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Biodiesel : Its Synthesis and Application

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***Abstract* – The natural resources are rapidly depleting with time. All human beings are trying to solve this problem by conserving the natural resources or by using alternative resources which are less harmful and can be reused. By giving speed to our day to day life we forgot that the power source i.e. petrol, diesel are not renewable resources. If we want to save the existence of these resources in future then we have to use them judiciously as well as explore alternative fuels. Many projects are going on in different reputed institutes on the use of biodiesel as an alternative fuel. Many countries are using biodiesel blend because pure biodiesel is not as beneficial as petrol or diesel but blends are much useful as they are good for engine's health and cause less pollution. Industries are carrying out research to standardize procedure for synthesis of biodiesel at large scale by using waste materials from different industries and employing suitable biocatalyst. Plenty of raw materials such as soyabean oil, fatty acids etc are available for synthesis of biodiesel. Both batch and continuous reactor can be used for its production. Biodiesel is more eco-friendly as compared to petrol or diesel. In this review, we describe some processes used in synthesis of biodiesel and its applications.**

***Keywords* – Alternative Fuel, Biodiesel, Biofuel, Fatty Acids, Novozyme, Transesterification Reaction**

I. Introduction

Biodiesel can be categorized as alternative fuel that is similar to conventional diesel fuel and is produced from biological substrate like vegetable or animal oil by a chemical reaction. It is eco-friendly, biodegradable and nontoxic. It has low emission profiles and so is considered environmentally beneficial (Krawczyk, 1996). It can be produced from vegetable oil, animal oil/fats, tallow and waste cooking oil. It is produced by a chemical reaction between lipids and an alcohol producing fatty acid esters. The reaction is known as trans - esterification reaction. Oil crops such as rapeseed, palm and soybean can be used as a source of raw material utilized in production of biodiesel. However, the most important, cheap and widely used source of raw materials used in synthesis of biodiesel is waste vegetable oil discarded from restaurants, chips shops, industrial food producers etc. Though oil straight from the agricultural industry represents the greatest potential source, yet, it is not being produced commercially simply because the raw oil is too expensive. After the cost of converting it to biodiesel has been added on it is simply too expensive to compete with fossil diesel. Waste vegetable oil can often be sourced for free or sourced already treated for a small price. Biodiesel can be used in pure form or may be blended with petroleum diesel at any concentration in most injection pump diesel engines. Biodiesel has different solvent properties than petro-diesel, and will degrade natural rubber gaskets and hoses in vehicles. This has been known to break down deposits of residue in the fuel lines where petro-diesel is used. As a result, fuel filters may become clogged with particulates if a quick transition to pure biodiesel is made. Therefore, it is recommended to change the fuel filters on engines and heaters shortly after first switching to a biodiesel blend.

One hundred years ago, Rudolf Diesel tested vegetable oil as fuel for his engine (Shay, 1993). With the advent of cheap petroleum, appropriate crude oil fractions were refined to serve as fuel and diesel fuels and diesel engines evolved together. In emergency situations vegetable oils were used as blends in diesel fuels for time to time within the period of 1930s and 1940s. Recently, because of increases in crude oil prices, limited resources of fossil oil and environmental concerns there has been a renewed focus on vegetable oils and animal fats to make biodiesel fuels. Continued and increasing use of petroleum will increase the surrounding air pollution and magnify the global warming problems caused by CO_2 (Shay, 1993). But biodiesel fuel has the potential to reduce the level of environmental pollution. It can also reduce the risk of pollutants many of which are potential carcinogens (Krawczyk, 1996).Among the different sources for production of biodiesel, oil from algae, bacteria and fungi have been investigated. (Shay, 1993). Microalgae have been examined as a source of methyl ester diesel fuel (Nagel and Lemke, 1990). Terpenes and latexes also were studied as diesel fuels (Calvin, 1985).

Biodiesel is an environmental friendly replacement of petroleum diesel. It is pure, natural & clean and can be made from almost any fatty acid. It is beneficial to the environment as carbon dioxide and other harmful gases are not released during combustion of biodiesel. Therefore, it can be described as 'carbon neutral'. This effect occurs because when the oil crop grows it absorbs the same amount of CO_2 as is released when the fuel is burnt. Biodiesel is rapidly biodegradable and completely non-toxic. This reveals that biodiesel spillages are far less of a risk than fossil diesel spillages. Biodiesel has a higher flash point than fossil diesel and so is safer in the event of a crash. Flashpoint for biodiesel is higher than 150°C whereas the same is about 52°C for petroleum diesel, which makes it less combustible. Biodiesel is therefore safe to handle, store and transport.

Producing biodiesel is a cost worthy process. It takes less amount of energy for its formation. Biodiesel utilization improve not only economy but it shows a positive impact on environment and also on government policies. Biodiesel production process is a simple process. Its production can be carried out by way of a community based biodiesel production programme. It will definitely enhance local economy as farmers grow the raw material for biodiesel production. Thus in this way, it increases the energy security level and leaves a positive impact on nearby environment. The crude oil companies and to a greater extent countries will have less domination on other countries in the aspect of energy resources while using biodiesel. This will lead for a better balanced peaceful world. We cannot use petro-diesel in crude form. Even when it is refined there are emission of many toxic substances such as benzene and butadiene from it that pollutes the environment. On the contrarily, biofuel refineries releases less toxic chemicals.

Slowly, we are exploring the science and getting benefits from the product of it and also applying it in the variations present in the nature. Many countries show their keen interest in the production and utilization of biodiesel in their daily routines of life. This is an appreciable step towards betterment of nature. Brazil has turned sugarcane into ethanol, and there are some cars that can run on pure ethanol rather than as additive to fossil fuels. Biodiesel is being used as a common fuel in Europe.

II. Properties Of Biodiesel

The calorific value of biodiesel is about 37.27 MJ/kg. Variation in biodiesel energy density is more dependent on the feedstock used than the production process. It has been claimed that biodiesel gives better lubricity and more complete combustion thus increasing the engine energy output and partially compensating for the higher energy density of petrodiesel (Table 1 & 2). The color of biodiesel ranges from golden to dark brown, depending on the production method. It has higher cetane number (CN). The CN is a commonly used indicator for the determination of diesel fuel ignition quality. It measures the readiness of the fuel to auto-ignite when injected into the engine than diesel fuel and contains no aromatics, almost no sulfur and 10-20% oxygen by weight. The viscosity is generally measured to be around 52.76mm2/sec at 40°C. The methyl esters and the blends were observed to have viscosity within the ASTM limits. The diesel fuel sample generally have a density value of 0.836kg/l which is lower than edible, non edible oils, methyl esters and its blends.

Table1: Different forms of biodiesel and their properties

	Gross heating value (MJ/kg)	Hydrogen content (mass%)	Net heating value (MJ/kg)	Density (kg/l)	Net heating value (MJ/l)
B(100)	39.973	11.92	37.444	0.880	32.950
B(90)	40.565	12.15	37.987	0.868	32.973
B(80)	41.330	12.81	38.612	0.857	33.090
B(65)	42.124	13.69	39.219	0.839	32.905
B(50)	43.189	13.19	40.390	0.822	33.201
B(20)	45.346	14.42	42.286	0.788	33.321
GTL	47.015	14.98	43.836	0.764	33.491

III. Biodiesel Synthesis

Biodiesel can be synthesized both in batch reactor and in continuous reactor. But it was observed that the production will be finer in continuous reactor as compared to batch reactor. Almost all biodiesel is produced using base catalyzed transesterification reaction as it is the most economical process requiring only low temperatures and pressures and producing a 98% conversion yield.

IV. Biodiesel Feedstocks

A variety of oils can be used to produce biodiesel. These include:

- Virgin oil feedstock – rapeseed and soybean oils are most commonly used, soybean oil accounting for about half of U.S. production. It also can be obtained from Pongamia, field pennycress and jatropha and other crops such as mustard, jojoba, flax, sunflower, palm, coconut etc.
- Waste vegetable oil
- Animal fats including tallow, lard, yellow grease, chicken fat, and the by-products of the production of Omega-3 fatty acids from fish oil.
- Algae, which can be grown using waste materials such as sewage and without displacing land currently used for food production.
- Oil from halophytes such as *Salicorniabigelovii*, which can be grown using saltwater in coastal areas where conventional crops cannot be grown, with yields equal to the yields of soybeans and other oilseeds grown using freshwater irrigation
- Sewage Sludge - The sewage-to-biofuel field is attracting interest of major companies. One such example is Waste Management and startups company like Info Spi, which are of opinion that renewable sewage biodiesel can become competitive with petroleum diesel as regards to its price.

V. Biodiesel Production in Batch Reactor

Raw materials used in the production of biodiesel in a batch reactor include waste and virgin vegetable oil, methanol and potassium hydroxide. Potassium hydroxide (KOH) works as a catalyst in the batch method.

The reaction employed in a batch reactor for production of biodiesel is a transestrification reaction. Transesterification is the process of exchanging the organic group R″ of an ester with the organic group R′ of an alcohol (Fig1). These reactions are often catalyzed by the addition of an acid or base catalyst. The reaction can also be accomplished with the help of enzymes (biocatalysts) particularly lipases. The conventional batch reaction occurs in a reactor where vegetable oil and/or animal fats & oils are mixed with methanol at 55^0C. Potassium hydroxide (KOH) is added as a catalyst to the reactants in the reactor and after the reaction is complete, methyl ester-biodiesel is obtained as a product (Fig2). This reaction is reversible and produces some by-products such as residual methanol, residual caustic etc. The batch process with potassium hydroxide (KOH) catalyst for production of biodiesel may produce soap and glycerol as side products that have to be removed before use. Soap can be removed by washing the product with water.

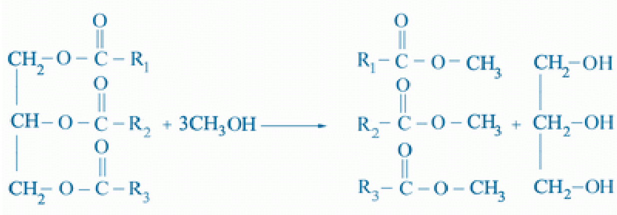

Fig. 1. Transesterification reaction for biodiesel production

The quality and quantity of biodiesel produced in a batch reactor is assessed by GC or Mass Spectrometer and Bomb Calorimeter.

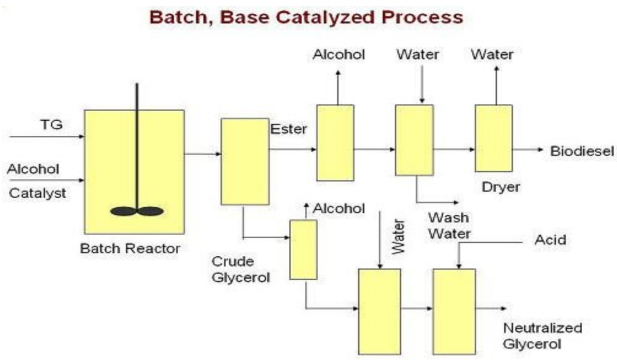

Fig. 2. Biodiesel production in batch reactor

VI. Biodiesel Production In Continuous Reactor

The raw materials required for production of biodiesel in continuous reactors comprise of waste and virgin vegetable oil and ethyl acetate. Novozyme-435 or lipase enzyme is used as a catalyst in the reactor. The raw materials react within the continuous reactor in the presence of biocatalyst. Transesterification process is also carried out in the continuous reactor in the presence of Novozyme 435 to produce the product biodiesel (Fig 3).Reactor is allowed to run for nearly 6 hours for optimal reaction. The continuous process produces biodiesel and triacetin. Triacetin is a known fuel additive which does not have to be removed from the biodiesel before use.Novozym-435 is a dynamic kinetic solution of alcohols coupled with ruthenium catalyst. It also consists of an amine coupled with metal racemizing agent. This enzyme has substrate specificity for esters and alcohols. The optimum temperature for working of the enzyme is 40-60°C (Fig 4).

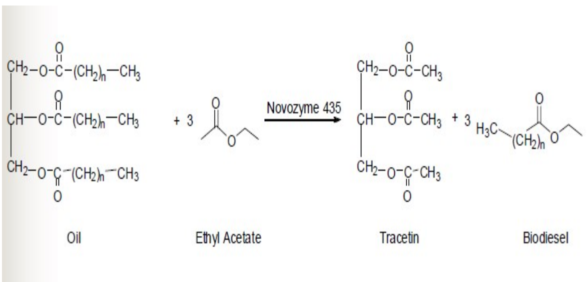

Fig. 3. Transesterification reaction using biocatalyst

Quality assurance tests are carried out for the presence and quality of biodiesel by GC or Mass Spectrometer and Bomb Calorimeter.

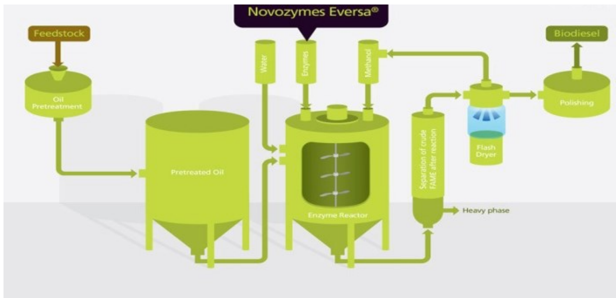

Fig. 4. Production of biodiesel in continuous reactor

The optimal reaction time for oil to be completely converted to biodiesel is 6 to 8 hours. The duration of the reaction time was determined by an indirect method of measuring the calorific values of samples taken at different points during the reaction process. Further testing showed that after this time period, the equilibrium point was reached for the reaction and it began to shift back to the reactant side. It was also observed that as the concentration of ethyl acetate in decreased in the reaction, the calorific value increased. Lipase enzyme can be used effectively as a substitute for Novazyme 435 as a catalyst for production of biodiesel in continuous reactor. Ethyl acetate is a good alternative to methanol as excess ethyl acetate can be distilled and reused.

The calorific value can be used as an indirect method for measuring the rate of conversion of vegetable oil to biodiesel. If we plot a graph of conversion of the reactant in some time intervals we come across the results that give some information about the conversion percentage and accumulation of biodiesel in the reactor (Fig 5).

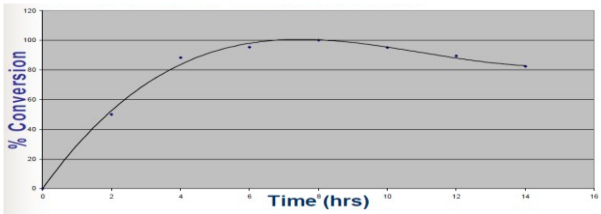

Fig. 5. Conversion of reactants to biodiesel with time

On comparison of data of production of biodiesel both in batch reactor as well as in continuous reactor, we get results in the form of different values of properties of oils. Experimental data show that the continuous reactor is more beneficial for the production of biodiesel as compared to batch reactor because it gives better calorific value and viscosity.

VII. Fuel Efficiency

The power output of biodiesel depends on its blend, quality, and load conditions under which the fuel is burnt. The thermal efficiency of B100will vary as compared to B20 due to the BTU content of the various blends. Thermal efficiency of a fuel is based in part on fuel characteristics such as viscosity, specific density and flash point. These characteristics change with the change in the percentage of biodiesel in the blends and cause a variation in the quality of biodiesel. Lower blends of biodiesel up to B20(20% biodiesel and 80% petroleum diesel) are mostly commercialized because of its consumption and efficiency as compared to pure form of biodiesel that is B100. The pure form of biodiesel is not much beneficial because the fuel efficiency is not good. The observations shows that B100 has low efficiency when compared with fossil fuels. But the blends are useful for the car engines by providing lubricity and other factors that play important role in increasing the efficiency.

VIII. Economic Impact

Multiple economic studies have been performed regarding the economic impact of biodiesel production. One study, commissioned by the National Biodiesel Board, reported that in 2011, production of biodiesel supported 39,027 jobs and generated more than $2.1 billion as household income. The growth in biodiesel also helps to increase GDP significantly. In 2011, biodiesel created more than $3 billion in GDP. Judging by the continued growth in the Renewable Fuel Standard and the extension of the biodiesel tax incentive, the number of jobs can further increase with a great hike in the income. Global demand for food is expected to double within the coming 50 years and global demand for transportation fuels is expected to increase even more rapidly. There is a great need for renewable energy supplies that do not cause significant environmental harm and do not compete with food supply. Biodiesel provides 93% more usable energy than the fossil energy needed for its production, reduces green house gases by 41% compared to diesel, reduces several major air pollutants, and has minimal impact on human and environmental health.

IX. Conclusion

Due to less number of harmful effects on environment, it attracts the scientist's interest. These potentially include reductions in greenhouse gas emissions, deforestation, pollution and the rate of biodegradation. Soil degradation is twice the rate when petroleum diesel is used instead of biodiesel. Toxic status of biodiesel is very low. Research carried out at various laboratories has shown very little toxic effects of biodiesel on the experimental animals like rabbit and also on plants. This is a matter of great satisfaction to the scientists that the use of biodiesel has less harmful ejections that pollute the environment as compared to petroleum diesel. Particulate emissions at the time of burning of biodiesel are much less as compared to petroleum diesel emissions.

The largest market for biodiesel probably will be as a fuel additive, because EPACT requirements are unlikely to increase significantly over the next 20 years. The ultra-low-sulfur diesel program will offer an opportunity for biodiesel as a lubricity additive and perhaps as a cetane booster as well. Biodiesel may also be marketed for applications in which reducing emissions of particulates and unburned hydrocarbons are paramount, such as school and transit buses. Since the additives improve diesel fuel properties, therefore it can be sold for a price above that of the diesel fuel. The oil produced by the rape seeds can be used for production of biodiesel. However, if there were a major shift of land into production of vegetable oil crops for energy these byproducts could likely be used for direct combustion or for production of ethanol. For the future, innovative and better ways of making biofuels need to be worked out. Process can be standardized to make biodiesel from grasses and saplings, which contain more cellulose. Cellulose is the tough material that makes up plants' cell walls, and most of the weight of a plant is cellulose. If cellulose can be turned into biofuel, it could be more efficient than current biofuels, and will emit less carbon dioxide. Thus in future, most of the vehicles will run on biodiesel blends as people understand the value of biodiesel not only as fuel but also as lubricant and additive.

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