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The downside of biodiesel fuel – A review

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Abstract

Biodiesel is a very hot topic of current scientific researches all across the globe as biodiesel is an unsurpassed alternative fuel source intended to extend the value to fossil fuels and the longevity and cleanliness of diesel engines. Biodiesel can be prepared by conventional transesterification reactions. Nowadays, however, the use of various heterogeneous catalysts has tremendously increased its production and efficiency in the diesel engine. However, in spite of numerous specifications, biodiesel is known to have a number of drawbacks that makes its excessive usage questionable. Therefore, this review summarizes and highlights the major problems related to the usage and production of biodiesel. The major issues related to biodiesel fuel include air pollution due to increased production of NO_X emissions and change in atmospheric composition, water pollution due to contaminants, fertilizers runoff causing eutrophication and water degradation. Increased use of biodiesel also results in land pollution in many ways including degradation of land. Severe health problems are also being reported due to biodiesel toxic effects. Some other issues like food vs. fuel debates, ethical and technical disadvantages and hurdles faced during the manufacturing of biodiesel fuel are also mentioned in this review. These are the problems which have to be solved. So, more researches and developments are required to improve the quality of biodiesel, to ensure the cleaners environment and to guarantee a sustainable future.

Key words: Biodiesel, fossil fuels, transesterification, NOx emissions, water pollution, eutrophication, environmental degradation

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1. Introduction

Depletion of existing petroleum resources increased emissions of greenhouse gases by uncontrolled combustion and their day-by-day increasing prices made renewable fuel more attractive [1]. Reservoirs of petro-diesels are limited and are concentrated in certain regions of the world [2]. Biofuels have a tendency to reduce the use of fossil fuels, improve energy security and lesser emission of greenhouse gases. Besides other auspicious alternative diesel fuels like renewable diesel fuel, hydrotreated vegetable oil and biomass to liquid fuels, biodiesel is one of these fuels that are feasible and in use today. Biofuels will help to fulfil future energy demands as well as help to reduce the emissions of greenhouse gases. Good biodiesel quality is fundamental for its continued success as a fuel. Biodiesel is such an alternative diesel fuel that comes from renewable biomass and it is known as a biodegradable, non-hazardous, oxygenated, sulfur free and eco-friendly diesel fuel.

Biodiesel is the mono-alkyl-esters of long chain fatty acids gained from renewable sources, like animal fats, vegetable oil and used cooking oil and is referred as B100. The quality of biodiesel must be according to the specification given by ASTM and EN standards. Biodiesel must meet the stringent quality standards to consider it as an appropriate transportation fuel. Either catalytic or non-catalytic, transesterification is the most convenient and simple process for the production of biodiesel. There is a variety of feedstock for biodiesel production including palm oil, coconut, soybeans, rapeseeds and even waste cooking oil. Rapeseed oil is commonly used in Europe for biodiesel production and soybean in the United States because these are native corps and climatic conditions of these regions favor their growth. Triglycerides are converted into fatty acid methyl esters that are the active compounds of biodiesels via catalytic transesterification. This process uses methanol and catalyst such as potassium hydroxide for the conversion of triglycerides and methanol into glycerol and methyl esters. Reaction equation for FAME production using methanol is shown below, this reaction mechanism allows for easy phase separation of the glycerol and methyl esters [3].

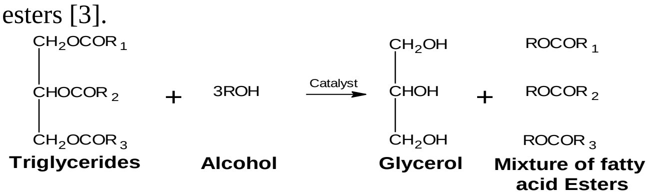

Fig 1 General transesterification process [3]

Biodiesel is a fuel that has gained worldwide attention being environmentally friendly and renewable in nature and is being appreciated all over the world. Biodiesel has many advantages over petroleum based diesels as: vehicles powered by petro diesel produce high amount of air pollutants, and unfortunately, these pollutants are dangerous for the environment. Biodiesel is agriculture-oriented, biodegradable, non-toxic and renewable fuel. Due to the presence of oxygen atoms in the fuel molecule, it has a high cetane number, low sulfur and low volatility. Most bright aspect of biodiesel is that it can also be mixed with other energy resources in different proportions to run the engines.

Biodiesel is used since 1893 but still have some problems that must be resolved before petroleum diesel is fully replaced by biodiesel. The current literature reveals the problems, associated with the use of biodiesel that could result in decreasing engine performance. Although this topic is very contentious, currently many studies are ongoing. This review will be purposive to give a brief overview of certain aspects of the biofuel issue. It will provide updates about the advancement in the production, types, feedstocks and technologies of biofuels, role of biofuels in the transportation sector, and some of the possible environmental, socio-economic and political issues that rises by the excessive use of biofuels. Considering the need for engine and vehicle performance, longevity and finest possible operation of engine and vehicle technologies, "worldwide fuel charter" is trying to introduce high quality and compatible fuels on a global basis. Biofuel that will fulfil these objectives will be beneficial for the consumers, fuel markets, facilitate trade and help governments to achieve public policy goals.

Although scientific attentions are focused on biodiesel production in the last recent years, it is not without disadvantages. One of the major problems faced by the use of biodiesel is increased emission of NOx which can result in the formation of smog and acid rain. Biodiesel has lower energy output as compared to petro-diesel. Hence, in order to get the same amount of energy, more biodiesel is used than petro-diesel. Also, the use of valuable cropland to grow biodiesel crops could result in the increase of food prices and furthermore cause food scarcity [4]. However, it must also consider that many documented problems are also associated with biodiesel that we should be aware of. These problems may include air, water and land pollution with its negative health problems. There are also food security issues and ethical and technical problems.

2. Downside of Biodiesel Fuel

Biodiesel has number of advantages over petroleum diesel being environmentally friendly, economically favorable and sustainable energy resource however some major disadvantages of biodiesel needs to be overcome in order to enhance the quality and quantity of biodiesel.

2.1 Biodiesel and Air Pollution

Air pollutants include oxides of nitrogen and sulphur, ozone, carbon monoxide, particulate matter and lead. The World Health Organization reported that about 2 million premature deaths occur all across the world every year because of air pollution. Following issues are related to the usage of biodiesel fuel.

2.1.1 Vehicular Emissions by Using Biodiesel Fuel

It has been investigated that biodiesel utilization in engines can lessen the emission of CO, SOx, total hydrocarbon and particulate matter [5]. Use of 100% biodiesel reduces PM and CO emissions up to 50% and hydrocarbon emission approximately 70%. Net emission of CO_2 from biodiesel is less than that emitted by petro diesel when looking at the biodiesel's production cycle. However, use of biodiesel increases NO_x emission [6]. NO_x initiates the ozone formation at ground-level and itself is toxic for human health, which causes strict regulatory limits.

Biodiesel is prepared by different feedstocks including canola oil, waste cooking oil, rapeseed oil, palm oil, olive oil, soybean oil and coconut oil. Emissions of gas-phase compounds and particulate matter were studied for the biodiesel produced from different sources and ultralow sulfur diesel during their use in diesel generators with different engine load. Except for coconut oil, all other biodiesels cause fewer THC emissions than ULSD while less CO is produced by soybean oil, palm oil and olive oil.

Nevertheless, particulate matter emissions are less for all biodiesels. But, emission of CO_2 and NO (at low load) by the combustion of biodiesels were higher than ULSD. It was concluded from different experimental results that engines with methyl esters of vegetable oil emit fewer hydrocarbons as compared to petroleum diesel due to oxygenated nature of biodiesel where more oxygen is available for the combustion. Carbon monoxide produced by partial combustion of hydrocarbons and sufficient availability of oxygen converts CO into CO_2.

2.1.2 Increase NO_x Emission

NOx gases are produced when nitrogen and oxygen react at the very high temperature and pressure in a combustion cylinder, where temperature can reach up to 4000°F. Generally excess of oxygen and high temperature leads to increased production of NOx. These reaction conditions are easily available in diesel engines because they operate at a lean air-fuel mixture and high compression ratios [7]. It was observed that the use of biodiesel increased the emission of NOx to about 12%. The NOx emissions are the very hazardous parameters for the environment as these cause acid rain and diseases in humans [8].

Environmental Protection Agency concluded that pure biodiesel causes an average 10% increase in NO_x emissions compared to petroleum based diesel [9]. It is reported that biodiesel emits more NO_x due to recent trends in injection timing, less radiative heat transfer, the higher degree of unsaturation, delay in combustion and high oxygen content. Use of biodiesel in diesel engine has widely been increased but the greater NO_x emissions could become hurdle in its commercialization.

2.2 Biodiesel Fuel and Water Pollution

Water is a precious resource used for many purposes. However, in some regions of the world, there is a scarcity of water reservoirs. Increased biofuels production will likely to add pressure to the water management challenges the nation already faces. There are the following issues of water pollution due to the usage of biodiesel fuel.

2.2.1 Eutrophication

In Asia, excessive use of chemical fertilizers due to biofuels could damage the coastal environment, mainly damaging the livelihood of local fishing industries [10]. Many studies measure the influence of biofuel production on water quality. Increase in the concentrations of some specific nutrients such as phosphorous and nitrogen, encourage the growth of plants and decomposition of aquatic ecosystems. This water pollution cause increased in hazardous phytoplankton, decrease in the concentration of oxygen in water, increased turbidity, loss of biodiversity, lessen the commercially beneficial fish and other harmful ecological effects [11].

Production of biodiesel feedstocks needs excess of nitrogen and phosphorous fertilizers, their runoff from fields into water bodies can cause eutrophication. The increased concentration of nitrogen in water bodies, especially coastal areas, can disturb the natural chemical balance that is harmful to the ecology of the system [12]. The potential of biodiesel from edible seed has about five times more tendency to cause eutrophication than that of conventional diesel fuel [13].

2.2.2 Dumping of Untreated Palm Oil Mill Effluent in Waterway

Water quality is getting worse by the overflow or dumping of polluted palm oil mill effluent into water bodies, which is harmful to the community health and aquatic diversity. This polluted water carries crushed shells and fat residues. Most palm oil mills have outdoor wastewater tanks to store and detoxify effluent by adding oxygen, but due to heavy rain or excessive production periods, these tanks can overflow. Some companies also allow the effluent to flow into the rivers without any pretreatment [14]. A mill can produce 1,200 cubic meters of wastewater per day with a potential of sixty tons of fresh fruit bunches per hour and this is equivalent to the wastewater produced by a city of 75,000 people.

As other agricultural and industrial activities, cultivation and processing of palm oil also cause environmental problem. Large quantities of water in mills are used for the processing of palm oil, where oil is extracted from the palm fruits and 50% effluent is produced. It is reported that 5-7.5 tons of palm oil mill effluent are generated for every 1 ton of crude palm oil [15]. In major oil palm producing nations like Indonesia and Malaysia, approximately 3 billion pounds of palm oil effluent is produced annually.

2.2.3 Water Degradation Due to Large-Scale Use of Biofuels

The cultivation of oil palms need pesticides and fertilizers for maximum yield, which sometimes leach into rivers and contaminates the water. For the oil palm plantation, around twenty-five, different pesticides are used but their use is not monitored as it is reportedly not controlled or documented. Parquet dichloride is a commonly used weed killer, which is very hazardous and accumulates in the soil due to excessive use which negatively affects the water quality [14].

2.3 Biodiesel Fuel and Land Pollution

The land is one of the fundamental resources of nature and excessive use of biodiesel degrades it. Degradation includes physical (loss of land and loss of soil structure) and chemical erosion (loss of fertility). Land degradation and all other problems are discussed below.

2.3.1 Loss of Habitat, Biodiversity and Ecosystem Services

In order to produce biodiesel, it is necessary to cultivate oil crops and more land must be brought into use for this purpose. Immaculate rainforests are being cleared for monoculture plantations. It is reported that 20% worldwide emissions of greenhouse gases are caused by deforestation and most of the forest land is being cleared for palm production. At the same time, landscapes with high levels of oil crops had low habitat diversity and significantly reduced biocontrol services in these fields [10]. Most of the arable lands were required for the cultivation of first generation biodiesel crops to meet the world’s fuel demand, which caused crucial ecological imbalances as various countries around the world are cutting down forests for this purpose. Therefore, these feedstocks could cause deforestation in tropical regions including Malaysia and Indonesia that meet about 80% supply of the world palm oil.

It has been documented that the increased oil crop production in the last few years to fulfil the world’s biodiesel demand caused deforestation on a massive scale. Eventually, execution of biodiesel as an alternative of petroleum-based diesel fuel could cause severe damage to environment and wildlife in those regions [16]. Such trends have caused serious erosion and loss of wildlife habitat of endangered species. Loss of biodiversity and associated bio-control services in agriculture is another problem that arises when rainforests are being cut down for cultivation of monoculture feedstock. Deforestation and peat land for oil palm cultivation cause a rapid increase in carbon dioxide emission. In Southeast Asia, the clearing of rainforest and peat lands is considered to cause 8% of global carbon dioxide emissions annually [17].

2.3.2 Soil Erosion

The extent of sediment erosion is directly related to land use for agriculture, the more will be the use greater will be the erosion. As compared to pastures and woodland, more sediment abrades from row crop fields. Biofuel-crop cultivation can cause soil erosion and may affect the nutrient and organic contents of soil, which leads to the use of fertilizer. For example, if residues of crops are removed from the field and used for the production of biofuel, then it will increase the chances of soil erosion and fewer nutrients and less organic matter will be going back to the soil [18]. This will decrease the permeability of the land, will cause loss of soil faunal activity, and compact the land, all of these will increase top soil runoff and causes soil erosion. Sediment starts to accumulate in rivers and streams. Flooding rapidly increase in the rainy season and there is a water shortage in the dry season due to interrupted or low water flow [14].

2.4 Biodiesel Fuel and Health Problems

In search of a cleaner-burning fuel, the interest in biodiesel has been increased that must also be compatible with petroleum based oil. Although, biodiesel has many advantages as fuel some health problems are also associated with it. NO_X emissions are increased by the use of biodiesel and these gases cause various health problems such as headaches, respiratory irritation, edema of lungs, emphysema, eye irritations, loss of appetite and corrosion of teeth. Most affected peoples are children, asthmatics and individuals with chronic bronchitis, emphysema or other chronic respiratory diseases [19].

2.4.1 Jatropha Biodiesel Health Issue

In United States, South Africa, Australia and Puerto Rico, Jatropha is known as invasive species. The Global Invasive Species Programmed has suggested that it should not be used for biodiesel production. In Western Australia due to the poisonous and invasive nature of this plant, it is recognized as a toxic weed. Government of state warns that jatropha oil has carcinogenic substances and cause serious human and animal health hazards [20]. It is documented that the oil constitutes curcanoleic acid, which may cause skin cancer and may start skin allergy to the farmers [21].

2.4.2 Cytotoxicity Assessments

Cytotoxicity assessment is necessary to find environmental and human health problems caused by exposure to chemicals. Various methods are used to investigate the cytotoxicity of air pollutants. Air pollutants have a greater tendency to harm cells that depends on the time of exposure and concentration, reactive oxygen species induce severe cytotoxicity to the cells [22]. Fossil fuels have been experimented for many years and the results revealed that the air pollutants enhance toxicity and apoptosis of animals and human cells. Biodiesel causes an increase in cytotoxicity effects when compared to diesel fuel or no much difference in cytotoxicity of both exhausts [23].

2.5 Biodiesel Fuel and Food Security Issues

On May 2, 2008, in his background note calling upon the UN Human Rights Council to convene a special session on the current world food crisis, the Special Rapporteur on the Right to Food pointed that biofuel demand is one of the determining factors. This has caused evictions and marginalization that leads to undermining the income of most groups in society. Resultantly, many individuals, either alone or in community with others, are not able to enjoy physical and economic approaches to food supplies.

2.5.1 The Food vs. Fuel Debate

Use of traditional food and feed crops for biofuel production, a farmer has an opportunity to sale the same crop for food, or for non-biofuel crops. This trend can decrease food availability and may allocate food and feed production to less productive land, thus decreases yields, food security and raises food prices [24]. The main source for the production of biodiesel is fat or oil and these oils come from crops, which otherwise could be used as a source of food. Conversion of food crops into fuel has an adverse effect on food supply. The biodiesel production process utilizes methanol as a reactant [25]. The food versus fuel issue is one of the challenges that need to be addressed. Palm oil is used in cooking oil and in different processed foods including margarine and biscuits and also as chemical derivatives for detergent. Production of biodiesel from palm oil is potentially competing for the food industry. Prices of edible oils are likely to increase as biodiesel demand increases, leads to an increase in the prices of food. Therefore, the use of edible oil for biodiesel production is not economically feasible [16].

2.5.2 Cost of Biodiesel

The cost of biodiesel is a hurdle to its commercialization as compared to petroleum diesel because about 60–70% of the raw material cost comes on edible oil that is used as biodiesel feedstock. Production of cheap fuel is very challenging due to the high value of soybean oil or canola oil as a food product. Utilization of such edible oil for biodiesel production is not suitable because of a difference in the need and supply of such oils as food. There are different factors that affect the cost of biodiesel including feedstock cost, capacity of plant, feedstock quality, processing technology, net energy balance, nature of purification and its storage. Two main factors are the feedstock prices and the cost of processing, it has been found that feedstock cost accounts for 75% of the total cost of biodiesel [26].

2.6 Biodiesel Fuel and Ethical Problems

There are also some ethical problems when we use biodiesel fuel. These include energy security and economic development.

2.6.1 Energy Security

There is lower energy output from biodiesel than petro diesel. As compared to petro diesel more biodiesel is used to achieve the same energy output. In United States typical No. 2 diesel gives about 8% more energy per gallon than biodiesel or 12.5% more energy per pound. This difference in two energy outputs is because of a higher density of biodiesel than petro diesel fuel. All biodiesel provide approximately the same amount of energy per gallon or per pound regardless of feedstock used for the production. However, some reference values are shown in table 1.

Table 1 Energy contents of diesel and biodiesel fuel Btu is British thermal unit

Type of Biodiesel	Btu/Ib.	Btu/gal
Typical Diesel No. 2	18,238	129,488
Typical Biodiesel (100)	16,377	119,550

The difference in energy contents between petroleum diesel fuel and biodiesel can be noticeable with B100 [27]. About fuel cost, the most important point for the consumer interest is that biodiesel especially B20 gives only 117,000 BTUs of heat energy per gallon than 131,000 BTU per gallon of typical #2 diesel fuel. This difference is because about 11% of biodiesel contains oxygen by weight and this oxygen does not contribute to the energy value. Less energy value of the fuel means less mileage per gallon and less power, during the road operation there can be a loss of power and also a decrease in miles per gallon of 0.5-1.0 mile per gallon. A truck that covers only 7-8 miles per gallon with typical #2 diesels fuel, this loss of mileage is very important [28].

2.6.2 Economic Development

Another drawback of biodiesel is that it lessens the fuel economy. Energy efficiency is the percentage of the fuel thermal energy that is used as engine output, and any test engine biodiesel has not shown any prevalent effect on energy efficiency. Volumetric efficiency, is more used term by consumers, it is referred as distance covered in miles per gallon or the per liter by a fuel [29]. Pakistan is a developing country and the economic position of Pakistan is not very stable. Therefore, there is need of huge investment to stand a biofuels industry. Few researchers [25] states that the drawback of biofuel blends is high cost that comes on their production and leads to higher prices at the pump. Agricultural products are mostly used for the biodiesel production due to which production cost rises very rapidly. This prevents stakeholders to show their interest in the biofuel production.

2.7 Biodiesel Fuel and Technical Problems

Technical problems with biodiesel that have persisted to the present are high viscosity, clogging in engine, negative effect on lubricants and many other factors as briefly explained below. Solving these problems at a time has proven difficulty because solution of one problem often encourages the other problem.

2.7.1 Biodiesel Effect on Engine Lubricants

As biodiesel is less volatile than conventional diesel fuel thus it has greater chance of partial combustion. Non-combusted fuel passes through the rings of piston and assembles at the piston sides, on scratching it moves down the piston and stores in the crankcase oil pump and dilute the oil. This dilute oil enhances the chances of severe problems such as it has negative effect on the properties of oil to avoid wear (changes in the viscosity of oil by dilution causes change in the thickness of the oil film), oil degradation, corrosions and engine deposits.

Biodiesel oil on dilution can increase the extent of engine deposits and sludge because polymerization of the biodiesel ester occurs and sludge-like deposits start to appear in the oil. This can be very problematic if deposits are formed within the upper side of the cylinder because this can cause piston ring sticking and even more severe problem of soot blow by an increase in the contamination of the crankcase oil. Chemical properties of the biodiesel mixture tend to cause coagulation in the fluid at cold temperature, which stops fuel injection in engines [30]. Biodiesel at its cloud point will start to solidify into a wax like material. If the temperature is lower than cloud point, the fuel will become completely wax-like and engine will not be able to use it. This temperature control is a barrier in the commercialization of biodiesel as an alternative for petroleum based diesel.

2.7.2 Clogging in Engine

Water and sediment impurities are the main problems associated with biodiesel. Water can be either in the form of dissolved water or suspended water droplets. Biodiesel is known to be insoluble in water as it actually needs relatively more amount of water than diesel fuel. Maximum 1500 ppm water can be dissolved in biodiesel while diesel fuel carries only 50 ppm. Sediments include dirt particles and suspended rust or it may appear as insoluble compounds from the fuel formed during fuel oxidation. Level of water and sediment impurities are tested by centrifuging 100 mL of biodiesel at 1870 rpm for <0.005 vol% [31]. The hydrolysis reaction of biodiesel also starts at high water contents that convert biodiesel to free fatty acids which also leads to fuel filter blockage [32]. Biodiesel may freeze or convert into the gel in winters, gel formation can clog filters and become so viscous that it cannot be pumped into the engine [27].

2.7.3 Water Contamination

Because of the oxygen contents, biodiesel makes hydrogen bonding with water molecules that is why water is not evaporated during processing or storage in tanks. Presence of water lowers the heat of combustion and results in more smoke formation. Water can cause corrosion of engine, the most direct form of corrosion is rust, but with time water may become acidic and lead to acidic corrosion that can attack fuel storage tanks. Although it only causes light corrosion there the resultant organic acid salts accumulate and form deposits in the fuel pump and injector. Metallic salt is formed by the further reaction of metallic and organic acids. These salts are precipitated and pass through the fuel filter and accumulate at the surfaces of the fuel pump and fuel injector. Polymer, sludge and oxidation products are additional immiscible substances, which often cause fuel filter blockage [33].

Kaul et al. [34] studied the rate of corrosion from different biodiesels produced from different feedstocks such as jatropha, mahua and karanja and compared with diesel fuel. They concluded that biodiesel from jatropha and salvadora caused more corrosion of both ferrous and non-ferrous metals. Geller et al. [35] concluded from the immersion test of fat based biodiesel for different ferrous and non-ferrous metals that there are more chances of copper alloys' corrosion than ferrous alloys. These experiments also revealed that fuel parameters like density and viscosity were also altered by metal contact. Water contamination can also promote microbial growth. At the bottom of a storage tank, species of yeast, fungi and bacteria can grow at the interface of the fuel and water. Some microbes convert sulfur into sulfuric acid which can cause corrosion of the fuel tanks [32].

2.7.4 High Viscosity

Viscosity is measured by considering the time taken by oil to pass through an aperture of a specific size. Viscosity has a direct impact on the injector lubrication and fuel atomization. For the precise fitting of fuel injection pumps, a low viscos fuel may not provide enough lubrication, which causes leakage or increased wear resistances. More viscos diesel fuels form larger droplets (poor atomization) during injection that results in partial combustion, increased emissions and exhaust smoke. The viscosity of biodiesel is the most important character that is close to petroleum based diesel because it affects the efficiency of the fuel injection equipment, especially at low temperatures, the viscosity increases that affect its fluidity. The viscosity of the biodiesel is higher than petro diesel because of the presence of more electronegative oxygen atoms. Biodiesel is more polar than diesel fuel and heating value of the biodiesel is also lower than diesel fuel due to the presence of elemental oxygen. Higher molecular mass and large chemical structure of biodiesel make kinematic viscosity of biodiesel 10–15 times higher than conventional diesel fuels. Sometimes, at low temperature, biodiesel becomes very viscous or even solidified. Some literature stated that volume flow and injection spray characteristics of engines are affected by higher viscosity of biodiesel [36].

2.7.4 Oxidation Stability

Oxidation of biodiesel during storage and operability causes the formation of peroxides, deposits, acids, deposits and gums, these products have adverse effects on the fuel systems. Therefore, the oxidation stability of FAME is a barrier in the commercialization of FAME. FAME molecules have many double bonds that oxidize very easily. At the start, the oxidation process produces hydrogen peroxide, which ultimately forms acids. Rancimat method is a fast oxidation test that is carried out at high temperatures in the presence of air that results in autoxidation in a few hours, instead of weeks or months. Jain and Sharma [37] stated that biodiesel comprises long chain fatty acid esters coming from feedstocks which have more or less unsaturated fatty acids that are vulnerable to rapid oxidation during storage in the presence of air and at high temperature may generate polymerized compounds. Autoxidation of biodiesel can disturb the fuel quality by affecting the stability parameters such as storage, oxidation and thermal stability. Instability of biodiesel regarding oxidation can result in the generation of oxidation products including shorter chain carboxylic acids, aldehydes, alcohols, insoluble gum and sediment. Autoxidation of lipids such as biodiesel generates free radicals through hydrogen abstraction in the presence of different initiators including light, heat, peroxides, hydroperoxides and transition metals. These free radicals again react exothermically with molecular oxygen to generate peroxides, which further react with un-oxidized lipids to generate additional free radicals [38]. This oxidative degradability of biodiesel has adverse effects on standard acid value and viscosity which are given by ASTM D6751 and EN 14214 biodiesel standards [39].

2.7.5 Variation in Quality of Biodiesel

The properties of biodiesel depend on various factors as the type of feedstock and the refining process. Biodiesel producers that follow standard procedures have a better opportunity for fuel production that meets the specifications. With the use of proper equipment, everyone can produce biodiesel, but most of the producers do not try to meet standard values of biodiesel fuel quality parameters. A survey by the National Biodiesel Board in 2006 stated that among 200 different fuel companies less than 50% gain a minimum quality standard. ASTM D6571 gives guidelines for the biodiesel production parameters, including alcohol content and glycerin content, both of these parameters can be met in the manufacturing process. It is a key point to have such fuel which meets these particular standards to eliminate fuel problems. Contamination of the final product with impurities of the manufacturing process can lead to serious issues of the fuel system and injector. Excess alcohol content, from the methanol wash, is another common issue in out-of-spec biodiesel; excess alcohol has an impact on the auto-ignition temperature and causes rough running of diesel engines. It is important for a biodiesel user, to make sure that the fuel they use, meet the ASTM standards of biodiesel.

2.7.6 Biodiesel Low-Temperature Operability

Crystallized saturated FAME of biodiesel in winter causes problems of fuel shortage and operability as solid like materials clog in the fuel lines and filters moreover by further decreasing the temperature material reaches the pour point (lowest temperature at which it will stop to flow). B20, common form of biodiesel, shows poor fluidity property in winter; at temperatures between 30-50°F, it converts into thick and cloudy biomass. Due to this reason, some biodiesel producers do not refer to its use in the cold season. Biodiesel fuels are more problematic due to the flow products than petroleum based diesel. Different biodiesel specifications of numerous biodiesel batches in the market can vary the effectiveness of cold flow properties. The type of feedstock also affect the cold flow properties of the fuel as monoglycerides can significantly raise the cloud point and affect the filter plug point of biodiesel [30].

Different feedstocks produce different amounts of various monoglycerides (saturated or unsaturated), which give different cold flow products. Monoglycerides of soybean and canola oils are less saturated and have adverse effects on cold flow properties than palm oil or tallow. Typical cold flow and anti-gel agents do not enhance the fluidity of B20 because they are prepared to remove paraffin wax crystals which are present in petroleum; not for the components of the vegetable oil phase which produces a gel. For the gelling problem of the biodiesel, "Bio Dee-Zol Plus" is used, it contains a component that controls wax formation from the fuel and modifies the viscosity that improves the fluidity of the vegetable at low temperatures [40].

2.7.8 Issues with Storage of Biodiesel

Dunn [40] states that the blending of conventional diesel fuel with biodiesel aggravates the problem, as the accumulation of solid residues in fuel dispensers and vehicles clog fuel filters. Biodiesel blends have sufficient storage ability for normal use, but for a long period of storage safety measures should be taken. Use of a stability additive is directed to store the biodiesel for months and oxidative stability of the fuel must also be checked monthly. During the storage period and flow processes, the temperature fluctuates periodically in day and night. This gives rise to the following problems:

- ❖ At low temperatures wax separate from fuel and deposits in the fuel tank
- ❖ The wax that deposited at low temperatures does not melt again when temperature increases but this fluctuation in temperature increases the amount of wax

Limit of storage period is a standard for fuel quality. Derivatives of vegetable oil make the situation more critical due to hydrolytic and oxidation reactions. Their degree of unsaturation makes them receptive to thermal and oxidative polymerization, which results in the generation of insoluble products that harm the fuel system, especially injection pump [41].

2.8 Biodiesel Fuel and Manufacturing Problems

Biodiesel is a renewable and alternative of fossil fuels, with some tendency to take the place of petro diesel in the market. It is produced by transesterification of triglycerides of vegetable oils and animal fats. Besides its benefits, there are many issues arising during the manufacturing of biodiesel fuel.

2.8.1 Variable Chemical Composition of Feedstock

The physiochemical characteristics of feedstocks such as fatty acid composition, free fatty acid content, moisture and impurities affect both the biodiesel production procedure and the product. For example, chain length and unsaturation of the component fatty acids affect the fuel parameters of the biodiesel such as oxidative stability, cetane number, cloud point, flash point, and heat content. Singh *et al*. [42] state that biodiesel produced by the same raw material can show varied properties and this change in properties is because of different parts of the plant used for the production of biodiesel.

Commercially, the fats and oils used for the biodiesel production constitute 10 types of fatty acids that contain 12 to 22 carbons and above 90% of these have 16 to 18 carbons. These chains may be saturated, monounsaturated or polyunsaturated. According to the specification limits, some fuel quality parameters of biodiesel depends on saturation levels and due to different proportions of saturated, monounsaturated and polyunsaturated fatty acids, every feedstock is different from others. Commonly, saturated fatty acid methyl esters have high cetane numbers and cloud points and are more stable. Increase in unsaturation causes a decrease in the cetane number and cloud point and thus decreases the natural stability of FAME. The cetane number and stability can be easily improved by traditional additives, while the cloud point cannot be improved easily.

2.8.2 Free Fatty Acid and Moisture Contents

Free fatty acid and moisture contents are important conditions for evaluating the feasibility of vegetable oil transesterification. For successful base-catalyzed transesterification, a free fatty acid value must be less than 3%. Higher will be the acidity of the oil, lesser will be the conversion rate. 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. Although biodiesel is produced from both edible and low-cost oils, the problem is that these low-cost oils and fats often contain an excess of free fatty acids that cannot be transesterified by using an alkaline catalyst. Free fatty acids also lead to soap formation when alkali catalyst is used [3]. Wright et al. [43] investigated that the raw materials used for alkali catalyzed transesterification must fulfil some standards. The acid value of the glyceride should be less than 1 and all materials should be anhydrous, if the acid value will be higher than 1, then for the neutralization of FFAs more NaOH will be used. Freedman reveals that ester production was decreased when reactants did not follow these specifications. Sodium hydroxide or sodium methoxide react with moisture and carbon dioxide in the air, which reduced their catalytic activity [44]. In addition, alcohol vapor facilitated this process. FFA in biodiesel may also affect fuel parameter as low temperature performance, oxidative stability, kinematic viscosity and relatively high lubricity [45].

2.8.3 Problems with Usage of Catalysts

Enzyme catalysts like lipases have the tendency to catalyze transesterification in both aqueous and non-aqueous systems, but the cost of a lipase catalyst is significantly high. Use of enzyme as a catalyst is not feasible because its catalytic activity is lost at high reaction condition, so until now it cannot be used on a commercial scale [75]. Alkali catalysts are very sensitive to water and free fatty acids and require a high amount of carbinol. Alkali catalysts also lead to saponification reaction which makes the separation of biodiesel and glycerin difficult. Use of sodium methoxide as a catalyst for the biodiesel production leads to the generation of many by-products mainly sodium salts, which is considered as waste. Moreover, high quality oil is needed for this catalyst [46].

Truck et al. [47] studied the adverse effects of base catalyzed transesterification containing a considerable amount of free fatty acid, basic catalyst react with these free fatty acids and results in soap formation, cause of some of the catalyst that no longer will be available for transesterification. Soap formation also caused an increase in viscosity because of the formation of gels. Base catalyzed transesterification has various other disadvantages: it needs high energy, separation of glycerol is difficult, recovery of catalyst is also a hard task, a lot of wastewater, and free fatty acid and water interfere with the reaction.

2.8.4 Influence of Impurities

Triglycerides are the raw materials for FAME production and impurities such as diglycerides and mono-glyceride are the reaction intermediate. Recently, it has been revealed that these contaminants cause sludge formation and deterioration of low temperature fluidity. Some saturated fatty acids like glycerides have a high pour point, as the pour point of stearic acid is about 40°C, while mono-glyceride, diglyceride and triglyceride of stearic acid have pour point up to 50~80°C, and among these mono-glyceride has the highest pour point. In the European FAME standard, the upper concentration limit of the glycerides was measured. Now, it has been cleared that the upper limit of the petrodiesel may lower down when it mixed with biodiesel and may lead to some problems. When Goto et al. [33] analyzed the substances that caused plugging of the filters, it was revealed that saturated fatty acid mono glycerides were the major elements. It is also considered that methanol that is used as raw material worked as a co-solvent to help in the dissolution of these compounds, and when the temperature is increased during flow process, methanol evaporates that decreases the dissolving performance and phase separation. Biodiesel that is produced from highly saturated fatty acid materials such as palm oil and beef oil in a cold region or season, it is essential to be very careful while estimating their further countermeasures [33].

3. Conclusions

Cooperative global efforts are focused on the search of alternative and nonrenewable diesel fuel that can be used in future to overcome energy crisis and biodiesel is the outcome of these global efforts. Although there are number advantages that biodiesel have over petro diesel including lesser emissions of greenhouse gases and nonrenewable nature etc. But biodiesel has also some downsides that must be kept in consideration before making it commercialized. Emission of carbon monoxide is less in case of biodiesel combustion because higher oxygen contents in biodiesel convert carbon monoxide into carbon dioxide along with higher emission of NO_X because of the excess of oxygen and high temperature and other water and land pollution problems that cause severe health hazards. In most of the countries, the edible seeds oil are used as feedstock that will compete with the food industry and also higher cost of biodiesel. Most of the biodiesel producers do not follow the standard procedures with the recommended specification. The use of enzyme as a catalyst is not advantageous as they are expensive and their catalytic activity is lost at higher reaction conditions, while some problems are also related to homogenous catalysts such as difficult to recover, a lot of wastewater is produced, soap formation and separation of the product are also difficult. Biodiesel is less volatile than conventional diesel fuel that increases the chances of the partial combustion which is responsible for deposit formation in the fuel engine. Higher water and sediment contents in the biodiesel promote microbial growth and corrosion of engine. Due to the higher molecular weight and large molecular structure, the viscosity of biodiesel is higher than that of conventional diesel fuel that affects the volume flow and injection spray characteristics in the engine. At low temperature, it becomes so viscous that wax starts to deposit that does not melt again even at a higher temperature. Biodiesel can be oxidized very easily due to a greater number of double bonds and this can disturb the fuel quality by affecting the stability parameters such as storage, oxidation and thermal stability.

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