BIODIESEL – AN ALTERNATIVE TO REDUCE WATER & ENVIRONMENTAL POLLUTION FOR MARINE APPLICATIONS: A REVIEW

[1]*JHALA, KISHORSINH B.; [2]MEHTA, ABHAY KUMAR AND [3]BANDHIYA, RAJESHKUMAR D.

DEPARTMENT OF FARM MACHINERY AND POWER ENGINEERING
COLLEGE OF AGRICULTURAL ENGINEERING AND TECHNOLOGY
JUNAGADH AGRICULTURAL UNIVERSITY
JUNAGADH – 362 001, GUJARAT, INDIA

EMAIL: jhalakb@jau.in

1Associate Professor, Department of Farm Machinery and Power Engineering, CAET, JAU, Junagadh
[2]Director of Research, Maharana Pratap University of Agriculture and Technology, Udaipur.
[3]Agricultural Assistant, Department of Farm Machinery and Power Engineering, CAET, JAU, Junagadh

ABSTRACT

Environment compatible fuels (Chemically modified vegetable oils) have positioned themselves among alternative fuels/additives, having fuel properties similar to diesel. The objective of the survey was to determine use friendliness of the alternate source of energy in respect to water pollution and environmental considerations. The study on different components of the exhaust gases after feeding biodiesel to diesel engine and its handling reveals that use of biodiesel on an average reduces Hydrocarbons (45-52%), Carbon monoxide (40-47%), Carbon dioxide (1%) with slight increase in Oxides of nitrogen (10-13%). This increment can be still reduced by slight modification in engine timing (retard of 3-5^{o}), so that an engine develops minimum of oxides of nitrogen for using biodiesel as a fuel in diesel engine used on marine boats. Due to reduction in HC, CO, CO_2 and NOx, the suspended particles in air also reduces, which in turn reduces the chances of polluting the water and environment.

KEY WORDS: Biodiesel, Marine, Pollution

INTRODUCTION

Environment, etymologically means surroundings, is a composite term for the conditions in which organisms live and thus consists of air, water, food and sunlight which are the basic needs of all living creatures and plants to carry on their life functions. It is the sum of all social, economical, biological, physical or chemical factors, which constitutes the surrounding of man, who is both creator and molder of environment around him. It also includes other living things, temperature, wind, electricity etc. The environment for any living organism has never been static but it is changing slowly, rapidly or drastically. The two types of the environment are:

1. Natural, which operates through self-regulating mechanism also called as homeostatic environment mechanism "Any change in natural ecosystem brought about by natural process is counter balanced by changes in other components of the environment". The components such as air, water, soil, radiation, land, wild life transportation, energy generation

and industrial revolution etc. are among the important components.

2. Man-made environment in which, man is the most powerful environmental agent spearheaded by modern technologies are capable of modifying environment according to his needs.

Environmental pollution is one of the most horrible ecological crisis to which we are subjected today. It can be defined as undesirable change in any physical, chemical or biological characteristics of our basic amenities causing harmful effect on our life or that of desirable species and cultural assets. The automobile exhausts are responsible for more than 75 per cent of the total air pollution. They release huge amount of poisonous gases such as carbon monoxide (77%), oxides of nitrogen (8%), and hydrocarbons (14%), in addition to leaded gas and particulate lead as a result of incomplete combustion of fuel which reacts with oxides of nitrogen in presence of sunlight and forms photochemical smog highly toxic in nature (Sharma and Kaur, 1993). On road engines have been identified as the sources of atmospheric emission and strict regulations for minimizing are laid down, but the effects of marine engine use on the quality of air as well as water are seldom studied.

Biodiesel

Biodiesel is a clean-burning diesel fuel additive produced from vegetable oils instead of petroleum. Biodiesel (classified as food for transport) is used in marine compression ignition (diesel) engines to enhance engine combustion performance, improve engine lubrication, and reduce air and water pollution caused by its exhaust. No engine conversions are required, unless an engine has old fuel lines. Biodiesel and a 20 per cent blend of biodiesel in petroleum diesel are designated as alternative fuels. Biodiesel is registered as a fuel additive with the Environmental Protection Agency (EPA). Biodiesel and the 20 per cent blend meet clean diesel standards established by the California Air Resources Board (CARB), particularly since the biodiesel contains no sulfur and no aromatics. The National Biodiesel Board and American Society for Testing and Materials had developed a provisional ASTM standard for biodiesel production in the United States. In 1998, Biodiesel as a 20 per cent blend ("B-20") with petroleum diesel was designated an "alternative fuel" under the Energy Policy Act. Mass production can lower down the prices for consumers.

Biodiesel production technique

Biodiesel is produced from vegetable oils by converting the triglyceride oils to esters (methyl or ethyl) with a process known as transesterification. In transesterification process alcohol reacts with the oil to release three "ester chains" from the glycerin backbone of each triglyceride. The reaction requires heat and a strong base catalyst (e.g., hydroxide or lye), to achieve complete conversion of the vegetable oil into the separated esters and glycerin. The glycerin can be further purified for sale to the pharmaceutical and cosmetic industries. The mono-alkyl ester is the biodiesel, with one-eighth the viscosity of the original vegetable oil. Each ester chain, usually 18 carbons in length for soy esters, retains two oxygen atoms forming the "ester" and giving the product its unique combustion qualities as an oxygenated vegetable based fuel. Biodiesel is nearly 10 per cent oxygen by weight. Petroleum diesel, in contrast, is made up of hundreds of different hydrocarbon chains (roughly in the range of 14 -18 carbons in length), with residues of sulfur and crude oil remaining. Diesel fuel sold today, even "low sulfur, low aromatic" diesel, contains 20-24 per cent aromatics (benzene, toluene, xylenes, etc.) have toxic & volatile compounds, responsible for the fire/health hazards and pollution associated with petroleum diesel (Randall von Wedel)

Impact on marine environment

Water pollution is also be reduced by using biodiesel in boat engines since there will be more efficient burning of the fuel mixture, less carbon (soot) accumulation and particulate (smoke) emissions. Faster starting and smoother operation also should reduce the discharge of unburned fuel. Any accidental discharges of small amounts of biodiesel should have relatively little impact on the environment compared to petroleum diesel, which contains more toxic and more water-soluble aromatics. Nonetheless, the methyl esters could still cause harm.

1.Low toxic to marine plants and animals

From 1994 – 1996, CytoCulture conducted a series of tests in collaboration with the California Department of Fish & Game (Office of Oil Spill Prevention & Response) to document the impact of vegetable methyl esters on various native species of marsh plants and marine organisms. As larval forms of fish and shell fish are much more sensitive than the adult forms, all of the marine toxicity studies were performed with larvae of established test species. The studies indicated that the Biodiesel, while not completely harmless to the larvae of crustacea and fish, is much less toxic than petroleum fuels and crude oil. In research conducted for CytoCulture in 1994, the LC50 (concentration required to kill 50 per cent of the population) for larval test fish (*Menidia Beryllina*) exposed to soy methyl ester Biodiesel was 578 ppm relative to an LC50 of 27 ppm for reference fuel oil (CytoCulture, 1997b). In larval shrimp (*Mysidopsis Bahia*) toxicity assays, the LC50 for the soy methyl ester Biodiesel was 122 ppm compared to the LC50 of 2.9 ppm for the reference fuel oil. In 1996 follow-up acute toxicity bioassays were performed by a different laboratory on recycled cooking oil methyl esters for CytoCulture using the same protocol and the same two test species. The recycled cooking oil Biodiesel had an average LC50 of 736 ppm in the Menidia fish larvae tests compared to the average LC50 of 39 ppm for the reference fuel oil. In the Mysidopsis toxicity bioassay, the recycled cooking oil Biodiesel had an LC50 of 124 ppm compared to the LC50 of 5.9 for the reference fuel oil. In subsequent gas chromatography studies on the solubility of Biodiesel methyl esters, it was determined that much of the apparent toxicity observed in abalone, shrimp and fish larvae was due to suffocation or coating of exposed gills as the tiny larvae swam into dispersed globules of the methyl esters. The concentrations for the reported LC50's exceed the saturation concentration for Biodiesel in seawater, further indicating that the observed marine toxicity is probably due to the formation of globules rather than due to a true chemical toxicity of dissolved-phase product. In other words, the Biodiesel methyl esters have very low solubility in water (7 ppm in San Francisco Bay seawater) compared to petroleum diesel that contains benzene, toluene, xylene and other more water-soluble, highly toxic compounds. However, when the Biodiesel is vigorously blended into water (requirement of EPA test protocols), the methyl esters form a temporary emulsion of tiny droplets that appear to be harmful to the swimming test larvae.

2.Solubility and biodegradation of biodiesel in bay water

Biodiesel methyl esters are actually quite insoluble in fresh or seawater, with a saturation concentration of 7 ppm (sea) and 14 ppm (fresh) at 17^0C, whereas petroleum diesel can partition aromatics into water in concentrations of hundreds of ppm. The dissolved phase of the biodiesel methyl esters was shown to breakdown by the biodegradation action of naturally occurring bacteria present in San Francisco Bay seawater. The half-life for the biodegradation of the vegetable methyl esters in agitated SF Bay water was less than 4 days at 17 Deg. C., about twice as fast as petroleum diesel (CytoCulture, 1997a).

3.Biodegradability in the aquatic environment

A study conducted at the University of Idaho in 1995 determined that rapeseed biodiesel would biodegrade about twice as fast as petroleum diesel. Further, the biodiesel has shown to enhance the biodegradation rate for diesel fuel in a blend. CytoCulture also confirmed, hydrocarbon-degrading bacteria can metabolize both, biodiesel and petroleum diesel at the same time. The biodegradation rate of rapeseed biodiesel in shake flasks with fresh water was found to be comparable to dextrose (a test sugar) and about twice as fast as for petroleum diesel. In the Idaho study (Peterson *et al.,* 1996), the 95 per cent of rapeseed esters were degraded, whereas only 40 per cent degraded after 23 days.

4.Spills of biodiesel and the environment

Biodiesel should have less impact to aquatic and marine organisms than petroleum diesel if accidentally spilled or inadvertently discharged over the side. However, the US EPA still considers spills of animal fats and vegetable oils harmful to the environment. Spilling Biodiesel into the water would be as illegal as discharging petroleum fuels overboard. Waterfowl and other birds, mammals and fish that get coated with vegetable oils could die from hypothermia or illness, or fall victim to predators. Even though the biodiesel is relatively non-toxic and less viscous than vegetable oil, it can still have a serious impact on marine and aquatic organisms in the event of a big spill. It can be recommended that the biodiesel always be handled like any other fuel to avoid contamination of our bays and waterways. The complexity of the chemical structure of the hydrocarbons presents in the fuel /makes it difficult to biodegrade, as the case is with diesel.

5.Sailboats with auxiliary diesel engines

Recreational sailboats powered by auxiliary diesel engines have proven to be a reliable and high profile market for biodiesel. Cytoculture (1997a) in the San Francisco Bay area found that 97 per cent of the vessels using biodiesel were sailboats (30 to 50 ft range with small diesel engines, 12-50 HP) consuming relatively little fuel. Sailboaters tend to be more conscious of environmental concerns, they are sensitive to smoke and odor from engine exhaust. Emphasis should be given on using Biodiesel in boats operating on lakes, rivers and confined bays that are more sensitive to air and water pollution.

5.1Blending ratios for biodiesel in boat fuel

Biodiesel mixes easily with diesel as a fuel additive for use in blends of up to 20 per cent (almost all properties of the mixture comes close to that of diesel (Peterson *et al.*, 2000) with regular petroleum diesel or use the blending chart. Biodiesel mixes quickly with petrodiesel once the boat is moving. Biodiesel is little heavier with has a specific gravity of 0.87 compared to 0.79-0.80 for reformulated petrodiesels. Higher concentrations, up to 100 per cent (neat) biodiesel, are used in Europe to operate diesel engines in boats and vehicles with good performance results and excellent emissions reductions, biodiesel are only to be sold as an additive for use in boat engines at ratios not to exceed 20 per cent. In France, diesel sold for vehicle fuel in the entire country posses 1 to 5 per cent rapeseed. Biodiesel in a blend and some urban buses routinely operate on a 30 per cent blend.

6.Emissions reductions with biodiesel

Since biodiesel is made entirely from vegetable oil, it does not contain any sulfur, aromatic hydrocarbons, metals or crude oil residues. The absence of sulfur means a reduction in the formation of acid rain by sulfate emissions which generate sulfuric acid in our atmosphere (over the crops). It also reduces the levels of corrosive sulfuric acid accumulating in the engine crankcase oil over time. The lack of toxic and carcinogenic aromatics (benzene, toluene and xylene) in biodiesel reduces impact on human health and the environment. The high cetane rating of biodiesel (ranges from 49 to 62) is another measure of the additive's ability to improve combustion efficiency. In addition, biodiesel blends have reduced emissions of polyaromatic hydrocarbons, less carcinogenic compared to those of petroleum.

6.1 Hydrocarbon emissions

Biodiesel burns cleanly and also improves the combustion efficiency of blends with petrodiesel. This in turn reduces air and water pollution from boats operated on biodiesel blends. In a 20 per cent blend, there will be a noticeable change in the odor and smoke in the exhaust. The studies documented the reduction in hydrocarbons. Biodiesel hydrocarbon chains are generally 16 to 20 carbons in length, and they are all oxygenated at one end, making the product an excellent fuel. Southwest Research Institute in 1994 reports that Biodiesel in a 20 per cent blend has shown to reduce particulate matter (PM) by 14 per cent in new engines, catalytic converter can further reduce. SWRI 1998 reports reduction of 20 to 31 per cent in hydrocarbon emissions was observed depending upon the engine for the B-20 blend. There was a drop of 72 to 94 per cent in total hydrocarbons for engine fueled with 100 per cent biodiesel as compared to No. 2 low sulfur diesel fuel. Colorado Institute for Fuels & High Altitude Engine Research reports a drop of 12.7 per cent drop in total hydrocarbons in 20 per cent blend.

6.2 Smoke and soot

Smoke (particulate material) and soot (unburned fuel and carbon residues) are of increasing concern to urban air quality problems, as they are causing a wide range of adverse health effects for citizens, especially in terms of respiratory impairment and related illnesses. A boat engine operating with biodiesel (absence of heavy petroleum) oil residue will nave less smoke and less soot production. Due to lack of heavy petroleum oil residues in the vegetable oil a boat engine operating with biodiesel will have less smoke, and less soot produced from unburned fuel. Since biodiesel contains more oxygen there is an increased efficiency of combustion even for the petroleum fraction of the blend. The improved combustion efficiency lowers particulate material and unburned fuel emissions especially in older engines with direct fuel injection system. Older engines have also shown less soot under load and less carbon black during startup. Independent research programs in Europe and the U.S. have shown that biodiesel in a 20 per cent blend with petroleum diesel created a significant reduction in visible smoke and odor. Southwest Research Institute in 1996 concluded that a B-20 blend (approximately 2% oxygen for RME-20) reduces particulate soot by approximately 30 per cent (from 0.06 for diesel no. 2 to 0.04 g/hp-hr for rapeseed methyl ester at 20%). A survey (1997) of recreational boaters using biodiesel on the San Francisco Bay confirmed these findings. Clean emission of diesel engine exhaust is a major driving force for biodiesel in the marine market. In a survey 98 per cent reported an improvement in the exhaust odor (smells more like french fries), 91 per cent reported a reduction in smoke, and 56 per cent indicated a reduction in soot deposits on the transoms and decks of their boats. New England Journal of Medicine 1993 which suggests that "fine particulate air pollution, or a more complex pollution mixture associated with fine particulate matter, contributes to excess mortality in certain U.S. cities."

6.3 Carbon monoxide emissions

Carbon monoxide gas is a toxic byproduct of all hydrocarbon combustion that is also reduced by increasing the oxygen content of the fuel. More complete oxidation of the fuel results in more complete combustion to carbon dioxide rather than leading to the formation of carbon monoxide. Southwest Research Institute in 1998 found a reduction of 8 to 22 per cent with a B-20 blend, depending on the type of engine. A drop of 28 to 37 per cent in the carbon monoxide emission was observed with neat biodiesel as compared to diesel. Many other studies documented similar drop (Nine *et al.*, 2000; Monyem *et al.* 2001).

6.4 Polyaromatic hydrocarbon emissions

Polyaromatic hydrocarbons (PAHs) consisting of multiple benzene ring structures make them insoluble, slow to burn and carcinogenic. In 1998, SWRI reports that the Cummins N-14 engine had a 12 per cent drop in PAH emissions when operating on B-20 blend relative to petrodiesel, and a 74 per cent drop with neat biodiesel. The Detroit Diesel engine had a 29 per cent reduction while operating on B-20 and a 68 per cent reduction with neat biodiesel. These data suggest major gains in improving the air quality around diesel engines in vehicles and boats operating on biodiesel. Polyaromatic hydrocarbons found in smoke and soot of petroleum diesel are complex, multi-ring compounds having anthracene and naphthalene that are carcinogenic and toxic. Water dosed with biodiesel exhaust at a 50 per cent engine load had non-detectable levels of PAHs.

6.5 Nitrogen oxides

The nitrogen oxides (major contributor to ozone formation) resulting from the oxidation of atmospheric nitrogen at the high temperatures inside the combustion chamber of the engine, rather than forms a contaminant present in the fuel. They are also a reality of operating internal combustion engines. There are consistent reports of slight increase in NOx emissions with biodiesel blends that are attributable, in part, to the higher oxygen content of the fuel mixture. More oxygen and better combustion of the fuel also means more formation of NOx emissions with biodiesel blends. In several research studies conducted since 1993 in the U.S. and Europe, EPA-regulated emissions from an unmodified engine operating on a 20 per cent biodiesel blend were shown to be lower than those for petroleum diesel, except for NOx (nitrogen oxides) emissions, which can be 2-5 per cent above baseline emissions. Retarding the timing of ignition can attain some reduction in NOx emission. Southwest Research Institute's study in 1988 reveals a 7 per cent rise in NOx emissions accompanied by 45 per cent drop in particulate matter and 65 per cent reduction in hydrocarbons using oxidation catalyst. In the case of the Transient Cycle Emissions Test, a one-degree timing change in the diesel engine did result in a net reduction of NOx emissions by 2 per cent, but at the expense of slightly less dramatic reductions in the particulate matter (40%), hydrocarbons (58%) and carbon-monoxide (34%).

6.6 Biodiesel reduce greenhouse gases

Biodiesel and other biofuels are produced from renewable agricultural crops that assimilate carbon dioxide from the atmosphere to become plants and vegetable oil. The carbon dioxide released this year from burning biodiesel, will be recaptured next year by crops growing in fields to produce more vegetable oil starting material. Fossil fuel combustion accounts for 70 per cent of the total anthropogenic CO_2 contribution. Supplementing our dwindling fossil fuel reserves with biomass-based fuels (Biodiesel for diesel and biomass-based alcohols or hydrogen for gasoline) helps reduce the accumulation of CO_2.

Safety and aesthetic advantages of biodiesel

User friendliness of biodiesel is that it has no noxious odors and is considered as harmless to handle as salad oil, but as a safety precautions avoid splashing it in your eyes, on your clothes, on your boat or into the water. The product smells and feels like cooking oil. In an early study sponsored by the National biodiesel Board (1993), the product had less toxicity in animal testing than table salt (grams per kg body weight).

1.No noxious or carcinogenic fumes

Vegetable oil ester contains no volatile organic compounds that would give rise to any poisonous or noxious fumes. There is no lead or sulfur to react and release harmful or corrosive gases. However, in blends with diesel significant fumes are released by the benzene and other aromatics present in the petroleum fraction (80%) of the blend.

2.No risk of explosion from vapors

Since the biodiesel has no volatile components (vapor pressure of less than 1 mm Hg) and a high flash point (over 360^0F), the product posses no risk of explosion caused by fumes accumulated below deck. The only significant fire risk would be from the spontaneous combustion of rags and paper towels soaked in biodiesel and stored in an area with low ventilation, or high temperatures

CONCLUSION

Major component 75 per cent of the environmental pollution (air or water) is contributed through on road or off road transport. The gases released by automobile exhausts are carbon monoxide, carbon dioxide hydrocarbons, nitrogen oxides, oxides of sulfur etc. Petroleum diesel hydrocarbons lack oxygen which makes them more difficult to biodegrade and in many cases toxic also. Vegetable oil (Biodiesel) having fuel properties comparable to those of commercial diesel. Biodiesel as an alternative fuel or as additive to the low sulfur commercial diesel have shown a considerable reductions in majority of the poisonous gases (CO, CO_2, HC, NOx SO_2, etc) along with the benefits of being indigenous in production, renewable in source of energy, low solubility and high biodegradability in water and land, low toxicity to the plants and animals and other resources or assets. Tiny droplets formed by vigorous blending of water and methyl ester are harmful to the swimming larvae. The use of biodiesel is beneficial in terms of financial and environmental considerations and therefore it should be promoted as it makes the nation self sufficient in terms of energy security.

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