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BIODIESEL

In a 1912 speech, Rudolf Diesel said, "the use of vegetable oils for engine fuels may seem insignificant today, but such oils may become, in the course of time, as important as petroleum and the coal - tar products of the present time". The revival of biodiesel derived from vegetable oils started as a result of agricultural surplus in some European countries and under Kyoto protocol the need of reducing greenhouse gas CO_2 emissions.

Biodiesel is a renewable fuel that is produced from a variety of edible and non-edible vegetable oils and animal fats.

The term “biodiesel” is commonly used for methyl or ethyl esters of the fatty acids in natural oils and fats, which meet the fuel quality requirements of compression-ignition engines.

Straight vegetable oils (SVO) are not considered as biodiesel. The straight vegetable oils have a very high viscosity that makes flow of these oils difficult even at room temperatures. Moreover, presence of glycerine in the vegetable oil causes formation of heavy carbon deposits on the injector nozzle holes that results in poor and unacceptable performance and emissions from the engine even within a few hours of operation.

Biodiesel Production – Esterification of Oils

Biodiesel is produced by reacting vegetable oils or animal fats with an alcohol such as methanol or ethanol in presence of a catalyst to yield mono-alkyl esters. The overall reaction is given in Fig. 8.6. Glycerol is obtained as a by-product.

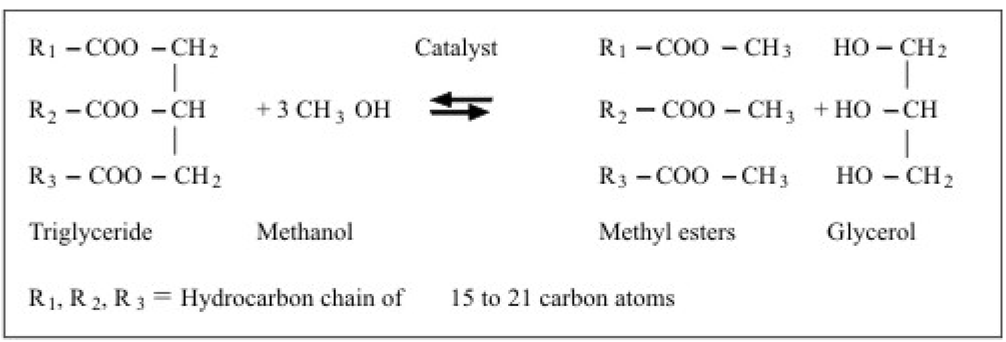

Figure 8.6:	Esterification reaction for vegetable oils and fats.’

Properties of Biodiesel

A variety of vegetable oils such as soybean, rapeseed, safflower, jatropha-curcas, palm, and cottonseed oils have been used for production of biodiesel. Waste edible oils left after frying/cooking operation etc., have also been converted to biodiesel for study of their performance. The biodiesel are also known as fatty acid methyl esters [FAME]. Recently non-edible oil produced from jatropha-curcas seeds has gained interest in India as this plant can be easily grown on wastelands. The properties of methyl esters of rapeseed and jatropha oils are given in Table 8.18.

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Table 8.18

Properties of Biodiesel Derived from Some Vegetable Oils

Properties	Rapeseed methyl ester	Jatropha methyl ester
Molecular weight	˜300	˜293
Hydrogen/carbon ratio, m/m	0.15	0.157
Oxygen content, % m/m	9-11	10.9
Relative density @ 15° C	0.882	0.88
Kinematic viscosity @ 40° C, mm2/s	4.57	4.4
Cetane number	51.6	57.1
Lower heat of combustion, MJ/kg	37.7	38.45
Sulphur content, %m/m	<0.002	< 0.020

The vegetable oil esters are practically free of sulphur and have a high cetane number ranging from 46 to 60 depending upon the feedstock. Due to presence of oxygen, biodiesels have a lower calorific value than the diesel fuels. European specifications for biodiesel or fatty acid methyl esters (FAME), EN 14214 have been issued in 2003.

Emissions

The influence of biodiesel on emissions varies depending on the type of biodiesel (soybean, rapeseed, or animal fats) and on the type of conventional diesel to which the biodiesel is added due to differences in their chemical composition and properties. The average effects of blending of biodiesel in diesel fuel on CO, HC, NO_x and PM emissions compared to diesel as base fuel are shown in Fig.8.7.The Table 8.19 gives change in emissions with 20 % blend of biodiesel in diesel and 100% biodiesel compared to diesel alone. These show the average of the trends observed in a number of investigations.

Use of biodiesel results in reduction of CO, HC and PM, but slight increase in NO_x emissions is obtained.

- Reduction in CO emissions is attributed to presence of oxygen in the fuel molecule.
- A slight increase in NO_x emissions results perhaps due to advancement of dynamic injection timing with biodiesel. The methyl esters have a lower compressibility, which results in advancement of dynamic injection timing with biodiesel compared to diesel.
- Lower SOF with biodiesel and advanced injection timing also results in lower PM emissions.
- Volumetric fuel consumption with biodiesel is higher than diesel due to its lower heating value. An increase of 10-11 % in fuel consumption compared to diesel may be expected when comparing their heating values. An increase in volumetric fuel consumption by 0.9-2.1% with 20% blends has been obtained.

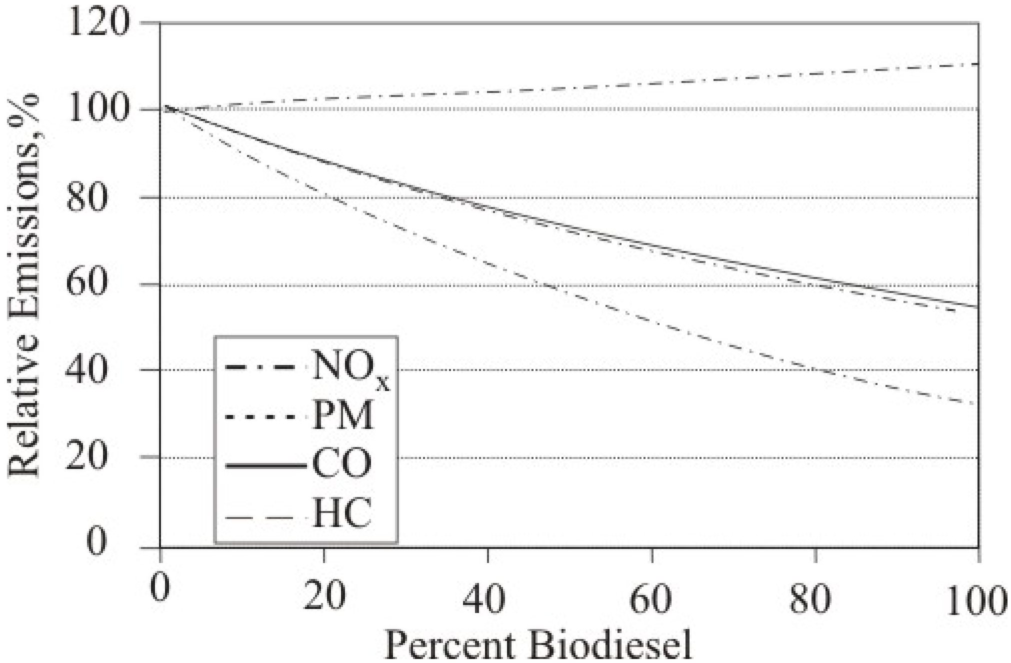

Figure 8.7:	Average effect on diesel engine emissions resulting from addition of biodiesel in diesel fuels

Table 8.19

Average reduction in emissions with use of biodiesel and 20% biodiesel blends compared to diesel alone

Emission	B100	B20
HC	- 93	-30
CO	- 50	-20
PM	- 30	-22
NOx	+13	+2
PAH	- 80	-13
Sulphates	- 100	-20

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Hydrogen

Interest in hydrogen as a potential alternative automotive fuel has grown due to need of reducing greenhouse gas, CO_2 emissions and to minimize dependence on fossil fuels. Hydrogen can be produced from a variety of fossil and non-fossil sources.

Hydrogen is a colourless, odourless and non-toxic gas. It burns with an invisible and smokeless flame. The combustion products of hydrogen consist of water and some nitrogen oxides. The major hurdles in the use of hydrogen as a fuel are lack of production, distribution and storage infrastructure. On board storage of hydrogen is another major challenge. Hydrogen has very low boiling point (–253º C) and very low volumetric energy density.

Volumetric energy density of compressed hydrogen is just one-third of energy density of natural gas. Liquid hydrogen also has a very low volumetric energy density, which is about one-fourth of gasoline. Hydrogen can be stored as compressed gas, as iron, magnesium, titanium or nickel hydride, or in liquefied form. The liquid, hydride and compressed hydrogen storage methods are compared in Table 8.20 for storing 19 litres of gasoline equivalent in energy. Hydrogen storage space required is at least 10 to 12 times higher than for gasoline. Storage and fuel weight for hydrides is 27 times and for compressed H_2 is 4 to 5 times of gasoline.

Table 8.20

Comparison of Hydrogen Storage Methods

	Gasoline	Liquid H_2	Hydride Fe-Ti (1.2%)	Compressed H_2 (70MPa)
Energy (LHV) stored, MJ	600	600	600	600
Fuel mass, kg	14	5	5	5
Tank mass, kg	6.5	19	550	85
Total Fuel System mass, kg	20.5	24	555	90
Volume, l	19	178	190	227

Combustion characteristics of hydrogen and its impact on emissions are given below;

- Hydrogen octane rating is 106 RON making it more suitable for spark-ignited engines.
- The laminar flame speed of hydrogen is 3 m/s, about 10 times that of gasoline and methane.
- Hydrogen has very wide flammability limits ranging from 5 to 75% by volume (f = 0.07 to 9), which may lead to pre-ignition and backfiring problems.
- Its adiabatic flame temperature is higher by about 110º C compared to gasoline.
- If inducted along with intake air, the volume of hydrogen is nearly 30% of the stoichiometric mixture decreasing maximum engine power.
- Hydrogen on combustion produces water and there are no emissions of carbon containing pollutants such as HC, CO and CO_2 and air toxics.
- Trace amounts of HC, CO and CO2 however, may be emitted as a result of combustion of lubricating oil leaking into engine cylinder.
- NO_x is the only pollutant of concern from hydrogen engines. Very low NO_x emissions can be obtained with extremely lean engine operation (f < 0.05) and/or injection of water into intake manifold or exhaust gas recirculation which in this case consists primarily of water vapours.

NO_x emissions of 0.013 g/km have been obtained which are about 1/10th of the US Tier 2 regulations.

- Hydrogen fuelled engines produces almost no CO_2 and its global warming potential is insignificant.

Hydrogen fuelled IC engines however are not considered a long term option when compared to fuel cell. Hydrogen fuel-cell vehicles are expected to have more commercial potential in the long run. Though it is believed that significant production volumes for customers will not be available until the 2017-2020 time frame.

Greenhouse Gas Emissions with Alternative Fuels

Fossil fuels currently supply about 80% of all primary energy and are expected to remain fundamental to global energy supply for at least the next 20 to 30 years. . Presently, it is estimated that power generation accounts for about 40% and surface transport contributes nearly 20% of global CO_2 emissions.

The Kyoto Protocol signed in December 1997 commits the industrialized countries to legally binding reductions in emissions of greenhouse gases by 2008-2012. Strategy to achieve reduction in CO_2 emissions from transport sector involves essentially the following:

- Reduction in fuel consumption of vehicles.
- Increased use of low carbon alternative fuels and bio fuels.

European Union countries have introduced CO_2 emission regulations for the automobiles. A voluntary target of 140 g/km average CO_2 emissions for new car sales to be met in 2008 was set that had to be relaxed. By the year 2012, a goal of 130 g/km of CO_2 to be achieved by engine and vehicle technology, and further reduction to 120g/km by use of renewable fuels has been set by European Union.

When comparing different fuel and power plant alternatives, life cycle CO_2 equivalent GHG emissions are to be considered. It should account for CO_2 and other GHG emissions generated during production, transportation and use in the vehicles. Lifecycle CO_2 emissions for liquid petroleum fuels, LPG, natural gas and biodiesel for heavy vehicle application are compared in Fig 8.8. The CO_2 emissions yielded during fuel production and during fuel utilization stage in engines are shown separately. Among the alternative fuels, natural gas having lower carbon content in the fuel molecule has advantage over gasoline and diesel fuels as far as CO_2 emissions are concerned. From natural gas vehicles, the greenhouse effect of the fugitive methane emissions as a result of leakage from the transportation and distribution systems is also to be accounted for as methane is nearly 20 times more potent than CO_2 in causing global warming. LPG lies in between the natural gas and liquid petroleum fuels. The bio fuels such as ethanol and biodiesel have much lower lifecycle CO_2 emissions as the carbon dioxide produced on their combustion would be the same that has been fixed from atmosphere during growth of the agriculture crops. These fuels do contribute to net CO_2 emissions resulting from manufacture of fertilizers and other ingredients used for crops and, during processing of these fuels and making them suitable for use in the engines.

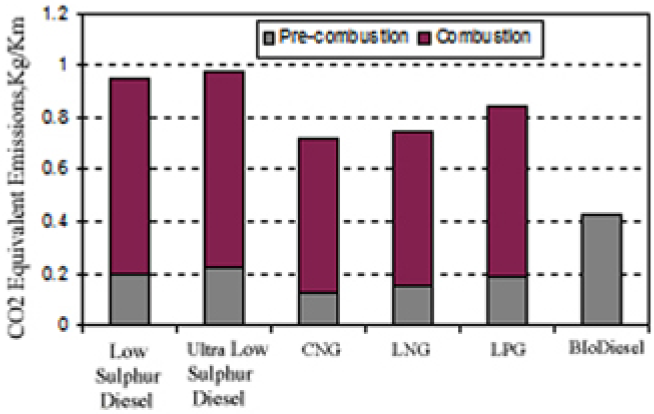

Figure 8.8:	Lifecycle GHG carbon dioxide emissions with different transport fuels.

Example 8.2: Calculate GHG carbon dioxide (CO_2) emissions per unit release of energy when methane is completely burned.

Solution:

Complete or stoichiometric combustion reaction of methane in air is;

$$CH_4 + \left(1 + \frac{4}{4}\right)(O_2 + 3.76N_2) = CO_2 + 2H_2O + 7.52N_2$$

Mass of reactants

Methane	+ Air	=	CO2 +	Water +	Nitrogen
16	+ 2 (32 + 3.76 x28)	=	44	+ 2x 18	+ 2 x3.76x 28
16	+ 274.56		44	+ 36	+ 210.56

From Example 1 the energy released when 1 kg of methane is burned = 50 MJ/kg the above CO_2 produced per kg of methane burned = 44/16 = 2.75 kg CO_2/kg of methane

CO_2 produced = 2.75/50 = 0.055 kg/MJ or 55 g/MJ of energy released. Ans

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Questions

(8.1) A diesel fuel when tested has the same ignition characteristics as the mixture of 40% n-cetane and 60% hepta-methyl nonane. What is its cetane number? The fuel at 15º C has density of 825 kg/m^3 and mid-boiling point (T_{50}) of 240º C. Find the calculated cetane index of the fuel. How much error results in using CCI instead of CN?

(8.2) What are the changes in volumetric efficiency for a gasoline (C_8H_{15}) engine when it is converted -by retro- fitment for operation on methane or hydrogen? Assume inlet conditions as 1 bar, 298 K and the engine size and geometry remain unchanged. Gasoline also enters the engine cylinder mostly as liquid.

(8.3) Calculate energy content of 1 m^3 of stoichiometric mixtures with air of gasoline (C_8H_{15}), ethyl alcohol, methanol and hydrogen. Compare your results with those in Table 8. 13. Take standard conditions of 1 atmosphere (101 kPa) and 298K.

(8.4) Rate the fuels methane, ethanol, gasoline, high aromatic gasoline, and diesel in terms of their potential to produce NO emissions based on adiabatic flame temperature data.

(8.5) Calculate mass of CO_2 per MJ of energy for gasoline, diesel, propane and ethanol when burned as stoichiometric mixtures. Check your results with the data given in Table 8.13.

(8.6) Find the contribution of 0.1% sulphur in fuel to PM as percentage of Euro 1 to Euro 4 heavy duty PM emission limits.

(8.7) Discuss why Supreme Court of India could have ordered replacement of all the diesel buses by CNG buses in early 2003? How the CNG buses could meet those goals?

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