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Biodiesel production from liquid biomass: An outline

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Abstract
The energy demand has been growing worldwide tremendously and was projected that the world energy consumption will increase by 53 %, from 505 quadrillion Btu in 2008 to 770 quadrillion Btu in 2035. The exponential increase in fossil fuel consumption and combustion of fossil fuel worldwide has resulted in green house gas (GHG) emissions which have further led to global climate change. The unexpected energy demands have thus boost up the scientific community to think about the alternative source of energy in coming era. In this context, biomass plays a vital role to meet the world's growing energy needs. In fact, biomass ranks fourth as an energy source and provides, approximately 14% of the world's energy needs. The additional benefit to earn carbon credit from the use of renewable energy provides bonus to the biomass based fuel like biodiesel. Biodiesel (i.e. the fatty acid alkyl ester) is a renewable biofuel and can be processed through the conventional transesterification process. However, the transesterification process has both positive attributes and limitations. In this review article the authors endeavored to sum up the potential conversion of biodiesel from various oil bearing biomass crops including its fuel properties.

Key words: Biodiesel, FAME, liquid biomass, fuel properties, applications

1.0. Introduction
Currently, energy demand has been growing worldwide tremendously. As per the report of U.S. Energy Information Administration (International Energy Outlook, 2011) it was projected that the world energy consumption will increase by 53 %, from 505 quadrillion Btu in 2008 to 770 quadrillion Btu in 2035. According to the report, the role of coal is expected to remain important but natural gas, petroleum and other liquid fuels will play a major role as largest global energy source with an increase of 26.9 million barrel per day and energy consumption together in China and India will account for half of the projected increase as presented in Figure 1 [1]. The exponential increase in fossil fuel consumption and combustion of fossil fuel worldwide has resulted in green house gas (GHG) emissions which have further led to global climate change. Hence the world is presently confronted with the twin crisis of fossil fuel depletion and environmental degradation. The progressive depletion of conventional fossil fuels with increasing energy consumption and GHG emissions have led to a move towards alternative, renewable, sustainable, efficient and cost-effective energy sources with lesser emissions [2-5]. Under this precarious scenario, the renewable energy sources such as solar energy, wind energy, hydro energy, and energy from biomass and waste provides a sustainable platform to meet the

world growing energy needs [6]. Most of the current renewable energy options (e.g., wind, solar, and hydro-energy) are suitable for the production of electrical energy while more than a half of the current energy consumptions are based on liquid fuels. However, the interest is in producing liquid biofuels derived from biomass for transportation applications using first or second generation technologies [7-9].

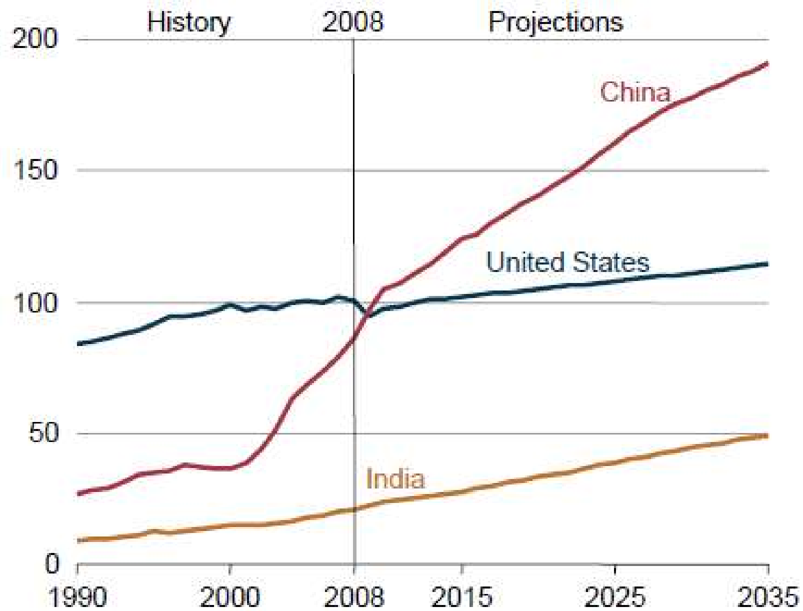


Fig.1 Energy consumption in the United States, China, and India, 1990-2035 (quadrillion Btu)

2.0. Liquid biomass as potential energy source

Biomass ranks fourth as an energy source and provides, approximately 14% of the world's energy needs. Today, biomass is considered as the most promising energy source to mitigate the greenhouse gas emissions and is important for implementing the Kyoto protocol to reduce CO_2 emissions by reducing consumption of fossil fuels. Liquid biomass (i.e. vegetable oil) being renewable in nature is also useful to earn carbon credit as envisaged from Kyoto protocol. In addition, the recent steep hikes in crude oil and petroleum products prices and decline of production have heightened interest in renewable feedstocks (biomass) as a source of fuel and energy related products. According to the International Energy Agency (IEA, 2007), bio-energy offers the possibility to meet 50% of our world energy needs in the 21st century. Hence, it is predicted that renewable energy from biomass will enter the energy market intensively in the near future to diversify the global energy sources [10, 11].

The term biomass (Greek; bio, life + maza or mass) refers to all organic plant matters as well as organic waste derived from plants, humans, animals, and aquatic or marine life [12]. There are three general classes of feedstocks derived from biomass that are appropriate for the production of renewable fuels: starchy feedstocks (including sugars), triglyceride feedstocks, and lignocellulosic feedstocks. Among all the three feedstocks, the most abundant is the lignocellulosic feedstock which is mainly comprised of energy crops and waste biomass such as switch grass, agricultural residues, municipal wastes and waste generated from wood processing [13]. The starchy feedstocks (sugarcane, sweet corn etc.) are mainly composed of glucose polysaccharides which could be easily hydrolyzed into the sugar monomers for the preparation of first generation biofuel such as bioethanol. The triglyceride feedstocks are the most investigated feedstock among all the biomass sources. Triglycerides, or animal fats and vegetable oils, are found in the plant and animal kingdom and consist of water insoluble, hydrophobic molecules that are made up of one glycerol unit and three fatty acids. More than 350 oil-bearing crops are known, and those with the greatest potential for fuel production, according to Peterson, are sunflower, safflower, soybean, cottonseed, rapeseed, canola, corn, and peanut. Currently, vegetable oils are being used for the production of biodiesel by transesterification [14, 15]. Despite their wide range of possible sources, biomass feedstocks are remarkably uniform in many of their fuel properties, compared with competing feedstocks such as coal or petroleum. Thus biomass can serve as an excellent alternative source to meet the present and future energy demands [16].

The two most common and successful biofuels are biodiesel and bioethanol which are aimed at replacing mainly the conventional liquid fuels like diesel and petrol [17]. Again, among the liquid biomass fuels, biodiesel (vegetable oil ester) is noteworthy and research on its production as fuel for compression ignition engines is a rapidly growing technology. In addition the biodiesel is environmentally benign in nature and has the potential to reduce the level of pollutants as well as that of potential or probable carcinogens [12, 18]. Thus the substitution of diesel oil by biodiesel produced within the country could not only solve increasing ecological problems but also improve the economy.

3.0. Biodiesel (FAME)

The term "biodiesel" was coined by the National Biodiesel Board, U.S. in 1992. The board was the pioneer in the commercialization of biodiesel in the U.S. Chemically, biodiesel is defined as a fuel composed of monoalkyl esters of long-chain fatty acids derived from vegetable oils or animal fats and its fuel properties are found similar to petro-diesel as reported elsewhere (Table 2). Moreover, the use of biodiesel in a conventional diesel engine substantially reduces emissions of unburned hydrocarbons, carbon monoxide, sulfates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons, and particulate matter [12, 19-22].

Biodiesel production from liquid biomass/vegetable oils is not a new aspect. In fact, one hundred and eighteen years ago, the very first usage of vegetable oil was demonstrated by Rudolf Diesel who used peanut oil to run one of his engines in Paris Exposition of 1900. He did extensive research on vegetable oil and pioneered the concept of using it as fuel but the availability of petroleum at cheaper price during those days did not widespread such a novel concept and after his death the use of vegetable oil as alternative fuel was also elapsed [23,24]. Due to high density, high viscosity and structural hindrance, the vegetable oils cannot be used directly in CI engine and after appropriate processing only it can be used in CI engines. There are four major techniques proposed to reduce the viscosity of vegetable oil namely, dilution, micro–emulsification, pyrolysis and transesterification. Among all these methods, transesterification is the most preferred method where a new transesterified liquid fuel called biodiesel is produced in the process. However, the researchers have also introduced new methods for biodiesel production such as supercritical alcohol process [25-27], biox co-solvent [28, 29] and in situ biodiesel process [30, 31].

3.1. Feedstocks for biodiesel production

A large number of investigations have been carried out worldwide to establish the suitability of different feedstocks available for biodiesel (FAME) production. The availability of feedstock for producing biodiesel depends on the regional climate, geographical locations, local soil conditions and agricultural practices of any country. Globally there are many oil-bearing crops which have been identified for biodiesel production and are classified as edible, non-edible feedstocks. Apart from these crops, waste cooking oil and animal fats are also proposed as feedstocks for biodiesel synthesis. The utilization of edible vegetable oil for biodiesel production interferes with the food security of a country like India where there is a big gap between the demand and supply of edible oils and the prices of edible vegetable oils are also higher than that of diesel fuel. The rapidly growing population and rising consumption of biofuels are increasing demand for both food and biofuels. Thus, food and fuel shortages may together be exaggerated.

Table 1 Fatty acid profile of different liquid biomass [12, 32-37]

Oil	Palmitic (C16:0)	Palmitoleic acid (C16:1)	Stearic acid (C18:0)	Oleic acid (C18:1)	Linoleic acid (C18:3)	Linolenic (C18:3)	Other acids
Corn	6.0	-	2.0	44.0	48.0	-	-
Cottonsed	28.3	-	0.9	13.3	57.5	-	-
Olive	14.6	-	75.4	10.0	-	-	-
Palm	42.6	0.3	4.4	40.5	10.1	0.2	1.1
Peanut	11.4	-	2.4	48.3	32.0	0.9	9.1
Rapeseed	3.5	0.1	0.9	54.1	22.3	-	0.2
Safflower	7.3	0.1	1.9	13.5	77.0	-	-
Soybean	11.9	0.3	4.1	23.2	54.2	6.3	-
Sunflower	6.4	0.1	2.9	17.7	72.9	-	-
Tallow	29.0	-	24.5	44.5	-	-	-
J.curcus	14.2	0.7	7.0	44.7	32.8	0.2	-
P.pinnata	10.2	-	7.0	51.8	17.7	3.6	-
M.Indica	24.5	-	22.7	37.0	14.3	-	-

Generally it is expected that the feedstock for biodiesel should fulfill two main requirements which are – low production costs and large production scale. Therefore, the food-for-fuel controversy plaguing the biodiesel industry has shifted the interest of stakeholders and scientists alike to non-edible, waste oils and animal fats. Some of the non edible oil feedstocks investigated exclusively for biodiesel production is *Terminalia belerica* Robx, *Jatropha curcus*, *Pongamia pinnata*, *Mesua ferrea* L., *Camellia oleifera* Abel oil [38-44].

Recently, microalgae have been introduced as third generation feedstock for biodiesel production. Because of its high photosynthetic efficiency to produce biomass and high oil content compared to edible/non edible oil feedstocks, it is considered as promising feedstock for biodiesel production. They are easier to cultivate than many other plants and it could be grown in farm or bioreactors. However the main limitation in the commercialization of microalgae is the high production cost arising due to various factors needed during cultivation. The emergence of closed photo-bioreactors which can control the various factors such as light requirement, CO_2, water, inorganic salts adds to the overall production cost, making it an expensive process [12, 45-46].

3.2. Biodiesel production using transesterification method

Conversion of vegetable oil into its corresponding ester and glycerol by reacting oil with appropriate alcohol (usually methanol) in the presence of a suitable catalyst is referred as transesterification. At present, transesterification is regarded as the most suitable method among other approaches for biodiesel production due to its low cost and simplicity. The chief product of this process is biodiesel and glycerol is another important by-product produced during the reaction which can be burnt for heat or be used as feedstock in the cosmetic industry. The simplified form of this chemical reaction is represented in Figure 2. Transesterification reaction is dependent upon several factors including type of oil, oil alcohol molar ratio, type of alcohol, type and amount of catalyst used, reaction time, reaction temperature, and mode of operation (continuous or batch type) etc. Although vegetable oils could only replace a very small fraction of transport fuel, considerable efforts have been made to develop vegetable-oil derivatives that approximate the properties and performance of hydrocarbon-based diesel fuels. Among all these methods transesterification process has been widely used to reduce the high viscosity of triglycerides and produce biodiesel with higher cetane number [38, 47-48].

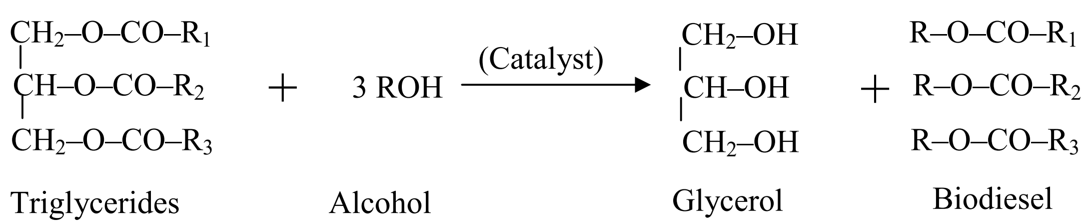


Fig.2 A reaction scheme for biodiesel production (transesterification reaction)

Where, R_1, R_2, R_3 represents the fatty acid chains.

Transesterification is mainly affected by the methanol and oil molar ratio – which is used to drive the reaction towards forward direction, catalyst – which depends on the amount of free fatty acid present in the vegetable oil/animal fat, reaction temperature and reaction time. Different types of alcohols are also used which includes methanol, ethanol, butanol etc. and based on the type of alcohol employed for biodiesel production the product is named. For example, when methanol is used, biodiesel is called as fatty acid methyl ester while it is called as fatty acid ethyl ester when ethanol is used. In order to obtain the maximum conversion yield, these variables must be optimized. Generally, the biodiesel production via transesterification can be catalyzed in four basic routes viz. base- catalyzed, direct acid catalyzed, enzyme catalyzed and non catalytic transesterification using methanol or methanol with a co-solvent [49-51].

3.3. Mechanism of transesterification

The transesterification reaction proceeds well in the presence of some homogeneous catalysts such as potassium hydroxide (KOH) and sodium hydroxide (NaOH) or heterogeneous catalysts such as metal oxides or carbonates. A catalyst is usually used to improve the reaction rate and biodiesel yield while excess alcohol is used to shift the equilibrium towards the product. The transesterification process consists of a sequence of three consecutive reversible reactions, which include conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides. Finally, the monoglycerides are converted into glycerol and yield one ester molecule in each step [52, 53]. This is represented in three steps as shown in Figure 3.

$$\text{Triglycerides} + \text{ROH} \xrightarrow{\text{(Catalyst)}} \text{Diglycerides} + \text{R}'\text{COOR} \longrightarrow \text{(Step I)}$$

$$\text{Diglycerides} + \text{ROH} \xrightarrow{\text{(Catalyst)}} \text{Monoglycerides} + \text{R}''\text{COOR} \longrightarrow \text{(Step II)}$$

$$\text{Monoglycerides} + \text{ROH} \xrightarrow{\text{(Catalyst)}} \text{Glycerol} + \text{R}'''\text{COOR} \longrightarrow \text{(Step III)}$$

Fig.3 Conversion of triglycerides into biodiesel (FAME)

Eckey [53] formulated the mechanism of the most widely used alkali-catalyzed transesterification process that takes place in consecutive three steps as summarized below:

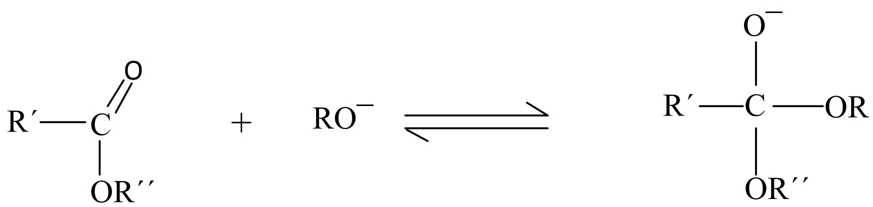
Pre-step:

$$OH^{-} + ROH \rightleftharpoons RO^{-} + H_2O, \text{ or}$$

$$NaOR \rightleftharpoons RO^{-} + Na^{+}$$

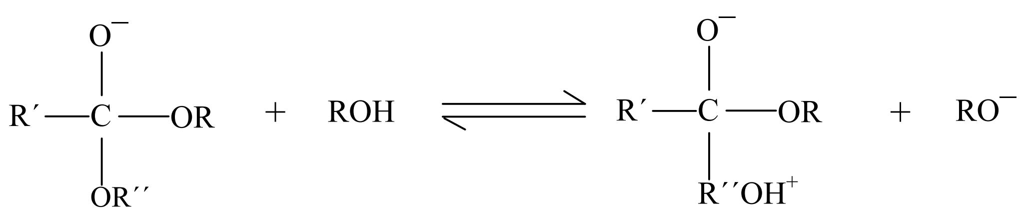
Step I

Carbonyl carbon atom of the triglyceride molecule is attacked by the anion of the alcohol to form tetrahedral intermediate.



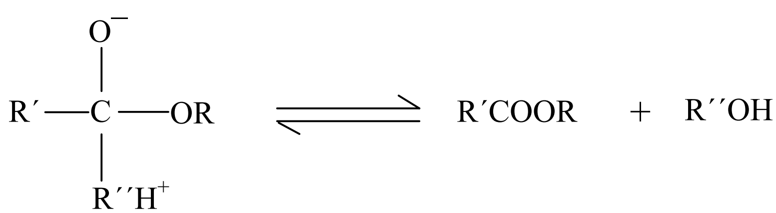
Step II

The tetrahedral intermediate reacts with an alcohol to regenerate the anion of alcohol



Step III

Tetrahedral intermediate rearrange itself to form fatty acid methyl ester and a diglyceride.



Accordingly, base catalysts such as NaOH or KOH react with alcohol to form alkoxide group which takes part in the reaction leading to the formation of fatty acid esters. It was also reported by different researchers that the alkali catalyzed transesterification proceeds 4,000 times faster than acid catalyzed transesterification and hence is commercially well-liked [54]. The key step in acid catalysis is the protonation of the carbonyl oxygen which in turn increases the electrophilicity of the adjoining carbon atom, making it more susceptible to nucleophilic attack. Hence in the case of acid catalysis formation of electrophilic species is ultimately responsible for the observed activity.

The transesterification process is a sequence of three reversible reactions, in which the triglyceride molecule is converted step by step into diglyceride, monoglyceride and glycerol. In order to shift the equilibrium to the forward, methanol is added in an excess over the stoichiometric amount in most commercial biodiesel production plants. Normally, the reaction is carried out at 60-65 ^{o}C using methanol as reactant with oil just above 6:1 molar ratio in presence of NaOH, or KOH as homogeneous catalyst (1% wt of oil). Recently, the heterogeneous catalysts of reusable nature are being investigated by researcher as the substitute of homogeneous catalyst. In addition, ethanol could be suitable replacement of methanol as the former is a purely renewable precursor if derived from biomass materials [21, 39, 55]. Biodiesel so produced can be utilized in unmodified diesel engine either directly or blending with Petroleum diesel. In order to use biodiesel efficiently in engine one must follow the fuel standard specified for CI engine. ASTM and European Nations separately specified the fuel standards as listed in Table-1.

Table 2 Fuel properties of biodiesel and petro-diesel [20-22]

Fuel properties	Unit	ASTM method	ASTM D6751 (Biodiesel)	ASTM D975 (Petro-diesel)
Density	g/cm^3	D 5002	0.86-0.90	0.834
Specific gravity	g/cm^3	D 287	0.88	0.851
Kinematic viscosity	mm^2/s	D445	1.9-6.0	1.9-4.1
Pour point	°C	C D97	-15to 16	-35 to -15
Cloud point	°C	D2500	-3.0 to 12	-15 to 5
Flash point	°C	D93	1 to 170	60-80
Sulfur contents	(%)	D4294	0.05	0.05
Acid number	mgKOH/g	D664	0.5	0.5

4.0. Advantages and limitations of transesterification process

Biodiesel fuel is a renewable and biodegradable fuel, eco-friendly in nature. After production biodiesel can be purified and separated and can be blended with diesel in any proportion or directly use in CI (diesel engine) without any engine modification. It emits less NOx and SOx as compared to diesel and lower amount of aromatic compounds during combustion and has higher cetene values than diesel fuel.

Although FAME has been used as diesel fuel for many years, the use of FAME is connected with some problems as compared to the use of petroleum-based diesel fuel. FAME damages some construction materials of the fuel system (seals). Detergent properties of FAME cause elution of impurities and plugging of some parts of the fuel system. This phenomenon is significant especially when changing mineral diesel fuel for diesel fuel containing FAME. FAME also tends to form sludge and deposits, especially during long-term storage no matter whether pure FAME or diesel fuel containing FAME are stored. High content of FAME in diesel fuel or combustion of pure biodiesel usually leads to faster degradation of motor oil. Relatively high solubility of water in FAME can cause larger corrosion of metal parts in comparison to mineral diesel fuel. Majority of the negative effects of FAME usage can be minimizing the content of FAME in diesel fuel. On the other hand, small content of FAME inhibits its larger utilization. Beside FAME production, there are other possibilities of vegetable oil processing for motor fuel production [56, 57].

5.0 Summary and conclusion

About 83 % requirement of petroleum products of our country is being compensated by imported crude oil. Transesterification of liquid biomass/vegetable oil could be integral parts of petroleum refining Industry. In our country the actual crude oil refining capacity is still higher than our demand of petroleum products. If the processes for utilization of non-edible vegetable oil and blending practices are implemented inside the refinery, a major problem of utilizing biodiesel and blends can be sorted out, as the quality control laboratories in the refinery are well set. Only the oil seed and vegetable oil market needs to be developed near the farm lands. If the production of oilseeds can be afforded using wasteland, degraded forest area, railway sides, highway side and by-lane sides cultivating high oilseed bearing plants such as Jatropha, Karanja, Mesua ferrea etc. our country can save over 10-20 % of the money spent for importing crude oil. This fraction of money will improve the income of the farmers and also help to save foreign exchange.

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