



A Comprehensive Review on Generations of Biofuels: Current Trends, Development and Scope

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ABSTRACT: The energy crisis and global warming due to rapid increase in Industrialization are the issues which compelled the scientist and the environmentalist to think about the more environment friendly solution which will satisfy the current energy consumption. Biofuel which is a fuel made by contemporary biological process is one such solution which gives energy security and economic development to our motherland. The researchers foresee an urgency in use of viable & reliable alternative fuel. This is due to already extensive damage of our natural resources in form of depleting fossil fuel levels, increasing concentration of greenhouse gases in the atmosphere, production of harmful gases due to the combustion of fossil fuels. This paper examines the growth pattern in synthesis procedures among the varied generation of biofuels in order to not only provide scope; but also, developments in the fields for subcontinent. Focusing primarily on India. On in-depth study, this particular paper has classified the developments in the field of biofuels into 4 generations which also provides a technological solution to drastically reduce the cost of extraction as a bio-fuel in comparison to the same done for current alternatives like gasoline and other fossil fuels.

Keywords: Bioethanol, Biodiesel, syngas, algae, microbes, triacylglycerol.

I. INTRODUCTION

Biofuels are the category of fuels which are derived from the natural sources which can be replenished by nature, i.e. renewable resources. Due to its natural derivative, these fuels burn more cleanly as compared to current gasoline and produce same amount of energy as non-conventional source with lesser pollutant emission. Four generations of biofuels have been known in which first generation biofuels are made of mostly edible sugar and starch components, second generation biofuels which are also known as advance biofuels contains various type of biomass, third generation Biofuels composition comprises of algae and the fourth-generation biofuels composition comprises of oils from genetically advanced algae and microbes.

II. BIOFUELS: HISTORY

The awareness and use of fuels derived from plant sources and feedstocks began in the mid-19th century. It was at that moment that the cheaper prices of fossil fuels suppressed the idea of naturally derived fuels. In 1897, German Engineer Rudolf Diesel designed a prototype engine which ran successfully on peanut oil in the Paris exhibition. Similarly, Henry Ford who laid down the foundation of automobiles and being a pioneer engineer developed prototype engines which ran on ethanol. These Visionaries expected that their

machines would run on biofuels, but surging need of fuel requirement was there during the world war era and at that time fossils fuels proved to be a cheaper and easily transportable fuel, hence depriving these young ideas.

During the mid-1970's there was again a need of an alternative source of fuel as petroleum cost was increasing, political instability among the OPEC countries which threatened the supply and ozone depletion had been at a critical level. Scientists started exploring various options from tidal power to solar power, etc. but the most promising scope turned to be biofuels. During the late 90's the biofuels again at though small scale but came back to the synthesis procurement.

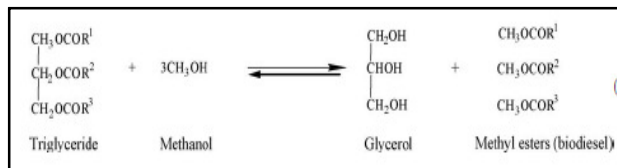
III. CLASSIFICATION OF BIOFUELS

Biofuels are generally classified into 4 categories-

A. First Generation Biofuels

The very first generation of biofuels began in the late 1990's when corn farmers of the United States of America synthesized fuel out of corn to meet the need to run their machinery. The first Generation of Biofuel was derived from sugarcane, feedstocks, corn, vegetable oils. The procedure followed in the extraction of first generation biofuels opts the way, at very first stage the oils are extracted from the plants or feedstocks which has been used as the source. Then the oils are

filtered for further impurity separation. Now the feasibility of the oil is checked by allowing it to set for an hour in a closed container. A mixture of sodium hydroxide (NaOH) and methanol is then prepared to get sodium methoxide and added to settled oil. The process of trans-esterification is carried out and allowed to set for about 2-3 hours under suitable conditions. An observation is done for the appearance of a white line separating the light yellow oil from glycerin and as this line is visible the glycerin is separated by using a suitable filtration method and the left over light yellow oil is biodiesel.



Generally, from results obtained from using 1000ml mustard oil, 20 ml KOH, 200 ml NaOCH₃ gave a yield of 900ml of washed cleaned biodiesel. Corn is most widely accepted source of feedstock as it gives the maximum yield per liter of the raw material (960ml/liter).

The Characteristic Value of Biodiesel obtained in first generation is as follows: -

Oxygen Concentration (%)	11
Sulphur (ppm)	<1
Heating value (MJ/Kg)	38
Distillation (degree C)	340-355
Cloud Point (degree C)	-5 to +15
Specific gravity	0.88
Cetane	50-65
Stability	Marginal

This generation had a disadvantage as the United Nations report [UN Report 2003] clearly stated that these first-generation biofuels may cause an adverse impact on the human life as there will be shortage of food resources for mankind which may endanger a lot of animal's species also. There will also be potable water crisis as irrigation requires a lot of water, to grow corn (1700 gallons water per gallon ethanol P.A.).

The first-generation biofuel currently being in use are biodiesel, ethanol, syngas, bio alcohols (UK Biofuel Organization Report 2013). "It is increasingly understood that 1st generation biofuels (produced primarily from food crops such as grains, sugar beet and oil seeds) are limited in their ability to achieve target oil-product substitution, climate change mitigation, and economic growth," (IEA, 2008), "Their sustainable production is under review, as is the possibility of creating undue competition for land and water used for food and fiber production," (Sims, 2008).

B. Second Generation Biofuels

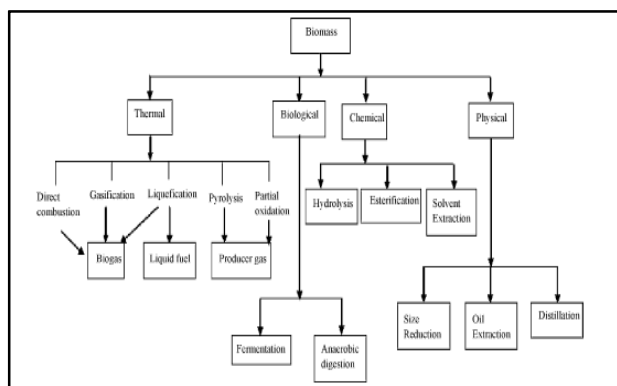
The beginning of 21st century marked the entry of second generation of biofuels in the market. The second generation also marked the introduction of advanced biogenesis in this field. In second generation biofuels, the roots of certain sugar producing or sugar rich plants were cultured in a special way such that directly oil is extracted from the roots. This generation was almost Carbon free or Carbon negative in terms of CO₂ released in the whole process.

Common second-generation biofuel sources include lignocellulosic feedstocks, grasses, Jatropha, seed crops, waste vegetable oil, and solid waste and forest residues. The main motto of second generation is to use crops which are unfit for human consumption. In the United States switchgrass is commonly preferred. Switchgrass is a perennial grass i.e. it reduces the cost of repeated planting. It has a very high growth rate and can directly (without any pre-treatment steps) can be used as biomass. The main quality of switchgrass is that it has high energy yield about 540% (according to UK's Biofuel Organization). Although having so many qualities it cannot be commercially used since switchgrass has some main drawbacks. Being a grass it requires a high content of water for its harvesting which contradicts with 1st generation. It also requires extensive phase processing to be converted into ethanol. These factors increase the production cost dramatically and more over there is a lack of technology to harness the source optimally. Another very popular seed crop is the jatropha seed, with a unique ability to yield high energy per seed about 240%. It is an important candidate for the biodiesel synthesis. India being one of the leaders in Jatropha seed based biodiesel export but this too failed to be commercially viable as it grows well only on fertile land and when used in marginal lands the quality of output is reduced. High amount of water is required to cultivate it on fertile land as compared to marginal land. The capital cost at the time of setup is quite high. The most promising was the used vegetable oils and corn Stover but the only problem they face is that used oils is spread around restaurants and households, cornstovers are used by farmers to prepare their compost.

There are two methods followed in this generation for obtaining liquid biofuels from biomass. First is the Thermochemical Processing and the other one is the Biochemical Processing. Thermochemical Processing is generally more preferred over the Biochemical Processing because of the fact that it can convert all organic components of the Biomass as compared to Biochemical process which focuses on the conversion of polysaccharides. Thermochemical processing defines the conversion of biomass into a range of products, by thermal decay and chemical reformation, and

essentially involves heating biomass under aerobic conditions.

The flow chart indicates the process in thermochemical Process: -



The Process to obtain biodiesel is to first culture the genetically modified trees and then extract the sugars from the roots of the tree. The process of transesterification is applied to the extracted sugar after which Biodiesel-2 (green diesel) is obtained.

Green diesel obtained in the second generation is more effective than that of the first generation as it has more stability and comparatively higher values in properties as shown below-

Oxygen Concentration (%)	0
Sulphur (ppm)	<1
Heating value (MJ/Kg)	44
Distillation (degree C)	265-320
Cloud Point (degree C)	-10 to +20
Specific gravity	0.78
Cetane	70-90
Stability	Good

Although having several advantages this generation has demerits too like lack of technological approach to reduce the cost, pretreatment of biomass for getting cellulosic sugars, economic instability and is declared currently unfit for mass scale manufacturing. The major concern is difficulty in gathering sources as they are unevenly distributed around the world.

C. Third Generation Biofuels

The third-generation biofuels are considered more energy dense as compared to previous generations (yield per area of harvest). It produces 30 times more energy than land crops such as *Jatropha*. There are expected to be 200,000-800,000 types of algae but only 40,000 are recorded officially. They are low cost, high yield producing plants. Algae are the crops used as third-generation fuel sources. The advantage of algae is that it can grow anywhere in any type of water bodies and is a nitrogen fixing plant. This would reduce the dependency and relieve the use of arable land, fresh water bodies. This generation is considered most

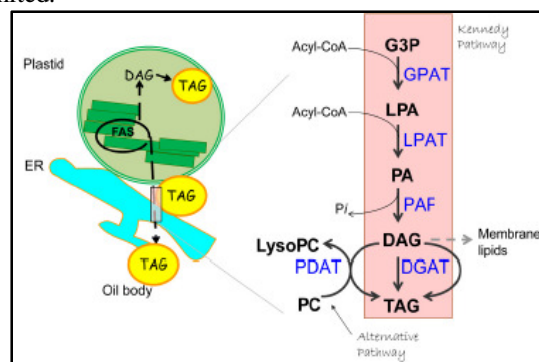
suitable because of the ability of algae that it can grow in sewage water, waste water, salt water bodies. It can accumulate 60% oil per dry weight under stress conditions. Cost of cultivation and oil extraction under photobioreactors and open pond lakes are quite high on which current research is being done to lower the cost.

Algae also face a challenge that all species are not suitable for industrial use. Fatty acid composition of microalgae lipids may not be optimal for use of biodiesel, stress conditions needed to accumulate lipids result in arrest of cell growth and division, causing a strong limitation of biomass production.

Process of Microalgae lipids to Biodiesel. It is found that microalgae synthesize large variety of lipids and fatty acids, the composition of which often reflect adaptation to external factors (environmental conditions). The building block of all membranes and storage lipid are the fatty acids produced in plastid. On applying stress all microalgae produce oil (triacylglycerol's-TAG's), the major form of storage lipids in eukaryotic cells. One triacylglycerol molecule is made of three often different fatty acids which are esterified to the 3 hydroxyl groups of a glycerol backbone. In genetic engineering in the field of microalgae the primary focus has been on modification of fatty acids.

Decoupling oil synthesis from arrest of cell. The type of species and factors under which it is cultivated determines the amount of oil produced, substantial oil accumulation almost always requires stress conditions. The most effective way to trigger stress is nitrogen deprivation. However, nitrogen starvation limits the overall productivity of the system. On large scale the maximum lipid yields obtained are 10-20 times lower than the theoretical maximum (5000-15000 gallons per acre per year).

Harnessing the complexity of lipid metabolism. Current technology on oil biosynthesis from microalgae is still limited.



The current pathway involves three major spatially separated biochemical steps, i.e. plastidial fatty acid synthesis, acylation of fatty acids to glycerol, and

deposition as oil bodies, the sub-cellular compartment destined for oil storage.

The best known is an acyl-CoA-dependent pathway, catalyzed by ER membrane bound enzymes (Riekhof, *et al.*, 2005), similarly to what occurs in plants. An alternative route to oil synthesis is present in both plants and yeast, and is catalyzed by phospholipid: diacylglycerol acyltransferase (PDAT) contributing to the synthesis of triacylglycerol using phosphatidylcholine as anacyl donor and *sn*-1,2-diacylglycerol as an acyl acceptor. A recent pathway proposed by Fu and Xan in 2011 indicated that least part of the triacylglycerol synthetic pathway is present in the plastid of *C. reinhardtii*. They further also observed that under Transmission Electron Microscope (TEM), some of the oil droplets formed in the plastid can be secreted and relocated to cytosol.

Major algae crop. Some of the major crops on which research is being carried out and further developments being made are: *-Chlamydomonas reinhardtii*, *Chlorella* sp, *Ostreococcus tauri*, *Phaeodactylum tricorutum*, *nannochloropsis* sp.

Fourth Generation Biofuels. This generation of biofuels is still in the development phase and none of the practically synthesized compounds have been tested. Till present date it is the most promising and referred to as the most advanced generation of biofuels. The theoretical concepts on which the principals of forth generation are laid are: Development of genetically modified plants which will consume more dioxide (CO₂) from the atmosphere. Combination of oil seeds and algae plants to stimulate a successful high yield cross genetics species. Currently only few companies are working on this, most popular is the Synthetic Genomics by Craig Venter which is currently prototyping the microorganisms which can directly produce fuel from carbon dioxide (CO₂). It is expected that by 2050 this generation shall become fully developed and shall have a major stake in the power sector of the world.

V. TRENDS

Out of all replacements for conventional sources only biofuels have been most promising in both economically and Environmentally. It is because of the studies made which clearly show that not only biofuels reduce CO₂ emission rather they also have ability to absorb more CO₂. The trend's is being approached are divided into two categories:

A. International Trends

The major international scope revolves around the moves made by the United States of America, recently a report by International Energy Agency (IEA) stated that by 2050 it is achievable that a new generation of sustainable biofuels could provide over a quarter of the

world's transport fuel. Most of the current biofuels being produced in the USA are dependent on corn and algae. More the production of corn more is the production of biofuels in USA. Since the government is overutilizing corn for only biofuels the economic market has suffered a lot as there is a steady increase by \$47 per capita since July 2006 according to a report by CNN. This also led to the increase of pork prices by 8.4%, poultry by 5%, beef by 4%. Corn production has been on an increase by 44% but the export rate declined by about 63%, USA being a corn dependent country may even face a sharp increase in food prices by about 200-500% if this declined rate of corn export prevails. The key focus has been made on USA because it alone produces 40% of the total world's corn even moreover, many countries are dependent on USA because 70% of its production is exported. For every increase in the cost of production of corn by \$1, the ethanol industry faces a decline in stocks by \$1 billion P.A. Current mass scale manufacturing process is still more using generation 1 techniques.

To get 1 gallon ethanol- 2600 gallons of water is required (including the water for harvesting the corn). The Biodiesel prices currently are:

Source of Raw material	Cost (in \$)/ per liter
Aviation Grade by oils from algae	2
From seed plants like sunflower, canola, etc.	1
Small plants like corn, cane, etc.	0.1

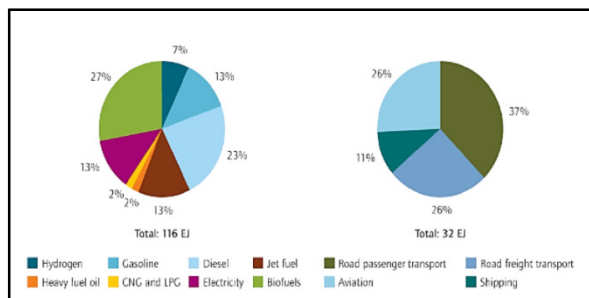
B. Trends in India

India is currently a second-generation biofuel manufacturer. It uses *Jatropha* seed as the source for powering its biofuel industry. As *Jatropha* is ideally grown in India, it utilizes its wasteland also providing CO₂ fixture. *Jatropha* oil is obtained from the *Jatropha Curcas*, this oil is then stored and preserved by the locals of a particular region. Later when the oil is collected in large quantities they are supplied to the Manufacturing plant for further by-products. The prices of bio ethanol in India is regulated by the Government of India and currently is being fixed at Rs.48.50-Rs.49.50. The major Bio-energy producer in India is IOC (Indian Oil Corporation) Biofuels Limited which aims and produces its bio-products from non-food energy crops. India being in the tropic region has the ability to grow almost any type of crops, but *Jatropha* was given an upper hand because of its main advantage that the oil extracted from *Jatropha* can be directly converted into biodiesel without any refining processes which reduces its manufacturing cost. The current price of bio-diesel in India is Rs.58-Rs.64 depending upon the quality of oil used. India does not use the biodiesel it produces for its domestic use rather it exports 74% of

its produce. The current scenario suggests that: India being the third largest exporter of biodiesel of 2nd generation produces 5940.87MW of biomass power with, Andhra Pradesh and Bihar being the leading producing states with production of 389.75MW, 43.42MW. It exports 1.16 million tons of bio power. The total domestic requirement is of 3.5 million tons, out of which only 1.57 million tons is being produced.

VI. SCOPE

There is a lot of future present in the biofuel developments and large scale commercialization. In the recent years, it has also drawn the attraction of UN, World bank, etc. various valuable organization which are spreading awareness and hence supporting research based on the further development. The main motto like fourth generation will remain clear that biofuel till 2050 should be synthesized from crops which not only release less co2 on combustion of oil but also should have genetic ability to absorb more co2 from the atmosphere. In a recent survey in the United States, the Department of Energy estimated that if all petroleum based fuels are replaced by biofuels, it would require 15000 square miles of land, which is achievable by USA as it is roughly about the size of Maryland. There are certain guidelines given by the EU meet in 2009 to the private sector regarding generation of biofuels stating that: A pro-biofuel must be generated which encompasses the agriculture, transport, and manufacture industry all together. Testing of genetically modified biofuel should be carried out in places which have proper security measures and is declared fit for testing by the respective country's law. Developments of new business models should be made which promote the interest of farmers to grow crops for biofuels. It should create a greater diversity for the availability of the feedstocks. Proper discussions of the trials impact under conditions to the consumer. The grade and purpose for which the fuel is designed should be specified.



The above figure global energy use in transport sector (left) and the use of biofuels in different transport modes (right) by 2050.

VII. CONCLUSION

The main point that can be concluded is that switch to biofuel is already in progress but an escalated speed is required before it is too late because the current emissions from automobile industries clearly indicate that the ozone layer depletion is at a high rate and by 2030 a new alternative is essentially required. The fourth generation can even work according to our research with the combination of oil produced from algae and Canola seeds oil, other variants can also be tried under NTP conditions. When combined the Calorific value increases of the mixture and it is experimentally also found that the use of biodiesel in engine reduces the wear and tear of parts by 40%.The principle defining sustainable biofuels should include the Carbon conservation, preservation of biodiversity, sustainable water utilization, healthy air quality, soil conservation, compliances with the laws, land rights, social issues (like storage, transportation, health effects, etc.) and most importantly it should have fair labor practices.

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