 3.812	
m-0.121m – 1.452n	= 3.812	
0.819m – 1.452 n	= 3.812	
-n + 0.5640m	=2.6253	(2)
Add (1) and (2)		
0.28816 m	= 10.7248	
m	= 37.2182	
n-0.27524m	= 8.0995	
n-0.27524 x 37.21.82	= 9.0995	
n	= 8.0995 + 0.27524 x 37.2182	
n	= 18.343	

Taking n=19, m=37 and r=2

The molecular formula for Neem Oil Methyl Ester is $\mathbf{C_{19}\ H_{37}\ O_2}$

The Structural formula is $\mathbf{C_{17}\ H_{34}\ COO\ CH_3}$

4.3 Derivation of molecular and structrural formula for B25

Similar to NOME the molecular formula for B25 is also derived as given below

75% Diesel + 25% NOME

$0.75\ (C_{10}\ H_{22}) + 0.25\ (C_{17}H_{34}COOCH_3)$

$0.75\ (C_{10}\ H_{22}) + 0.25\ (C_{19}H_{37}O_2)$

$(0.75\ C_{10}\ 0.75\ H_{22}) + (0.25\ C_{19}\ 0.25H_{37}\ 0.25O_2)$

$(0.75\ C_{10} + 0.25\ C_{19})\ (0.75\ H_{22} + 0.25H_{37})\ (0.25O_2)$

(0.75*10 C + 0.25*19 C) (0.75*22 H + 0.25*37 H) (0.25 *2O)

(7.5 C + 4.75 C) (16.5 H + 9.25 H) 0.5 O

12.25 C 25.75 H 0.5 O

12.25*4 C 25.75*4 H 0.5*4 O

49C +103H + 2O

$C_{49}\ H_{103}\ O_2$

The Molecular formula of B25 is $\mathbf{C_{49}\ H_{103}\ O_2}$

The Structural Formula of B25 is $\mathbf{C_{47}\ H_{100}\ COOCH_3}$

5.THEORETICAL CALCULATIONS OF THE PROPERTIES OF DIESEL, NOME AND B25

5.1 AIR-FUEL RATIO OF DIESEL, NOME AND B25 by mass basis

The calculations of stoichiometric air-fuel ratio for various fuels used are given below.

5.1.1 A/F ratio of Diesel

Balanced chemical equation of Diesel

$C_{10}H_{22} + 15.5\ (O_2+3.76N_2) \rightarrow 10CO_2 + 11\ H_2O + 58.28N_2$

Reactant side Product side

$(A/F)_S$ by mass $= \frac{15.5\ (O_2 + 3.76N_2)}{C_{10}H_{22}}$

$= \frac{15.5\ (32 + 3.76 \times 28)}{10\times12 + 22\times1}$

$= 14.98$

$(A/F)_S$ by mass $= 15$

5.1.2 A/F ratio of NOME

Balanced chemical equation of NOME

$C_{17}H_{34}COOCH_3 + 27.25\ (O_2+3.76N_2) \rightarrow 19CO_2 + 18.5\ H_2O + 102.46N_2$

Reactant side Product side

$(A/F)_S$ by mass $= \frac{27.25\ (O_2 + 3.76N_2)}{C_{17}H_{34}COOCH_3}$

$= \frac{27.25\ (32 + 3.76 \times 28)}{19\times12 + 37\times1 + 2\times16}$

$= 12.595$

$(A/F)_S$ by mass $= 12.6$

5.1.3 A/F ratio of B25

Balanced chemical equation of B25

$C_{47}H_{100}COOCH_3 + 73.75\ (O_2+3.76N_2) \rightarrow 49CO_2 + 25.75\ H_2O + 277.3N_2$

Reactant side Product side

$(A/F)_S$ by mass $= \frac{73.75\ (O_2 + 3.76N_2)}{C_{47}H_{100}COOCH_3}$

$= \frac{73.75\ (32 + 3.76 \times 28)}{49\times12 + 103\times1 + 2\times16}$

$= 10124.4/723$

$(A/F)_S$ by mass $= 14.0$

5.2 AIR FUEL RATIO OF DIESEL, NOME AND B25 by mole basis

5.2.1 A/F ratio of Diesel

Balanced chemical equation of Diesel

$C_{10}H_{22} + 15.5\ (O_2+3.76N_2) \rightarrow 10CO_2 + 11\ H_2O + 58.28N_2$

Reactant side Product side

$(A/F)_S$ by mole basis $= \frac{15.5\ (O_2 + 3.76N_2)}{C_{10}H_{22}}$

$= \frac{15.5\ (1 + 3.76)}{1}$

$= 73.78$

$(A/F)_S$ by mole basis $= 74$

5.2.2 A/F ratio of NOME

Balanced chemical equation of NOME

$C_{17}H_{34}COOCH_3 + 27.25\ (O_2+3.76N_2) \rightarrow 19CO_2 + 18.5\ H_2O + 102.46N_2$

Reactant side Product side

$(A/F)_S$ by mole basis $= \frac{27.25\ (O_2 + 3.76N_2)}{C_{17}H_{34}COOCH_3}$

$= \frac{27.25\ (1 + 3.76\ )}{1}$

$= 129.71$

$(A/F)_S$ by mole basis $= 130$

5.2.3 A/F ratio of B25

Balanced chemical equation of B25

$C_{47}H_{100}COOCH_3 + 73.75\ (O_2+3.76N_2) \rightarrow 49CO_2 + 25.75\ H_2O + 277.3N_2$

Reactant side — Product side

$$(A/F)_S \text{ by mole basis} = \frac{73.75\ (O_2 + 3.76N_2)}{C_{47}H_{100}COOCH_3} = \frac{73.75\ (1 + 3.76)}{1} = 351.05$$

$(A/F)_S$ by mole basis = 351

5.3 PERCENTAGE OF CARBON, HYDROGEN AND OXYGEN BY WEIGHT OR MASS BASIS

5.3.1 Percentage of carbon and hydrogen for Diesel

The chemical formula for Diesel is $C_{10}H_{22}$

Molecular weight of Diesel = 12 x 10 + 1 x 22 = 142

Molecular weight of carbon = 12 x 10 = 120

Molecular weight of hydrogen = 22 x 1 = 22

Percentage of carbon in fuel (Diesel) = $\frac{Molecular\ weight\ of\ carbon\ in\ Diesel\ fuel}{Molecular\ weight\ of\ Diesel\ fuel}$ x 100

= (120/142)*100

= 84.5%

Percentage of Hydrogen in fuel (Diesel) = $\frac{Molecular\ weight\ of\ hydrogen\ in\ Diesel\ fuel}{Molecular\ weight\ of\ Diesel\ fuel}$ x 100

= (22/142)*100

= 15.5%

5.3.2 Percentage of carbon, hydrogen and oxygen for NOME

The chemical formula for NOME is $C_{17}H_{34}COOCH_3$

Molecular weight of NOME = 12 x 19 + 1 x 37 + 2 x 16 = 297

Molecular weight of carbon (NOME) = 12 x 19 = 228

Molecular weight of hydrogen (NOME) = 37 x 1 = 37

Molecular weight of oxygen (NOME) = 16 x 2 = 32

Percentage of carbon in fuel (NOME) = $\frac{Molecular\ weight\ of\ carbon\ in\ NOME\ fuel}{Molecular\ weight\ of\ NOME\ fuel}$ x 100

= (228/297)*100

= 76.8%

Percentage of hydrogen in fuel (NOME) = $\frac{Molecular\ weight\ of\ hydrogen\ in\ NOME\ fuel}{Molecular\ weight\ of\ NOME\ fuel}$ x 100

= (37/297)*100

= 12.4%

Percentage of oxygen in fuel (NOME) = $\frac{Molecular\ weight\ of\ oxygen\ in\ NOME\ fuel}{Molecular\ weight\ of\ NOME\ fuel}$ x 100

= (32/297)*100

= 10.8%

5.3.3 Percentage of carbon, hydrogen and oxygen for B25

The chemical formula for B25 is $C_{47}H_{100}COOCH_3$

Molecular weight of B25 = 12 x 49 + 1 x 103 + 16 x 2 = 723

Molecular weight of carbon (B25) = 12 x 49 = 588

Molecular weight of hydrogen (B25) = 1 x 103 = 103

Molecular weight of oxygen (B25) = 16 x 2 = 32

Percentage of carbon in fuel (B25) = $\frac{Molecular\ weight\ of\ carbon\ in\ B25\ fuel}{Molecular\ weight\ of\ B25\ fuel}$ x 100

= (588/723)*100

= 81.33%

Percentage of hydrogen in fuel (B25) = $\frac{Molecular\ weight\ of\ hydrogen\ in\ B25\ fuel}{Molecular\ weight\ of\ B25\ fuel}$ x 100

= (103/723)*100

= 14.25%

Percentage of oxygen in fuel (B25) = $\frac{Molecular\ weight\ of\ oxygen\ in\ B25\ fuel}{Molecular\ weight\ of\ B25\ fuel}$ x 100

= (32/723)*100

= 4.42%

5.4 HIGHER CALORIFIC VALUE OF DIESEL, NOME AND B25

5.4.1 Higher calorific value of Diesel

Higher calorific value of Diesel $= \frac{1}{100}[35000\,C + 143000\left(H - \frac{O}{8}\right) + 9160\,S]$

$= \frac{1}{100}[35000 * 84.5 + 143000\,(15.5 - 0) + 9160 * 0]$

= 51740 kJ/kg

5.4.2 Higher calorific value of NOME

Higher calorific value of NOME $= \frac{1}{100}[35000\,C + 143000\left(H - \frac{O}{8}\right) + 9160\,S]$

$= \frac{1}{100}[35000 * 76.76 + 143000\,(12.45 - \frac{10.77}{8}) + 9160 * 0]$

= 42744 kJ/kg

5.4.3 Higher calorific value of B25

Higher calorific value of B25 $= \frac{1}{100}[35000\,C + 143000\left(H - \frac{O}{8}\right) + 9160\,S]$

$= \frac{1}{100}[35000 * 81.33 + 143000\,(14.25 - \frac{4.42}{8}) + 9160 * 0]$

= 48053 kJ/kg

5.5 LOWER CALORIFIC VALUE OF FUEL DIESEL, NOME AND B25

5.5.1 Lower calorific value of Diesel

Lower calorific value of Diesel = Higher calorific value - $\frac{9}{100}\ x\ H\ x\ \ 2460$

= 51740 - $\frac{9}{100}\ x\ 15.5\ x\ \ 2460$

= 48308 kJ/kg

5.5.2 Lower calorific value of NOME

Lower calorific value of NOME = Higher calorific value - $\frac{9}{100}\ x\ H\ x\ \ 2460$

= 42744 - $\frac{9}{100}\ x\ 12.45\ x\ \ 2460$

= 39999 kJ/kg

5.5.3 Lower calorific value of B25

Lower calorific value of B25 = Higher calorific value - $\frac{9}{100}\ x\ H\ x\ \ 2460$

= 48053 - $\frac{9}{100}\ x\ 14.25\ x\ \ 2460$

= 44898 kJ/kg

5.6 PERCENTAGE OF FUEL, AIR IN THE REACTANT SIDE FOR DIESEL NOME AND B25.

5.6.1 % of fuel and air in the reactant side of Diesel fuel

Balanced chemical equation of Diesel on the reactant side is shown below

$C_{10}H_{22}$ + 15.5 (O_2+3.76N_2)

The total molecular weight of reactant side =12 x10 + 1 x22 +15.5 (16 x 2 + 3.76*14 x 2)

=120+22+15.5 (32 +28 x 3.76) = 2269.84

Molecular formula of Diesel fuel = $C_{10}H_{22}$

Molecular weight of Diesel fuel = 12 x 10 + 1x 22 = 142

Molecular formula of air in the Diesel fuel = 15.5 (O_2+3.76N_2)

Molecular weight of air in the Diesel fuel = 15.5 (16 x 2+ 3.76 x 14 x 2) = 2127.84

Percentage of Diesel fuel in the reactant side $= \frac{Molecular\ \ weight\ of\ Diesel\ fuel}{Total\ molecular\ \ weight\ of\ reactant\ \ side}\ x\ 100$

$= \frac{142}{2269.84}\ x\ 100$ = 6.26 %

Percentage of Air in the Diesel fuel $= \frac{Molecular\ \ weight\ of\ air\ in\ the\ Diesel\ fuel}{Total\ molecular\ \ weight\ of\ reactant\ \ side}\ x\ 100$

$= \frac{2127.84}{2269.84}\ x\ 100$ = 93.74%

5.6.2 % of fuel and air in the reactant side of NOME fuel

Balanced chemical equation of NOME on the reactant side is shown below

$C_{17}H_{34}COOCH_3$ + 27.25 (O_2+3.76N_2)

The total molecular weight of reactant side =12 x19 + 1 x 37+ 16 x 2+27.25 (16 x 2 + 3.76*14 x 2)

=228+37+32+27.25 (32 +28 x 3.76)

= 228+37+32+3740.88

= 4037.88

Molecular formula of NOME fuel = $C_{17}H_{34}COOCH_3$
Molecular weight of NOME fuel = 12 x 19 + 1x 37 + 16 x 2 = 297
Molecular formula of air in the NOME fuel = 27.25 (O_2+3.76N_2)
Molecular weight of air in the NOME fuel = 27.25 (16 x 2+ 3.76 x 14 x 2) = 3740.88
Percentage of NOME fuel in the reactant side $= \frac{Molecular\ weight\ of\ NOME\ fuel}{Total\ molecular\ weight\ of\ reactant\ side}\ x\ 100$

$= \frac{297}{4037.88}\ x\ 100 = 7.36\ \%$

Percentage of Air in the NOME fuel $= \frac{Molecular\ weight\ of\ air\ in\ the\ NOME\ fuel}{Total\ molecular\ weight\ of\ reactant\ side}\ x\ 100$

$= \frac{3740.88}{4037.88}\ x\ 100 = 92.64\%$

5.6.3 % of fuel and air in the reactant side of B25 fuel

Balanced chemical equation of B25 on the reactant side is shown below

$C_{47}H_{100}COOCH_3$ + 73.75 (O_2+3.76N_2)

The total molecular weight on reactant side =12 x49 + 1 x 103 + 16 x 2+73.75 (16 x 2 + 3.76*14 x 2)
=588+103+32+73.75 (32 +28 x 3.76)
= 723+10124.4 = 10847.4

Molecular formula of B25 fuel = $C_{47}H_{100}COOCH_3$
Molecular weight of B25 fuel = 12 x49 + 1 x 103 + 16 x 2 = 723
Molecular formula of air in the B25 fuel = 73.75 (O_2+3.76N_2)
Molecular weight of air in the B25 fuel = 73.75 (16 x 2+ 3.76 x 14 x 2) = 10124.4
Percentage of B25 fuel in the reactant side $= \frac{Molecular\ weight\ of\ B25\ fuel}{Total\ molecular\ weight\ of\ reactant\ side}\ x\ 100$

$= \frac{723}{10847.4}\ x\ 100 = 6.67\ \%$

Percentage of Air in the B25 fuel $= \frac{Molecular\ weight\ of\ air\ in\ the\ B25\ fuel}{Total\ molecular\ weight\ of\ reactant\ side}\ x\ 100$

$= \frac{10124.4}{10847.4}\ x\ 100 = 93.33\%$

5.7 % OF CO_2, H_2O AND N_2 ON THE PRODUCT SIDE OF DIESEL, NOME AND B25 FUEL.

5.7.1 % of CO_2, H_2O and N_2 for Diesel fuel

Balanced chemical equation of Diesel on the product side is shown below

10CO_2 + 11 H_2O + 58.28N_2

The total molecular weight on product side = 10 (12x1 + 16x2) + 11(1x2 + 16x1) + 58.28 (14x2)
= 440 + 198 + 1631.84 = 2269.84

Percentage of CO_2 in Diesel fuel $= \frac{Molecular\ weight\ of\ carbon\ dioxide\ in\ the\ Diesel\ fuel}{Total\ molecular\ weight\ of\ product\ side}\ x\ 100$

Percentage of CO_2 in Diesel fuel $= \frac{440}{2269.84}\ x\ 100\ = 19.38\ \%$

Percentage of H_2O in Diesel fuel $= \frac{Molecular\ weight\ of\ water\ vapour\ in\ the\ Diesel\ fuel}{Total\ molecular\ weight\ of\ product\ side}\ x\ 100$

Percentage of H_2O in Diesel fuel $= \frac{198}{2269.84}\ x\ 100\ = 8.72\ \%$

Percentage of N_2 in Diesel fuel $= \frac{Molecular\ weight\ of\ nitrogen\ in\ the\ Diesel\ fuel}{Total\ molecular\ weight\ of\ product\ side}\ x\ 100$

Percentage of N_2 in Diesel fuel $= \frac{1631.84}{2269.84}\ x\ 100\ = 71.90\ \%$

5.7.2 % of CO_2, H_2O and N_2 for NOME fuel

Balanced chemical equation of NOME on the product side is shown below

19CO_2 + 18.5 H_2O + 102.46N_2

The total molecular weight on product side = 19 (12x1 + 16x2) + 18.5(1x2 + 16x1) + 102.46 (14x2)
=836 + 333 + 2868.88 = 4037.88

Percentage of CO_2 in NOME fuel $= \frac{Molecular\ weight\ of\ carbon\ dioxide\ in\ the\ NOME\ fuel}{Total\ molecular\ weight\ of\ product\ side}\ x\ 100$

Percentage of CO_2 in NOME fuel $= \frac{836}{4037.88}\ x\ 100\ = 20.70\ \%$

Percentage of H_2O in NOME fuel $= \frac{Molecular\ weight\ of\ water\ vapour\ in\ the\ NOME\ fuel}{Total\ molecular\ weight\ of\ product\ side}\ x\ 100$

Percentage of H_2O in NOME fuel $= \frac{333}{4037.88}\ x\ 100\ = 8.25\ \%$

Percentage of N_2 in NOME fuel $= \frac{Molecular\ \ weight\ of\ nitrogen\ \ in\ the\ NOME\ fuel}{Total\ molecular\ \ weight\ of\ product\ \ side}\ x\ 100$

Percentage of N_2 in NOME fuel $= \frac{2868.88}{4037.88}\ x\ 100$ = 71.05 %

5.7.3 % of CO_2, H_2O and N_2 for B25 fuel

Balanced chemical equation of Diesel on the product side is shown below

$49CO_2 + 25.75\ H_2O + 277.3N_2$

The total molecular weight on product side = 49 (12x1 + 16x2) + 25.75(1x2 + 16x1) + 277.3 (14x2)
=2156 + 463.5 + 7764.4 = 10383.9

Percentage of CO_2 in B25 fuel $= \frac{Molecular\ \ weight\ of\ carbon\ \ dioxide\ \ in\ the\ B25\ fuel}{Total\ molecular\ \ weight\ of\ product\ \ side}\ x\ 100$

Percentage of CO_2 in B25 fuel $= \frac{2156}{10383.9}\ x\ 100$ = 20.77 %

Percentage of H_2O in B25 fuel $= \frac{Molecular\ \ weight\ of\ water\ \ vapour\ \ in\ the\ B25\ fuel}{Total\ molecular\ \ weight\ of\ product\ \ side}\ x\ 100$

Percentage of H_2O in B25 fuel $= \frac{463.5}{10383.9}\ x\ 100$ = 4.46 %

Percentage of N_2 in B25 fuel $= \frac{Molecular\ \ weight\ of\ nitrogen\ \ in\ the\ B25\ fuel}{Total\ molecular\ \ weight\ of\ product\ \ side}\ x\ 100$

Percentage of N_2 in B25 fuel $= \frac{7764.4}{10383.9}\ x\ 100$ = 74.77 %

5.8 ACTUAL AIR FUEL RATIO FOR DIESEL, NOME AND B25

The general formula used for calculating the actual air fuel ratio for any fuel is given below

$$(\frac{A}{F})_{actual} = \frac{N_2C}{33\ (CO + CO_2)}$$

Where

CO_2 - Percentage of carbon dioxide by volume.

CO – Percentage of carbon monoxide by volume.

O_2 – Percentage of oxygen by volume.

N_2 – Percentage of nitrogen by volume. = 100 – (CO+CO_2+O_2)

C – Percentage of carbon by weight in a given fuel.

Note : The values of CO_2, O_2, CO and N_2 is recorded from the exhaust gas analyser while experiment is conducted in a given engine.

5.8.1 Actual air-fuel ratio for Diesel

The products of combustion of Diesel fuel in volume by percentage are given below

CO=0.01%, CO_2=9%, O_2=10%, N_2=100–(10+0.01+9)=81 % and C= 84.5% (by weight)

$$(\frac{A}{F})_{actual} = \frac{N_2\mathrm{C}}{33\ (CO + CO_2)}$$

$$(\frac{A}{F})_{actual} = \frac{81\ x\ 84.5}{33\ (0.01 + 9)}$$

$(\frac{A}{F})_{actual}\ for\ Diesel\ fuel = 23$ kg/kg of fuel

5.8.2 Actual air-fuel ratio for NOME

The products of combustion of NOME fuel in volume by percentage are given below

CO=0.02%, CO_2=9.6%, O_2=9.3%, N_2=100–(0.02+9.6+9.3)=81.1 % and C= 76.8% (by weight)

$$(\frac{A}{F})_{actual} = \frac{N_2C}{33\ (CO + CO_2)}$$

$$(\frac{A}{F})_{actual} = \frac{81.1\ x\ 76.8}{33\ (0.02 + 9.3)}$$

$(\frac{A}{F})_{actual}\ for\ NOME\ fuel = 20.3$ kg/kg of fuel

5.8.3 Actual air-fuel ratio for B25

The products of combustion of B25 fuel in volume by percentage are given below

CO=0.03%, CO_2=9 %, O_2=9%, N_2=100–(0.03+9+9)=81.97 % and C= 81.33% (by weight)

$$(\frac{A}{F})_{actual} = \frac{N_2C}{33\ (CO + CO_2)}$$

$$(\frac{A}{F})_{actual} = \frac{81.97\ x\ 81.33}{33\ (0.03 + 9)}$$

$(\frac{A}{F})_{actual}\ for\ B25\ fuel = 22.37$ kg/kg of fuel

5.9 PERCENTAGE OF EXCESS AIR IN A FUEL FOR DIESEL, NOME AND B25

5.9.1 Percentage of excess air for Diesel fuel

Percentage of excess air for Diesel = $\frac{\text{Actual air fuel ratio of Diesel} - \text{stomichiometric air fuel ratio of Diesel}}{\text{Stomichiometric air fuel ratio of Diesel}} \times 100$

$= \frac{23-15}{15} \times 100 = 53.33$ %

5.9.2 Percentage of excess air for NOME fuel

Percentage of excess air for NOME = $\frac{\text{Actual air fuel ratio of NOME} - \text{stomichiometric air fuel ratio of NOME}}{\text{Stomichiometric air fuel ratio of NOME}} \times 100$

$= \frac{20.3-12.6}{12.6} \times 100 = 61$ %

5.9.3 Percentage of excess air for B25 fuel

Percentage of excess air for B25 = $\frac{\text{Actual air fuel ratio of B25} - \text{stomichiometric air fuel ratio of B25}}{\text{Stomichiometric air fuel ratio of B25}} \times 100$

$= \frac{22.37-14}{14} \times 100 = 59.79$ %

6. CALCULATION OF CETANE NUMBER OF DIESEL, NOME AND B25

Introduction

The fuel properties of bio-diesel play a significant role in the combustion process. One of such prop erties is cetane number. It influences the combustion process and the engine performance. The cetane number is commonly used indicator for the determination of Diesel fuel ignition and quality. It measures the readiness of the fuel to auto-ignite when injected into the engine. Many performance characteristics such as density, heating value are related to cetane number. Cetane number is the parameter used to determine the quality of bio-diesel. It is proportionate to the fuel delay time in CI engine.

Cetane of a fuel is define as the percentage by volume of normal cetane in a mixture of normal cetane and α-methyl naphthalene which has the same ignition characteristics (ignition delay) as the test fuel, when combustion is carried out in astandard engine under specified operating condition. Afuel of higher cetane number gives lower delay period and provides smoother engine operation. Bio-diesel has a higher cetane number than petro-diesel because of its higher oxygen content. The ignition delay is defined as the time period between the start of the injection of the fuel and the start of the combustion of the fuel (commonly known as ignition).

Benefits of cetane number

A higher cetane number, indicating a shorter ignition delay time, usually means more complete combustion of the fuel. This translates into:

- The faster the fuel will ignite and the more completely it will burn.
- Improved cold starts.
- Improved fuel efficiency
- A reduction of harmful emissions such as hydrocarbon, carbon monoxide and particulate matter.
- Less wear and tear on the starter and batteries
- Quicker pumping of protective lubricating fluids throughout the system
- Less engine noise and knocking.
- Reduced white smoke and warm-up-time.
- Fewer misfires
- Higher energy content
- Significantly improves combustion efficiency.
- More power.

6.1 Calculation of cetane number for Diesel

According to Stavrovet.al (1981) Diesel cetane number is expressed as follows

Cetane number of Diesel = $(KE_{20} + 17.8)(\frac{1.5879}{DE_{20}})$

Where KE_{20} = Kinematic viscosity of Diesel fuel at 20°C in mm^2/sec

DE_{20} = Density of Diesel fuel at 20°C in g/cm^3

The KE20 = 4

DE20 = 0.85

Cetane number of Diesel $= (4+17.8)(\frac{1.5879}{0.85})$

$= 40.72$

$= 41$(say)

6.2 Calculation of cetane number for NOME

A recursion analysis was used to develop an equation to estimate the cetane number of NOME using the given fatty acid profile, The equation obtained to credit the cetane number is given by the equation below.

Cetane No = 61.3+0*L+0.1025*M+0.133*P+0.152*S-0.001*PA–0.037*O-0.243*LI-0.395 * LINO

Where

L - Percentage of Lauritic fatty acids
M - Percentage of Mystic fatty acids
P - Percentage of Palmitic fatty acids
S - Percentage of Stearic fatty acids
PA - Percentage of Palmitoleic fatty acid
O - Percentage of Oleic fatty acid
LI - Percentage of Linolic fatty acid
LINO - Percentage of Linolenic fatty acid

Cetane Number = 61.3+0.1025*M+0.133*P+0.152*S-0.0376*O-0.243*LI
= 61.3+0.1025*7+0.133*10+0.152*11-0.0376*30-0.243*42
Cetane number = 53.68 = 54 (say)

6.3 Calculation of Cetane number of B25

Cetane number of B25 = 75% of Diesel cetane number + 25% of NOME cetane number
= 0.75 * 41 + 0.25 * 54
= 44.25

Note: The percentage of free fatty acids have been taken from the table 3.

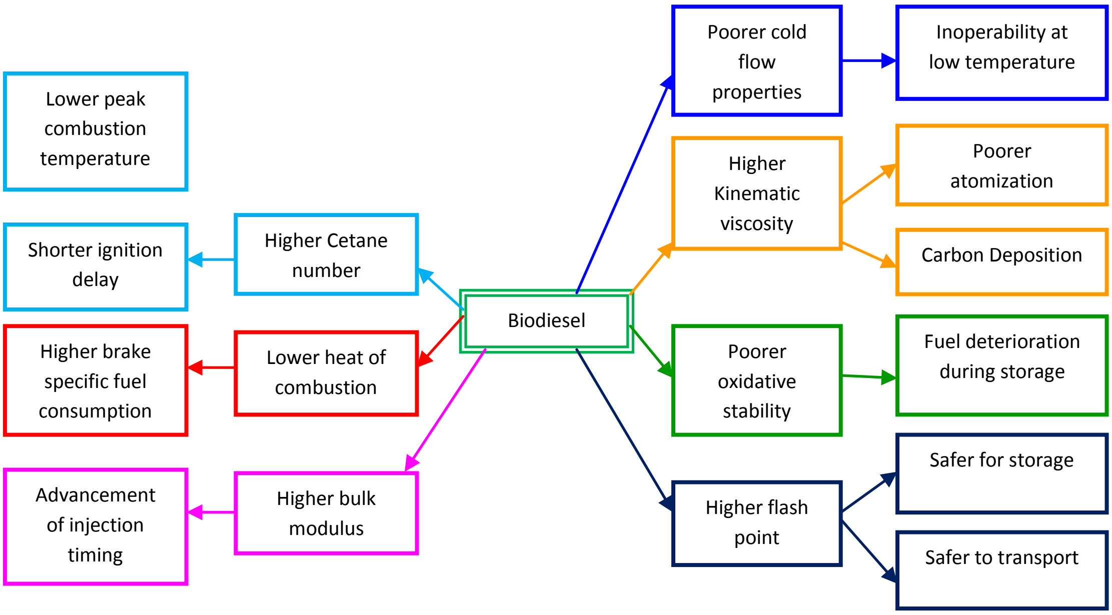
Table 3 Calculated values of properties of fuels

Property	Diesel	NOME (100%)	B25
Chemical formula	$C_{10}H_{22}$	$C_{19}H_{37}O_2$	$C_{49}H_{103}O_2$
Stochiometric Air Fuel ratio (by weight)	15	12.6	14
Stochiometric Air Fuel ratio (by mole)	74	130	351
% of carbon (by weight)	84.5	76.8	81.33
% of hydrogen (by weight)	15.5	12.4	14.25
% of oxygen (by weight)	-	10.8	4.42
Higher calorific value of fuel(MJ/kg)	51.74	42.74	48.05
Lower calorific value of fuel (MJ/kg)	48.31	39.99	48.9
% of fuel	6.26	7.36	6.67
% of air	93.74	92.64	93.33
% of CO_2	19.38	20.7	20.77
% of H_2O	8.72	8.25	4.46
% of N_2	71.9	71.05	74.77
Actual A/F ratio	23	20.3	22.37
% of excess air	53.33	61	59.79
Cetane number	41	54	44.25
Density @ 25°C(g/cc)	0.85	0.880	0.86
C/H ratio by Weight basis	5.45	6.19	5.71

7. BIO-DIESEL

Bio-diesel is defined as the mono-alkyl esters of fatty acids derived from vegetable oils and animal fats. In simple terms bio-diesel is the product obtained when a vegetable oils or animal fat is chemically reacted with an alcohol to produce fatty acid alky esters. A catalyst such as potassium or sodium hydroxide is required. Glycerol is produced as a co-product or a by-product. The approximate proportions of the reaction are 100 kg of oil + 10 kg of methanol → 100 kg of Bio-diesel + 10 kg of glycerol.

The bio-diesel properties and their associated impact on engine operation, storage and transportation as compared to fossil fuel are shown in Fig.11.



(Source: Jo-Han Ng et al. 2009)

Fig. 11 Bio-diesel fuel properties and their associated impact on engine operation, storage and transportation as compared to fossil fuel

The properties of bio-diesel are, has better lubricating properties, bio-diesel addition reduces the fuel system wear, the higher cetane number gives shorter ignition delay and lower peak temperature, the lower heat of combustion provide higher brake specific fuel consumption, the higher bulk modulus enable advancement of injection timing, poor cold flow properties give in-operability at low temperature, higher kinematic viscosity enables fuel deterioration during storage, high flash point provides safe storage and transportation and more complete combustion thus increasing the engine energy output and partially compensating for higher energy density of petro-diesel.

The properties of bio-diesel have an effect on emissions as given below:

- Higher cetane number of bio-diesel enables shorter ignition delay period, lower peak temperature and a reduction in NOx.
- Higher bulk modulus of bio-diesel provides advancement in injection timing, stronger pre-mixed combustion phase, higher peak temperature and NOx increase.
- Higher oxygen content of bio-diesel enables limited rich combustion, more complete combustion, high peak temperature, NOx increase, CO, HC and particulate decrease.
- Higher kinematic viscosity enables spray droplets with larger mean size, slower evaporation, incomplete combustion, HC and particulates increased.
- Lower aromatics content leads to lower adiabatic flame temperature and NOx decrease.
- Lower sulphur content provides lesser sulphate adsorption on soot and decreased particulates **(**Jo-Han Ng et al. 2009).

Reasons for encouraging the development of bio-diesel:

- It provides a market for excess production of vegetable oils and animal fats.
- It decreases the countries dependence on imported petroleum.
- Bio-diesel is renewable and does not contribute global warming due to its closed carbon cycle.
- Bio-diesel has excellent lubricating properties and hence the life of span is increased.
- The exhaust emissions from bio-diesel are lower than with regular Diesel fuel (Van Gerpen et al. 2004).

Direct impact and corresponding interaction of bio-diesel properties on emissions as compared to fossil Diesel are shown in Fig. 12.

*PAH – Polycyclic aromatic hydrocarbons, **MAH – Monocyclic aromatic hydrocarbons, ***PM - particulate matter

(Source: Jo-Han Ng et al. 2009)

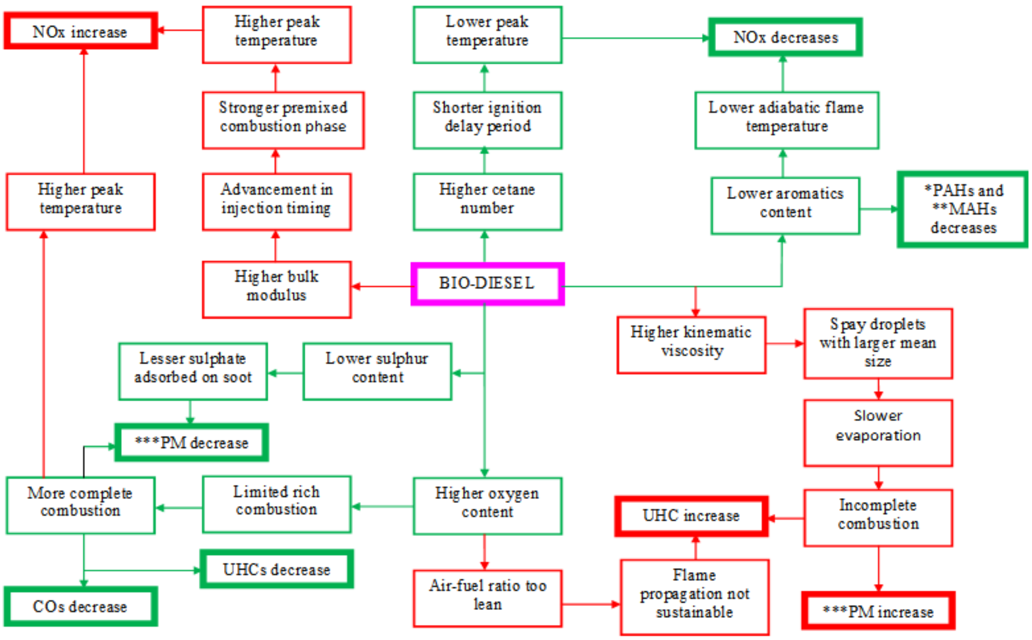


Fig. 12 Direct impact and corresponding interaction of biodiesel properties on emission compared to fossil Diesel

The benefits of bio-diesel are:

- Higher combustion efficiency due to higher oxygen content improves the combustion process.
- Compatible with catalyst for emission control due to lower sulphur content thus reducing catalyst poisoning.
- Bio-diesel can be used in the existing engine without any modifications
- Bio-diesel obtained from vegetable sources does not contain any sulfur, aromatic hydrocarbons, metals or crude oil residues.
- Bio-diesel is an oxygenated fuel, and hence emissions of carbon monoxide and soot tend to reduce.
- Bio-diesel has been classified as a non-flammable liquid by the occupational safety and health administration.
- Bio-diesel is mostly obtained from renewable vegetable oils or animal fats and hence it may improve the fuel or energy security thus leading to economy independence.
- Esters have lower viscosity than the parent oils. Accordingly they improve the injection process and ensure better atomisation of the fuel in the combustion chamber.
- Cetane number of esters is greater than those of both vegetable oils and No.2 Diesel fuel.
- 90% reduction in cancer risks.
- Provides a domestic and renewable energy supply.
- Bio-diesel is bio-degradable and non-toxic
- Bio-diesel has a high flash point and ignition temperature of about 149°C compared to petroleum Diesel fuel of 52°C, hence it is safer to transport.
- Auto ignition, fuel consumption, power output and engine torque are relatively unaffected by bio-diesel.
- Bio-diesel is an oxygenated fuel thus implying that their oxygen content plays a role in making fatty compounds suitable as a Diesel fuel by "cleaner" burning (Babu et al. 2003).

Bio-diesel has the following limitations:

- Bio-diesel is not economical
- Energy is required to produce bio-diesel fuel from plants for sowing, fertilising, harvesting etc.
- Use of bio-diesel decreases engine power compared to Diesel.

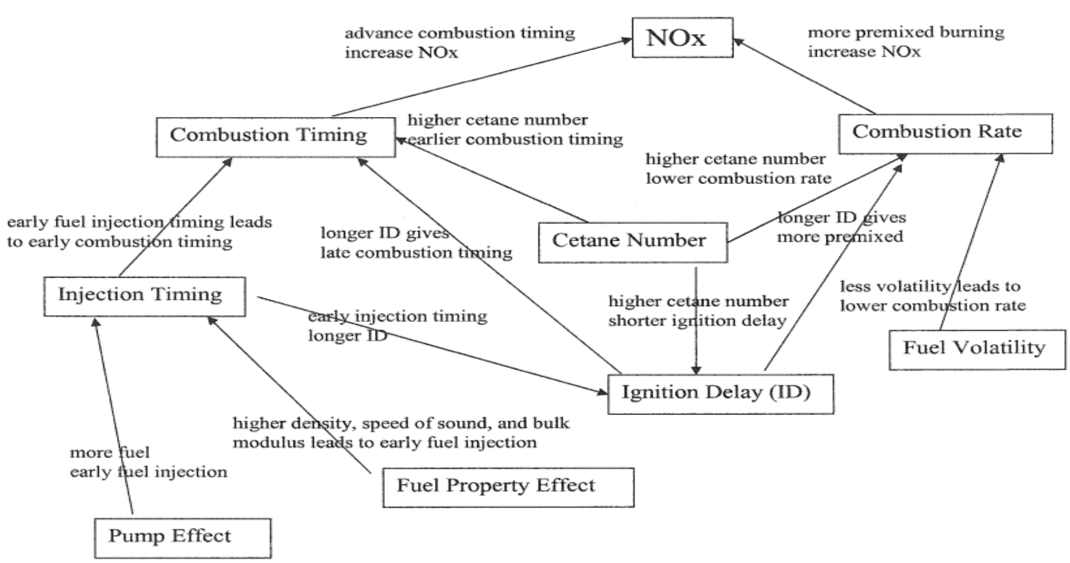
- Bio-diesel has higher NOx emissions compared to Diesel.
- Bio-diesel has to be used as soon as it produced. The fuel quality of bio-diesel is susceptible to deterioration after long term use or storage, particularly in high temperature or pressure operating environments. Oxidation and thermal stability of bio-diesel are poor. Hence, antioxidants are added to bio-diesel to improve them.
- Seals, hoses, glues, plastics and gaskets that are exposed to bio-diesel for a prolonged period may experience softening, seepage or degradation. Hence Nylon, Viton, Teflon and fluorinated plastics have been found to be compatible in place of polyvinyl, polypropylene, Tygon and Nitrile rubber compounds which are particularly incompatible with bio-diesel.
- Bio-diesel's cloud and pour point are higher than those of petro-diesel which can cause fuel lines and filters to clog in cold weather. Adequate cold flow improver must be used with bio-diesel.
- Water content of bio-diesel cause problems in engines (Bhaskar et al. 2014).

8. CONCEPT OF OXIDES OF NITROGEN

NOx production of Diesel engines is very complex, because it is influenced by many factors and many of these factors interact at different levels. The concept map depicted in Figure 13 shows the interrelationships between NOx emissions and the Diesel engine combustion parameters, such as combustion timing and premixed combustion.

As shown in Fig. 13, there are two main combustion characteristics that will determine the temperature in the cylinder and thus the NOx emission. These are the combustion timing and combustion rate. Combustion timing relates to the start of combustion relative to the piston position in the cylinder. Early combustion timing causes combustion to occur closer to TDC and during the compression process, increasing the pressure, temperature, and NOx emission (Lyn et al. 1968). The cetane number of biodiesel is higher than Diesel fuel. Higher cetane number shortens the ignition delay time and advances the combustion timing. Early injection timing and higher cetane number advance the combustion timing which tends to increase the NOx emission (Wong et al. 1982). Biodiesel has lower energy content than Diesel fuel and when a greater volume of fuel is injected, some fuel injection pumps will advance the start of injection timing, causing an additional increase in NOx emission. Biodiesel also has different physical properties such as higher density, speed of sound, and bulk modulus, which can also lead to an earlier start of injection (Tat et al. 1999).

Combustion rate, as indicated by the heat release rate, also has an effect on NOx production. More premixed combustion means a high initial rate of combustion which increases NOx emission. Premixed combustion corresponds to the fuel that is mixed with air and prepared to burn during the ignition delay period. When this fuel auto ignites it usually bums very quickly. Cetane number and fuel volatility are the two most important fuel properties that determine the combustion rate. High cetane number and low volatility lowers the combustion rate.



(Source: Mustafa Ertunc Tat 2003)

Fig. 13 Concept map of NOx emission and combustion characteristics

9. COST ANALYSIS

Introduction

Any product introduced in the market is dependent upon the cost factor as it is embedded in human mind, as to what it will cost to buy the new product when compared to products available already in the market.
An estimation of small bio-diesel production cost from Neem seeds have been undertaken on average production per month which accounts crushing 3000 kgs of neem seeds.

Production unit: A small bio-Diesel production unit needs the following equiptments, apparatus and glass wares for producing Neem oil methyl ester and B25.

- decorticator,
- oil expeller with capacity of 40 kgs per hour,
- settling tank,
- micro-filtration unit,
- trans-esterification unit and
- other instruments like hot air oven,
- pensky apparatus for flash and fire point,
- hydrometer,
- kinematic viscometer and
- all the glass wares.

The total production unit for calculation of production cost of biodiesel Neem oils it a capacity of 25 kgs works out of Rs.10 lakhs which includes the mentioned equipments.

Chemicals and Reagents: The production of biodiesel from neem seeds have been taken through transesterification process. Transesterification is the process of exchanging of organic group R' of an ester with organic group R' of an alcohol (methanol or ethanol). These reactions are often catalysed by the addition of an acid (H_2SO_4) or (NaOH or KOH) as catalyst and which requires the following chemicals and reagents under the study alkali method was employed because free fatty acids of Neem is less than 5%. The Chemical and Reagent need for biodiesel production for 3000 kgs of Neem seeds is shown in Table 4.

Table 4 Chemical and Reagent need for biodiesel production for 3000 kgs of Neem seeds.

S. No.	List of Chemicals and Reagents	Quantity	Rate per unit/litre/kg	Amount in Rs.
1.	Iso propyl alcohol	1 litre	1000	1000
2.	Phonolphthalein Indicator	1 litre	100	100
3.	Methanol	200 litres	60	12000
4.	Sodium hydroxide	5 kgs	300	1500
Total				14600

Products obtained in the bio-diesel production process: The clean seeds were crushed in mechanical expeller. During the process seed cake have been obtained as by product and oil as major product. The oil have been subjected to transesterification where oil have been converted to bio-diesel and glycerine and it is shown in Table 5.

Table 5 products obtained in the process of biodiesel production for 3000 kgs of neem seeds.

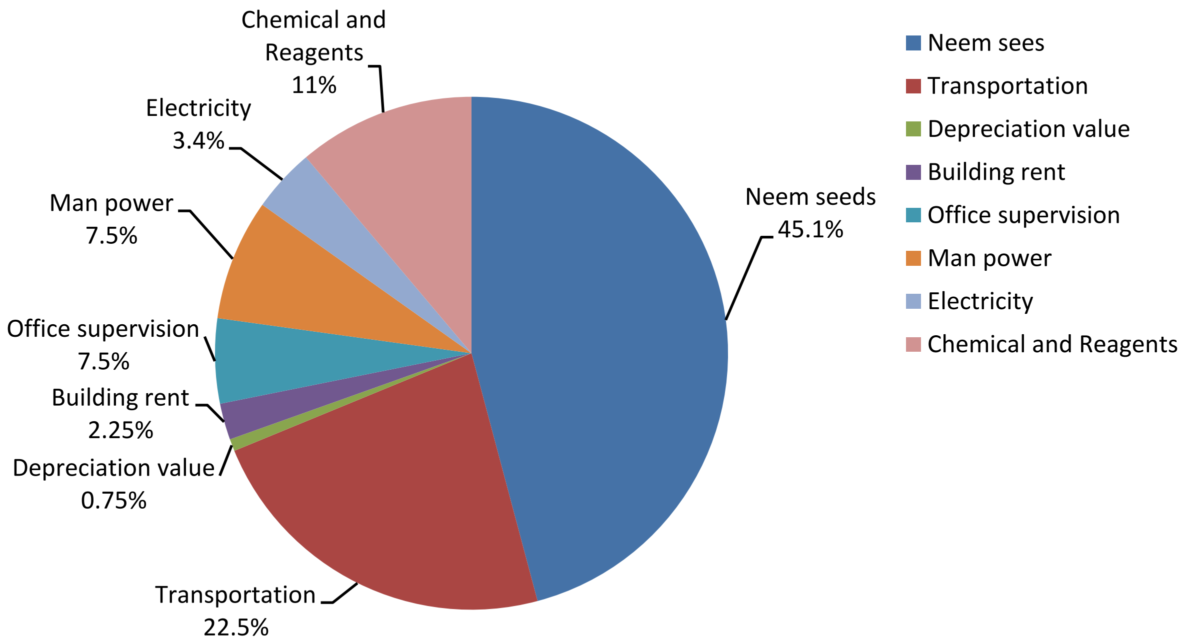
S.no.	Products	Quantity
1.	Neem oil	750 litres
2.	Neem seed cake	2000 kgs
3.	Bio-diesel (Neem oil methyl ester)	700 litres
4.	Glycerin	120 litres

Total cost of production including operating cost: Total cost of biodiesel is generally depends upon the feed stock cost. The neem seeds are to be purchased with a price of Rs. 20 per kg from the local market. The fixed cost includes Building rent, machine depreciation value. (It was calculated with depreciable life of 15 years.) The escalation rate at the rate of 1% per year, labour cost, office expenditure, electricity cost have been included but the cost of working capital and value added taxes (VAT) on biodiesel have excluded in this study and it has been shown in Table 6.

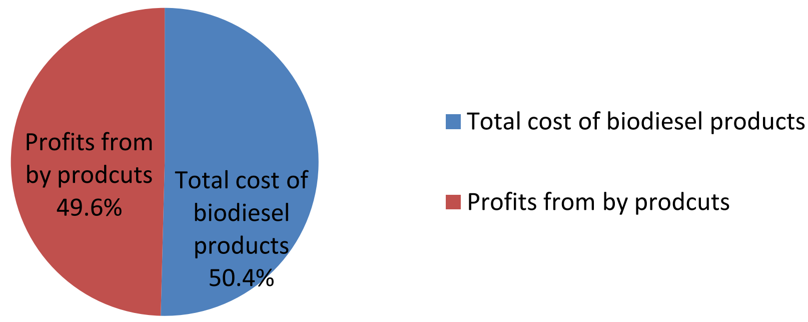
Table 6 Production cost of biodiesel from 3000 kgs of Neem seeds

S.No.	Description / particulars	Quantity	Rate (Rs.)	Amount(Rs.)
I.	**Total cost of production**			
1.	Neem seeds	3000 kgs	20	60000
2.	Transportation charges	3000 kgs	10	30000
3.	Chemical and Reagents	-	-	14600
4.	Electricity	750 units	6.00	4500
5.	Man power (6 days) and Helpers (2 nos.)	2	5000	10000
6.	Office superivision	-	-	10000
7.	Production unit building Rent per month	-	-	3000
8.	Depreciation value at the rate of 1% per month	-	-	1000
Total				**133100**
II.	Income from the by products			
9.	Neem seed cake	2000 kgs	25	50000
10.	Glycerine	120 litres	45	5400
Total				**55400**
Net production cost of biodiesel for 750 litres				
11.	Total Cost of biodiesel production	-	-	133100
12.	Profits from byproducts	-	-	55400
Total				44600

The cost of biodiesel for 750 litres is Rs.44600 and per litre Rs.59.50/- whereas the cost of Diesel is Rs.57/- per litre. Bio-diesel during the study it was found that the major factor that affected the cost of production where cost of feed stock which was accounted 45.1% of the total cost of production which is shown in Graph 1 followed by chemical and reagents used to convert oil into bio-diesel of 11% with operating cost. The study revealed that the second most major factor for the total cost of production was chemical solvents used in the trans-esterification process. The total cost of bio-diesel production is of 50.4% and profits from byproducts is of 49.6% which is shown in Graph 2.



Graph 1 Total cost of biodiesel production for 3000 kgs of neem seeds



Graph 2 Return shares from by products from 3000 kgs of Neem seeds.

Neem oil has the unique advantage of yielding a number of marketable bio-products when compared to other bio-diesel oils. These by-products are widely used in pharmaceutical (mosquito repellant), agricultural (manure), cosmetics (soap making) and other sectors. This will set of the excess cost of NOME especially in a country like India where traditional agro by products are still used in bulk. The present movement "to go green" will further spur the urge to purchase the neem by-products for mass use. Hence the high cost of NOME compared to conventional Diesel oil should not be a deterrent for its use in engines. Further the law of economics has show that when a new product is launched the initial cost of production will be high, but as demand curve goes up the cost must come down because of the law of demand and supply.

Conclusion

1. The bio-diesel can be produced from edible or non edible oils. For developing countries like India with a large population, there is an increasing demand for edible oil for human consumption. Hence, production of bio-diesel from edible oil is not an affordable solution for India. Instead non-edible oil can be considered as good option.
   In the present work Neem Oil Methyl Ester (NOME) produced from non-edible neem oil is chosen as alternative fuel for Diesel engine due to the following reasons
   - Is less expensive to cultivate with little amount of water
   - Requires less maintenance even at the seeding stage and small development period.
   - Can grow on all the climatic conditions and soils
   - Yield is high and the extraction of oil is also maximum
   - Provides higher rate of output
   - Has the ability to grow well on poor and infertility soil.
   - Can be harvested for 50 years
   - Can give multiple products like bio-diesel, soap, mosquito repellent and organic fertilizer.
2. The possibility of using NOME and B25 in a DI compression ignition as an alternative fuel without any modifications in the engine. Further the emissions such as carbon monoxide, unburnt hydrocarbons, smoke density of bio-diesel and its blends with Diesel comparatively reduced than Diesel fuel except oxides of nitrogen.
3. The fuel recommended through this investigation is a Bio-diesel (NOME) derived from non-edible vegetable oil which is available in plenty. Utilising NOME as a fuel for CI engine will not affect the food industry and will not reduce the land availability for growing food crops. In addition to the above advantages, NOME is indigenously available and utilising it as an alternative fuel for Diesel will reduce India's dependence on oil import which is about 200 million tons per annum.
4. NOME and B25 produced meets the standard bio-diesel specifications. The production and consumption of NOME and B25 would be increasing in future due to
   - low environmental impact,
   - ease of handling
   - Possibility of use without need for major adjustments of existing engines.

- Production and use of bio-diesel leads to savings in foreign exchange,
- Improves energy security of the nation,
- Provides employment to rural masses,
- Produce sustainable and relatively inexpensive fuel and
- Start propagating the concept with village population to supplement their income with the existing tree population.

It is concluded that bio-diesel blends can be used satisfactorily in Diesel engines without any major modifications in the hardware of the system.

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