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REVIEW ARTICLE

PLANT BIOFUEL: TOMORROWS FUEL

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ABSTRACT

The use of Biofuels has been gaining more popularity over the past few years because of their ability to reduce the dependence on fossil fuels. The present review covers the approach for making plant as Biofuel more economically and competitive with petro diesel. As a renewable energy source, Biofuels can be a viable option for sustaining long-term energy needs if they are managed efficiently. More specifically, we investigate the use of ethanol, Jatropha plant, Palm oil, soyabean oil, vegetable oil , Neem oil and algae that can potentially be used as alternative fuels in place of petrol and diesel. In context of climatic changes and soaring prices per barrel of petroleum, renewable carbon source, transport fuels are needed to displace petroleum derived transport fuel, which contribute to global warming and are of limited availability. Biofuels derived from oil crop is a renewable and carbon source alternative to petroleum fuel. As discussed here, Biofuel from plants including micro algae seems to be the most promising renewable Biofuel that has the potential to completely replace petroleum-derived transport fuel without adversely affecting supply of food and other crops products.

INTRODUCTION

Biofuels are the biologically derived fuels, it can be renewable, sustainable, and expandable, biodegradable, non-hazardous and safer for air, water and soil and its use reduces the emission of greenhouse gases. They have the potential to be domestically and globally available for energy security, with most being carbon source i.e. introducing no additional carbon to the global carbon cycle, or potentially carbon negative and supportable within the current agricultural infrastructure. An ever increasing demand of fuels has been a challenge for today's scientific workers. The fossil fuel resources are dwindling day by day. Biofuels seems to be a solution for future. Biofuels is an environmentally viable fuel. Out of the four ways viz. direct use and blending, micro-emulsions, thermal cracking and transesterification, most commonly used method is transesterification of vegetable oils, fats, waste oils, etc. Yield of biodiesel is affected by molar ratio, moisture and water content, reaction temperature, stirring, specific gravity, etc (Sharma *et al*., 2008). As energy demand increasing the global supply of fossil fuels decreasing, causing inflation, instability and war. The emissions from fossil fuels cause immediate harm to human health and contribute to the greenhouse effect, and deforestation and the destruction of agricultural lands threaten to turn this Earth into a desert bit by bit. There is no doubt that the end of the fossil fuel age is not far off. Using waste biomass to produce energy can reduce the use of fossil fuels, reduce greenhouse gas emissions and reduce pollution and waste management problems. A recent publication by the European Union highlighted the potential for waste-derived bioenergy to contribute to the reduction of global warming. The report concluded that 19 million tons of oil equivalents are available from biomass by 2020, 46% from bio-wastes: municipal solid waste (MSW), agricultural residues, farm waste and other biodegradable waste streams (Marshall, 2007).

It was recently discovered that living plants also produce methane. The amount is 10 to 100 times greater than that produced by dead plants in an aerobic environment but does not increase global warming because of the carbon cycle (*Frank* et al*, 2006)*. It is a critical stage for global oil consumers. After many years of growth the world has started consuming more crud oil than it could discover. Nearly 944 billion barrels of oil has been extracted and about 1200 billion barrels remain underground. The reserves would last for only 40 years (British petroleum, 2006). However based on available data in predicting the discovery and drying of oil wells, the end of oil as an abundant and cheap energy resource is near. Even the supply of underground oil is continued for several more decades. We have to look for an alternative fuel in response to the potential threat of global warming. Global energy demand is rising rapidly in this century due to population growth, increasing standards of living and the energy intensity of developing economies. To meet this demand we have to look for an alternative fuel that is Biofuels. India is a diesel based economy. Diesel consumption

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is about five times that of petrol. Diesel is the fuel for trucks, agricultural machinery and water pump sets (Auto fuel policy, 2002). The Biofuels such has ethanol are produced from sugarcane, corn, cellulose from agricultural and forest residues. Diesel can be obtained from coal using fischer-Tropsch synthesis. Biodiesel can be produced from plants like seeds of Jatropha, *Pongamia pinnata* etc. Biofuels could supply some 30% of global demand in an environmentally responsible manner without affecting food production (Koonin, 2006). India is likely account for 15% of the world's oil demand by 2040 (Anon, 2006).

Replacement of petrol by ethanol

Ethanol is replacing the petrol. Ethanol is a Biofuel which can be obtained by fermentation of sugar. Sugar can be derived from a variety of feedstock such as sugarcane molasses, cane juice and starch-containing corps like corn. Ethanol produced from corn starch already is used as a substitute or octane booster for gasoline. This has limited potential for substantial improvements in volume and cost. Biotechnology offers the promise of dramatically increasing ethanol production using cellulose from plant waste as post-harvest corn plants and timber residues or from suck high-biomass crops as poplar trees. Most petrol engines can operate on a petrol-ethanol blend of up to 10% with minor or zero modification and the modification for greater blending ethanol are modest.

The heating value of ethanol 29MJ/Kg is about a third lower than that of petrol 42MJ/Kg. Blending ethanol would lead to a decrease in the engine mileage per unit volume fuel. However, unlike petrol and diesel, ethanol contains oxygen resulting in improved combustion and lower emission of unburnt hydrocarbons, CO and particulate matter (Bharadwaj *et al,* 2007). India imports 70 percent of its petrol-some 111 million tones in 2004-2005. This is projected to double by 2020. The commission proposed increasing the proportion of Biofuels used in India from five to 20 percent by 2012 (Padma, 2005). Encouraged by the success of the pilot projects and R&D studies and after discussions with all the concerned authorities, including State Governments, the Government of India issued a notification on 12 September 2002 mandating supply of 5% ethanol-blended petrol in nine States - Andhra Pradesh, Goa, Gujarat, Haryana, Karnataka, Maharashtra, Punjab, Tamil Nadu and Uttar Pradesh and four Union Territories - Chandigarh, Dadra & Nagar Haveli, Daman & Diu and Pondicherry with effect from 1 January 2003 (Samagra, 2003).

As mentioned above Biodiesel can be produced from cellulose. Cellulose the most abundant biological material on earth allows the development of ethanol and reduces net CO2 emission. The conversion of cellulose to ethanol is a very complicated and expensive multi step involves thermo chemical and biological methods. It has 3 steps. (1) Thermo chemical treatment of raw biomass to render the complex polymers more accessible to enzymatic breakdown. (2) Production and application of special enzyme preparations that break down plant cell wall constituents into a mixture of simple sugars and (3) Fermentation mediated by Bacterial or Yeast, to convert these sugars to ethanol. The hydrolysis of cellulose for fermentation is difficult because of its strong, rigid nature. Making the conversion of cellulose to ethanol more economical and practical will require the development of a science base for molecular redesign of numerous enzymes, biochemical pathways and full cellular system (Houghton, 2005; Bilal. M. McDowell Bomani *et al.,* 2009). The following figure depicted ethanol production.

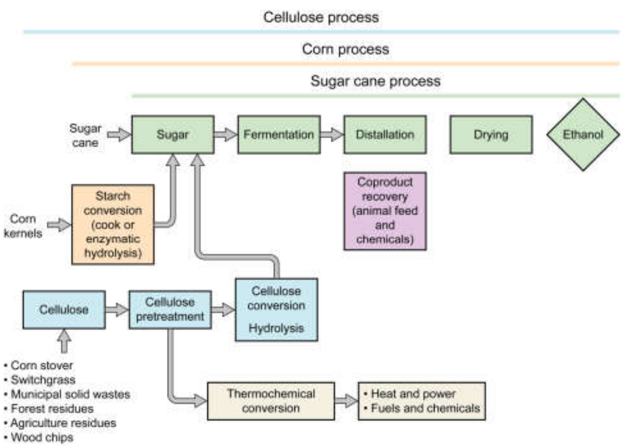

Figure 1.—Ethanol production flowchart (Ref. 12).

Replacement of Diesel by Jatropa oil

Jatropha curcas belongs to the family Euphorbiaceae, commonly known as the Physic Nut, is an oil-bearing plant which is able to tolerate arid climates, rapidly growing, useful for a variety of products. Jatropha is used as Biodiesel by extraction of oil from seed can yield up to two tons of biodiesel fuel per year per hectare. Jatropha can yield about 1,000 barrels of oil per year per square mile (Brook and Bhagat, 2004). In such quantities, Jatropha, like Biofuels in general cannot become a replacement for oil. But it requires minimal inputs, stabilizes or even reverses desertification and has use for a variety of products after the Biofuel is extracted. Moreover, diesel fuel with biodiesel additives causes far less pollution. Oil can also be extracted from many other plant species like *Pongamia pinnata,* palm, sunflower etc. Jatropa is the first choice for biodiesel. An average of about 5 tons of seeds per hectare can be produced under optimum conditions. The oil content of the seed is 55-60%, which can be converted into biodiesel by transesterification (Brook and Bhagat, 2004).

Biodiesel eliminates carbon dioxide emissions, reduces emission of particulate matter by 40-65%, unburned hydrocarbons by 68%, carbon monoxide by 44-50%, sulphates by 100%, polycyclic aromatic hydrocarbons (PAHs) by 80%, and the carcinogenic nitrated PAHs by 90% on an average (Brook and Bhagat, 2004). The biodiesel molecules are simple hydrocarbon chains free of the aromatic substances and sulfur associated with fossil fuels. Although biodiesel does produce more Nitrogen Oxide emissions than petrodiesel (Planning Commission, 2003) these emissions can be reduced through the use of catalytic converters. In petro diesel vehicles, catalytic converters have generally not been included because the sulfur in the fuel destroys them, but biodiesel does not contain sulfur. Biodiesel can be used in any diesel engine or burner without adaptation. It has a higher cetane number of biodiesel compared to petrodiesel, indicating potential for higher engine performance and causing less knocking. Due to solvent power of biodiesel, especially older engines can get clogged. Biodiesel can clean it, dissolving the residues left by petrodiesel. Engine efficiency is also increased by its superior lubricating properties and the more complete combustion of hydrocarbons due to its higher oxygen content (up to 10%). Finally, Biofuel is safer to store because of its higher flash point. One drawback especially of undiluted biodiesel (BD100) is its cold-clogging point of 0 degrees Celsius. This is one of the reasons it is usually mixed with conventional diesel, especially in cold countries. This is not a serious problem. According to Katwal (Brook and Bhagat, 2004), Director General of the Indian Council of forestry Research and Education, said that the Union government of India had drawn up a blueprint to plant Jatropha trees on 50,000 hectares at a cost of Rs 1,430,000 (Brook and Bhagat, 2004). Biofuels are gaining importance in the light of increasing energy demand, especially fossil fuels which are non-renewable. The production of biodiesel in India is very less compared to its potential. If 10 million hectares (100,000 square kilometers or 38,000 square miles) of India's vast and sometimes destructive wastelands were used for biodiesel production, with a modest estimate of 1.5 tons of seeds per hectare, 4 million tons of biodiesel would be produced- one tenth of the country's annual oil requirement. If one person was employed per hectare, that would mean 10 million new jobs.

And, for use or sale, 11 million tons of organic seedcake fertilizer or livestock feed and 0.4 million tons of technical grade glycerol would be produced (Brook and Bhagat, 2004). Here is a problem with biomass energy production. This may convert the agricultural land from food to fuel in a hungry world. To over come the “food or fuel" dilemma-the waste lands which are unsuitable for growing other crops are used to cultivate the Jatropa. By growing Jatropa drought and water shortages which would ruin food crops can be survived, if grown in addition to food crops, as mentioned above it can literally protect them from animals, insects and desertification and its seed cakes can be used as fertilizer. The most difficult problem is as always cost. In remote areas where fossil fuels are not readily available, biodiesel is already a feasible alternative especially considering wasteland reclamation, rural employment and income generation from Jatropha biodiesel and its by-products. This is important to consider in India where electricity is always in short supply- biodiesel can power generators, lights and farm equipment as well as cars. On the current global market, however, biodiesel generally cannot directly compete with petrodiesel at least not yet.

Biodiesel from Algae

The yields of oil from algae are orders of magnitude higher than those for traditional oilseeds. As a comparison, a single acre of algae ponds can produce 15 000 gal of biodiesel, an acre of soybeans produces up to 50 gal of biodiesel per acre, an acre of jatropha produces up to 200 gal per acre, coconuts produce just under 300 gal per acre, and palm oil produces up to 650 gal of biodiesel per acre (Briggs and Michael, 2009). Table 1, lists the gallons of oil per acre per year for corn, soybeans, safflower, sunflower, rapeseed, palm oil and microalgae. Berzin (2009) has developed a method of capturing carbon dioxide from smokestack emissions using algae and turning the result into Biodiesel, ethanol and even a coal substitute. His process based on technology he developed for NASA in the late 1990s, captures more than 40 percent of emitted CO_2 (on sunny days, up to 80 percent) along with over 80 percent of NOx emissions. In turn, it produces Biodiesel at rates per acre that could make a full conversion to Biofuel for transportation readily achievable. Berzin calculates that just one 1000-MW power plant using his system could produce more than 40 million gal of biodiesel and 50 million gal of ethanol per year. Bullock (Bullock, 2006) conducted a 6-month test in a small plant to demonstrate Green Fuel Technologies Corporation’s process that uses micro algae in a Photo Bioreactor to sequester carbon dioxide from furnace gases. Research into algae for the mass production of oil is mainly focused on micro algae capable of photosynthesis that are less than 2 mm in diameter as opposed to macro algae (seaweed). This preference towards micro algae is due largely to its less complex structure, fast growth rate and high oil content (for some species). Some commercial interests into large-scale algae-cultivation systems are looking to tie into existing infrastructures, such as coal power plants or sewage treatment facilities. This approach not only provides the raw materials for the system such as carbon dioxide and nutrients but it changes those wastes into resources.

Table 1: Annual yields of oil per acre of various Biofuel feedstocks

Feedstock	Yield, Gal
Corn	18
Soybeans	48 to 50
Safflower	83
Sunflower	102
Rapeseed	127
Jatropha	200
Coconut	300
Palm	635
Micro algae	5000 to 15 000

(Briggs & Michael, 2009; Riesing & Thomas, 2009)

Economics of algal Biodiesel production

Some of the Indian experts suggest that the Sundarbans delta archipelago of 100 islands, spread over approx 4,260 sq.km on the Bay of Bengal, can be used for algal cultivation and extraction of biodiesel (Molina *et al.,* 2003). The Biodiesel from algae can be competitive with petroleum sourced fuel, as these fuels at present are the least expensive transport fuels in India. Whether micro algal Biodiesel is competitive or not is mainly depends on the cost of algal Biomass production (Banerjee *et al.,*2002). Micro algal oils have potential to completely replace petroleum as a source of hydrocarbon feedstock for the petrochemical industry. For this to happen micro algal oil needs to be produced at a price which is less than the price of crude oil (Banerjee *et al.,*2002; Bajhaiya *et al .,*2010).

It can be conclusively established that the economics of Biodiesel production can be improved by advancing the production technology. As the yield per acre of micro algal oil is already far more than the yield of oil from palm and jatropha plant (Tyson, 2001). While Jatropha take 2-3 year for commercial yield, algae start yielding from 2-3 days of plantation, therefore algae oil can be harvested every day. After the conversion of algal oil into biodiesel the left over part serves as an excellent source of high value protein and can be used to supplement as cattle feed or rich carbon source to be used as soil additive in mulching also as biofertilizer.

Algal Biodiesel performances

The micro algal biodiesel have many advantages over the traditional diesel fuel, it can reduce net carbon dioxide emission by 78% on a life-cycle basis as compared to traditional diesel fuel (Sawayama *et al.,* 1995; Timothy *et al*., 2008). Bio diesel also contain little or no sulfur or aromatic compound; in conventional diesel, the sulfur lead to formation of sulfur oxide and sulfuric acid, while the aromatic compound also increase particulate emission and are considered carcinogens. In addition to reduce CO and particulate emission, the use of Biodiesel confers additional advantages including a higher flashpoint, faster biodegradation and greater lubricity. The higher flashpoint helps in safer handling and storage, whereas biodegradability of biodiesel is particularly advantageous in environmentally sensitive areas (Knothe *et al*.,2005). The lubricity of biodiesel is also greater than conventional diesel fuel and blending Biodiesel with low sulfur fuel restores lubricity (Hill *et al* ., 2006). However, the biggest advantage of algal Bio diesel is that, it's a sustainable source of liquid transportation fuel and derives energy from sun (Sawayama *et al* ., 1995). The combustion of Biodiesel in place of conventional diesel fuel can also reduce green house gas emission up to 40%.

Biofuel from Neem oil

Neem oil is generally light to dark brown, bitter and has a rather strong odour that is said to combine the odours of peanut and garlic. It comprises mainly triglycerides and large amounts of triterpenoid compounds, which are responsible for the bitter taste. It is hydrophobic in nature and in order to emulisify it in water for application purposes, it must be formulated with appropriate surfactants. Neem oil also contains steroids (campesterol, beta-sitosterol, stigmasterol) and a plethora of triterpenoids of which Azadirachtin is the most well known and studied. The Azadirachtin content of Neem Oil varies from 300ppm to over 2000ppm depending on the quality of the neem seeds crushed. Experiments conducted by Radha and Manikandan (2011) demonstrated that the biodiesel produced using neem oil could reduce smoke and Carbon monoxide emissions, significantly while the Nitrogen oxide emission changed slightly. The temperature increases yield of methyl ester at 55 ^{0}C and a molar ratio of 1:12 were found to be beneficial . Thus, the ester of this oil can be used as environment friendly alternative fuel for diesel engine (Radha and Manikandan, 2011).

Table 2. Properties of Neem oil (Radha and Manikandan, 2011)

Properties	Quantity	Fatty Acid	Weight %
Moisture content (wt %)	0.4	Oleic acid	51.3
Free Fatty Acid Content (wt %)	5.7	Palmitic acid	17.8
Refractive Index	1.47	Linoleic acid	14.7
Gum Content (wt %)	0	Steric acid	14.4
Iodine Value	80	Arachidic acid	1.6
Density(kg/m3)	1024	Myristic acid	0.03

Biodiesel from Palm Oil

Demand for palm oil is rising and is expected to climb further, particularly for use as a biodiesel fuel. The demand for palm oil usage is forecast to double by 2020 (Basiron Yusof and Simeh Mohd Arif , 2005). To achieve that production increase, 1160 new square miles will have to be planted every year for 20 years. Malaysia, where the palm tree has been grown since the 1870s, and Indonesia account for 85 percent of the world's production of palm oil. Indonesia has 26 300 square miles of forest land officially allocated for new palm oil plantations while Malaysia has almost 3000 square miles more than that. The expected thousands of square miles of new plantings on the islands of Sumatra and Borneo have the potential to eliminate the remaining orangutans, rhinos, and tigers. The environmental impact of the growth and further development of palm oil plantations is a serious threat that cannot be accurately predicted because of the amount of political pressure on palm oil countries. An independent study commissioned by the Malaysian government in 2006 has shown that palm oil requires an input of only 30 to 40 percent of fossil fuel energy to produce a given amount of energy compared with an input of up to 60 percent fossil fuel energy in the process of making Biofuels from maize, rapeseed, or soybeans.

Palm oil was transesterified using NaOH as catalyst and methanol to form biodiesel. The conversion was 92% at 600c. The fuel properties like viscosity, density,flash point ,fire point and calorific value of the the transesterified product(biodiesel) compare well with accepted biodiesel standards i.e Indian biodiesel standards.The basic properties of palm oil biodiesel–diesel fuel blends were measured according to the corresponding Indian standards. High flash point and hence safe to transport and store ,Oxygenated fuel and hence clean burning. Low viscosity and hence improved injection and atomization, Ceatane no. of esters is greater, Reduced emissions , 90% reduction in cancer risk, Provides domestic, renewable energy (Venkata Ramesh Mamilla *et al*., 2012).

Biodiesel from Soybean and vegetable oil

Liu *et al*., (2008) studied transesterification of soybean oil to biodiesel using CaO as a solid base catalyst. The reaction mechanism was proposed and the separate effects of the molar ratio of methanol to oil, reaction temperature, mass ratio of catalyst to oil and water content were investigated. Their experimental results showed that a 12:1 molar ratio of methanol to oil, addition of 8% CaO catalyst, 65 °C reaction temperature and 2.03% water content in methanol gave the best results, and the biodiesel yield exceeded 95% at 3 h. The catalyst lifetime was longer than that of calcined K2CO3/γ-Al2O3 and KF/γ-Al2O3 catalysts. CaO maintained sustained activity even after being repeatedly used for 20 cycles and the biodiesel yield at 1.5 h was not affected much in the repeated experiments.

He *et al*.(2007) developed a system for continuous transesterification of vegetable oil using supercritical methanol by utilizing a tube reactor. Increasing the proportion of methanol, reaction pressure and reaction temperature can enhance the production yield effectively. However, side reactions of unsaturated fatty acid methyl esters (FAME) occur when the reaction temperature is over 300 °C, which lead to much loss of material. There is also a critical value of residence time at high reaction temperature, and the production yield will decrease if the residence time surpasses this value. The optimal reaction condition under constant reaction temperature process is: 40:1 of the molar ratio of alcohol to oil, 25 min of residence time, 35 MPa and 310 °C. However, the maximum production yield can only be 77% in the optimal reaction condition of constant reaction temperature process because of the loss caused by the side reactions of unsaturated FAME at high reaction temperature. To solve this problem, They proposed a new technology: gradual heating that can effectively reduce the loss caused by the side reactions of unsaturated FAME at high reaction temperature. With the new reaction technology, the methyl esters yield can be more than

96%. Alkali-catalyzed transesterification of waste cooking oils with methanol was carried out in a laboratory scale reactor by Phan and Phan (2008). Biodiesel yield of 88-90% was obtained at the methanol/oil ratios of 7:1-8:1, temperatures of 30-50 °C and 0.75 wt% KOH. Biodiesel and its blends with diesel were characterized for their physical properties referring to a substitute for diesel fuel. They showed that the biodiesel experienced a higher but much narrower boiling range than conventional diesel. Carbon residue content was up to 4 wt%. Blends with a percentage of the biodiesel below 30 vol% had their physical properties within EN14214 standard, which indicated that these could be used in engines without a major modification.

Recently, Chodchanok Attaphong *et al*. (2012) reported the phase behavior of carboxylate-based extended surfactant micro emulsion systems with the goal of formulating optimized systems for Biofuel. It was found that carboxylate-based extended surfactants were able to form reverse micelle microemulsions without salt addition, thereby eliminating the phase separation and precipitation which had been observed with sulfate-based extended surfactants. In addition, fuel properties such as viscosity and temperature dependence were favorable and thus support the continued development of these surfactant-based fuel systems for use in diesel engines. Stella Bezergianni *et al.,* (2012) opined that catalytic hydroprocessing is an effective technology with various applications in the petrochemical industry that are lately expanding in the area of Biofuels production. The selection of a hydroprocessing catalyst is a critical step defining the hydrotreating products' yields and their corresponding quality as well as the expected run-length of the process. Their work involves the process of selecting a suitable hydroprocessing catalyst for the conversion of waste cooking oil into Biofuels. In particular three commercial catalysts are evaluated: a hydrotreating catalyst, a mild-hydrocracking catalyst and a severe hydrocracking catalyst.

Conclusion

Now, the world has to perish in the pollution and War there is no other choice. The Biofuel industries have to grow up fast. The government should give tax concessions or other financial incentives to Biofuels companies and consumers to speed up the progress, and urge other nations to do the same. With Biofuels, we can help heal and preserve the air, land and our own physical health and peace. The production of Biofuels from suitable feedstock could also generate economic and environmental benefits in a number of developing countries, create additional employment, reduce energy import bills and open up potential export market. In particular, the production of Bioethanol could offer a feasible alternative for some sugar producing countries.

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