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Biomass to Biofuel: A Review of Technologies of Production and Future Prospects

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Abstract - **Biomass is an eminent starting material for the future fuel production due to its sustainable nature. Inadequacy of fossil fuels has engendered enormous interest of researchers and technologists in biofuels. Biofuel can be viewed as a major solution to defeat the dependence on fossil fuels, climate change and emission of greenhouse gases. Fuels derived from crude oil is mixture of various hydrocarbons hence by removing the oxygen in carbohydrates, biomass can be effectively converted into hydrocarbons. [12] The transformation of biomass to biofuel has resulted into generation of various liquid and gaseous biofuels such as bioethanol, biodiesel and biogas that can be used for transportation, industrial and domestic purposes. [12] In recent years, there has been exorbitant development in the biofuel production. [18] In this work we have comprehensively outlined the different production technologies for conversion of biomass to biofuel as well as given a pithy overview on the recent research in the field of biofuels – Biofuel from Jatropha seeds, marine micro algae and chemical catalysts like zeolites.**

Keywords: Biomass, fossil fuels, hydrocarbons, Jatropha seeds, Micro algae, zeolites

1. INTRODUCTION

Most of the world's energy supply is furnished by fossil fuel (Coal, crude oil and gas). Fossil fuel demands have been increased extensively due to increased power production, transportation and industrialization. Coal is the main fuel used in power production; gasoline and diesel are the main transportation fuels. Rapid consumption of the fuels having limited sources and the greenhouse gases emission due to use of fossil fuels have accelerated the need for renewable and green sources for energy production. Biofuels have received substantial attention due to renewable and environment friendly nature. It is also believed that biomass takes same amount of CO2 while growing as it releases during consumption.[35] Biomass is nothing but the natural organic matter such as wood, trees, manure, sewage, timber waste, grass cuttings, rice husk etc. All this natural organic material is a source of green energy called as 'biofuel'. Alcohol biofuels can replace gasoline in spark ignition engines, biodiesel and green diesel can replace diesel in compression ignition engines whereas LPG can be successfully replaced by the biogas.[29] The comprehensive objective of this paper is to outline the possible pathways and production technologies for the conversion of biomass to biofuels.

2. BIO-REFINERY SYSTEM

A Bio-refinery is a system consisting of various conversion processes and equipment which converts biomass into fuels, chemicals and power. Deep insight of chemistry, production and conversion technology is required to transform biomass to useful products. Bio-refineries can be classified based on variety of bases such as technology implementation status, type of raw material used, type of intermediate produced and main type of conversion process applied.[3] Based on the technological implementation bio-refineries can be classified as first, second and third generation bio-refineries. Various conversion technologies have been used for effective conversion of biomass to biofuels such as thermochemical conversion, biological conversion, chemical conversion and physical conversion depending upon the required product. [35] Detailed flow chart of various conversion processes used in bio-refinery is shown in Fig: 1.

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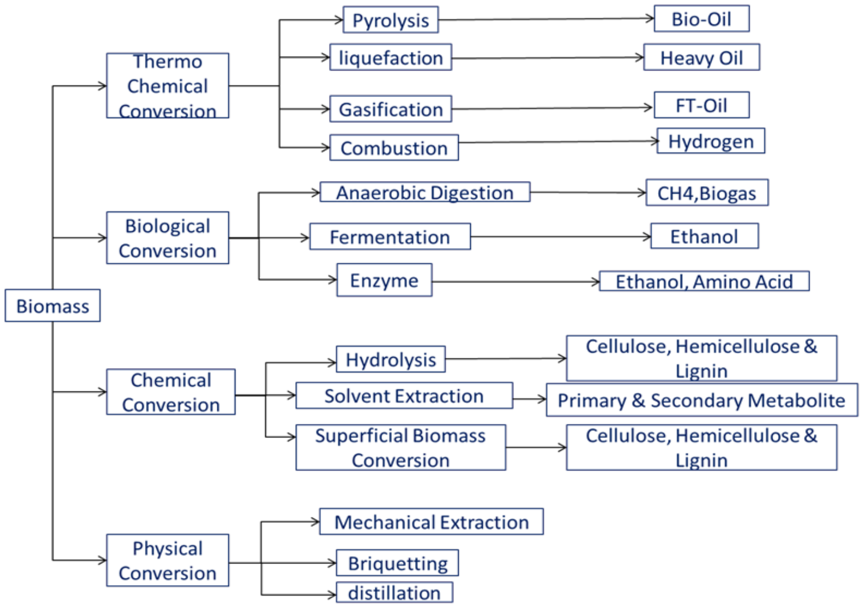

Figure 1: Biomass conversion processes [35]

3. FIRST GENERATION BIOFUEL

Feedstock for the first generation bio-refinery is mainly food crops.[8-9],[14],[31] The biofuels produced from sugars, grains or seeds are first generation biofuels. Bioethanol and biodiesel are the main biofuels produced commercially. Ethanol is produced from the fermentation of starch or sugar whereas biodiesel is produced from the transesterification of vegetable oil, residue oil and fats [6],[10],[13],[19].

3.1. Transesterification

The reaction produces fatty acids of methyl esters from vegetable oils (tri-glycerides).[27] The transesterification reaction is a reversible reaction in which homogeneous catalyst is present in liquid phase. Glycerol, a high value coproduct is obtained in this reaction.[23]

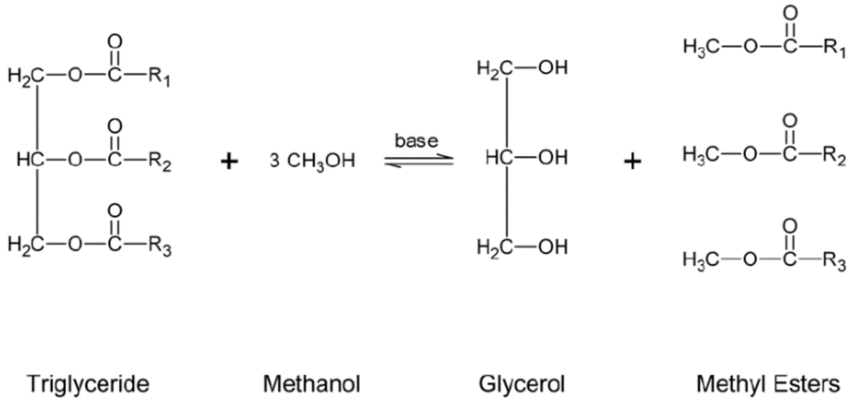

Figure 2: Chemistry of transesterification

3.2. Ethanol conversion processes

Various raw materials (sugars and starch) containing carbohydrates can be converted into bioethanol by fermentation process. Due to activity of enzymes secreted by microorganisms, metabolic conversion of organic substrate takes place. Depending upon the necessity of oxygen for the process it can be aerobic or non-aerobic fermentation.[35]

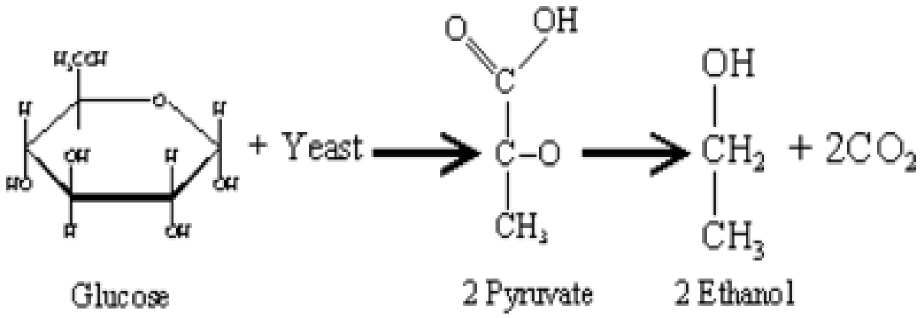

Figure 3: Production of ethanol from glucose

Due to use of edible feedstock it has resulted into following concerns.

a) Competition with food, water and land used for fiber production.[2], [4], [34]
b) High processing and production cost to compete with petroleum products.

Despite of these problems, large amount of first generation biofuel is produced worldwide. First generation conversion is an established technology. There are a variety of processing methods available and various advancements in technologies have been done in recent years.

4. SECOND GENERATION BIOFUEL

Second generation biofuels are produced from non-edible feedstock. Non edible feedstock contains stalks of wheat, wood, corn and waste biomass. Lignocellulosic biomass is the major constituent of second generation feedstock and it does not disturb the food chain. Bio-ethanol is one of the vital biofuel that can be produced from Lignocellulosic feed stock.[24] 2G biomass can be converted to biofuels via two basic routes:

- Thermochemical processing- Thermal energy is used to convert biomass into synthesis gas (e.g. Gasification/pyrolysis) which can be further processed chemically on basis of Fischer-Tropsch synthesis to get hierarchy of chemicals and fuels.
- Biochemical processing- Enzymes secreted by microorganisms can substantially convert cellulosic material to sugars which can be converted to bio-ethanol by Fermentation.

Biochemical processing focuses only on conversion of polysaccharides whereas thermochemical processing can effectively convert all the organic components of the biomass.[24]

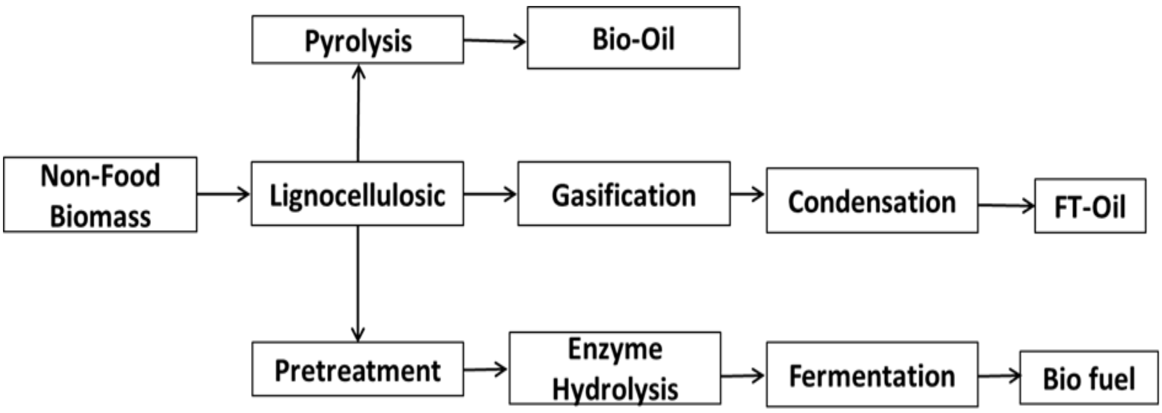

Figure 4: Second generation conversion

4. Lignocellulosic biomass to bioethanol

Bioethanol produced by this method can directly replace gasoline in spark ignition engines or can be successfully blended with gasoline. Basic steps involved in this process are pretreatment, enzymatic saccharification, fermentation and separation by distillation.[22]

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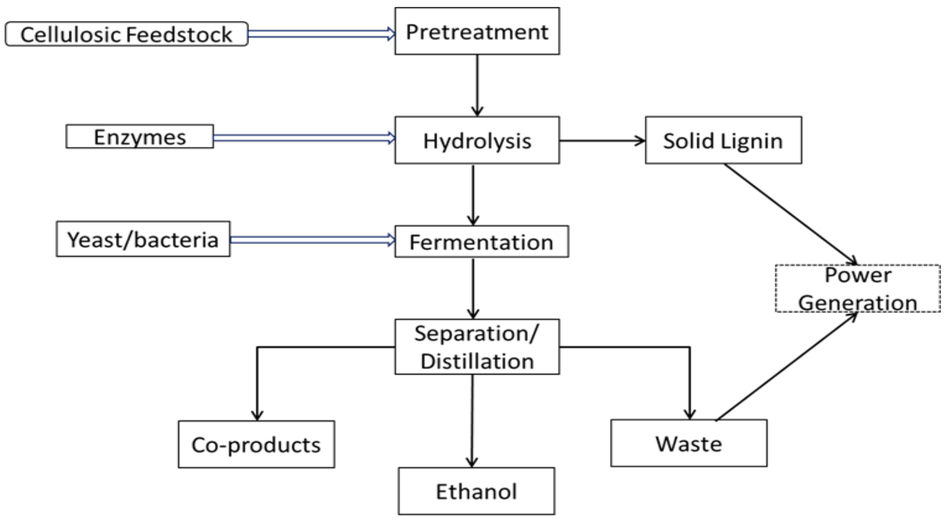

Figure 5: Lignocellulose biomass to bioethanol

Pretreatment separates cellulose, hemicellulose and lignin. Enzymatic hydrolysis breaks down the complex carbohydrate polymer molecules of cellulose and hemicellulose into fermentable sugars.[37] Hemicellulose is a sugar comprised of 5 carbons which can be further broken down into its constituent sugars like xylitol and pentose.[15],[36-37] Fermentation of these constituent sugar will result into formation of alcohol. To convert 5 carbon sugars into ethanol (fermentation) is an arduous process and hence requires adept microorganisms such as yeast and bacteria. Lignin contains phenols and hence cannot be fermented. Lignin is recovered and used as fuel to produce power.[15],[36-37] Final products are separated by distillation. Microorganism like Neurospora, Paecilomyces, Monilia and Fusarium can directly convert cellulose directly into ethanol by simultaneous saccharification and fermentation.[35]

4.2. Gasification

The feedstock is heated to higher temperatures to produce gases which further undergo chemical reaction to produce synthesis gas. The process can either be catalytic or non-catalytic. For non-catalytic conversion, it requires very high temperatures but catalytic conversion can be achieved at lower temperatures as well. Further advances in the catalysts can significantly reduce the operating temperature from the current value of 900^o C.[1] Reaction of biomass with air and steam produces gaseous mixture of CO, H_2, CO_2, N_2 and CH_4.[30] Synthesis gas produced can be used in production of wide range of chemicals and fuels using different technologies.[1],[30]

Name	Thermal Efficiency	Syngas CO Conversion	Selectivity
Fischer-Tropsch Synthesis	˜60%	Able to achieve 50-90% conversion of the CO in the syngas with recycling of the off-gas into the catalyst stream.	The gasoline product fraction has a maximum selectivity of 48% (using Fe catalyst), although under actual process conditions is only 15-40%. The maximum selectivity of diesel product fraction is closer to 40%(using Co)
Methanol Synthesis	˜79%	Per pass, the maximum conversion is 25%, although values are only 4-7%. Can convert 99% of the syngas to methanol with recycling	>99.5% selectivity for methanol
Mixed Alcohols Synthesis	62-68%	Single pass conversions are generally 10-40%,but producing mainly methanol	Selectivity to methanol, ethanol and higher alcohols varies due to hydrocarbon production but on a CO2 free basis ranges from 60-90%
Syngas Fermentation	Not stated	Depends on the mass gas-liquid transfer rates, microorganism growth and activity, if recycled	Given the correct microorganism solely ethanol can be made (100% selectivity)

Table 1: Syngas Conversion Processes

4.3. Pyrolysis

Thermal degradation of the biomass in the absence of oxygen leads to production of bio-oil, charcoal and gaseous fuel products.[7] This method has been used commercially to produce fuels, chemicals, solvents from biomass feed stock.[16] The main objective of this process is to recover biofuel with medium-low calorific value. The pyrolysis liquid consists of acids, alcohols, aldehydes and ketones.[2] Table describes the conversion technologies used, operating conditions and products.[2]

Technology	Residence Time	Heating Rate	T (˚C)	Products
Carbonation	days	Very low	400	charcoal
Conventional	5-30 min	low	600	Oil, gas, char
Fast	0.5-5s	Very high	650	Bio-oil
Flash-Liquid	< 1s	high	<650	Bio-oil
Flash-gas	< 1s	high	<650	Chemicals, gas
Ultra	< 0.5s	Very high	1000	Chemicals, gas
Vacuum	2-30s	Medium	400	Bio-oil
Hydro-pyro	< 10s	high	<500	Bio-oil
Methano-pyro	< 10s	high	>700	Chemicals

Table 2: Conversion Technologies used in Pyrolysis

5. THIRD GENERATION BIOFUELS

In case of second generation biofuels, the feedstock does not compete with food; however it indirectly affects the food chain by competing land usage, deterioration of forest cover and water scarcity. Third generation biofuels are produced by microorganisms.[25],[26],[38]

Microalgae are observed as a potential feedstock for production of biofuels. Microbes have the ability to store fatty acids which qualifies them as substrate for biodiesel production.[25],[26],[33],[38] 3G biomass can be converted into biofuels via two basic routes:

- Thermochemical processing- Processes such as gasification, pyrolysis and liquefaction can be used for conversion of microalgal biomass to biofuels by use of thermal energy.
- Biochemical processing- Biomass can also be converted into biofuels by processes such as photo biological hydrogen production, fermentation and anaerobic digestion.

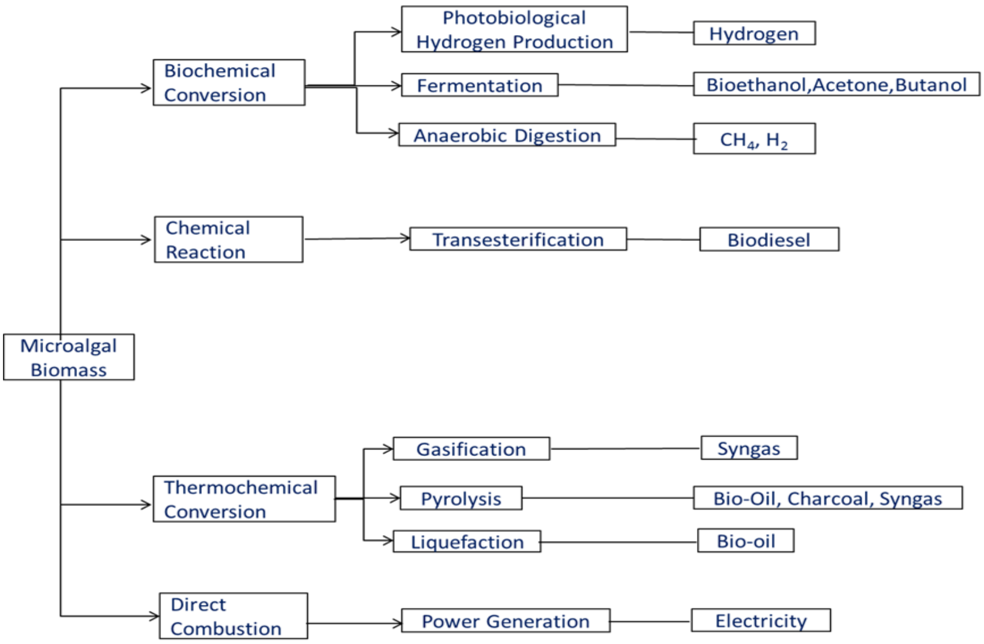

Figure 6: Third generation conversion [26]

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There are some drawbacks for this process like:

- Efficient algal strain
- Designing the metabolic pathways to achieve desired lipid content by engineering the reaction that controls lipid synthesis.
- Strain cultivation at optimum growing rates
- Efficient recovery of oil from algal strains

6. FOURTH GENERATION BIOFUELS

Fourth generation biofuels are derived from oxygenic photosynthesis using metabolically engineered algae. The main difference between fourth generation biofuel and the previously discussed methods is that previous methods applies 'cell factory' concepts or processing of biomass to produce biofuels whereas in fourth generation the solar energy drives the photosynthetic microorganisms using CO2 as raw material. Major advantage of fourth generation is that microorganisms will directly secrete the final products out of the cell avoiding the cost of fermentation and biomass feedstock processing.[21] The number of steps for the conversion is significantly reduced as compared to third generation. Table 4 represents some completed microalgal genome sequences for oxygenic photosynthesis.

Condition	Phylum	Species	Strain	GenBank	Length (nt)	Genes	Proteins
Complete (nuclear genome sequencing)							
	Chlorophyta						
		Chlamydomonas reinhardtii	CC-503 cw92 mt+	ABCN00000000	105,192,443	14,354	14,412
		Chlorella variabilis	NC64A	ADIC01000000	46,200,000	9,791	9,791
		Micromonas pusilla	CCMP1545	ACCP00000000	21,706,984	10,248	10,242
		Micromonas sp.	RCC299	CP001335- CP001574	20,900,00	10,128	10,128
		Ostreococcus lucimarinus	CCE9901	CP000581- CP000601	13,200,000	7,651	7,615
		Ostreococcus tauri	OTH95	CR954201- CR954220	12,560,000	8,166	8,166
		Volvox carteri f. nagariensis	Eve	ACJH00000000	125,467,762	14,437	14,436
	Ochrophyta						
		Phaeodactylum tricornutum	CCAP1055/1	ABQD00000000	24,612,623	9,479	9,488
		Thalassiosira pseudonana	CCMP1335	AAFD00000000	29,453,142	10,747	10,660
	Rhodophyta						
		Cyanidioschyzon merolae	10D	AP006483(DDBJ)	16,728,945	5,331	5,017

Table 3: List of microalgal of genome sequences

Although fourth generation is very effective fuel production technique, there are some problems in fourth generation fuel production.

- Understanding of algal metabolism and growth
- Accumulation of metabolites which will be toxic to host cells

Impact of this method on energy market will not be possible without technological advancements. It requires better understanding to make it economically feasible and hence fourth generation fuel production is not yet commercialized.

7. CURRENT RESEARCH

Currently, a lot of research is being conducted for the production of bioethanol from biomass using technologies that are economical as well as sustainable keeping the environment in mind. Following is a terse overview of a few methods that have been developed in the lab scale and are in the process of being scaled up.

7.1. Biodiesel from Jatropha seeds

Jatropha seeds are obtained from the Jatropha fruit. The fruit is deshelled in the deshelling machine. The seed thus obtained is used for extracting Jatropha oil, which is then neutralized with alkali to remove excess free fatty acid. An antioxidant is added and sparging the oil with dry air is done to reduce the moisture content. It is then reacted with methanol to form methyl ester and glycerol. The husk from the deshelling machine is used as a biomass gasifier for power and to produce process heat, thus making the technology self-sufficient in energy.[41]

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Figure 7: Biodiesel and allied products from Jatropha fruits

The advantages of using Jatropha seeds to produce bioethanol are:

- Biodiesel is produced directly from plant materials, under ambient conditions with least energy input and minimum effluent formation.
- The yield is between 94-98% based on neutralized oil.
- The crude is washed with methyl ester to extract as much of the methanol, catalyst and other impurities to eliminate froth formation.
- Utilize a part of crude glycerol for production of glycerol ether to reduce the cloud point of the biodiesel.
- The methanol can be distilled in the glycerol layer for reuse after drying.
- The alkaline glycerol layer can be treated with SO_x to convert the spent catalyst into solid fertilizer grade potassium sulphate that can be filtered and washed.

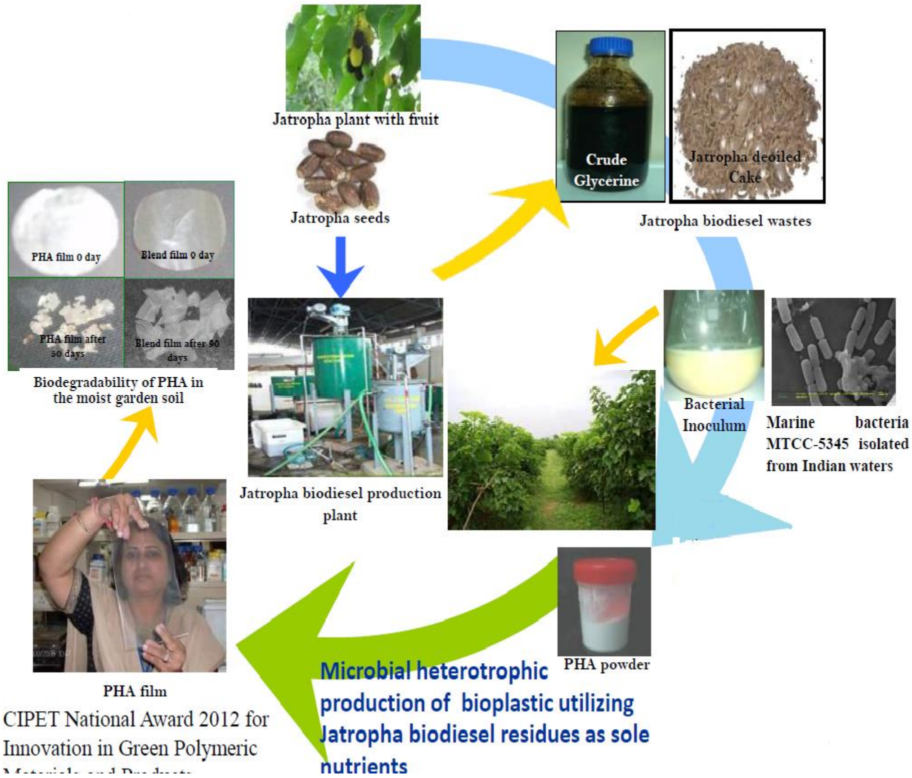

Figure 8: Flowchart of biodiesel from Jatropha fruit

7.2. *Biodiesel from marine microalgae*

Naturally occurring microalgal mat formed from a consortium of algae *Microspora ATCC* and *Cladophora sp. ATCC* including oil bearing ones were found at site 1– Longitude 68˚59.876' and Latitude 22˚23.975' and site 2- Longitude 70˚54.959' and Latitude 20˚42.391'.[42]

The method used in the above discovery is as follows:[42]

- Collect marine microalgal mats containing oil bearing algae like *Chlorella.*
- Separate the oil bearing algae like *Chlorella.*
- The outdoor mass cultivation of *Chlorella* is conducted in salt farms.
- Drying and grinding is carried out to form biomass.
- Transesterification of biomass is done to form biodiesel.
- The spent biomass and waste is heated to produce biogas and power the entire process.

This biodiesel was first tested on Tavera in India which operated on 20% biodiesel (B-20). The Tavera gave 12.4 km better mileage than the 10-11 kms recorded by diesel run SUV's.

The aim is now to run the test vehicle on B-100 (neat biodiesel) marine micro algae biodiesel and evaluate the economic viability.

7.3. *Chemical catalysis*

Chemical processes use catalysts along with energy to convert raw materials to fuels. Many of the routes to biomass transformation involve several steps including de-polymerization followed by separation and upgrading processes.[44]

For biofuel production, you need to remove as much of oxygen to gain energy density. At the same time, the cost for oxygen removal needs to be minimized. With the help of techniques like high resolution transmission electron microscopy, X- ray photoelectron spectroscopy and extended X-ray absorption fine structure spectroscopy, the mechanism of interaction of atoms on the catalyst surface with plant lignin material was understood. Consequently it was found that metals like palladium can be used along with iron to yield higher rates.[45]

Pretreatment and Deconstruction: Recently, work has been done on developing an ammonia based method referred to as AFEX. The ammonia breaks the lignin structure that leads to an improvement in the efficiency of the enzyme action.

Multifunctional Catalysts: The most common problem encountered with the use of catalysts for fuel production is the increased cost due to the involute nature of the process, including separation techniques and regular upgrades. Therefore, there is an urgent need for the development of heterogeneous catalysts to convert biomass to fuel.

Zeolite catalysts have proven to be breakthrough in this field as potential biomass catalysts. ZSM-5 is a quintessential material due to low molecular weight, low coking tendency and high deoxygenation activity. The addition of certain base metals to the zeolite has found to increase the selectivity. For example, addition of Nickel has increased the conversion of oxygenates.

8. CONCLUSION

This paper delineates the various methods of production of biofuels. Although first generation is efficient, it involves edible food stock due to which second generation is more lucrative. However, second generation involves land costs, depleting land cover etc. which is eliminated by third generation biofuels which involves production from microalgae. Fourth generation biofuels eliminates the fermentation step involved in all the previously mentioned mechanisms by directly using sunlight for photosynthesis of raw materials. A lot of research is on-going in this field to make synthesis of biofuels sustainable and economically viable. We have a long way to go for producing B-100 biofuels. Literature reports of catalysts and enzymes provide interesting impetus for the future. The potential of these methods needs to be adjudged on the basis of techno-economic analysis of the process. The biotransformation of raw materials faces some critical challenges due to which there is no scale up of these methods. This is one of the main areas to focus on for future development.

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