MODELLING OF EXHAUST EMISSION
OF → FROM.
VEGETABLE OIL BASED DIESEL FUEL

A DISSERTATION

Submitted in partial fulfilment of the
requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
CHEMICAL ENGINEERING
(With Specialization in Industrial Pollution Abatement)

By

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CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in the dissertation entitled **"MODELLING OF EXHAUST EMISSION OF VEGETABLE OIL BASED DIESEL FUEL "**, in the partial fulfillment of the requirements of the award of the degree of Master of Technology in Chemical Engineering with specialization in Industrial Pollution Abatement, submitted in the Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, Uttarakhand (India), is an authentic record of my own work carried out during the period from June 2007 to June 2008 under supervision of **Dr. SHISHIR SINHA**, Assist. Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee,

I have not submitted the matter, embodied in this dissertation for the award of any other degree or diploma.

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CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge and belief.

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ABSTRACT

The demand of biodiesel is the need of the day because it have two advantage one is the renewable sources of energy due to the depletion in fossil fuel it is necessary that an alternative fuel is necessary which fulfill environmental and energy needs all the requirement without sacrificing operating performance and second is the ecofriendly it is give the less emission then to the fossil fuel but it have some problem like as the higher viscosity but it is decrease by some modification (Transesterification, Blending, Pyrolysis, microemulsification). In this work we will discuss about the modeling of the exhaust emission of two type of biodiesel which made from the two type of vegetable oil namely the sunflower oil and soyabean oil and variation in exhaust emission due to the variation in the Free fatty acid content of vegetable oil and develop a generalized equation which describe all the emission in one equation and find that it was the best fit between the two type biodiesel and their exhaust emission approximately same between theoretical and experimental data.

Keywords: non-edible vegetable oil, emission, free fatty acid, diesel fuel

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NOMENCLATURE

a0, a1, a2, a3	Specific constant for model equation
B0	100% diesel no biodiesel
B10	90% diesel 10% biodiesel
B20	80% diesel 20% biodiesel
B30	70% diesel 30% biodiesel
B40	60% diesel 40% biodiesel
B50	50% diesel 50% biodiesel
D2	Crude diesel fuel
C01	Blending ratio
C02	Carbon dioxide
C03	Carbon mono-oxide
C04	Nitrogen oxide
NOx	Nitrogen oxides
SOx	Sulfur oxides

CHAPTER 1

INTRODUCTION

1.1 GENERAL

Today fossil fuel are the major sources of the world energy demand and due to the limited reserves of petroleum and the storage goes to the end and the ratio of demand to supply increases which lead to increase in diesel fuel prices day by day of then so attention about the alternative of diesel fuel which is fulfill environment and energy security needs without sacrificing operating performance. Global air pollution is a serious problem. Much of this pollution is caused by the use of fossil fuels for transportation. Therefore, engine manufacturers have designed alternatively fueled engines and fuel systems, which provide sufficient power while staying within regulatory emission-limits. At the same time, a great deal of research and development on internal-combustion engines has taken place not only in the design area but also in finding an appropriate fuel. Many researchers have concluded that biodiesel holds promise as an alternative fuel for diesel engines, since its properties are very close to those of diesel fuel. Therefore* biodiesel can be used in diesel engines with few or no modifications. Diesel-fuel blends with biodiesel have superior lubricity, which reduces wear and tear on the diesel engine and makes the engine components last longer. Biodiesel mixes well with diesel fuel and stays blended.

Biodiesel has a higher cetane number than petroleum diesel fuel, no aromatics, and contains 10-11% oxygen by weight. These characteristics of biodiesel reduce the emissions of carbon monoxide (CO), hydrocarbons (HC), and particulate matter (PM) in the exhaust gas compared with diesel fuel. However, NOx emissions of biodiesel increase because of combustion and some fuel characteristics. When a higher percentage of biodiesel is used in the diesel engine during cold weather, it thickens more than diesel fuel and special systems may be required. Equipment made before 1993 may have rubber seals in the fuel systems that could fail if 100% biodiesel is used. Therefore, it is recommended that a blend of 20% biodiesel with diesel fuel may be used without changing any parts.

So the vegetable oil (Biodiesel) is a good substitute of diesel fuel. Replacing of diesel fuel by vegetable oils (biodiesel) is not a new concept [1]. The uses of vegetable oil as an alternative fuel could solve two problems namely fossil fuel depletion and environmental pollution. These fuels are non-toxic, renewable source of energy, which do not increase the net CO_2 in the global. Vegetable oils have a very large potential and to be used as an alternative fuel for diesel engine due to their renew ability and emit less green house gases [2]. Biodiesel from vegetable oil are considered as a renewable alternative diesel fuel. Waste vegetable oil and non-edible oil are potential raw material for biodiesel production but the price of refined oils such as sunflower, soybean oil and palm oil are high as compared to that of diesel so this increases the overall production cost of the biodiesel. Biodiesel production from refined oils would not be viable as well as economical for the developing countries like India. Hence* it is better to use the non-edible type of oils for biodiesel production. In India non-edible type oil yielding trees such as linseed, castor, karanji, neem, rubber, jatropha and cashew are available in large number. The production and utilization of these oils are low at present, because of their limited end usage. Utilization of this oils/biodiesel as fuels in internal combustion engines are not only reducing the petroleum usage, but also improve the rural economy. Efforts are made here to produce biodiesel from typical unrefined oil (rubber seed oil) and to use it as the fuel in diesel engines. Different techniques have been developed for producing biodiesel from vegetable oil and quality of biodiesel depends on the vegetable oil and the manufacturing process.

There are many type non-edible oils which are as Tobacco seed oil, Neem oil, Rubber seed oil, Cynara oil, Jojoba oil etc. Because these abundantly available every where and cheaply. Many low cost feed stocks are available for biodiesel production. Unfortunately, many of these feed stocks contain large amounts of free fatty acids (FFA). As discussed elsewhere, these free fatty acids will react with alkali catalysts to produce soaps that inhibit the reaction.

The following ranges of FFA are commonly found in biodiesel feed stock:

Refined vegetable oils < 0.05 %

Crude vegetable oil 0.3 – 0.7%

Restaurant waste grease 2 – 7%

Animal fat 5 – 30%

Trap grease 40 – 100%

Generally, when the FFA level is less than 1%, and certainly if it is less than 0.5%, the FFA can be ignored. Common catalyst amounts are:

Sodium hydroxide: 1% of triglyceride weight

Potassium hydroxide: 1% of triglyceride weight

Sodium methoxide: 0.25% of triglycerides weight

Soaps may allow emulsification that causes the separation of the glycerol and ester phases to be less sharp. Soap formation also produces water that can hydrolyze the triglycerides and contribute to the formation of more soap. Further, catalyst that has been converted to soap is no longer available to accelerate the reaction.

When FFA levels are above 1%, it is possible to add extra alkali catalyst. This allows a portion of the catalyst to be devoted to neutralizing the FFA by forming soap, while still leaving enough to act as the reaction catalyst. Since it takes one mole of catalyst to neutralize one mole of FFA, the amounts of additional catalyst can be calculated by the following formulas:

Sodium hydroxide: *[%FFA] (0.144) + 1 %*

Potassium hydroxide: *[%FFA] (0.197)/0.86 + 1 %*

Sodium methoxide: *[%FFA] (0.190) + 0.25 %*

Tobacco seed oil is non-edible oil extracted from tobacco seed unlike tobacco leaves, tobacco seed are not commercial product and are not collected from field [3]. Tobacco seed oil have around same properties as to the diesel fuel like as renew ability, minimal sulfur and aromatic content, better quality gas emission, higher flash point etc and tobacco seed oil is a by product of tobacco leaves production the seeds of tobacco plant are very small in size but they come in an extremely large quantity per plant. They can be preserved a long time if they are stored in dry conditions resistant to high humidity at normal temperature and have a strong shell. Tobacco seeds endosperm contains thin walled cells which is rich in oil. The oil extracted from tobacco seed is non-edible oil. Tobacco plant has pink flower and green capsules containing numerous small seeds. The average seeds are in the range of 0.08-0.09gm.The oil content of seed from 36% to 41% by weight [45] and the remaining part containing protein, crude fiber, carbohydrate and inorganic material. The leaf is the product of the plant and used in the production of cigarettes in tobacco processing industries. Tobacco seed oil is non-edible oil and it is not used in food industry and a small amount is collected from field because for the next year production and mostly are left unused.

Now we can start to deal with biodiesel. As you know, biodiesel is derived from vegetable oils. The major components of vegetable oils are triglycerides. The term triacylglycerols is being used more and more, but we will use the classical term in this discussion. Triglycerides are esters of glycerol (see above; an alcohol with a hydroxy group on each of its three carbon atoms) with long-chain acids, commonly called fatty acids. Tables4 and 5 list the most common fatty acids and their corresponding methyl esters. Note from the comparison of the rational names of the fatty acids with their structural formulas how the position of the double bonds is defined by numbers. The number of carbon atoms is counted by beginning with the first carbon having the functional group defining the fatty compound as acid or ester. As you can see from the former example (for example, 1-propanol and 2-propanol), this way of counting holds for other functional groups as well. The trivial names of fatty acids and their esters are far more commonly used than their rational names.

Table1.1. Chemical Structure of Common Fatty Acids and Their Methyl Esters

Fatty acid (trivial name / rational name)	**Structure**	**Common acronym**	**Methyl ester (trivial name / rational name)**
Palmitic acid / Hexadecanoic acid	$R-(CH_2)_{14}-CH_3$	C16:0	Methyl palmitate / Methyl hexadecanoate
Stearic acid / Octadecanoic acid	$R-(CH_2)_{16}-CH_3$	C18:0	Methyl stearate / Methyl octadecanoate
Oleic acid / 9(*Z*)-octadecenoic acid	$R-(CH_2)_7-CH=CH-(CH_2)_7-CH_3$	C18:1	Methyl oleate / Methyl 9(Z)-octadecenoate
Linoleic acid / 9(*Z*),12(*Z*)-octadecadienoic acid	$R-(CH_2)_7-CH=CH-CH_2-CH=CH-(CH_2)_4-CH_3$	C18:2	Methyl linoleate / Methyl 9(Z),12(Z)-octadecadienoate
Linolenic acid / 9(*Z*),12(*Z*),15(*Z*)-octadecatrienoic acid	$R-(CH_2)_7-(CH=CH-CH_2)_3-CH_3$	C18:3	Methyl linolenate / Methyl 9(Z),12(Z),15(Z)-octadecadienoate

a) R = COOH (CO_2H) or $COOCH_3$ (CO_2CH_3); $(CH_2)_7$ = $CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2$, etc.

Table1.2. Characteristic of Common Fatty Acids and their Methyl Esters

Fatty acid Methyl ester	Formula	Molecular weight	Melting point (°C)
Palmitic acid **Methyl palmitate**	$C_{16}H_{32}O_2$ $C_{17}H_{34}O_2$	256.428 270.457	63-64 30.5
Stearic acid **Methyl stearate**	$C_{18}H_{36}O_2$ $C_{19}H_{38}O_2$	284.481 298.511	70 39
Oleic acid **Methyl oleate**	$C_{18}H_{34}O_2$ $C_{19}H_{36}O_2$	282.465 296.495	16 -20
Linoleic acid **Methyl linoleate**	$C_{18}H_{32}O_2$ $C_{19}H_{34}O_2$	280.450 294.479	-5 -35
Linolenic acid **Methyl linolenate**	$C_{18}H_{30}O_2$ $C_{19}H_{32}O_2$	278.434 292.463	-11 -52 / -57

However, for increasing unsaturation, increasing NO*x* exhaust emissions are still observed. And second one is the jatropha oil. Jatropha oil is the second non-edible oil. Jatropha curcas can be grow in arid, semiarid, and wasteland and it require less water and fertilizer and can be easily grown in infertile soil and not to be eaten by cattle and it high yield for continuous 30-40 years. Crude jatropha oil is dark greenish yellow in colour and jatropha oil contains 14% free fatty acid which is higher than 1% free fatty acid which can be converted into biodiesel by transesterification process. Jatropha oil contain acid value 28±1% mg KOH /g corresponding to free fatty acid level 14±0.5% which is higher than the limit for transesterification.

Rubber seed oil which is also an alternative substitute of diesel fuel rubber seed have no major application in any field and uses and even natural production of seeds remains underutilized. Rubber seed kernels contain (50-60) seed which also contain 40-50% brown colored oil.

Jojoba oil is the another name which is also used for biodiesel this is a name that is increasingly common as an industrial crop in some country and also be one of the most genuinely Egyptian product[4]. Jojoba oil has half of the wt. of the seeds. Jojoba oil and its derivative are used commonly in cosmetics, pharmaceuticals and lubricants. Characteristic of jojoba oil are different from other common vegetable oils [5-7]. Its structure has long straight chain ester while other common vegetable oils have triglycerides (branched esters). Jojoba oil have no glycerides while other oil contain glycerides in which fatty acid are connected to glycerol molecule [8]. In the jojoba oil fatty acid directly connected to fatty alcohol which is alone in the group. Coconut oil is the another candidate which can be used for biodiesel manufacturing but coconut tree have less coconuts yield then to the other oil seeds tree because they are by small farmers. Coconut tree grows widely in coastel area of tropics and subtropics and dried kernel of coconut contains 65-70% oil because this is the mainly oil tree but every part of tree uses for some purposes like as shell is used to produce charcoal and activated charcoal, husk used for mat, nets and bags and stem used in construction and the leaves are used for thatch.

1.2. BASIC CHEMISTRY OF VEGETABLE OIL

Before steady of biodiesel it is necessary to know the basic chemistry of vegetable oil and their characteristic such as density, viscosity, calorific value etc. Distillation is one of the most known characteristic which make them different from gas oil and more similar to fuel oil but it is not done because vegetable oil have very high boiling point

The chemical composition of fat and oil esters is dependent upon the length and degree of unsaturation of the fatty acid alkyl chains. The carbon/hydrogen ratio of biodiesel from other sources will be slightly different, depending upon the degree of unsaturation. The most important compositional difference between D-2 and biodiesel is oxygen content. Biodiesel contains 10-12 wt% oxygen, which lowers energy density and, and as will be shown, lowers the particulate emission. Diesel can contain up to 500ppm sulfur by ASTM D-2622. Biodiesel is essentially sulfur free. Sulfur is converted to sulfur oxide in the tailpipe and a fraction of the sulfur oxide is converted to sulfuric acid, which is counted as particulate, a regulated pollutant. Sulfur oxides are also regarded as air pollutants although they are not regulated as such from diesel engines. Petroleum derived diesel also contains from 20 to 40 vol. % aromatic compounds. Aromatics are known to increase emissions of particulate and NOx. Biodiesel is essentially non-aromatic. Petroleum diesel contains essentially no olefinic bonds. Biodiesel can contain a significant number of these reactive, unsaturated sites.

All naturally occurring fats and oils are esters of the tri-alcohol, glycerol. These are known as glycerides, triglycerides, or triacylglycerides. With few exceptions, the carboxylic acids (fatty acids) from which the fats and oils are derived are all straight-chain compounds ranging in size from three to 18 carbons. Table 3 shows the chemical structure of the fatty acid chains found in the most common biodiesel source materials. Except for C3 and C5 compounds, only acids with an even number of carbons occur naturally. Acids may be saturated (contain only single bonds) or unsaturated (contain one or more double bonds). A saturated fat is one that cannot chemically add hydrogen. An unsaturated fat can be hydrogenated; for each degree of unsaturation, that is each double bond, one hydrogen molecule can be added per fatty acid. Table 3 also shows the melting and boiling points of the various fatty acids. The saturated acids exhibit higher freezing points than the unsaturated acids. Stearic acid, for example, is solid to 70°C, while oleic acid melts at 16°C. The only difference is the presence o a single double bond in the structure of oleic acid. For freezing point, chemical structure is very important. The boiling points of the acids, on the other hand, are dependent on the length of the carbon chain but nearly independent of the degree of unsaturation of the fatty acid. These observations regarding the effect of chemical structure on melting and boiling points also apply to esters of the fatty acids, although the boiling and melting points are significantly lower.

Table1.3. Fatty acid composition of sunflower oil and soyabean oil

Fatty acid	Sunflower oil, W%	Soyabean oil, W%
Myristric	0.06	0.09
Pentadecanoic	Trace	NA
Palmitic	6.08	11.75
Margaric	0.09	NA
Margaroleic	0.05	NA
Stearic	3.26	3.15
Oleic	16.93	23.26
Arachidic	0.00	NA
Linoleic	73.73	55.53
Linolenic	0.00	6.31
Gadoleic	0.08	NA
Behenic	0.00	0.00
Lignocenic	0.00	0.00

There are three structures given which give the basic comparison between vegetable oil, their methyl esters and hydrocarbons that are present in petroleum fuel. Their structure are very similar except that the two ester functional group

There are five types of chains that are common in soybean oil and animal fats (others are present in small amounts):

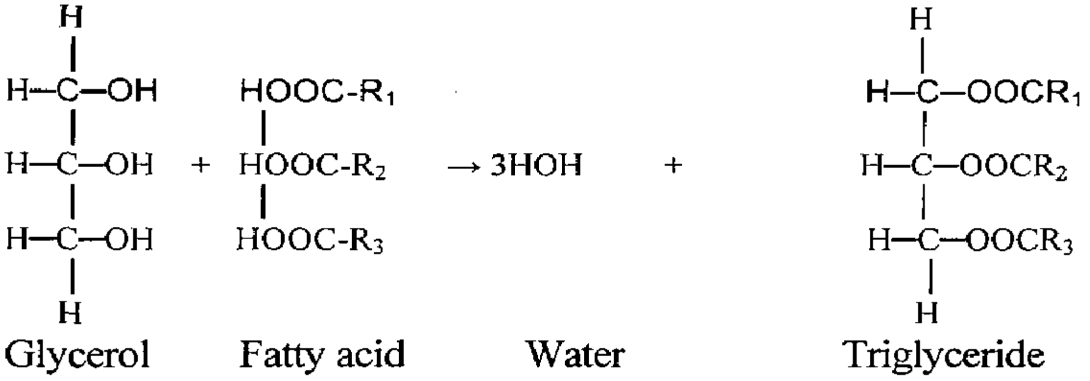
Palmitic: R = - $(CH_2)_{14} - CH_3$ 16 carbons, (including the one that R is attached to.) (16:0)

Stearic: R = - $(CH_2)_{16} - CH_3$ 18 carbons, 0 double bonds (18:0)

Oleic: R = - $(CH_2)_7 CH=CH (CH_2)_7CH_3$ 18 carbons, 1 double bond (18:1)

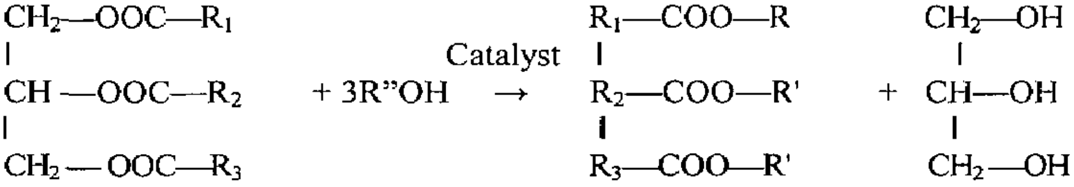
Linoleic: R = - $(CH_2)_7 CH=CH-CH_2-CH=CH (CH_2)_4CH_3$ 18 carbons, 2 double bonds (18:2)

Linolenic: R = - $(CH_2)_7 CH=CH-CH_2-CH=CH-CH_2-CH=CH-CH_2-CH_3$ 18 carbons, 3 double bonds (18:3)



$$\begin{array}{c}H\\ |\\ H-C-OH\\ |\\ H-C-OH\\ |\\ H-C-OH\\ |\\ H\\ \text{Glycerol}\end{array} + \begin{array}{l}HOOC\text{-}R_1\\ |\\ HOOC\text{-}R_2\\ |\\ HOOC\text{-}R_3\\ \text{Fatty acid}\end{array} \rightarrow \begin{array}{c}3HOH\\ \text{Water}\end{array} + \begin{array}{c}H\\ |\\ H-C-OOCR_1\\ |\\ H-C-OOCR_2\\ |\\ H-C-OOCR_3\\ |\\ H\\ \text{Triglyceride}\end{array}$$

Fig.1.1. Chemical structure of vegetable oil



$$\begin{array}{l}CH_2-OOC-R_1\\ |\\ CH-OOC-R_2\\ |\\ CH_2-OOC-R_3\end{array} + 3R''OH \xrightarrow{\text{Catalyst}} \begin{array}{l}R_1-COO-R\\ |\\ R_2-COO-R'\\ |\\ R_3-COO-R'\end{array} + \begin{array}{l}CH_2-OH\\ |\\ CH-OH\\ |\\ CH_2-OH\end{array}$$

Fig.1.2. Ester of vegetable oil and hydrocarbon

The properties of these oils can be studied by assuming the following: first is the hydrocarbon structure is same in all of these and behavior as combustibles requires weak molecular association and in hydrocarbon they have very small cohesion forces between their molecules and they have low density and viscosity. The density and viscosity of Methyl esters are a bit higher, but not very much, due to the characteristics of the functional group. In the case of vegetable oils, as every molecule has three hydrocarbon chains attached to a common group, Their density and viscosity are higher because intermolecular association is more important. Vegetable oil has a lower calorific power. Assuming the same chain length, hydrocarbons have a higher calorific power as the molecule does not contain oxygen as do vegetable oils and their derivatives. These differences are not very important [10].

Table1.4: Comparison of Properties of vegetable oils

Property	**Soybean oil**	**Sunflower oil**	**Jatropha oil**	**Tobacco seed oil**
Flash point(°C)	150	220	340	220
Pour point(°C)	-11	-15.0	NA	-14
Ash content (% by wt.)	0.063	<0.01	NA	0.008
Kinematic viscosity at 40°C (cST)"	4.5(mm^2/s)	33.21	38.8	27.7
Kinematic viscosity at 100°C (cST)	6.459	7.85	9.2	6.54
Carbon content (% by mass)	81.8	79.3	NA	NA
Iodine value	NA	NA	13	135
Calorific value (MJ/Kg)	42.21	37.05	39.7	39.4
Density (g/cm^2)	0.8831	0.923	0.9115	0.9175

1.3. PROBLEMS WITH VEGETABLE OILS

Every engine manufacturer want to maximize the thermal efficiency and power of the engine and want to minimize the pollution from the engine because the emission regulation become more stringent day by day [11,12] for the reduction of pollutant emission by the use of alternative fuels. Because the oxygenated or oxygen enriched fuel reduce the particulate emission [13, 14, 15] but it is increase the nitrogen oxides (NOx) which are related to soot/NOx trade off [16, 17]. The major problem are associated with their highly increased viscosity which is 10-12 times greater of the diesel fuel and their lower calorific value problems appeared when the engine running a long time then this create the problem in injector coking with trumpet formation, more carbon deposit, and piston oil ring sticking, as well as thickening and gelling of the engine lubricating oil. The problem associated with these oil higher viscosities, higher pour point Lower calorific value and lower volatility. Their oxidation values are lower they are hygroscopic and as solvent they may cause corrosion of component, attacking some plastic materials used for seal hoses, paints, and coatings. The effect of oxygen content and type of soot formation and oxidation process and NO formation mechanism are of importance.

It is expected that the widely difference in physical properties of fuels against the normal diesel fuel will play a major role in the fuel spray formation mechanism and consequently in the combustion and the related formed emission. A significant smoke opacity peak observed during the engine start process when biodiesel fuel used. This effect was caused by the increase in the relatively low start temperatures. At start low temperature the higher the viscosity and boiling point of biodiesel fuel make the fuel/air mixing and combustion difficult [18]. At full load of methyl ester give the higher NOx emissions. The increase in NOx emissions are around 5% at full load due to the higher temperature of the combustion chamber and presence of fuel oxygen [19, 20, 21]. There are negligible difference in between NOx emission of blend and the diesel fuel at partial load at around 50% load because more oxygen available at partial load the external oxygen supplied with air are less effective then the fuel borne oxygen in the production of NOx.

The characteristic of vegetable oil fall in narrow band and are quite close to those of diesel fuel vegetable oil have about 15% less heating value then that of the diesel fuel due to the oxygen content in there molecule and the kinematic viscosity of vegetable oil are several times higher then the diesel fuel the high viscosity of vegetable oil leads to problems in pumping and atomization in injection system of diesel engine. The combination of higher viscosity and low volatility causes poor cold engine start up, misfire, and ignition delay, hence it is necessary that the combustion related properties come closer to the diesel fuel. The fuel modification is mainly aimed at reducing the viscosity of vegetable oils to get rid of the flow related problems. Vegetable oil contain acid which causes corrosion so that it is necessary first the acid removal from unrefined vegetable oil to refined vegetable oil.

These problems can be divided in to two types 1: operational, 2: durability, the former included the ignition quality characteristic like as poor start up, formation, combustion of injector steps, ring sticking, and lube oil dilution and degradation.

1.4. METHOD FOR CONVERSION OF VEGETABLE OIL INTO BIODIESEL

There are many vegetable oils available which have been used as fuel components for diesel engines. These oils are Soybean, Cottonseed, Sunflower, and Safflower, Crude palm oil (CPO), Rapeseed, Peanut, Linseed and Castor. Diesel fuel which consist mostly of saturated hydrocarbon, while these vegetable oil are triglycerides consisting of glycerol ester of fatty acid. The oils which are mostly used are Soybean, Sunflower, Peanut and Cottonseed.

The major problem which attributes towards the limited use of vegetable oil as fuel-alternative Is viscosity. Solution to the viscosity problem has been approached in at least four ways: (a) By blending, (b) Transesterfication, (c) Micro emulsification, and (d) by pyrolysis. We will discuss those methods one by one.

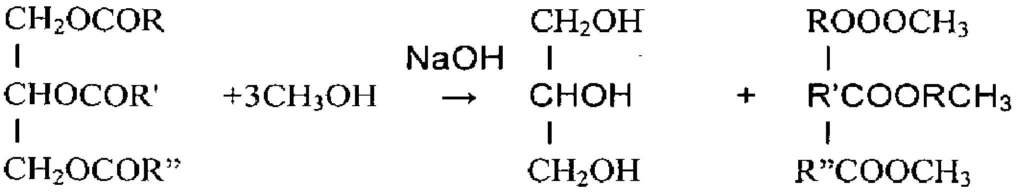
1.4.1 By blending

Blending means the mixing of the vegetable oil with the diesel fuel in a right proportion. Blending of vegetable oil with Neat diesel fuel lo improve the fuel properly of vegetable oil is one of the well known but not a very much recommended method. Dilution of sunflower oil with diesel fuel (1:3 V/V) provides a fuel with a viscosity of 4.88 cSt at 40°C which is higher than the maximum specified ASTM value of 4.0 cSt at 40 C, the viscosity is moderately less than that of neat Sunflower oil. However, Zlejewski et. [22] Concluded that the blend could not be recommended for long term use in the direct-injection diesel engine because of severe injector for long term use in the Direct-injection diesel engine because of severe injector nozzle coking and sticking. A comparable blend with high-oleic Safflower oil, replacing Sunflower oil, passed the 200-hour test. High order Safflower oil differs from typical Safflower and Sunflower oil in that it contains less unsaturation. The unsaturated oil is highly reactive and tends to oxidize and polymerize. If such products accumulate in the lube oil, they could lead to thickening of the lubricant. Therefore, frequent replacement of lube oil becomes necessary.

1.4.2 Transesterfication

The second method for reducing the viscosity is the conversion of the triglyceride oils to simple esters which In effect reduces the molecular weight of the original oil to 1/3 of its former value, reduces the viscosity. Because fatty esters are less viscous, they have performed well in long-term diesel engine tests. Following Figure shows the vegetable oil to methyl ester reaction:

$$\text{Vegetable oil} + \text{Alcohol} \rightarrow \text{Glycerol} + \text{Ester}$$



$$\begin{array}{lcclcl} CH_2OCOR & & & CH_2OH & & ROOOCH_3 \\ | & & & | & & | \\ CHOCOR' & +3CH_3OH & \xrightarrow{NaOH} & CHOH & + & R'COORCH_3 \\ | & & & | & & | \\ CH_2OCOR'' & & & CH_2OH & & R''COOCH_3 \end{array} \quad (1.3)$$

Fig.1.3. Transesterfication of vegetable oil

Alcohols are primary and secondary monohydric aliphatic alcohols having 1-8 carbon atoms. Among the alcohols that can be used in the transesterification process are methanol, ethanol, propanol, butanol and amyl alcohol. Methanol and ethanol are widely used and especially methanol because of its low cost, its physiochemical advantages with triglycerides and sodium hydroxide (NaOH) is easily dissolved in it. Physiochemical property of methanol includes molecular weight (32.04), boiling temperature (64.71°C) and specific gravity (0.792). As the molecular weight is low compared to other alcohol, less amount of methanol is required on mole basis for reaction. Since boiling temperature is also low compared to other alcohol, less energy required for reaction. Apart from alkali other catalysts such as acids, enzymes can be used for transesterification. Some of the alkalis include NaOH, potassium hydroxide (KOH), carbonates and corresponding sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide. Sulphuric acid, sulphonic acids and hydrochloric acid are usually used for acid catalysis. Alkali catalyzed transesterification is much faster than acid catalyzed transesterification and is most often used commercially. Transmethylation occur approximately 4000 times faster in the presence of alkaline catalyst than those catalyzed by the same amount of acid catalyst. Biocatalysts such as Lipases can be used as catalysts in transesterification reaction. The other important parameter is stirring speeds, which play a vital role in transesterification process.

The degree of homogeneity (emulsification) of alcohol in the triglyceride phase is of great importance in the transesterfication process after transesterification process the ester can be separated from glycerol by gravity and the ester has to be washed with slightly acidified water to remove traces of alkali. The reaction between triglyceride and methanol to form fatty ester and glycerin is shown in upper figure.

The stoichiometry of this reaction thus requires a 3:1 molar ratio of alcohol to triglyceride. In practice, the ratio needs to be higher to drive the equilibrium to a maximum ester yield. Although the ester Is the major product, desired recovery of glycerol Is important because of Its many Industrial uses. Further, alkali catalyzed transesterfication Is known to proceed much faster than acid catalyzed transesterfication. Fatty acid methyl esters are considered as a possible substitute or extender of conventional automotive diesel fuel. The engine performance with Soya bean methyl or ethyl ester differed little from diesel oil in the 200-hour test with the exception of some fuel filler plugging apparently caused by gum formation in the esters. Following table provides details about etherified vegetable oil (Rapeseed oil) and ordinary diesel.

Table1.5: Properties of the esterified vegetable oil and diesel oil [23]

Properties	**Esterified vegetable oil**	**Diesel fuel**
Density (20°C)	0.876	0.821
Viscosity (20°C)	7.16	4.01
Viscosity(40°C)	5.20	3.80
Flash point (°C)	100	60
Cetane number(-)	754	52
Sulfur content (%m)	<0.02	0.26
Energy(MJ/Kg)	37.02	43.47
Shear stress (dyne/cm^2)	*0.784*	*0.064*
Specific gravity	0.872	0.835
Pour point °C	-10	-16
Cloud point °C	-2	-1
Diesel index	50	45

As the above Figure shows, etherified vegetable oil is an attractive fuel; the viscosity is some what higher than Hint of diesel fuel. The gross healing value of the etherified vegetable oil is less than that of diesel. The cetane number is almost similar. High flash point for the ester makes it safer to handle than diesel fuel. Further, these esters do not emit polyaromatics or other harmful exhaust components such as carcinogenic hydrocarbons. Further, methyl esters are oxygenated, fuel combustion is improved 10 percent. The fuel contains virtually no sulfur compounds and therefore no sulfurous emission. With regard to engine performance, the slightly lower heating value of methyl esters is offset by its sulfur combustion performance.

1.4.3 Micro emulsification

To solve the problem of the high viscosity of vegetable oils, micro-emulsions with solvents such as methanol, ethanol and 1-butanol have been investigated. A micro-emulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimension generally in the 1-150 nm range, formed spontaneously from two normally immiscible liquids. They can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles. Short term performance of micro-emulsions of aqueous ethanol in soybean oil was nearly as good as that of diesel, in spite of the lower cetane number and energy content

These are mecellar system that may be formed with ionic or non-ionic amphiphiles [24].Schwab and Pryde [25] demonstrated the use of 2-octanol as an effective amphiphile in the mecellar solublization of methanol in triolein and soybean oil. Methanol has an economic advantage over ethanol and it can be derived from a large variety of base stocks. These include biomass, municipal waste, natural gas and coal. By microemulsion formation, it is possible to prepare alternative diesel fuels completely free of petroleum. Fuels formulated thus for as microemulsion have low cetane number

Preliminary engine tests gave the following results [26]:

1: Nonionic micro emulsions produced nearly as much engine power as diesel fuel, despite having a 19% lower heating value.

2: The non-ionic fuel gave slightly higher thermal efficiency, higher engine power and lower specific fuel consumption than Ionic emulsion.

3: Micro emulsions gave lower exhaust temperatures, reduced

4: exhaust smoke and lower carbon monoxide/nitrogen oxide emissions that are observed for diesel fuel.

5: Heat release pattern indicated that the micro emulsions fuels burnt faster than diesel fuel and have higher levels of premixed burning and lower levels of diffusion flame burning. According to Kaufman and Ziejewsk [27] a Sunflower micro emulsion fuel gave mixed results with their test. On the one hand, the fuel gave a good spray pattern, and injectors operated throughout the test in a satisfactory manner compared to the Sunflower oil fuel blend (1:3 ratios). On the other hand, carbon and gum deposits were higher and contamination of the lubricating oil was more severe. Goering and Fry [281] studied the soybean/diesel fuel microemulsion. They reported a soybean oil/diesel fuel microemulsion managed to give good results at starting but there are indicators that failure would have acquired had the engine been run on the fuel for a slightly lower period. A microemulsion consisting of soybean oil: 2-octanol: cetane number (52.7:13.3: 33.3: 1.0 by volume) also showed a good result as reported by a Goering [29] However, carbon accumulated around the orifices of the injector nozzles, and heavy deposits (380 times that found for diesel fuel) were left on the exhaust valves. The better performance was attributed to the solvent action and cooling effect of the alcohol in keeping the Injector needles and orifices clean.

1.4.4 Pyrolysis

Pyrolysis is the conversion of one substance into another by means of heat or by heat in presence of a catalyst. The paralyzed material can be vegetable oils, animal fats, natural fatty acids or methyl esters of fatty acids. The pyrolysis of fats has been investigated for more than 100 years, especially in those areas of the world that lack deposits of petroleum. Many investigators have studied the pyrolysis of triglycerides to obtain products suitable for diesel engine. Thermal decomposition of triglycerides produces alkanes, alkenes, alkadines, and aromatics and carboxylic acids. Thermal and catalytic decomposition of vegetable oils to produce substitutes for diesel fuel has been studied by a number of researchers using a variety of methods. The method involves cleavage of chemical bonds to yield smaller molecules. Engleri [30] in 1888 first studied vegetable oil pyrolysis when he attempted the synthesis of petroleum from vegetable oils in order to confirm the theory of origin of petroleum from organic matter. Since World War I, many Investigators have studied the pyrolysis of vegetable oils to obtain products suitable for fuel. Grossly [31] has studied the temperature effect on the type oi products obtained from heated triglycerides. Essentially three different methods of proco8slng vegetable oils to obtain fuel nave been used: (1) Passing of the oil over a heated catalyst In a tube, (2) Distillation of the oil while In the presence of metallic salts, and (3) Distillation of the oil under pressure or distillation of the oil followed by vapor-phase cracking. In some studies, the vegetable oil was first converted to soaps by hydrolysis and processed by the above three methods. Most of the research has been conducted using the aforesaid methods. The pioneering work using catalysts and/or metallic salt was performed by Mailhe In the early 1920s. Mailhe passed linseed oil vapours over heated balls of Cu mixed with MgO, Al_2O_3 or Kaolme at 550°C and obtained gas liquid products of a brown colour and strong odor.

A process patented In Britain in 1932 used activated carbon in the form of fibers to 350°C to 600°C and yielded a conversion of 75% of the vegetable oil to a liquid that contained hydrocarbons with a boiling range from 110-250°C. Also In our country, Dalai and Mehta [31] cracked vegetable oil in tubes of Fe and glass at various flow rates and also distilled vegetable oil In the presence of various proportions of $ZnCl_2$. They found that the percent of the oil cracked Increased with temperature, decreased with an increased amount of $ZncCl_2$. $ZnCl_2$ was more effective that $CaCl_2$ Mandikar et. Al [31] found the percent of crude diesel fuel decreased with an increase of Zinc Chloride from 0.5 to 2.5 percent when Sesame oil was distilled. Goswami et. al [32] discovered that pyrolysis of oleic acid at 350 to 385° C over a Cu catalyst resulted in a 50 percent conversion to mixed hydrocarbons, 49 percent of them distilling from 250 to 350°C. Recently fuel properties of pyrolyzed materials were characterized and compared by Dykstra et. al [33] with those of soya bean oil. The healing values for soya bean oil and its distillate are similar. Soyabean oil distillate has a higher cetane number than diesel fuel. The viscosity of the pyrolysed soya bean distillate was 10.2 cSt at 37.8°C higher than ASTM specified range for diesel fuel but still well below that viscosity of soyabean oil.

1.5. STUDY ABOUT PERFORMANCE AND EMISSION

Biodiesel is considerably less flammable than petroleum diesel, which burns at 50°C (120°F). Pure biodiesel does not ignite until 150°C (300°F). The flashpoint (the temperature at which it will ignite when exposed to a spark or flame) of a biodiesel blend falls somewhere between these temperatures, depending on the mixture. Because biodiesel is a mild solvent it is important to wipe up spills and dispose of rags safely. Biodiesel may deface some paints if left on painted surfaces for a long time. One of the most important characteristics of diesel fuel is its ability to auto ignite, a characteristic that is quantified by a fuel's cetane number or cetane index, where a higher cetane number or index means that the fuel ignites more quickly. Graboski and McCormick [46] .have summarized several experimental studies of biodiesel characteristics. They report that the cetane number for biodiesel ranges from 45.8 to 56.9 for soybean oil methyl esters, with an average of 50.9. In comparison the cetane index for petroleum diesel ranges from 40 to 52. They imply that careful production control could result in biodiesel products with cetane numbers in the high end of the range. Lubricity, another important characteristic of diesel fuel, is a measure of lubricating properties. Fuel injectors and some types of fuel pumps rely on fuel for lubrication. One study, published in 1998 and cited by the National Biodiesel Board, found that one-half of samples of petroleum diesel sold in the United States did not meet the recommended minimum standard for lubricity[47] Biodiesel has better lubricity than current low-sulfur petroleum diesel, which contains 500 parts per million(ppm) sulfur by weight. The petroleum diesel lubricity problem is expected to get worse when ultra-low-sulfur petroleum diesel (15 ppm sulfur by weight) is introduced in 2006. A 1- or 2-percent volumetric blend of biodiesel in low-sulfur petroleum diesel improves lubricity substantially. It should be noted, however, that the use of other lubricity additives may achieve the same effect at lower cost.

Biodiesel also has some performance disadvantages. The performance of biodiesel in cold conditions is markedly worse than that of petroleum diesel, and biodiesel made from yellow grease is worse than soybean biodiesel in this regard. At low temperatures, diesel fuel forms wax crystals, which can clog fuel lines and filters in a vehicle's fuel system. The "cloud point" is the temperature at which a sample of the fuel starts to appear cloudy, indicating that wax crystals have begun to form. At even lower temperatures, diesel fuel becomes a gel that cannot be pumped. The "pour point" is the temperature below which the fuel will not flow. The cloud and pour points for biodiesel are higher than those for petroleum diesel.

Vehicles running on biodiesel blends may therefore exhibit more drivability problems at less severe winter temperatures than do vehicles running on petroleum diesel [10] this is a potential concern during the winter in much. The solvent property of biodiesel can cause other fuel-system problems. Biodiesel may be incompatible with the seals used in the fuel systems of older vehicles and machinery, necessitating the replacement of those parts if biodiesel blends are used [49] the initial use of B20 or B100 in any vehicle or machine requires care. Petroleum diesel forms deposits in vehicular fuel systems, and because biodiesel can loosen those deposits, they can migrate and clog fuel lines and filters [50]. Another disadvantage of biodiesel is that it tends to reduce fuel economy. Energy efficiency is the percentage of the fuel's thermal energy that is delivered as engine output, and biodiesel has shown no significant effect on the energy efficiency of any test engine. Volumetric efficiency, a measure that is more familiar to most vehicle users, usually is expressed as miles traveled per gallon of fuel (or kilometers per liter of fuel). The energy content per gallon of biodiesel is approximately 11 percent lower than that of petroleum diesel [49]. Vehicles running on B20 are therefore expected to achieve 2.2 percent (20 percent x 11 percent) fewer miles per gallon of fuel.

About 11 percent of the weight of Biodiesel is oxygen. The presence of oxygen in biodiesel improves combustion and therefore reduces hydrocarbon, carbon monoxide, and particulate emissions; but oxygenated fuels also tend to increase nitrogen oxide emissions. Engine tests have confirmed the expected increases and decreases of each exhaust component from engines without emissions Controls Biodiesel users also note that the exhaust smells better than the exhaust from engines burning conventional diesel. Nitrogen oxide emissions from biodiesel blends could possibly be reduced by blending with kerosene or Fischer-Tropsch diesel. Kerosene blended with 40 percent biodiesel has estimated emissions of nitrogen oxide no higher than those of petroleum diesel, as does Fischer-Tropsch diesel blended with as much as 54 percent biodiesel [51]. These results imply that Fischer- Tropsch diesel or kerosene could be used to reduce nitrogen oxide emissions from blends containing 20 percent biodiesel, although the researchers did not investigate those possibilities. Blending di-tri-butyl peroxide into B20 at 1 percent is estimated to cost 17 cents per gallon (2002 cents), and blending 2-ethylhexyl nitrate at 0.5 percent is estimated to cost 5 cents per gallon. Oxides of nitrogen and hydrocarbons are ozone precursors. Carbon monoxide is also an ozone precursor, but to a lesser extent than unburned hydrocarbons or nitrogen oxides. Air quality modeling is needed to determine whether the use of biodiesel without additives to prevent Increases in nitrogen oxide emissions will increase or decrease ground-level ozone on balance. Particulate emissions are reduced for every mode as the concentration of any of the tested biodiesel fuels were increased in the blend despite the higher fuel/air ratio required in each mode necessary to compensate the lower heating value. These reductions are explained by the increase in oxygen content in the fuel which contributes to complete fuel oxidation even in locally rich zones, and by the lower final boiling point which guaranties a complete evaporation of the liquid fuel. This effect can also be observed in the hydrocarbons emissions and the smoke opacity which, unlike the particulate matter, were measured in hot and undiluted conditions. The particulate emission reduction is more significant at low load, because the cylinder temperature is relatively low, which in the case of a multi-component fuel such as the reference, could lead to some difficulties in evaporation and burning of heaviest hydrocarbons. The relative reductions in particulate emissions are more drastic from0% biodiesel to 25% than from this concentration to pure biodiesel. The biodiesel fuels are renewable source of energy derived by biomass feedstock. These fuels can be easily mixed with standard diesel and can be used in blends at any proportion. As far as impact on engine is concerned, there have been no evidence material compatibility problems using vegetable oil fuel when it is used in proportion of 20-30% blend with diesel.

Reports, 100% methyl ester of soybean oil indicated immersion incompatibility with certain rubbers and plastics, but not with metals. As far as durability is concerned most studies have shown no appreciable difference between vegetable oil based oil and petrodiesel. A study by the university Idaho showed that petrodiesel consistently produced higher concentration of iron, aluminum, chromium, and lead in crankcase oil as compared to vegetable based fuel [33]. In the same study while a slight decrease in oil viscosity was observed it remain with in allowable limits. This was attributed to fuel to fuel dilution of crankcase oil. A similar study confirmed the presence of unburned esters in the crankcase oil, and stated that the rate of dilution could be significantly reduced by lowering the blend level by adding ethanol to the fuel mixture or by modifying the injectors [34]. Vegetable oil fuel can be substituted for diesel with essentially no engine modifications particularly at lower blend level. Mechanics will not have to undergo retraining. Research has shown that sustained use of unprocessed oil in direct injected diesel engine will lead to severe coking and injector tip fouling. Infect, many researchers have reported less coking with vegetable oil fuel than petro diesel. Vegetable oil has advantage that they do not produce the explosive mixture with air.

A critical step in the diesel engine is the injection of fuel into combustion chamber. The fuel must be in the form of finely divided particles-a mist. If not it burns too slowly and unevenly, reducing engine efficiency, producing unburned pollutant in emission and forming carbon deposit in engine part. The principal problem in using crude vegetable oil as alternative fuel is as follows [35].

1: residual fines ,from the oil extraction process, phosphatide gums, waxes, and high melting fatty component clog the fuel lines and fuel filter.

2: higher inherent viscosity than the diesel fuel cause poor atomization, ignition, and combustion, resulting in carbon deposit on injection nozzle, chamber walls, and piston heads. Unsaturated fats can polymerize in storage and result in even higher initial viscosities.

3: polymerization of unsaturated component in the combustion chamber can also cause deposit on the cylinder walls. Polymerization of these compounds blow past the cylinder into the lubricating oil can cause undesirable thickening or formation of solids. All these problems have been reported using many kind of degummed, filtered seed oil, most unmodified diesel engines start easily and deliver nearly full power on a short term basis, whether direct or precombustion chamber indirect injection types this letter type has a cavity at the top of piston chamber that creates better fuel-air mixtures and improves combustion in DI engine fuel is sprayed directly into the cylinder. These general principle apply to most oils, there are some difference among them. For example in comparing the performance of cottonseed, peanut, soybean and sunflower oils Ryan and coworkers [36].found performance difference arising from both the degree of refining and source of the oil analysis of data from test on DI engine indicated that the most significant fuel properties were the linolenic-linoleic ratio the iodine number and the nitrogen content. The significance of oxygen and free fatty acid contents of the oils was minor compared to the other factor for indirect engine the result indicated essentially the same trends. The negative effect of nitrogen may be due to the interference with the combustion process through radical trapping or some other mechanism. The oxygen effect in the indirect injection engine was positive possibly because the presence of oxygen in the fuel accelerated the combustion process.

It is not unusual to compare the performance of unmodified ester or triglycerides blends with diesel fuels. Because diesel fuels is generally formulated with additive [37]. That enhances cold flow, increase cetane number, and inhibit corrosion, diesel fuels have built in performance advantage over unformulated diesel substitutes. Clark and coworkers[38] have shown that cetane improving additives commonly used with diesel fuel are effective with soybean oil esters as well Du Plessis and De Villiers [39] have demonstrated the value of antioxidants in methyl and ethyl sun flower oil esters. Vander wait and hugo [40] identified a few commercial additives that reduced injector coking but the chemical nature of the additives was not reported and could not correlated with their performance. The use of vegetable oil derivatives as diesel fuels would provide transportation energy from renewable sources and would thus slow the rise of atmospheric CO_2 resulting from combustion of fossil fuels. A good example of the ethyl alcohol from sugarcane the total CO_2 in the atmosphere is not affected because the CO_2 produced when the alcohol is burned is recaptured in the following year sugarcane growth. Since vegetable oil is practically sulfur free their use as fuel would also reduce the atmospheric SO_2. SO_2 and CO_2 reductions are clear, but other reduction of other emission is less clear Mittelbach and coworkers [41]. Compared the emission of rapeseed methyl ester fuel with diesel fuel for gases and particulates Hydrocarbon, CO, particulate, aldehyde, and polycyclic aromatic hydrocarbon emission were all in the same range for both type of fuel. NOx emissions are slightly higher for the ester fuels. A 50% particulate reduction in the compared to the petroleum fuel [42]. Hall and cowokers [43] suggest that the production and use of biofuels is more effective strategy than creating forest reserves for carbon dioxide absorption. While harvesting, transport, and processing requirements make biofuels more costly than growing trees to sequester carbon energy sales revenue can be taken as a credit against these costs. Because the prospects are good that these fuels can be produced competitively the net cost of offsetting CO_2 emission by substituting biofuels for fossil fuels could be near zero or even negative and thus less costly than establishing tree plantations for carbon sequestration.

Many of the points are applicable to diesel fuel substitute from vegetable oils. We conclude the following: The low sulfur content of biofuels results in little or no SOx emissions the precursor of acid rain. Oxygenated biofuels emit little NOx emissions a reactant in the formation of smog. The growth of biomass is the only practical way to remove CO_2 from atmosphere and ameliorate global warming. The use of biofuels can reduce the amount of the fossil fuels and the NOx, SOx, and unburned hydrocarbon they produce. The production of biofuels can provide job and economic development. Biofuels are import substitute for diesel fuels. Many petroleum based organic chemical can be derived from biomass. It is clear that the CO_2 and SOx reduction will occur with biofuels research on establishing the conditions that result in lesser amount of unburned hydrocarbon, particulate and NOx with these fuels is certainly important. Vegetable oil fuels have been reported to reduce emission in some cases but not in other depending on the factor such as type of engine, load on engine, and the use of blends. A clear definition of ways that vegetable oil fuels could improve the environment would accelerate the acceptance and use.

Particulate emissions are reduced as the concentration of any of the biodiesel fuels are increased in the blend. These reductions are mainly justified by the increase in oxygen content in the fuel which contributes to a complete fuel oxidation even in locally rich zones, and by the lower final boiling point which guarantees complete evaporation of the liquid fuel.

The presence of oxygen on the ester molecules is not lead to increases in NOx formation. On the contrary a certain decrease was observed at high load. Although increases in NOx emissions have often been attributed to the oxygen content of the fuel molecule, a balance on oxygen availability reveals that, even by including the oxygen of the ester molecule, the oxygen/fuel mass ratio remains below that of the conventional fuel. With respect to reference commercial fuel, the soot mass contained in the collected particulate matter was observed to strongly decrease as the concentration of biodiesel was increased, while the mass of adsorbed hydrocarbons remained approximately unchanged leading to increased soluble organic fraction at any engine load.

The proportion of adsorbed hydrocarbons on the particles surface increased with the biodiesel concentration. As such trends are not accompanied by any decrease of particle mean diameter with ester composition, it is concluded that particles remain unsaturated, and consequently, a decrease in the soot formation does not lead to any restriction on hydrocarbon adsorption.

The sulphate content in the particulate matter was also reduced, consistently with the sulfur reduction in the fuel. Highest reductions were found with sunflower methyl ester.

The presence of vegetable esters in the fuel led to dramatic decreases in the number of particles, along with the reduction on emitted particulate mass, and to slight increases on the mean particle size.

1.6. AIMS AND OBJECTIVE

The objective of the work is that find a model equations of the exhaust emission of vegetable oil based diesel fuel which gives an easy to find the emissions and the characteristic of the biodiesel which is used for the combustion.

CHAPTER 2

LITERATURE REVIEW

L. G. Schumacher, S. C. Borgelt, D. Fosseen, W. Goetz C & W. G. Hires (1996): Diesel Corporation diesel engine (9.0 1) was fueled on blends of 10, 20, 30 and 40% soydiesel/diesel fuel. The engine was tested using the Environmental Protection Agency (EPA) heavy duty engine test cycle in an EPA certification test cell. A 56.6 m3/min (2000 cfm) PDP-CVS dilution tunnel, gaseous bench and particulate bench provided full gaseous and particulate emissions data. Fueling with biodiesel/diesel fuel blends reduced particulate matter (PM), total hydrocarbons (THC) and carbon monoxide (CO), while increasing oxides of nitrogen (NOx). The optimum blend of biodiesel and diesel fuel was a 20/80 biodiesel/diesel fuel blend. Retarded fuel injection timing reduced NOx emissions, while CO, THC and PM remained essentially constant with a 20/80 biodiesel/diesel fuel blend

O. M. I. Nwafor & G. Rice (1996): The concept that 100% vegetable oil cannot be used safely in a direct injection diesel engine for long periods of time have been stressed by many researchers. Short-term engine tests indicate good potential for vegetable oil fuels. Long-term endurance tests may show serious problems in injector coking, ring sticking, gum formation, and thickening of lubricating oil. These problems are related to the high viscosity and non volatility of vegetable oils, which cause inadequate fuel atomization and incomplete combustion.' Fuel blending is one method of reducing viscosity. This paper presents the results of an engine test on three fuel blends. Test runs were also made on neat rapeseed oil and diesel fuel as bases for comparison. There were no significant problems with engine operation using these alternative fuels. The test results showed increases in brake thermal efficiency as the amount of rapeseed oil in the blends increases. Reduction of power-output was also noted with increased amount of rapeseed oil in the blends. Test results include data on performance and gaseous emissions. Crankcase oil analyses showed a reduction in viscosity. Friction power was noted to increase as the amount of diesel fuel in the blend increases.

J.A. Lopez Sastre, J. San Jose' Alonso, C. Romero-Avila Garc, E.J. Lopez Romero-Avila, C. Rodriguez Alonso (2002): properties of vegetable oils which make them suitable, either totally or in part, for replacing C-diesel oil (which is the most widely used combustible for this purpose in Spain) in thermal energy production are studied. Vegetable oils, due to their agricultural origin, are able to reduce CO_2 emissions to the atmosphere as well as improve energetic crops.

A.S. Huzayyin, A.H. Bawady , M.A. Rady , A. Dawood (2003): An experimental evaluation of using jojoba oil as an alternate Diesel engine fuel has been conducted in the present work. Measurements of jojoba oil chemical and physical properties have indicated a good potential of using jojoba oil as an alternative Diesel engine fuel. Blending of jojoba oil with gas oil has been shown to be an effective method to reduce engine problems associated with the high viscosity of jojoba oil. Experimental measurements of different performance parameters of a single cylinder, naturally aspirated, direct injection, Diesel engine have been performed using gas oil and blends of gas oil with jojoba oil. Measurements of engine performance parameters at different load conditions over the engine speed range have generally indicated a negligible loss of engine power, a slight increase in brake specific fuel consumption and a reduction in engine NOx and soot emission using blends of jojoba oil with gas oil as compared to gas oil. The reduction in engine soot emission has been observed to increase with the increase of jojoba oil percentage in the fuel blend.

Magı´n Lapuertaa,, Octavio Armas, Rosario Ballesteros, Jesu´s Ferna´ndez(2004): Methyl esters obtained from the most interesting Spanish oleaginous crops for energy use—sunflower and Cynara, cardunculus were both used as diesel fuels, pure and in 25% blends with a commercial fuel which was also used pure. A stationary engine test bed, together with the instrumentation for chemical and morphological analysis, allowed studying the effect of these fuels on the engine emissions, soluble organic fraction of the particulate matter, origin of adsorbed hydrocarbons, sulphate content, particle number per unit filter surface, and meaning particle diameter. Both the consideration of the thermo chemical properties of the tested fuels and the computations of a chemical equilibrium model were helpful for the results analysis. These results proved that the use of these vegetable esters provides a significant reduction on particulate emissions, mainly due to reduced soot and sulphate formation. On the contrary, no increases in NOx emissions or reductions on mean particle size were found.

O.M.I. Nwafor (2004): The world energy demand has, for the last two decades, witnessed uncertainties in two dimensions. Firstly, the price of conventional fossil fuel is too high and has added burden on the economy of the importing nations. Secondly, combustion of fossil fuels is the main culprit in increasing the global carbon dioxide (CO_2) level, a consequence of global warming. The scarcity and depletion of conventional sources are also cases of concern and have prompted research world-wide into alternative energy sources for internal combustion engines. Biofuels appear to be a potential alternative "greener" energy substitute for fossil fuels. The problem of using neat vegetable oils in diesel engines relates to their high viscosity. Experiments were designed to study the e6ect of reducing viscosity by increasing the inlet temperature of vegetable oil fuel on combustion and emission characteristics of diesel engine. The test results showed that the CO production with heated fuel is a little higher than the diesel fuel at higher loading conditions. The CO concentrations in the exhaust were higher for unheated oil operation compared to other fuels. The heated oil showed marginal increase in CO_2 emissions compared to diesel fuel. The hydrocarbon emissions were significantly reduced when running on plant oils. The fuel consumption was a little worse when running on plant fuel. The ignition delay was longer for unheated plant fuel operation.

Gerhard Knothe (2005): Biodiesel, defined as the mono-alkyl esters of vegetable oils or animal fats, is an alternative diesel fuel that is becoming accepted in a steadily growing number of countries around the world. Since the source of biodiesel varies with the location and other sources such as recycled oils are continuously gaining interest, it is important to possess data on how the various fatty acid profiles of the different sources can influence biodiesel fuel properties. The properties of the various individual fatty esters that comprise biodiesel determine the overall fuel properties of the biodiesel fuel. In turn, the properties of the various fatty esters are determined by the structural features of the fatty acid and the alcohol moieties that comprise a fatty ester. Structural features that influence the physical and fuel properties of a fatty ester molecule are chain length, degree of unsaturation, and branching of the chain. Important fuel properties of biodiesel that are influenced by the fatty acid profile and, in turn, by the structural features of the various fatty esters are cetane number and ultimately exhaust emissions, heat of combustion, cold flow, oxidative stability, viscosity, and lubricity.

Y.D. Wang , T. Al-Shemmeri , P. Eames , J. McMullan , N. Hewitt , Y. Huang , S. Rezvani (2005): Experimental tests have been carried out to evaluate the performance and gaseous emission characteristics of a diesel engine when fuelled with vegetable oil and its blends of 25%, 50%, and 75% of vegetable oil with ordinary diesel fuel separately. Tests on ordinary diesel fuel have also been carried out for comparison purposes. A series of tests are conducted and repeated six times for each of the test fuels. The engine works at a fixed speed of 1500 rpm, but at different loads respectively, i.e. 0%, 25%, 50%, 75% and 100% of engine full loads. The performance and the emission characteristics of exhaust gases of the engine are analyzed and compared. The experimental results show that the basic engine performance – power output and fuel consumption are comparable to diesel when fueled with vegetable oil and its blends. The emission of nitrogen oxides (NOx) from vegetable oil and its blends are lower than that of pure diesel fuel. This emission character found in the tests to some extent is of significance for the practical application of vegetable oil to replace ordinary diesel fuel.

Md. Nurun Nabi , Md. Shamim Akhter, Mhia Md. Zaglul Shahadat (2005): combustion and exhaust emissions with neat diesel fuel and diesel–biodiesel blends have been investigated. In the investigation, firstly biodiesel from non-edible neem oil has been made by esterification. Biodiesel fuel (BDF) is chemically known as mono-alkyl fatty acid ester. It is renewable in nature and is derived from plant oils including vegetable oils. BDF is non-toxic, biodegradable, recycled resource and essentially free from sulfur and carcinogenic benzene. In the second phase of this investigation, experiment has been conducted with neat diesel fuel and diesel–biodiesel blends in a four stroke naturally aspirated (NA) direct injection (DI) diesel engine. Compared with conventional diesel fuel, diesel–biodiesel blends showed lower carbon monoxide (CO), and smoke emissions but higher oxides of nitrogen (NOx) emission. However, compared with the diesel fuel, NOx emission with diesel–biodiesel blends was slightly reduced when EGR was applied.

A.S. Ramadhas, C. Muraleedharan, S. Jayaraj (2005): Recent concerns over the environment, increasing fuel prices and scarcity of its supply have promoted the interest in development of the alternative sources for petroleum fuels. At present, biodiesel is commercially produced from the refined edible vegetable oils such as sunflower oil, palm oil and soybean oil, etc. by alkaline-catalyzed esterification process. This process is not suitable for production of biodiesel from many unrefined non-edible vegetable oils because of their high acid value. Hence, a two-step esterification method is developed to produce biodiesel from high FFA vegetable oils. The biodiesel production method consists of acid-catalyzed pretreatment followed by an alkaline-catalyzed transesterification. The important properties of methyl esters of rubber seed oil are compared with other esters and diesel. Pure rubber seed oil, diesel and biodiesel are used as fuels in the compression ignition engine and the performance and emission characteristics of the engine are analyzed. The lower blends of biodiesel increase the brake thermal efficiency and reduce the fuel consumption. The exhaust gas emissions are reduced with increase in biodiesel concentration. The experimental results proved that the use of biodiesel (produced from unrefined rubber seed oil) in compression ignition engines is a viable alternative to diesel.

C.D. Rakopoulos , K.A. Antonopoulos, D.C. Rakopoulos, D.T. Hountalas, E.G. Giakoumis(2006): An extended experimental study is conducted to evaluate and compare the use of various Diesel fuel supplements at blend ratios of 10/90 and 20/80, in a standard, fully instrumented, four stroke, direct injection (DI), Ricardo/Cussons 'Hydra' Diesel engine located at the authors' laboratory. More specifically, a high variety of vegetable oils or bio-diesels of various origins are tested as supplements, i.e. cottonseed oil, soybean oil, sunflower oil and their corresponding methyl esters, as well as rapeseed oil methyl ester, palm oil methyl ester, corn oil and olive kernel oil. The series of tests are conducted using each of the above fuel blends, with the engine working at a speed of 2000 rpm and at a medium and high load. In each test, volumetric fuel consumption, exhaust smokiness and exhaust regulated gas emissions such as nitrogen oxides (NOx), carbon monoxide (CO) and total unburned hydrocarbons (HC) are measured. From the first measurement, specific fuel consumption and brake thermal efficiency are computed. The differences in the measured performance and exhaust emission parameters from the baseline operation of the engine, i.e. when working with neat Diesel fuel, are determined and compared. This comparison is extended between the use of the vegetable oil blends and the bio-diesel blends. Theoretical aspects of Diesel engine combustion, combined with the widely differing physical and chemical properties of these Diesel fuel supplements against the normal Diesel fuel, are used to aid the correct interpretation of the observed engine behavior.

Octavio Armas , Juan J. Herna´ndez, Marıa D. Ca´rdenas(2006): This work is focused on the measurement and analysis of the smoke opacity resulting from a Diesel engine fuelled with conventional fuel and biofuels under transient conditions. Methyl esters obtained from used cooking and unused vegetable oils were tested as diesel fuels, pure and blended with 30% and 70% of a commercial diesel fuel which was also used pure. A commercial engine was mounted in a test bench prepared for operating in different transient conditions. A smoke meter AVL 439 allowed for the study of the effect of these fuels on the smoke opacity under varied operating conditions. The thermo chemical properties of the test fuels and the engine parameters, such as fuel/air ratio or exhaust gas recirculation (EGR) ratio, were used for the analysis and interpretation of the results. The engine transient processes studied were (a) engine start, (b) load increase at constant engine speed and (c) engine speed decrease at constant torque. These results suggested that the use of the diesel blends containing vegetable esters is an interesting alternative for a significant reduction in smoke opacity not only in steady conditions but also in transient engine operation, the latter being the most usual condition in passenger vehicle

Magı´n Lapuerta, Octavio Armas, Jose´Rodrıguez Fernandez (2007): The call for the use of biofuels which is being made by most governments following international energy policies is presently finding some resistance from car and components manufacturing companies, private users and local administrations. This opposition makes it more difficult to reach the targets of increased shares of use of biofuels in internal combustion engines. One of the reasons for this resistance is a certain lack of knowledge about the effect of biofuels on engine emissions. This paper collects and analyzes the body of work written mainly in scientific journals about diesel engine emissions when using biodiesel fuels as opposed to conventional diesel fuels. Since the basis for comparison is to maintain engine performance, the first section is dedicated to the effect of biodiesel fuel on engine power, fuel consumption and thermal efficiency. The highest consensus lies in an increase in fuel consumption in approximate proportion to the loss of heating value. In the subsequent sections, the engine emissions from biodiesel and diesel fuels are compared, paying special attention to the most concerning emissions: nitric oxides and particulate matter, the latter not only in mass and composition but also in size distributions. In this case the highest consensus was found in the sharp reduction in particulate emissions.

CHAPTER 3

FUNDAMENTALS OF TRANSESTERIFICATION

3.1. GENERAL

Transesterification is the displacement of alcohol from an ester by another in a process similar to hydrolysis, except than alcohol is used instead of water. This process has been widely used to reduce the high viscosity of triglycerides. The transesterification reaction is represented by the general equation as Fig. 1.3. If methanol is used in this process it is called methanolysis. Transesterification is one of the reversible reactions and proceeds essentially by mixing the reactants. However, the presence of a catalyst (a strong acid or base) accelerates the conversion.

3.2. PRINCIPLE OF KINETICS

Derivation of the kinetics of a reaction is based upon a few generally accepted principles. The main ones are presented here, for use in the succeeding chapters. Chemical reactions are classified as either irreversible or reversible. An irreversible reaction proceeds in only one direction, which by convention is assigned to be from left to right:

$$FFA + OH^{-} \xrightarrow{k_{12}} A + W \qquad (3.1)$$

This reaction shows the saponification of free fatty acid by a hydroxide base, to form soap (*A*) and water (*W*). The reaction can only proceed in the direction that creates soap and water; it cannot make free fatty acids and hydroxide from soap and water. The rate of reaction is governed by the rate constant k_{12}.

A reversible reaction can proceed in either direction:

$$OH^{-} + ROH \underset{k1r}{\overset{k1}{\rightleftarrows}} RO^{-} + H_2O \qquad (3.2)$$

This shows the conversion between an alcohol and the hydroxide base on the left, and alkoxide and water on the right. Alkoxide is formed when the hydroxide hydrogen of an alcohol is removed by a base. This reaction can proceed in either direction. The forward rate is governed by the rate constant k_1, while the rate of the reverse reaction is governed by k_{1r}. With reversible reactions, it is important to control the conditions of the reaction to favor the desired direction of conversion. Kinetics describes the rate of chemical reactions. Rate equations are typically written in terms of the concentrations of the reactants, for example,

$$\frac{-d[TG]}{dt} = k[TG]^2 \qquad (3.3)$$

In words, this equation says that the rate of disappearance of triglycerides is proportional to the square of the molar concentration of triglycerides. This rate expression appeared in a recent paper (Darnoko 2000), it is not the expression used in the model described here. Rate equations can be obtained by application of the law of mass action (LMA), which relates the rate of reaction to the concentrations of reactants. For example, LMA applied to Equation (1-1) produces the rate expression

$$\frac{dW}{dt} = k_{12}[FFA]^1[OH^-]^1 \qquad (3.4)$$

Under LMA, the rate of reaction in a given direction is proportional to the products of the reactant concentrations, each raised to the power of its coefficient in the reaction. The law of mass action only applies to elementary reactions, those which reflect the mechanism at the molecular level, and which occur as a single event. Chemists use simplicity tests to determine whether a reaction is elementary. These include number of collisions, number of bonds broken, number of bonds formed, integer reaction coefficients, and simplicity of reverse reaction. Even with simplicity tests, the order of reactions predicted by LMA should be verified by experiment. When a reversible reaction proceeds at the same rate in the forward and reverse directions, it is said to be in equilibrium. The relative proportions of the reactants are given by the equilibrium constant. The equilibrium condition for Equation (1-2) is given by

$$K_1 = \frac{k_1}{k_2} = \frac{[RO^-][H_2O]}{[ROH][OH^-]} \qquad (3.5)$$

The overall reaction for transesterification can be written symbolically as

$$TG + 3ROH \xrightarrow{KOH} G + 3E \qquad (3.6)$$

This reaction occurs in three steps:

$$TG + ROH \Leftrightarrow DG + E \qquad (3.7)$$

$$DG + ROH \Leftrightarrow MG + E \qquad (3.8)$$

$$MG + ROH \Leftrightarrow G + E \qquad (3.9)$$

Where TG means triglycerides, DG means diglycerides, MG means monoglycerides, G means glycerol, ROH means alcohol, E means alkyl ester, and A means soap. The catalyst is usually either potassium hydroxide (KOH), or sodium hydroxide (NaOH), also known as lye. When the catalyst dissolves in the alcohol, it forms an ionic solution, in which the K+ or Na+ ions and the OH- ions are not directly bound to each other. The active ingredient is the hydroxide ion, OH-. When describing chemical reactions and rate equations, the K+ or Na+ ions are never written out explicitly. Hydroxide ion is the catalyst for base-catalyzed transesterification. It is also a reactant in the competing saponification reactions, in which it is consumed. Thus, saponification robs the transesterification reaction not only of reactants that could be made into biodiesel, but also of the catalyst needed for the reaction to proceed.

Transesterification of triglycerides produce fatty acid alkyl esters and glycerol. The glycerol layer settles down at the bottom of the reaction vessel. Diglycerides and monoglycerides are the intermediates in this process. The mechanism of transesterification is described in Fig. 3.1.

The step wise reactions are reversible and a little excess of alcohol is used to shift the equilibrium towards the formation of esters. In presence of excess alcohol, the foreword reaction is pseudo-first order and the reverse reaction is found to be second order. It was also observed that transesterification is faster when catalyzed by alkali.

The mechanism of alkali-catalyzed transesterification is described in Fig. 3.3. The first step involves the attack of the alkoxide ion to the carbonyl carbon of the triglyceride molecule, which results in the formation of a tetrahedral intermediate. The reaction of this intermediate with an alcohol produces the alkoxide ion in the second step. In the last step the rearrangement of the tetrahedral intermediate gives rise to an ester and a diglyceride.

$$\underset{\text{Ester}}{RCOOR^1} + \underset{\text{Alcohol}}{R^2OH} \xleftrightarrow{Catalyst} \underset{\text{Ester}}{RCOOR^2} + \underset{\text{Alcohol}}{R^1OH} \quad (3.10)$$

Transesterification can be catalyzed by Brownsted acids, preferably by sulfonic and sulfuric acids. These catalysts give very high yields in alkyl esters but these reactions are slow, requiring typically temperature above 100.8°C and more than 3 h to complete the conversion. However, it can be extended to di- and tri-glycerides.

The protonation of carbonyl group of the ester leads to the carbocation, which after a nucleophilic attack of the alcohol produces a tetrahedral intermediate. This intermediate eliminates glycerol to form a new ester and to regenerate the catalyst (Fig.3.4). The methanolysis of soybean oil in the presence of 1 % H_2SO_4 with an alcohol/oil molar ratio 30:1 was studied. At a reaction temperature of 65.8°C the conversion was observed to be completed in 20 h, while butanolysis at 117.8°C and ethanolysis at 78.8°C using the same quantities of catalyst and alcohol, take 3 and 18 h, respectively.

3.3. VARIABLES AFFECTING TRANSESTERIFICATION REACTION

The process of transesterification is affected by various factors depending upon the reaction condition used. The effects of these factors are described below.

3.3.1. Effect of free fatty acid and moisture

The free fatty acid and moisture content are key parameters for determining the viability of the vegetable oil transesterification process. To carry the base catalyzed reaction to completion; a free fatty acid (FFA) value lower than 3% is needed. The higher the acidity of the oil, smaller is the conversion efficiency. Both, excess as well as insufficient amount of catalyst may cause soap formation. Ma et al. [49] studied the transesterification of beef tallow catalyzed by NaOH in presence of free fatty acids and water. Without adding FFA and water, the apparent yield of beef tallow methyl esters (BTME) was highest. When 0.6% of FFA was added, the apparent yield of BTME reached the lowest, less than 5%, with any level of water added.

The products were solid at room temperature, similar to the original beef tallow. When 0.9% of water was added, without addition of FFA, the apparent yield was about 17%. If the low qualities of beef tallow or vegetable oil with high FFA are used to make biodiesel fuel, they must be refined by saponification using NaOH solution to remove free fatty acids. Conversely, the acid catalyzed process can also be used for esterification of these free fatty acids.

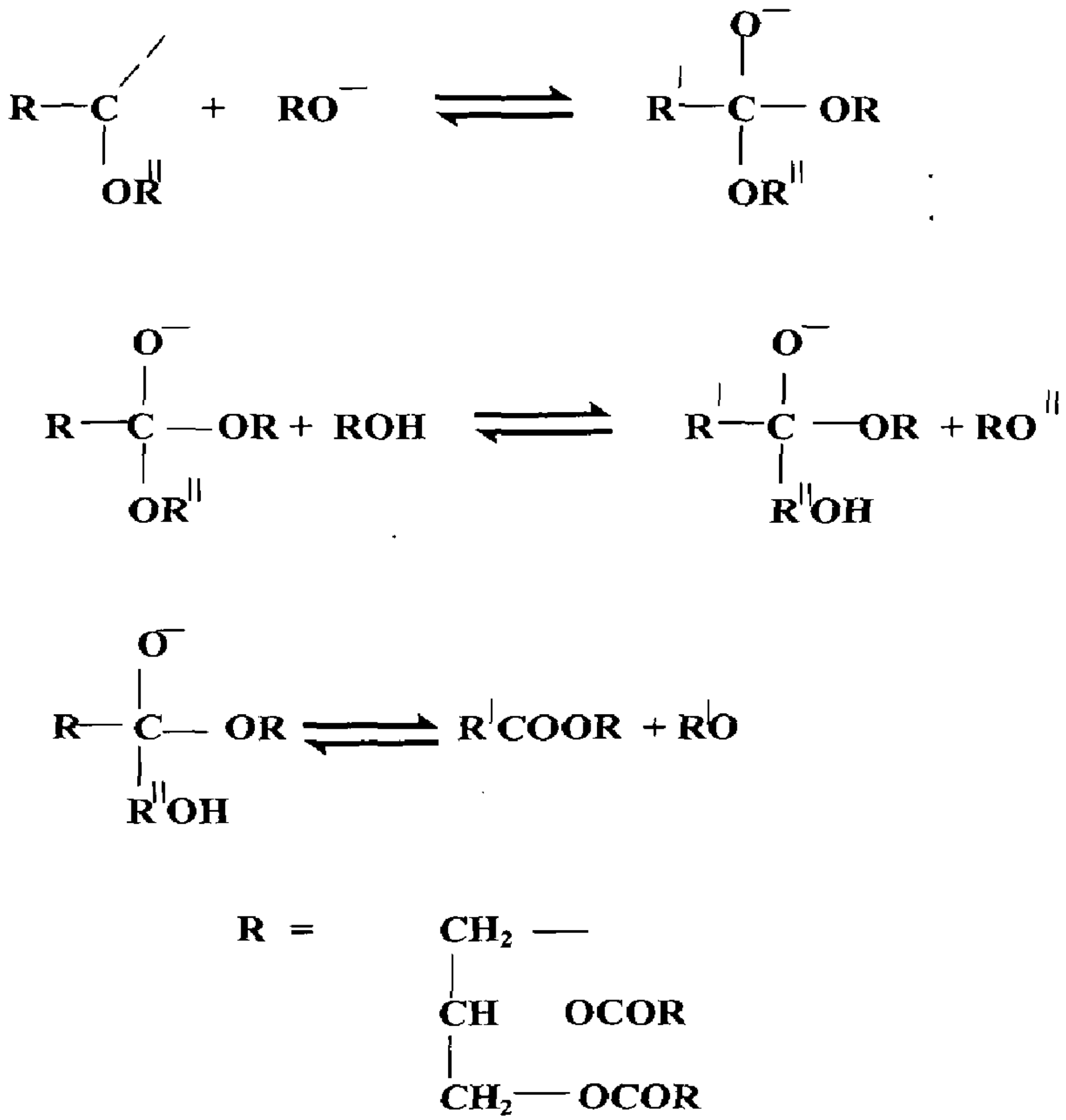
$$Triglyceride + R' \leftrightarrow Digleceride + RCOOR^1 \tag{3.11}$$

$$Digleceride + R'OH \leftrightarrow Monogleceride + RCOOR' \tag{3.12}$$

$$Monoglceride + R'OH \leftrightarrow Glycerol + RCOOR^1 \tag{3.13}$$

The starting materials used for base catalyzed alcoholysis should meet certain specifications. The triglycerides should have lower acid value and all material should be substantially anhydrous. The addition of more sodium hydroxide catalyst compensates for higher acidity, but the resulting soap causes an increase in viscosity or formation of gels that interferes in the reaction as well as with separation of glycerol. When the reaction conditions do not meet the above requirements, ester yields are significantly reduced. The methoxide and hydroxide of sodium or potassium should be maintained in anhydrous state. Prolonged contact with air will diminish the effectiveness of these catalysts through interaction with moisture and carbon dioxide.

Most of the biodiesel is currently made from edible oils by using methanol and alkaline catalyst. However, there are large amounts of low cost oils and fats that could be converted to biodiesel. The problems with processing these low cost oils and fats are that they often contain large amounts of free fatty acids that cannot be converted to biodiesel using alkaline catalyst. Therefore, two-step esterification process is required for these feed stocks. Initially the FFA of these can be converted to fatty acid methyl esters by an acid catalyzed pretreatment and in the second step transesterification is completed by using alkaline catalyst to complete the reaction. Initial process development was performed with synthetic mixture containing 20 and 40% free fatty acid prepared by using palmitic acid. Process parameters such as molar ratio of alcohol to oil, type of alcohol, amount of acid catalyst, reaction time, and free fatty acid level were investigated to determine the best strategy for converting the free fatty acids to usable esters. The work showed that the acid level of the high free fatty acids feed stocks could be reduced to less than 1 % with a two step pretreatment reaction. The reaction mixture was allowed to settle between steps so that the water containing phase could be removed. The two-step pretreatment reaction was demonstrated with actual feed stocks, including yellow grease with 12% free fatty acid and brown grease with 33% free fatty acids. After reducing the acid levels of these feed stocks to less than 1%, the transesterification reaction was completed with an alkaline catalyst to produce fuel grade biodiesel.

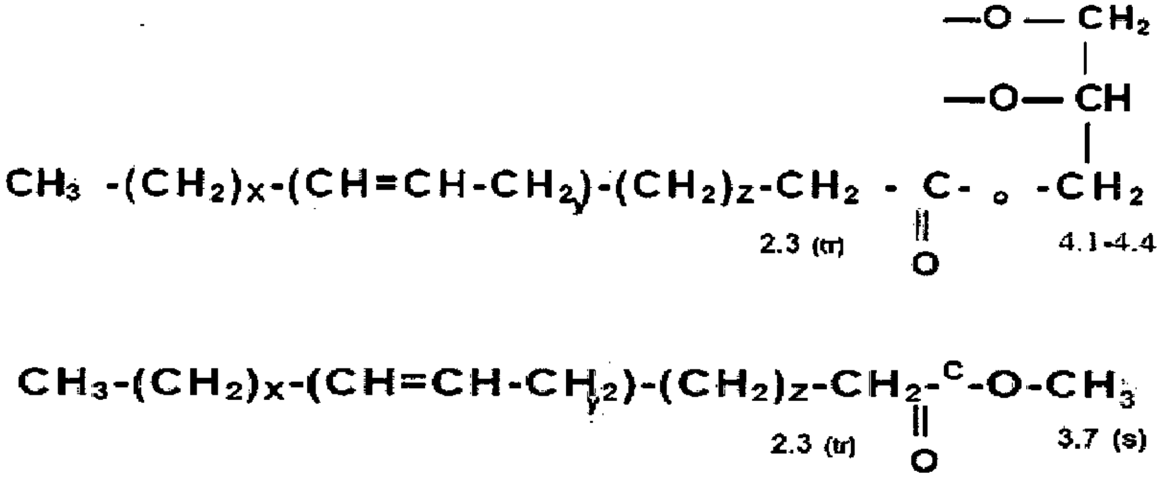


R' = Carbon chain of fatty acid

R = Alkyl group of alcohol

Fig.3.1. Mechanism of base catalyzed transesterfication

Turck et al. [50] have investigated the negative influence of base catalyzed transesterification of triglycerides containing substantial amount of free fatty acid. Free fatty acids react with the basic catalyst added for the reaction and give rise to soap, as a result of which, one part of the catalyst is neutralized and is therefore no longer available for transesterification. These high FFA content oils/fats are processed with an immiscible basic glycerol phase so as to neutralize the free fatty acids and cause them to pass over into the glycerol phase by means of monovalent alcohols. The triglycerides are subjected to transesterification, using a base as catalyst, to form fatty acid alkyl esters, characterized in that after its separation; the basic glycerol phase produced during transesterification of the triglycerides is used for processing the oils/fats for removal of free fatty acids. The minimum amount of catalyst required for this process was calculated, relative to 1000 g of the oil to be processed, as a function of the acid value and the mean molar mass of the oil/fat.



$$CH_3-(CH_2)_x-(CH=CH-CH_2)_y-(CH_2)_z-CH_2-\underset{\underset{O}{\|}}{C}-O-CH_2$$

$$CH_3-(CH_2)_x-(CH=CH-CH_2)_y-(CH_2)_z-CH_2-\underset{\underset{O}{\|}}{C}-O-CH_3$$

Fig.3.2. Assignment of shift of protons in transesterification reaction

3.3.2. Catalyst type and concentration

Catalysts used for the transesterification of triglycerides are classified as alkali, acid, enzyme or heterogeneous catalysts, among which alkali catalysts like sodium hydroxide, sodium methoxide, potassium hydroxide, potassium methoxide are more effective. If oil has high free fatty acid content and more water, acid catalyzed transesterification is suitable. The acids could be sulfuric acid, phosphoric acid, hydrochloric acid or organic sulfonic acid. Methanolysis of beef tallow was studied with catalysts NaOH and NaOMe. Comparing the two catalysts, NaOH was significantly better than NaOMe. The catalysts

NaOH and NaOMe reached their maximum activity at 0.3 and 0.5% w/w of the beef tallow, respectively. Sodium methoxide causes formation of several by products mainly sodium salts, which are to be treated as waste. In addition, high quality oil is required with this catalyst. This was different from the previous reports in which ester conversion at the 6:1 molar ratio of alcohol/oil for 1% NaOH and 0.5% NaOMe were almost the same after 60 min. Part of the difference may be attributed to the differences in the reaction system used. As a catalyst in the process of alkaline methanolysis, mostly sodium hydroxide or potassium hydroxide have been used, both in concentration from 0.4 to 2% w/w of oil. Refined and crude oils with 1% either sodium hydroxide or potassium hydroxide catalyst resulted successful conversion. Methanolysis of soybean oil with the catalyst 1% potassium hydroxide has given the best yields and viscosities of the esters. Attempts have been made to use basic alkaline-earth metal compounds in the transesterification of rapeseed oil for production of fatty acid methyl esters. The reaction proceeds if methoxide ions are present in the reaction medium. The alkaline-earth metal hydroxides, alkoxides and oxides catalyzed reaction proceeds slowly as the reaction mixture constitutes a three-phase system oil-methanol-catalyst, which for diffusion reason inhibits the reaction. The catalytic activity of magnesium oxide, calcium hydroxide, calcium oxide, calcium methoxide, barium hydroxide, and for comparison, sodium hydroxide during the transesterification of rapeseed oil was investigated. Sodium hydroxide exhibited the highest catalytic activity in this process. The degree to which the substrates were reacted reached 85% after 30 min of the process and 95% after 1.5 h, which represented a close value to the equilibrium. Barium hydroxide was slightly less active with a conversion of 75% after 30 min. Calcium methoxide was medially active. The degree to which the substrates were reacted was 55% after 30 min. eighty percents after 1 h and state of reaction equilibrium (93%) was reached after 2.5 h. The rate of reaction was slowest when catalyzed by CaO. Magnesium oxide and calcium hydroxide showed no catalytic activity in rapeseed oil methanolysis. Acid catalyzed transesterification was studied with waste vegetable oil. The reaction was conducted at four different catalyst concentrations, 0.5, 1.0, 1.5 and 2.25 M HCl in presence of 100% excess alcohol and the result was compared with 2.25 M H_2SO_4 and the decrease in viscosity was observed. H_2SO_4 has superior catalytic activity in the range of 1.5-2.25 M concentration. Although chemical transesterification using an alkaline catalysis process gives high conversion levels of triglycerides to their corresponding methyl esters in short reaction times, the reaction has several drawbacks: it is energy intensive, recovery of glycerol is difficult, the acidic or alkaline catalyst has to be removed from the product, alkaline waste water require treatment, and free fatty acid and water interfere the reaction. Enzymatic catalysts like lipases are able to effectively catalyze the transesterification of triglycerides in either aqueous or non-aqueous systems, which can overcome the problems mentioned above. In particular, the by-products, glycerol can be easily removed without any complex process, and also that free fatty acids contained in waste oils and fats can be completely converted to alkyl esters. On the other hand, in general the production cost of a lipase catalyst is significantly greater than that of an alkaline one.

3.3.3. Molar ratio of alcohol to oil and type of alcohol

One of the most important variables affecting the yield of ester is the molar ratio of alcohol to triglyceride. The stoichiometry ratio for transesterification requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid alkyl esters and one mole of glycerol. However, transesterification is an equilibrium reaction in which a large excess of alcohol is required to drive the reaction to the right. For maximum conversion to the ester, a molar ratio of 6:1 should be used. The molar ratio has no effect on acid, peroxide, saponification and iodine value of methyl esters. However, the high molar ratio of alcohol to vegetable oil interferes with the separation of glycerin because there is an increase in solubility. When glycerin remains in solution, it helps drive the equilibrium to back to the left, lowering the yield of esters. The transesterification of Cynara oil with ethanol was studied at molar ratios between 3:1 and 15:1. The ester yield increased as the molar ratio increased up to a value of 12:1. The best results were for molar ratios between 9:1 and 12:1. For molar ratios less than 6:1, the reaction was incomplete. For a molar ratio of 15:1 the separation of glycerin is difficult and the apparent yield of esters decreased because a part of the glycerol remains in the biodiesel phase. Therefore, molar ratio 9:1 seems to be the most appropriate.

The base catalyzed formation of ethyl ester is difficult compared to the formation of methyl esters. Specifically the formation of stable emulsion during ethanolysis is a problem. Methanol and ethanol are not miscible with triglycerides at ambient temperature, and the reaction mixtures are usually mechanically stirred to enhance mass transfer. During the course of reaction, emulsions usually form. In the case of methanolysis, these emulsions quickly and easily break down to form a lower glycerol rich layer and upper methyl ester rich layer. In ethanolysis, these emulsions are more stable and severely complicate the separation and purification of esters. The emulsions are caused in part by formation of the intermediates monoglycerides and diglycerides, which have both polar hydroxyl groups and non-polar hydrocarbon chains. These intermediates are strong- surface active agents. In the process of alcoholysis, the catalyst, either sodium hydroxide or potassium hydroxide is dissolved in polar alcohol phase, in which triglycerides must transfer in order to react. The reaction is initially mass-transfer controlled and does not conform to expected homogeneous kinetics. When the concentrations of these intermediates reach a critical level, emulsions form. The larger non-polar group in ethanol, relative to methanol, is assumed to be the critical factor in stabilizing the emulsions. However, the concentration of mono- and di-glycerides is very low, and then the emulsions become unstable. This emphasizes the necessity for the reaction to be as complete as possible, thereby reducing the concentrations of mono- and di-glycerides.

3.3.4. Effect of reaction time and temperature

The conversion rate increases with reaction time. Freedman et al. [51] transesterified peanut, cotton-seed, sunflower and soybean oil under the condition of methanol-oil molar ratio 6:1, 0.5% sodium methoxide catalyst and 60.8°C. An approximate yield of 80% was observed after 1 min for soybean and sunflower oils. After 1 h, the conversion was almost the same for all four oils (93-98%). Ma et al. [52] studied the effect of reaction time on transesterification of beef tallow with methanol. The reaction was very slow during the first minute due to mixing and dispersion of methanol into beef tallow. From one to 5 min, the reaction proceeds very fast. The production of beef tallow methyl esters reached the maximum value at about 15 min. Transesterification can occur at different temperatures, depending on the oil used. For the transesterification of refined oil with methanol (6:1) and 1% NaOH, the reaction was studied with three different temperatures. After 0.1 h, ester yields were 94, 87 and 64% for 60, 45 and 32.8°C, respectively. After 1 h, ester formation was identical for 60 and 45.8°C runs and only slightly lower for the 32.8°C run. Temperature clearly influenced the reaction rate and yield of esters.

3.3.5. Mixing intensity

Mixing is very important in the transesterification reaction, as oils or fats are immiscible with sodium hydroxide-methanol solution. Once the two phases are mixed and the reaction is started, stirring is no longer needed. Initially the effect of mixing on transesterification of beef tallow was study by Ma et al. [52]. No reaction was observed without mixing and when NaOH-MeOH was added to the melted beef tallow in the reactor while stirring, stirring speed was insignificant. Reaction time was the controlling factor in determining the yield of methyl esters. This suggested that the stirring speeds investigated exceeded the threshold requirement of mixing.

3.3.6. Effect of using organic cosolvents

The methoxide base catalyzed methanolysis of soybean oil at 40.8°C (methanol-oil molar ratio 6:1) shows that to form methyl esters proceeds approximately more slowly than butanolysis at 30.8°C. This is interpreted to be the result of a two phase reaction in which methanolysis occurs only in the methanol phase. Low oil concentration in methanol causes the slow reaction rate; a slow dissolving rate of the oil in methanol causes an initiation period. Intermediate mono- and di-glycerides preferentially remain in the methanol, and react further, thus explaining the deviation from second order kinetics. The same explanations apply for hydroxide ion catalyzed methanolysis. In order to conduct the reaction in a single phase, cosolvents like tetrahydrofuran, 1, 4- dioxane and diethyl ether were tested. Although, there are other cosolvents, initial study was conducted with tetrahydrofuran. At the 6:1 methanol-oil molar ratio the addition of 1.25 volume of tetrahydrofuran per volume of methanol produces an oil dominant one phase system in which methanolysis speeds up dramatically and occurs as fast as butanolysis. In particular, THF is chosen because its boiling point of 67.8°C is only two degrees higher than that of methanol. Therefore at the end of the reaction the unreacted methanol and THF can be co-distilled and recycled. Using tetrahydrofuran, transesterification of soybean oil was carried out with methanol at different concentrations of sodium hydroxide. The ester contents after 1 min for 1.1, 1.3, 1.4 and 2.0% sodium hydroxide were 82.5, 85, 87 and 96.2%, respectively. Results indicated that the hydroxide concentration could be increased up to 1.3 wt%, resulting in 95% methyl ester after 15 min. Similarly for transesterification of coconut oil using THF/MeOH volume ratio 0.87 with 1 % NaOH catalyst, the conversion was 99% in 1 min. A single-phase process for the esterification of a mixture of fatty acids and triglycerides were investigated. The process comprises forming a single-phase solution of fatty acids and triglyceride in an alcohol selected from methanol and ethanol, the ratio of said alcohol to triglyceride being 15:1-35:1. The solution further comprises a cosolvent in an amount to form the single phase. In a first step, an acid catalyst for the esterification of fatty acid is added. After a period of time, the acid catalyst is neutralized and a base catalyst for the transesterification of triglycerides is added. After a further period of time, esters are separated from the solution. An improved process was investigated for methanolysis and ethanolysis of fatty acid glycerides such as those found in naturally occurring fats and oils derived from plant animals. The processes comprise solubilizing oil or fat in methanol or ethanol by addition of a cosolvent in order to form a one-phase reaction mixture, and adding an esterification catalyst. The processes proceed quickly, usually in less than 20 min, at ambient temperatures, atmospheric pressure and without agitation. The co-solvent increases the rate of reaction by making the oil soluble in methanol, thus increasing contact of the reactants. The lower alkyl fatty acid monoesters produced by the process can be used as biofuels and are suitable as diesel fuel replacements or additives.

CHAPTER 4
DEVELOPMENT OF MODEL

4.1 GENERAL

This chapter describes the development of the mathematical expression to explain the change in the exhaust emission of the biodiesel fuel with the free fatty acid. We take

1. Blending ratio and CO
2. Blending ratio and CO_2
3. Blending ratio and NOx
4. Blending ratio, CO and CO_2
5. Blending ratio, CO and NOx
6. Blending ratio,CO_2 and NOx
7. Blending ratio, CO, CO_2 and NOx

A simple mathematical model based on the blending ratio and the exhaust emission are derived here first we derived the model equation from the experimental value given in paper "**HEAVY-DUTY ENGINE EXHAUST EMISSION TESTS USING METHYL ESTER SOYBEAN OIL/DIESEL FUEL BLENDS**" by "L. G. Schumacher, S. C. Borgelt, D. Fosseen, W. Goetz C & W. G. Hires " for soyabean oil.

4.2 ASSUMPTIONS

1. The variety of vegetable oil is same in respected season.
2. This model is valid only in the range of 10 to 50% blending ratio of biodiesel with diesel.
3. The process same for all the samples likes as the variable temperature, pressure and type of catalyst and the engine are same for all blending ratio.
4. The emission measuring method and instruments are same throughout the process.
5. The blending of biodiesel with diesel is to be uniform.
6. The injecting time is to be same for the entire sample throughout the measurement.

4.3 MODEL

The experimental data given in the above paper this is used here for develop model equation

referred in text?

Table4.1

Blending ratio	CO (g/hp-hr)	NOx (g/hp-hr)	CO2 (g/hp-hr)
B00	1.51	4.23	654
B10	1.43	4.38	657
B20	1.32	4.46	666
B30	1.14	4.80	675
B40	1.07	4.86	684
B50	1.01	4.96	690

By using the above data and polymath for develop the model equation for exhaust emission of biodiesel by the polymath the model equation for the blending ratio and the CO is given below.

1. Blending ratio and CO

Nonlinear regression (mrqmin)

Model: C01 = a1*C03+a2*C03^2

Variable	Ini guess	Value	95% confidence
a1	1	0.2939377	0.2265036
a2	0.2	0.2415497	0.1723831

2. Blending ratio and CO_2

Nonlinear regression (mrqmin)

Model: C01 = a1*C02+a2*C02^2

Variable	Ini guess	Value	95% confidence
a1	1	0.0149964	0.0021788
a2	0.2	-2.068E-05	3.244E-06

3. Blending ratio and NOx

Nonlinear regression (mrqmin)

Model: C01 = a0 + a1*C04

Variable	Ini guess	Value	95% confidence
a0	2	3.5928191	0.8512675
a1	1	-0.6159955	0.1841394

4. Blending ratio, CO and CO_2

Nonlinear regression (mrqmin)

Model: C01 = a0 + a1*C02 + a2*C03

Variable	Ini guess	Value	95% confidence
a0	2	6.9232144	14.033609
a1	1	-0.0096238	0.0184836
a2	4	0.228109	1.320391

5. Blending ratio, CO and NOx

Nonlinear regression (mrqmin)

Model: C01 = a0 + a1*C03 + a2*C04

Variable	Ini guess	Value	95% confidence
a0	-3	-2.5934076	10.833103
a1	0.09	1.4081565	2.4595737
a2	0.3	0.3440749	1.6853065

6. Blending ratio, CO_2 and NOx

Nonlinear regression (mrqmin)

Model: *C01 = a0+a1*C02+a2*C04*

Variable	Ini guess	Value	95% confidence
a0	3	8.4816168	5.7426307
a1	1	-0.0108599	0.0126857
a2	4	-0.0963481	0.6209392

7. Blending ratio, CO, CO_2 and NOx

Nonlinear regression (mrqmin)

Model: C01 = a1*C02+a2*C03+a3*C04

Variable	Ini guess	Value	95% confidence
a1	0.09	-0.0035725	0.0090137
a2	0.3	1.1828167	0.9264211
a3	0.4	0.3624197	1.0646661

The proposed model equation are given below for different emissions for

1. Blending ratio and CO

C01 = a1*C03+a2*C03^2

2. Blending ratio and CO_2

C01 = a1*C02+a2*C02^2

3. Blending ratio and NOx

C01 = a0 + a1*C04

4. Blending ratio, CO and CO_2

C01 = a0 + a1*C02 + a2*C03

5. Blending ratio, CO and NOx

.C01 = a0 + a1*C03 + a2*C04

6. Blending ratio, CO_2 and NOx

C01 = a0+a1*C02+a2*C04

6. Blending ratio, CO_2 and NOx

C01 = a1*C02+a2*C03+a3*C04

Is this the total work done?

Didn't the authors obtain these coefficients?

Plots?

CHAPTER 5

RESULT AND DISCUSSION

5.1 INTRODUCTION

In this chapter, results of the proposed model have been represented and discussed. The proposed model predicts the values of the coefficients with these estimated coefficients studies and check with the other experimental data published in the other paper graphically and numerically.

The theoretical curves calculated by the equations with constant obtained above were given in figure. A relatively good fit between one paper data to the other paper data can be noted.

The interdependence of the blending ratio and the exhaust emissions are studied. The exhaust emissions are varied with the variation in blending ratio. The exhaust emissions and the blending ratio can be calculated if we have the data of the other parameter which is required in the equation and the constant of the equation. The effect of the blending of biodiesel with diesel on the exhaust emission was studied.

When the blending ratio increased from 10% to 50% the curves shows that the effect of blending ratio on the exhaust emission in the figures when the blending ratio increased then the NOx concentration increased and this model is not valid above the blending ratio 50% because above 50% the coke formation takes place in the cylinder which give the emission problem and increase the CO and NOx emission to unrespectable level. There are few differences between the verifying value and the experimental value which are coming due to the incomplete mixing, geographical condition, and processing parameter like as temperature, pressure, catalyst type and quantity, storage condition and processing time etc which would affect the emission rate and quantity which give a negligible change which we ignore or do not consider.

5.2 ESTIMATION OF COEFFICIENT OF MODEL

A non-linear regression procedure was used to perform the mathematical fitting of the coefficients. The application of this algorithm to set of experimental data from ref[53].

The constant calculate from the experimental data for the different model equations are given below

1. Blending ratio and CO

Model: C01 = a1*C03+a2*C03^2

```
a1=0.29377
a2 = 0.2415497
```

2. Blending ratio and CO$_2$

Model: C01 = a1*C02+a2*C02^2

```
a1 = 0.0149964
a2 = -2.068E-05
```

3. Blending ratio and NOx

Model: C01 = a0 + a1*C04

```
a0 =  3.5928191
a1 = -0.6159955
```

4. Blending ratio, CO and CO$_2$

Model: C01 = a0 + a1*C02 + a2*C03

```
a0 = 6.9232144
a1 =-0.0096238
a2 = 0.2281090
```

5. Blending ratio, CO and NOx

Model: C01 = a0 + a1*C03 + a2*C04

```
a0 =-2.5934076
a1 = 1.4081565
a2 = 0.3440749
```

6. Blending ratio, CO$_2$ and NOx

Model: C01 = a0+a1*C02+a2*C04

```
a0 =8.4816168
a1 =-0.0108599
a2 =-0.0963481
```

7. Blending ratio, CO, CO$_2$ and NOx

Model: C01 = a1*C02+a2*C03+a3*C04

```
a1 =-0.0035725
a2 = 1.1828167
a3 = 0.3624197
```

Didn't the authors compare their data with some other data?

5.3 VALIDATION OF MODEL

Published data from ref[53]were used to check the validity of the model. Model predictions were in good agreement with those given by ref[54] and these results are given graphically. The reason of the slight variation are given below the slight variation due to the difference in the processing time and the processing parameters and the storage condition and time and the differ in the seed variety of vegetable oil and change in the testing engine specifications which give this difference in the exhaust emissions and the free fatty acid contents the free fatty acid give a bug difference in the exhaust emission because the change in the free fatty acid give the change in transesterification process and if the free fatty acid content is higher than soaps formation takes place and soaps may allow the emulsification that causes the separation of glycerol and ester phases to be less sharp. Soap formation also produces water that can hydrolyze the triglycerides and contribute to the formation of more soap. So that catalyst has been no longer available to accelerate the reaction. It is possible to add extra alkali catalyst and this give low quality triglycerides. So this gives the slight change in the emissions.

Orientation.

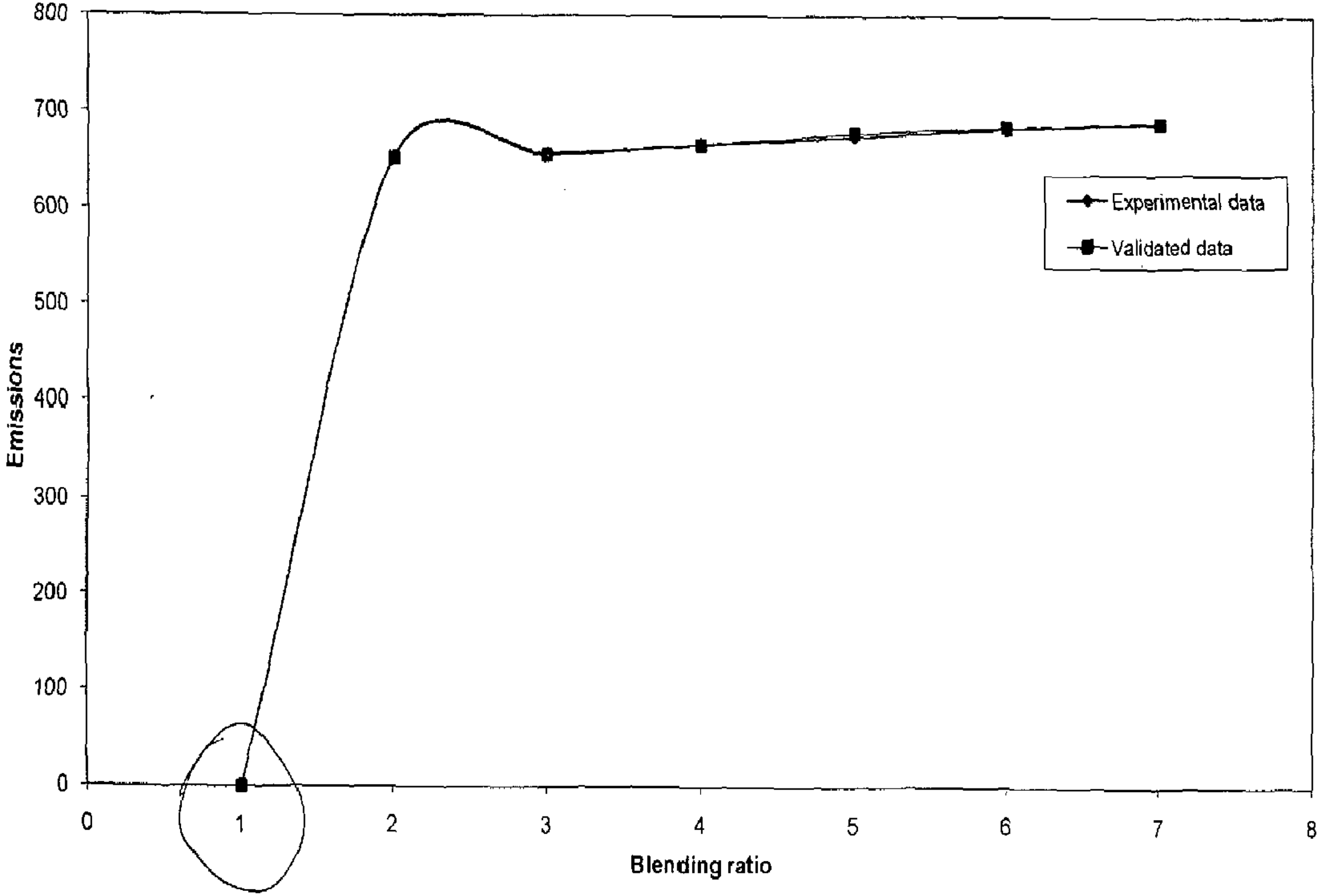


Figure5.1. Effect of Carbon dioxide emission in various blending ratio of soya bean oil with diesel

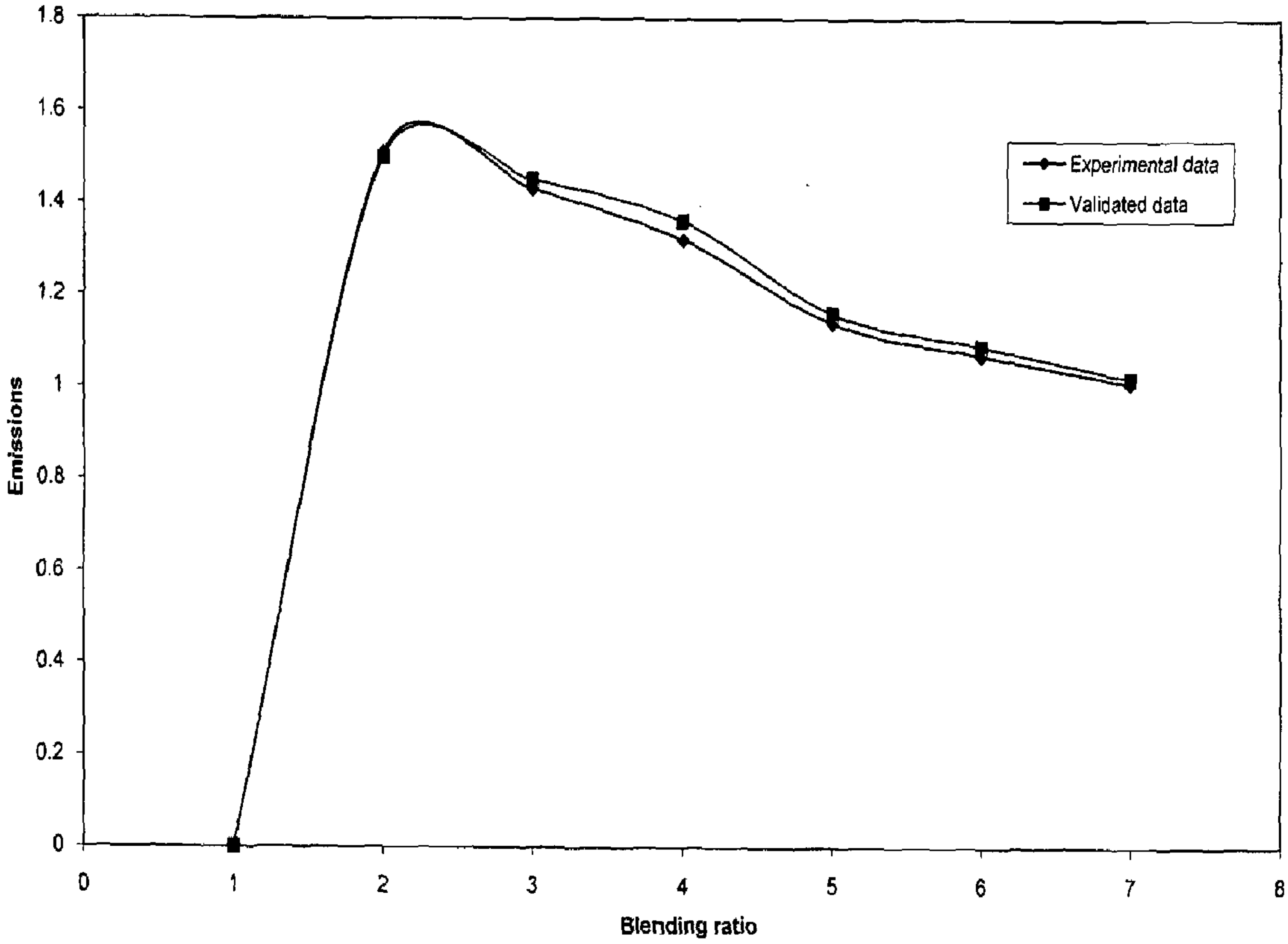


Figure5.2. Effect of Carbon monoxide emission in various blending ratio of soya bean oil with diesel

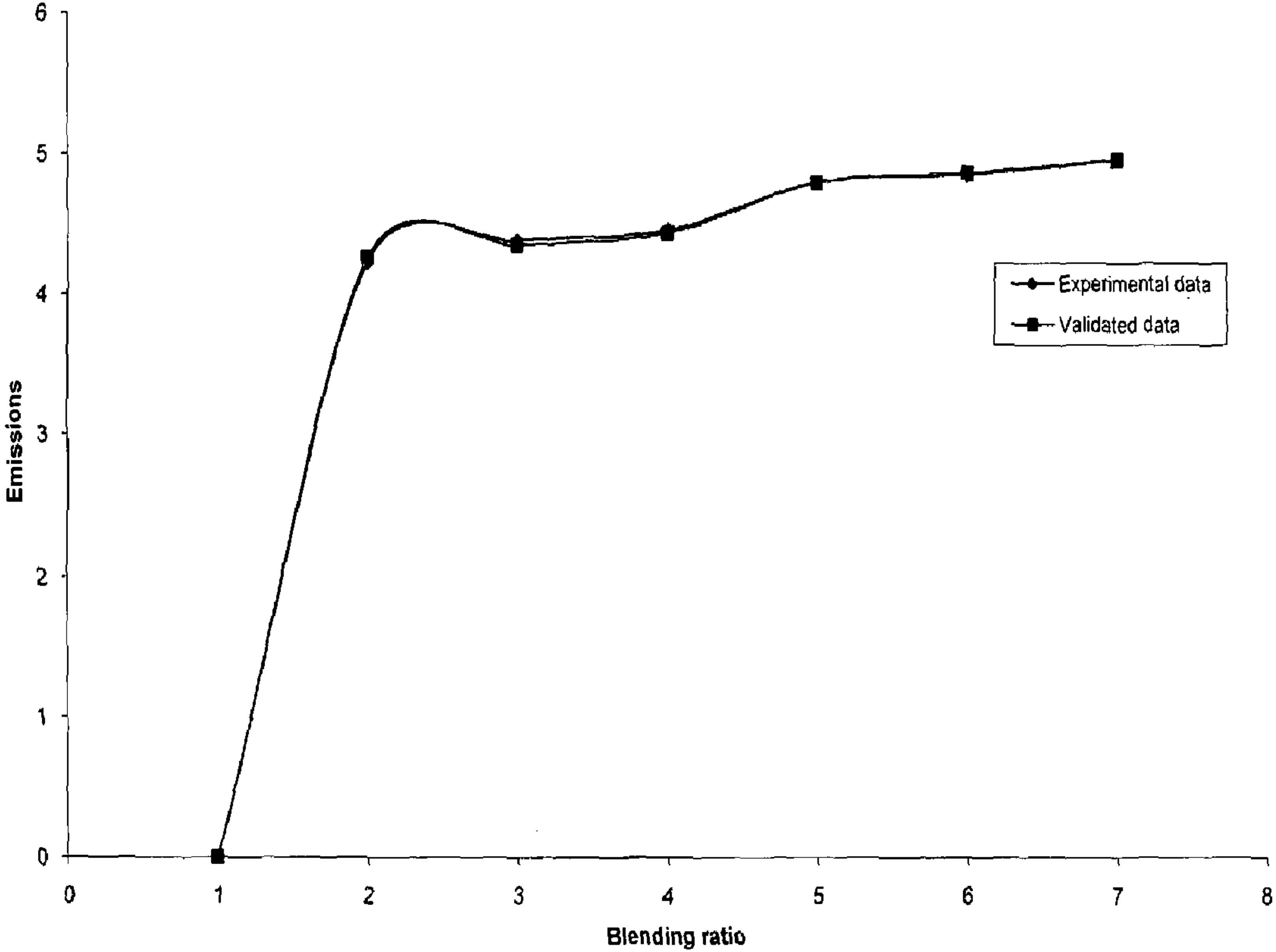


Figure5.3.Effect of Nitrogen oxide emission in various blending ratio of soya bean oil with diesel

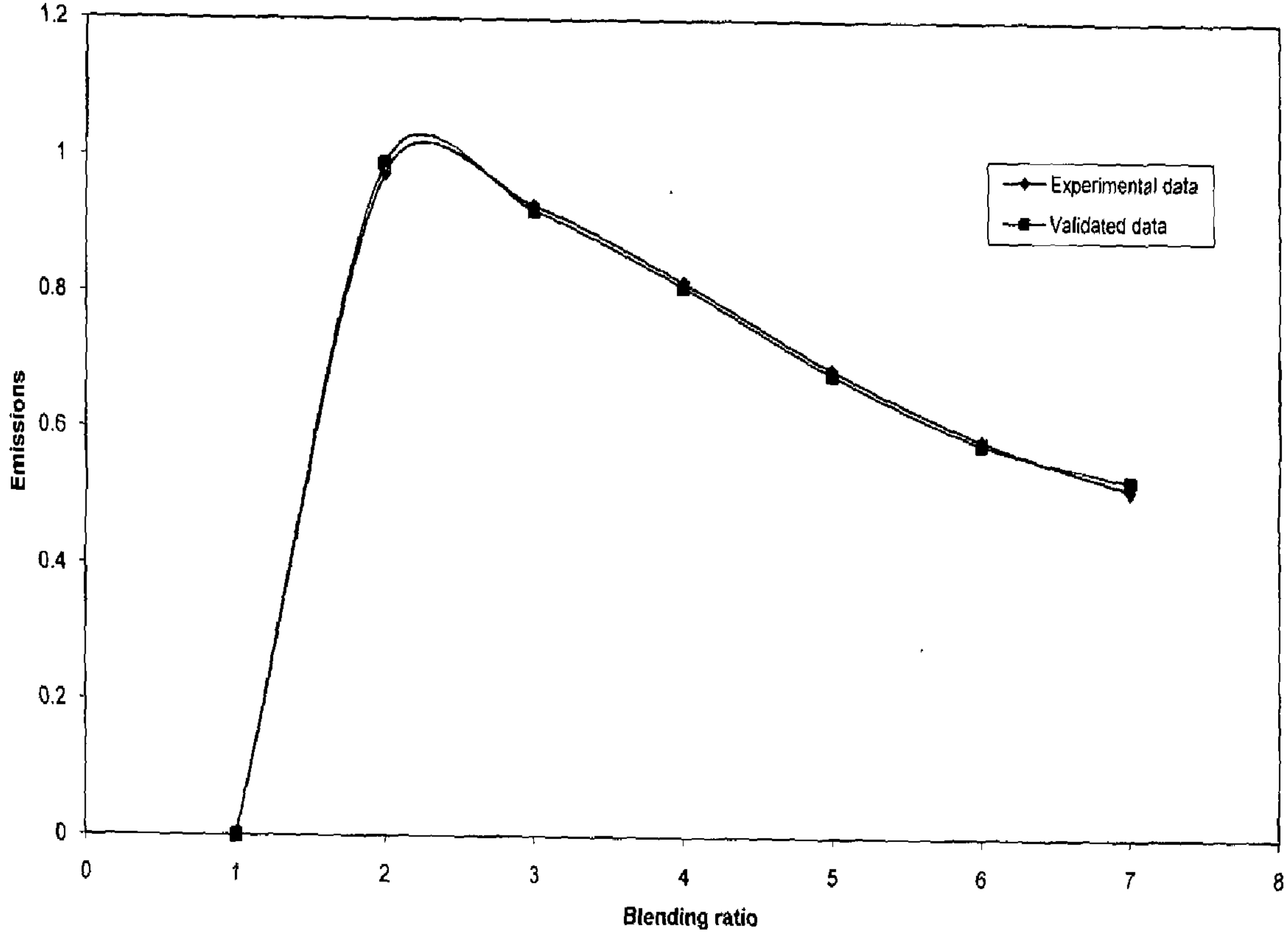


Figure5.4. Effect of Carbon di and mono oxide emission in various blending ratio of soya bean oil with diesel

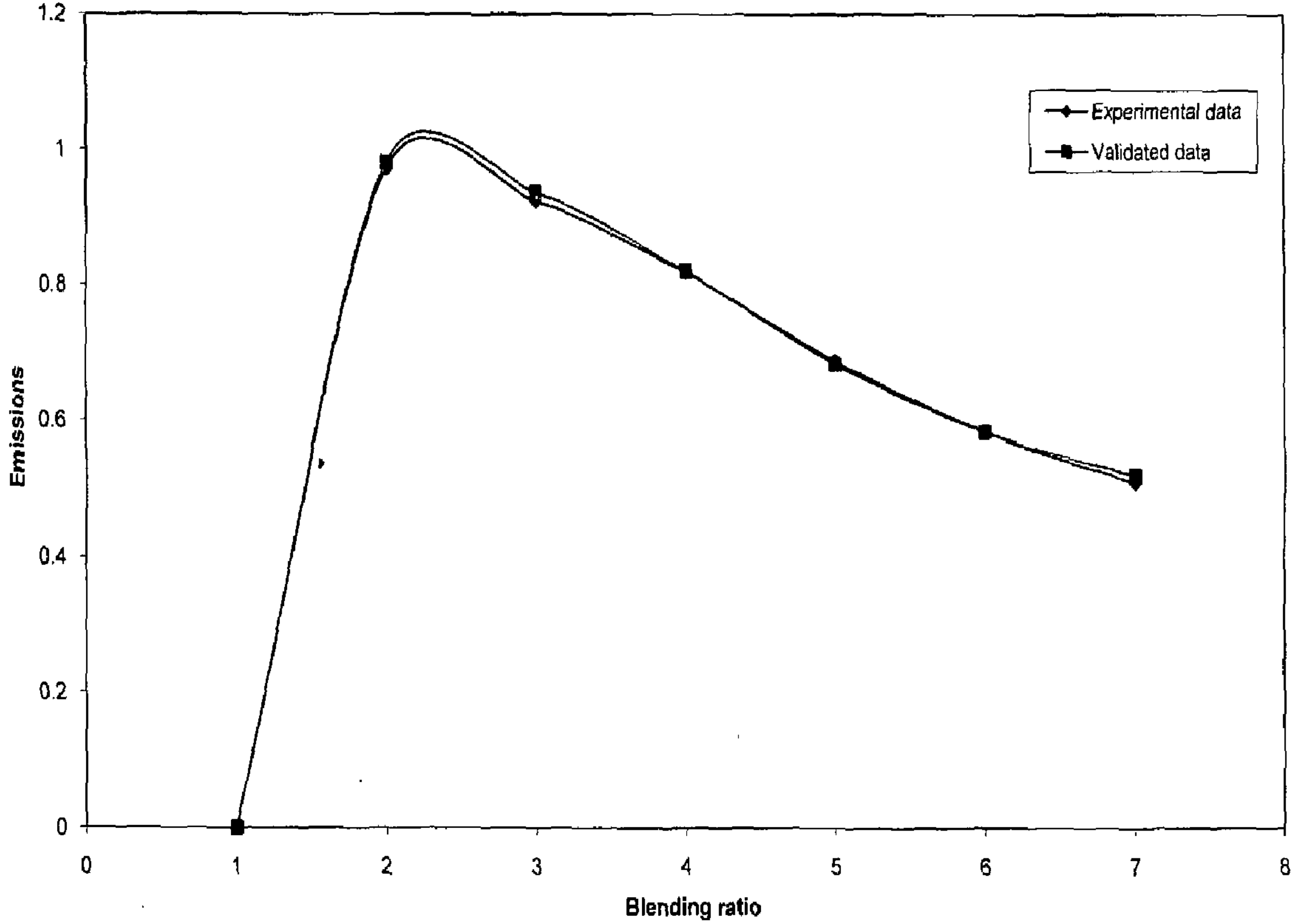


Figure5.5.Effect of Nitrogen oxide and Carbon dioxide emission in various blending ratio of soya bean oil with diesel

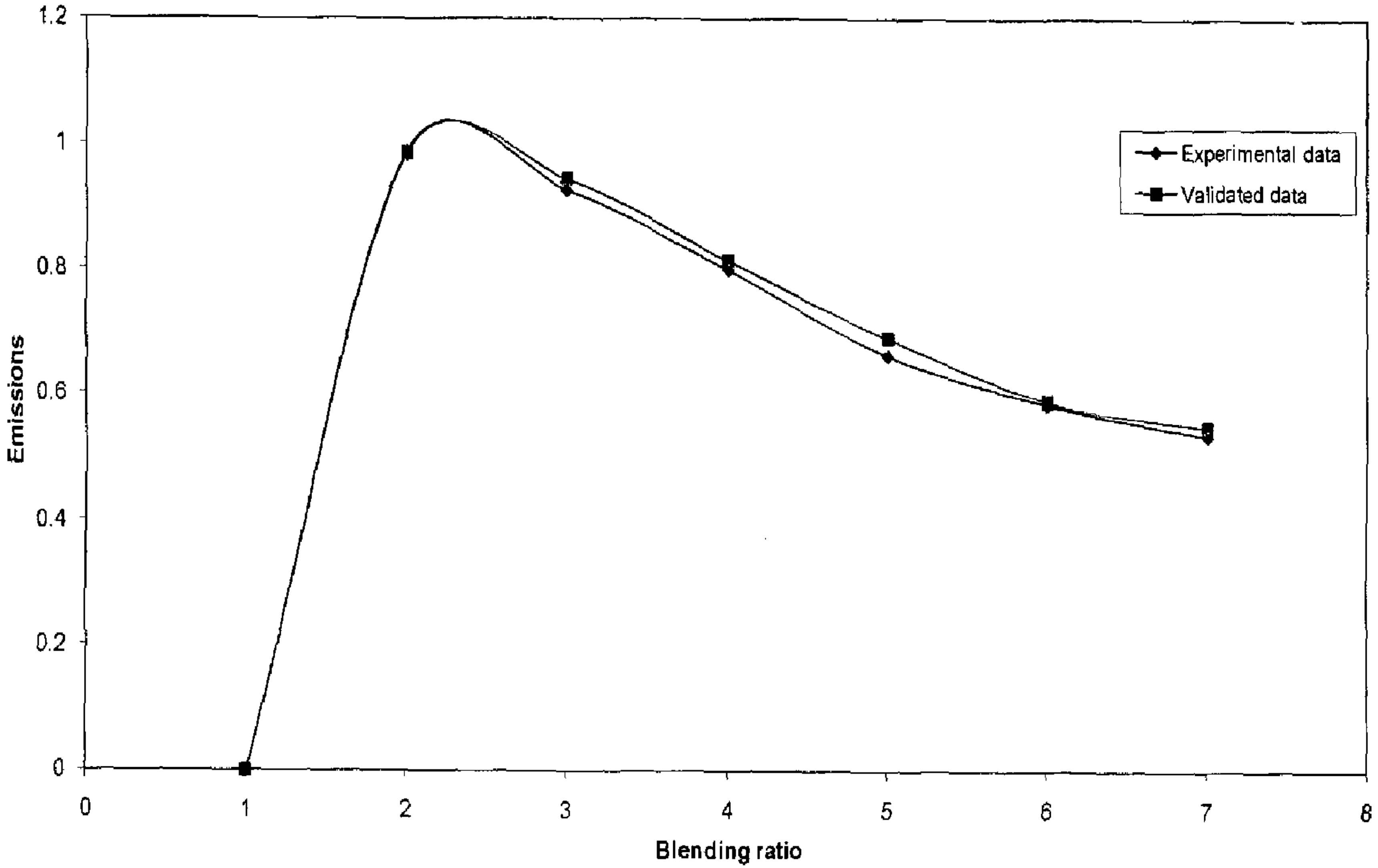


Figure5.6.Effect of Carbon monooxide and nitrogen oxide emission in various blending ratio of soya bean oil with diesel

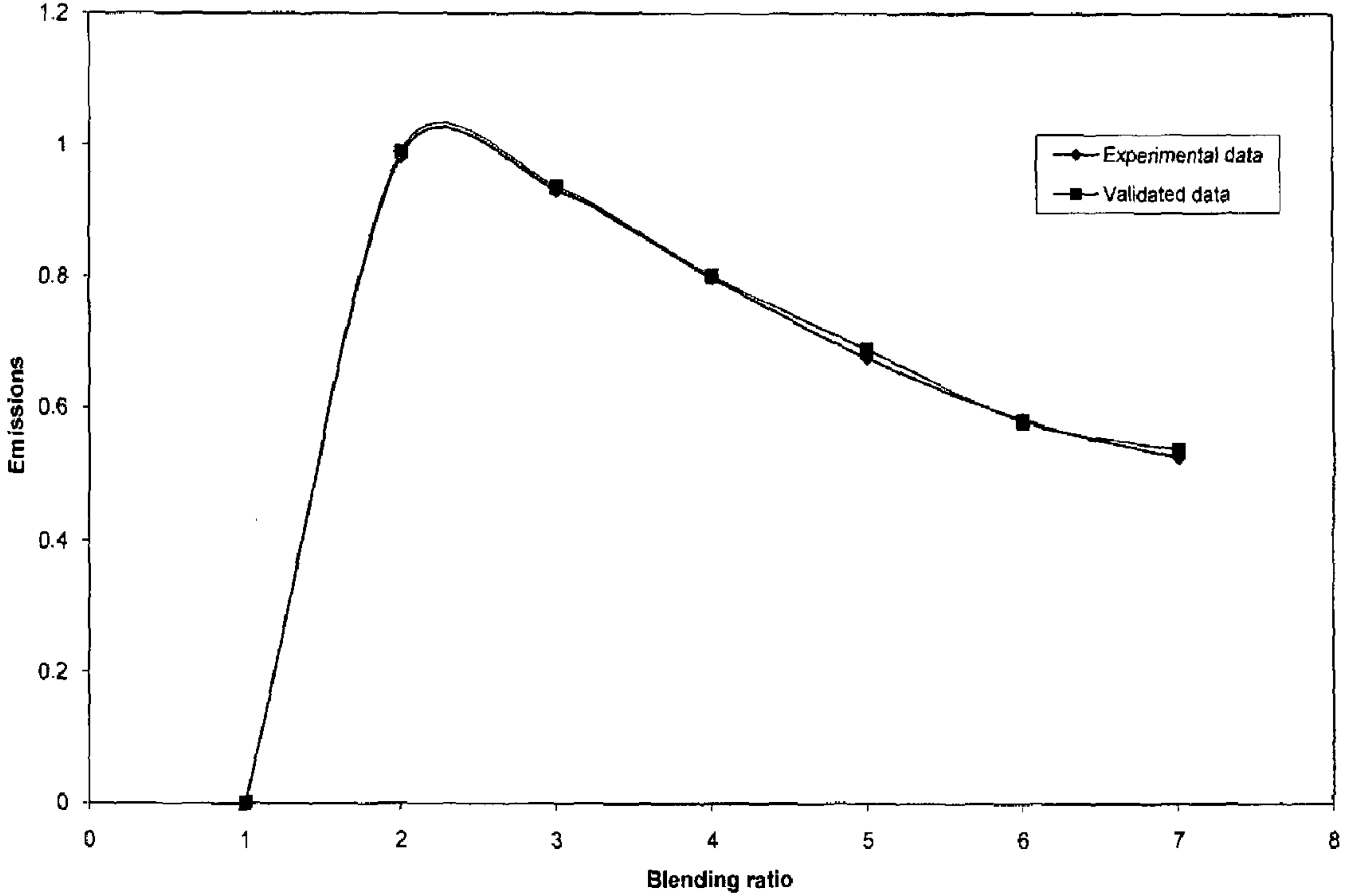


Figure5.7.Effect of Nitrogen oxide, Carbon di and mono oxide emission in various blending ratio of soya bean oil with diesel

⇒ Blending ratio 1 means what?

⇒ Why should blending ratio 2 produce maximum emissions?

CHAPTER 7

PAPER PUBLISHED OUT OF THE DISSERTATION WORK

I have one paper published in the CHEMCON-2007 in Dec.-2007 on the topic of **"Performance and Emission Study of Direct Injection Diesel Engine Using Non-Edible Vegetable Oils of Indian Origin"**

⇒ Not in ref.?

Abstract

Because of depletion in petroleum reserves the demand increases day by day the increase in the ratio of demand to supply lead to increase in diesel fuel prices. Moreover the demand for ecofriendly alternative fuel is the need of day keeping view of these fact diesel from vegetable oil is a good substitute because of higher viscosity and long carbon chain vegetable oil can not be used as such an alternative fuel this drawback may cause environment problem and reduce the performance of engine however the certain modification modification provide us various tools for the use of vegetable oil. A successful alternative fuel fulfills environmental and energy needs without sacrificing operating performance. After chemical modification (transesterification, microemulsification, pyrolysis and blending) vegetable oil can be used as a substitute for diesel fuel without compromising the environment and energy norms. In the present paper we will discuss the performance and emission study of five vegetable oil (especially Non-edible)in Indian context these oil are very much available in subcontinent.

CHAPTER 6

CONCLUSION

6.0 GENERAL

The following main conclusions may be drawn from the present study.

6.1 CONCLUSIONS

In the view of the fact we develop the model equation from the experimental data and verify from the another data which are we find approximately the same or have a negligible change which we ignore or leave and we have already describe in the result and discussion section that this change comes due the climatic change and depend on the storage condition, processing parameter like as the temperature, pressure, catalyst type and quantity, and the variety of the vegetable seed and after verifying the model equation from the different data we find that these model equation have a good fit and do not give a large difference between the one data to the other data. Finally we find the model equation and the constant are calculate from the given data by the non-linear regression fitting method and verify model equation which we find that these equation have no enough change and give the similar result that actual or experimental data.

6.2 FUTURE ASPECT RECOMMENDATION

The effect of the parameter such as the temperature, pressure, pH, storage condition, and mixing intensity and the free fatty acid effect on the quality of the biodiesel should be studied.

Which parameters determine quality of biodiesels?

CHAPTER 8

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APPENDIX

OBSERVATION TABLES

Table for Effect of Carbon dioxide emission in various blending ratio of soya bean oil with diesel

Carbon dioxide (g/bhp-hr)	Blending ratio (Experimental data)	Blending ratio (Validated data)
654	0.962413	0.961502
657	0.926068	0.920405
666	0.814798	0.814731
675	0.700178	0.718228
684	0.582207	0.578961
690	0.501699	0.505289

Table for Effect of Carbon monoxide emission in various blending ratio of soya bean oil with diesel

Carbon mono-oxide (g/bhp-hr)	Blending ratio (Experimental data)	Blending ratio (Validated data)
1.51	0.994603	0.992493
1.43	0.914276	0.924068
1.32	0.808874	0.816526
1.14	0.649007	0.655997
1.07	0.591064	0.605607
1.01	0.543282	0.543282

Table for Effect of Nitrogen oxide emission in various blending ratio of soya bean oil with diesel

Nitrogen oxide (g/bhp-hr)	Blending ratio (Experimental data)	Blending ratio (Validated data)
4.23	0.987158	0.978678
4.38	0.894759	0.903239
4.46	0.845479	0.847799
4.80	0.636041	0.638361
4.86	0.599081	0.59292
4.96	0.537481	0.537481

Table for Effect of Carbon di and mono oxide emission in various blending ratio of soya bean oil with diesel

Blending ratio (Experimental data)	Blending ratio (Validated data)
0.973689	0.970656
0.926569	0.920379
0.814863	0.812483
0.687189	0.683256
0.584607	0.581827
0.513178	0.515083

Table for Effect of Nitrogen oxide and Carbon dioxide emission in various blending ratio of soya bean oil with diesel

Blending ratio (Experimental data)	Blending ratio (Validated data)
0.971690	0.970519
0.924658	0.919268
0.819211	0.824577
0.688713	0.687201
0.585193	0.583370
0.510399	0.511259

Table for Effect of Carbon monooxide and nitrogen oxide emission in various blending ratio of soya bean oil with diesel

Blending ratio (Experimental data)	Blending ratio (Validated data)
0.988291	0.984594
0.984594	0.985153
0.799889	0.809385
0.663411	0.664740
0.585488	0.581317
0.535408	0.539531

Table for Effect of Nitrogen oxide, Carbon di and mono oxide emission in various blending ratio of soya bean oil with diesel

Blending ratio (Experimental data)	Blending ratio (Validated data)
0.982674	0.988863
0.931694	0.931622
0.798425	0.782779
0.676588	0.678706
0.583384	0.598920
0.527222	0.522622