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Biopolymer Materials, an Alternative to Synthetic Polymer Materials

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Abstract:

Reports have shown that the use of petroleum based polymers have numerous adverse impact on atmosphere. Most of the plastic waste ended up in the landfill creates pollution with the accumulation of chemicals, only 10% of plastics has been recycled. On the other hand, biopolymers converted into biomass with the help of living organisms which later use as manure in plants. Disposal of bio-waste in landfill creates environmental problems, due to the huge production of CO2 and NH3. Since the waste contains large amount of sugars, carbohydrates and cellulose in them, to utilize them in ecofriendly way for industrial use with the help of bacterial fermentation in a cost-effective way is the best approach. Biomass can be converted into biofuel, biogas and bio-oil in eco-friendly way with the help of mutagenesis technique. The use of bioplastics over conventional plastics limits due to its high cost but there are several other options to produce bioplastics from the biomass feedstock in cost effective way. The future market for biopolymers are significantly increasing due to its sustainability. The biotechnology of microorganism gives a new hope to bioplastic production could significantly influence the production to compete with current barriers. The motive of the review was discussed, and excellent results would have achieved which is a way to control marine pollution with the increasing use of biopolymers for the green economy.

Key Words: Biopolymers, Biodegradable, Petroleum based Polymers, Biomass, Biofuel, Biotechnology

Introduction:

Nowadays, people are more aware about the harmful effects of petrochemical derived plastic materials in the environment. Researchers have conducted many researches for managing plastic waste on earth by finding eco-friendly alternative to plastics. This ecofriendly alternative is Bioplastics, which are disposed in environment and can easily degrade through the enzymatic actions of microorganisms. The degradation of biodegradable plastics give rise to carbon dioxide, methane, water, biomass, humic matter and various other natural substances which can be readily eliminated [1]. In view of dwindling reserves of fossil resources industry is showing growing interest in Bioplastics. About 4% of the world's oil production is converted into plastics for use in products as varied as shopping bags and the external panels of cars. Another few percent are used in processing industries because oil-based plastics require substantial amounts of energy to manufacture. As oil runs out and the use of fossil fuels becomes increasingly expensive, the need for replacement sources of raw material for the manufacture of vital plastics becomes increasingly urgent. In addition, the use of carbon-based sources of energy for use in plastics manufacturing adds greenhouse gases to the atmosphere, impeding the world's attempts to cut CO_2 emissions [2,3]. An environmental dilemma with more far-reaching implications is climate change. The need for rapid and deep greenhouse gas (GHG) emissions cut is one of the drivers for the resurgence of industrial biotechnology generally, and the search for bio-based plastics more specifically. Bio-based has come to mean plastics based on renewable resources but this need not necessarily imply biodegradability.

If the primary purpose is GHG emissions savings, then once again plastics durability can be a virtue, if the end-of-life solution can be energy recovery during incineration or recycling. The pattern of production is shifting from the true biodegradable plastics to the bio-based plastics and that trend is likely to persist into the future [4]. Another environmental aspect of plastics manufacture is greenhouse gas generation. The Intergovernmental Panel on Climate Change (IPCC) trajectory to 2050 for stabilization of atmospheric GHG concentrations at 450 ppm CO_2 requires emissions reduction of 80% compared to the 1990 level [2]. This will be perhaps the biggest human challenge of the next generation. Several countries have adopted targets for such deep reductions in GHG emissions [3] and part of the strategy for many is the development of a biobased economy. The biobased economy first emerged as a policy concept within the OECD at the start of this century linking renewable biological resources and bioprocesses through industrial scale biotechnologies to produce sustainable products jobs and income [5]. These problems can be overcome. All the major oil-based plastics have substitutes made from biological materials. The polyethylene in a shopping bag can be made from sugar cane and the polypropylene of food packaging can be derived from potato starch. Plastics are irreplaceable, and will all eventually be made from agricultural materials. By finding an economically more advantageous synthesis solution for the plastic pollution with the deep understanding about the various types of biopolymers by describing their nature of biodegradable and compostable processes. The idea of review paper is to find a cost-effective way to produce biopolymers from the biomass. To enhance the use of biopolymers due to their excellent characteristics features which makes them so special, for example single use, disposable properties, and eco-friendly. Biodegradable plastics should have the needed performance characteristics in intended use, but after use should undergo biodegradation process in suitable environment. In the degrading process, a biodegradable plastic can be converted to carbon dioxide (CO_2) and water and composting done by without leaving any toxic residue. However, their applications are limited to some extent due to its high cost synthesis. [6]

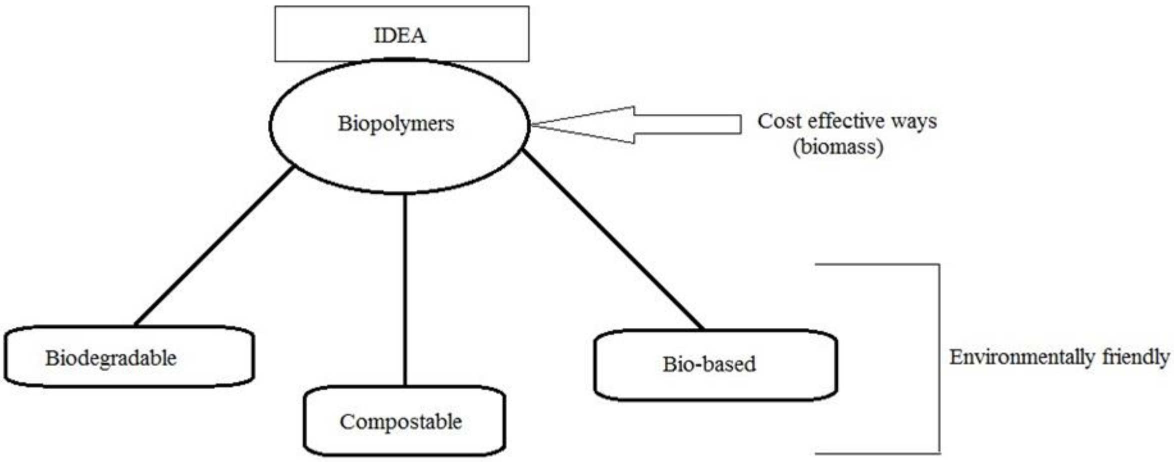

Figure 1. *Basic idea of research* [6]

The term biopolymers relate with the biodegradability of the polymers derived from organic matter goes directly into nature after the use is over. According to ASTM, biodegradation is defined as in Figure 8 the degradation or fragmentation of the polymer with the help of microorganisms like bacteria, algae and fungi into the natural environment that includes changes in chemical structure, physical appearance, loss of mechanical properties and structure properties which converts carbon into basic compounds like water, carbon dioxide (CO2), humic materials, biomass and minerals. The factors that are helpful in the conversion such as suitable temperature, humidity, oxygen. The process also knows as ultimate aerobic biodegradation. [7] (Systems, 2012)

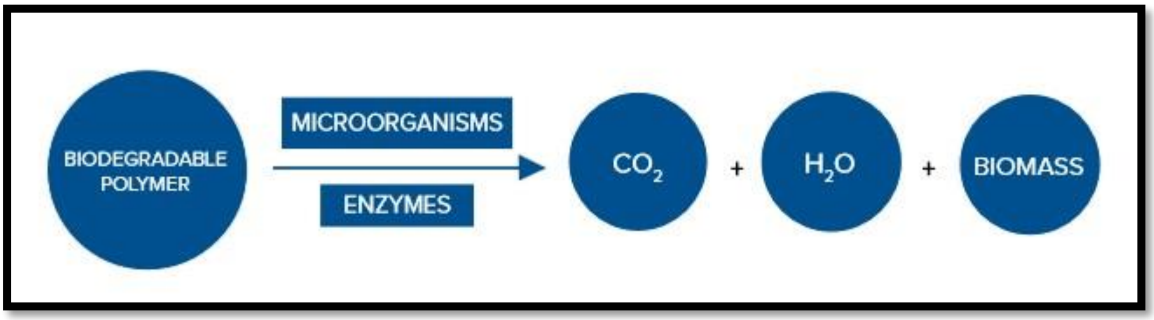

Figure 2. *The process of Biological degradation of biodegradable polymers [8]*

Some Important Definitions:

Biodegradation: A biological process in which, a polymer breaks into smaller particles with the help of microbial activity and converted into methane, water and carbon dioxide. The mechanism of bio degrades the polymer depends upon the thickness and composition of the material. [9]

Degradation: The process of disintegration of the polymer into smaller fragments by the action of abiotic factors such as UV radiation, oxygen attack, and biological attack. The most common degradable plastics are polyethylene.

Bio-based plastics: The term bio-based consists both plastics that are biodegradable and are bio-based, means those are derived from natural resources or biomass in some content. They may or may not be biodegradable but recyclable. The mechanical properties are quite similar as those derived from fossil for example, Bio- PVC, bio- PE derived from sugarcane (Braskem). [10]

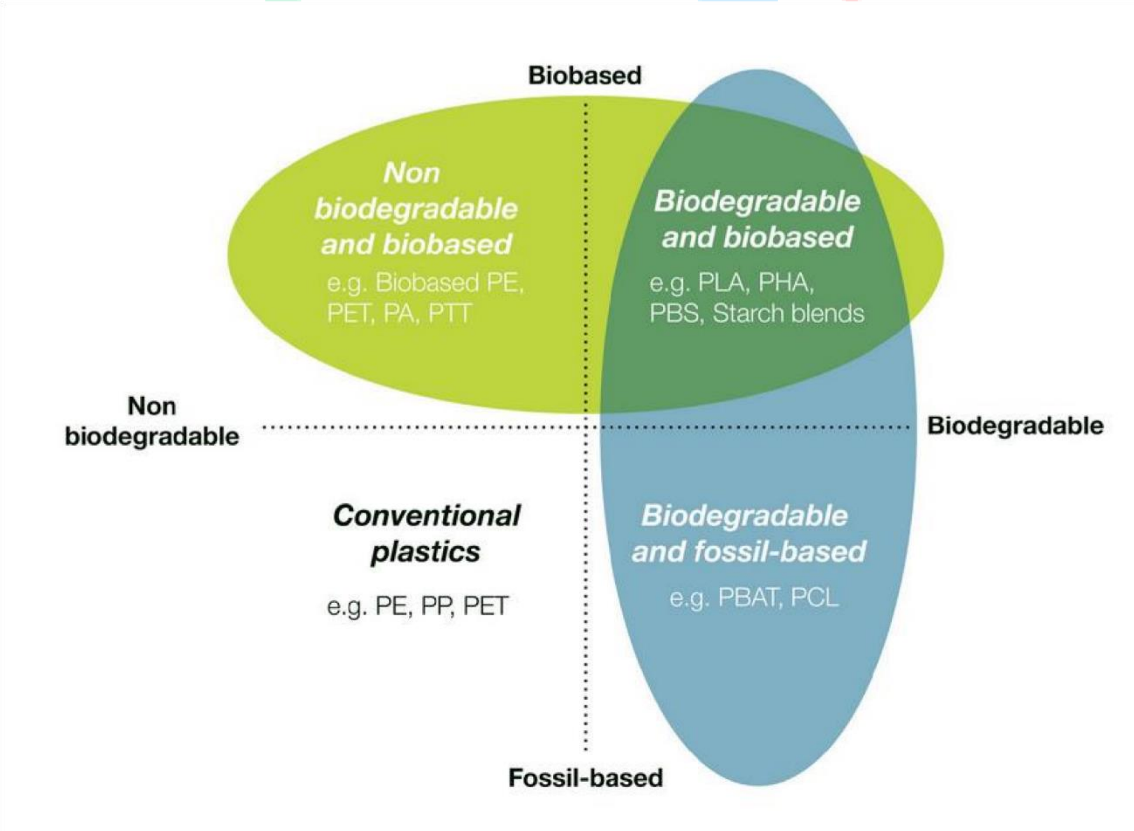

Figure 3. *Understanding the three different categories of bioplastics [11]*

Compostable plastics: A plastic that have capability to undergo biological decomposition in compost site and breaks down into carbon dioxide, water, inorganic compounds and biomass without leaving toxic substances to the atmosphere. The compostable products can also degrade by the mechanism of enzymes. For example, PLA is suitable for both methods to degrading completely. [9]

Conventional plastics: They are also known as petro-based plastics/ fossil based, synthetic plastic generally derived from non-renewable resources.

Types of Biopolymers

There are five main types of biopolymers based respectively on plants, microorganisms, animals, fossil based and bio-based (non- biodegradable) are systematically described in Table 1 below.

Table 1. Classification of biopolymers [12]

Biodegradable				Nonbiodegradable
Bio-based			Fossil-based	Bio-based
Plants	Microorganisms	Animals		
Cellulose and its derivatives[1] (polysaccharide)	PHAs (e.g., P3HB, P4HB, PHBHV, $PHBHH_x$)	Chitin (polysaccharide)	Poly(alkylene dicarboxylates) (e.g., PBA, PBS, PBSA, PBSE, PEA, PES, PESE, PESA, PPF, PPS, PTA, PTMS, PTSE, PTT)	PE (LDPE, HDPE), PP, PVC
Lignin	PHF	Chitosan (polysaccharide)	PGA	PET, PPT
Starch and its derivatives (monosaccharide)	Bacterial cellulose	Hyaluronan (polysaccharide)	PCL	PU
Alginate (polysaccharide)	Hyaluronan (polysaccharide)	Casein (protein)	PVOH	PC
Lipids (triglycerides)	Xanthan (polysaccharide)	Whey (protein)	POE	Poly(ether-esters)
Wheat, corn, pea, potato, soy, potato (protein)	Curdlan (polysaccharide)	Collagen (protein)	Polyanhydrides	Polyamides (PA 11, PA 410, PA 610, PA 1010, PA 1012)
Gums (e.g., *cis*-1,4-polyisoprene)	Pullulan (polysaccharide)	Albumin (protein)	PPHOS	Polyester amides
Carrageenan	Silk (protein)	Keratin, PFF (protein)		Unsaturated polyesters
PLA (from starch or sugarcane)		Leather (protein)		Epoxy
				Phenolic resins

HDPE, high-density polyethylene; LDPE, low-density polyethylene; P3HB, poly(3-hydroxybutyrate); P4HB, poly(4-hydroxybutyrate); PBA, poly(butylene adipate); PBS, poly(butylene succinate); PBSA, poly(butylene succinate-co-adipate); PBSE, poly(butylene sebacate); PC, polycarbonate; PCL, poly(ε-caprolactone); PE, polyethylene; PEA, poly(ethylene adipate); PES, poly(ethylene succinate); PESA, poly(ethylene succinate-co-adipate); PESE, poly(ethylene sebacate); PET, poly(ethylene terephthalate); PFF, poultry feather fiber; PGA, poly(glycolic acid), polyglycolide; PHA, polyhydroxyalkanoate; $PHBHH_x$, poly(3-hydroxybutyrate-co-3-hydroxyhexanoate); PHBHV, poly(3-hydroxybutyrate-co-3-hydroxyvalerate); PHF, polyhydroxy fatty acid; PHH, poly(3-hydroxyhexanoate); PLA, poly(lactic acid), polylactide; POE, poly(ortho ester); PP, polypropylene; PPF, poly(propylene fumarate); PPHOS, polyphosphazenes; PPS, poly(propylene succinate); PTA, poly(tetramethylene adipate); PTMS, poly(tetramethylene succinate); PTSE, poly(tetramethylene sebacate); PTT, poly(trimethylene terephthalate); PU, polyurethane; PVC, poly(vinyl chloride); PVOH, poly(vinyl alcohol).

[1] Acetyl cellulose (AcC) is either biodegradable or nonbiodegradable, depending on the degree of acetylation. AcC's with a low acetylation can be degraded, while those with high substitution ratios are nonbiodegradable.

Cost effective methods of producing biopolymers:

Due to the controversy regarding the negative impacts of biopolymers, as they are contributing global food crisis by using crops as feedstock. An alternative of that requires less valuable raw material such as agricultural waste and food industrial wastes [13]. Following are some researches of inexpensive ways to obtain the raw materials (carbon source) from discarded living items.

Microbial Polysaccharides: There are several approaches done by researchers to produce polysaccharides (Exopolysaccharides) such as pullulan, dextran, xanthan, levan can be obtained from syrups and molasses at low cost by using the method of pretreatment with sulfuric acid. The method of centrifugation and filtration in sugarcane molasses and sugarcane syrup has been used to obtain high yield of levan with the help of Zymomonas mobilis culture, for more details see Table 2. [14]

Sugar beet pulp: The waste left from sugar beets during the sugar production consists huge amount of starch, cellulose, hemicellulose and pectin that can be used to make composite materials from cheap cellulosic material. Extracting pectin from apple pomace waste from cider producing industries with hot aqueous mineral acid that can further isolated from the solution. [15]

Table 2: *Methods of extraction of microbial polysaccharides from biomass of food waste [14]*

EPS	Microorganism	Biomass	Pretreatment	Yield (time)
Curdian	*Agrobacterium sp.* ATCC 31749	CCS	Clarification by filtration	7.72g/L (120h)
Dextran	*L, mesenteroides* NRRL B512	Carob extract	Milling aqueous extraction	8.56g/L (12h)
Dextran	*L, mesenteroides* NRRL B512	Carob extract and cheese whey	Deproteiization of whey	7.23g/L (12h)
Dextran	*L, mesenteroides* V-2317D	Sugar beet M	No treatment	50g/L (9 days)
Gellan	*S. paucimobilis* ATCC-31461	Sugarcane M	Dilution	13.81g/L (48h)
Gellan	*S. paucimobilis* ATCC-31461	Cheese whey	Neutralization heat treatment	7.9gL (100h)
Levan	*Halomonas sp.* AAD6	Sugar beet M Starch M	Clarification by centrifugation pH adjustment acid hydrolysis TCP treatment AC treatment	12.4g/L (210h)
Levan	*Paenibacillus polymyxa* NRRL B-18475	Sugar beet M	Dilution Gel filtration chromatography Anion exchange chromatography	38.0g/L (5 days)
Levan	*P. polymyxa* NRRL B-18475	Sugarcane syrup	Clarification by filtration	`19.6g/L (5 days)
Levan	*Zymomonas mobilis* ATCC 31821	Sugarcane M	Clarification by centrifugation and filtration	2.53g/L (24h)
Levan	*Zymomonas mobilis* ATCC 31821	Sugarcane syrup	Clarification by centrifugation and filtration	15.5g/L (24h)
Pullulan	*Aureobasidium sp.* NRRL Y	CCS	Clarification by centrifugation	4.5g/L (9 days)
Pullulan	*A.Pullulans* SU-M18	Carob extracts	Aqueous extraction	6.5g/L (3 days)
Pullulan	*A.pullulans*	OMW	Clarification by filtration	8g/L
Pullulan	*A.pullulans* NRRLY-6220	OMW	No treatment	10.7gL (7 days)
Pullulan	*A.pullulans* NRRLY-6220	Grape pomace	Aqueous extraction	22.3g/L (7 days)
Pullulan	*A.pullulans* NRRLY-6220	Sugar beet M	Dilution	6.9g/L (7 days)
Pullulan	*A.pullulans*	Sugar beet M	Acid hydrolysis	32.0g/L

Biotechnology in biopolymer production:

Mutagenesis is a process of mutation for strain improvement in microorganism in order to increase their metabolic capacities (industrial strains) by making changes in genotypic and phenotypic behavior of microorganisms. Mutation can be achieved by different procedures such as gene transfer methods, protoplast fusion, gene cloning vectors and recombinant genes. [16]. Table 4 is describing the most frequently used microorganism for different methods of gene transfer in which the most commonly used method is transformation. These methods are used to increase molecular diversity and to improve chemical stability for the cheaper production of desired products. [17]

Table 3: *Most commonly used microorganisms (GGMs) for the process of gene transfer methods [17])*

Type of Organism	Industrial Applications	Gene Transfer Methods
Aspergillus	Food fermentations	Protoplastic transformation Electroporation Biolistic transformation
Yeasts	Food and beverage fermentations	Protoplast transformation Electroporation
Bacillus	Industrial enzymes Fine chemicals Antibiotics Insecticides	Transformation of competent cells Protoplast transformation Electroporation
Corynebacterium	Amino acids	Protoplast transformation Electroporation Conjugation
Escherichia Coli	Therapeutic protein production Biodegradable plastics	Transformation of competent cells
Lactic Acid Bacteria	Food fermentations Organic Acids	Protoplast transformation Electroporation
Pseudomonas	Plant biological control agents bioremediation	Electroporation Conjugation
Streptomyces	Antibiotics, antitumor, and antiparasitic agents Herbicides	Protoplast transformation Electroporation Conjugation

Biomass energy conversion:

The conversion of feedstock into bio-energy such as heat, electricity, fuel and gas. The process is used to replace the content of crude oil with biofuels in transportation needs while reducing the greenhouse gas emissions. The consumption of an alternative energy resource of renewable energy is increasing day by day due to the concern about climate change. The demand for fossil fuel energy is depleting by people because burning of fossil fuel creates many environmental problems. The carbon dioxide emits 1000 times more in case of fossil fuel as compared to biomass energy can be seen in Figure 4. According to the surveys the future energy sources would come up with CO2 neutral energy including solar and wind energy, bioenergy, nuclear fission and fusion, and fossil fuels with carbon capture technology [18]

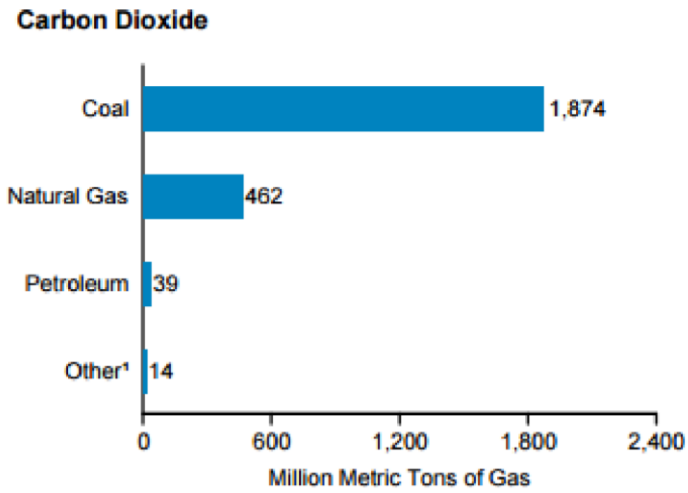

Figure 4. Carbon dioxide emissions from energy consumption in coal and natural gas [19]

The process consists two main steps are thermochemical and biochemical conversion, also mechanical extraction can be used during the production of energy from biomass. [20]

Thermochemical Conversion:

Biomass waste is an extraordinary source of producing biopolymer such as cellulose can be used as a raw material. The U.S. is one of the largest producing biological raw material, due to its excellent climate conditions that generates approximately 280 million tons of waste biomass (Committee on Bio-based Industrial Products, 2000) which further converted into 3 main products: two of them relates to heat and power generation and fuel for vehicles (biofuel) and the last one as a chemical feedstock. The residues including forest residues, primary mill residues, agricultural, urban wood waste can be used as feedstock for low-cost biomass energy production, it contains high content of cellulose and hemicellulose are shown in Table 3. [21] (Teixeira, 2010)

Table 4. Content of cellulose, hemicellulose and lignin in the discarded lignocellulose waste [21]

Lignocellulose waste	Cellulose (wt %)	Hemicellulose (wt %)	Lignin (wt %)
Barley straw	33.8	21.9	13.8
Corn cobs	33.7	31.9	6.1
Corn stalks	35.0	16.8	7.0
Cotton stalks	58.5	14.4	21.5
Oat straw	39.4	27.1	17.5
Rice straw	36.2	19.0	9.9
Rye straw	37.6	30.5	19.0
Soya stalks	34.5	24.8	19.8
Sugarcane bagasse	40.0	27.0	10.0
Sunflower stalks	42.1	29.7	13.4
Wheat straw	32.9	24.0	8.9

Several studies show that there is a possibility to produce biopolymer from the agro- industrial waste as it consists cellulose in it [22]. The thermochemical process can be done in four major steps including, combustion, pyrolysis, gasification and liquefaction are shown below in Figure 5. The aim of this process is to convert the feedstock by the process of gasification to convert it into hydrocarbons and liquefy biomass in the process of pyrolysis with high temperature into liquid fuel. [23]

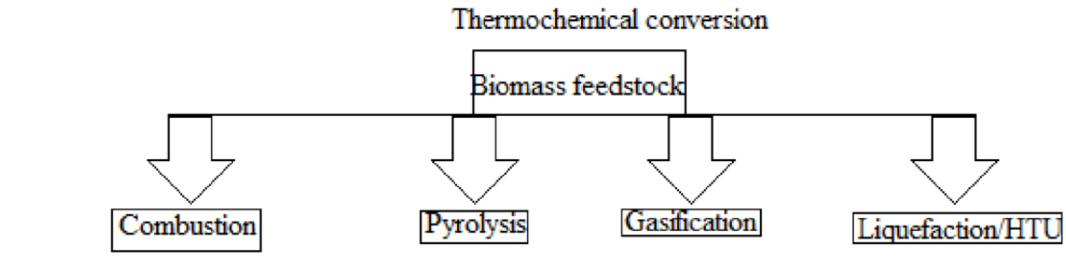

Figure 5. The processes in thermochemical conversion of biomass [20]

Combustion: The conversion of chemical process into heat process, by burning biomass in the air at temperature around 800-1000˚C. The moisture content needed to the biomass for the combustion process is <50%, the better conversion processes require high moisture content. [20]

Gasification: As the name indicates the conversion of biomass into combustible "gas" with the help of partial oxidation and high temperature around 800-900˚C. The product gas used as a feedstock syngas. The production of syngas from the gasification process are resulting in the production of methanol and hydrogen which is helpful in the biofuel. [20]

Pyrolysis: The process occurs in anaerobic conditions where the biomass transform into solid charcoal, liquid oils and gaseous fractions with the help of heating processes at the rate of different temperature and time as shown in Figure 6. The biochar used as a soil amendment for the growth of plants and stored as a stable carbon source in the ground that helps in decreasing the amount of carbon dioxide in nature. [24] There is possibility to produce bio-oil from the flash pyrolysis process at low temperature by condensation of vapours into liquid bio-oil, which can be used in engines and turbines. Most pyrolysis processes are designed for biofuel production. [20]

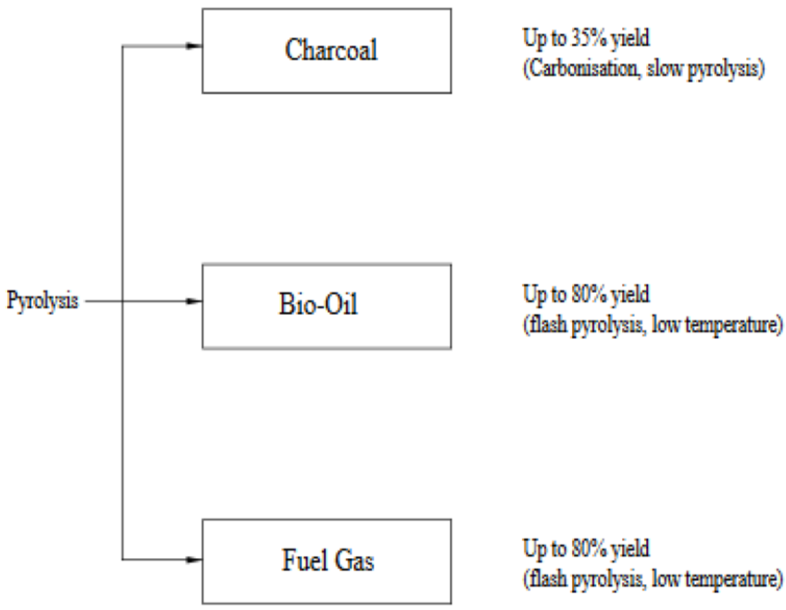

Figure 6. Generation of three energy products from the process of pyrolysis. [20]

Liquefaction and hydro thermal upgrading (HTU): The process of HTU is relatively an expensive process as compared to pyrolysis in which biomass converts into partly oxygenated hydrocarbons in the wet environment at high pressure. On the other hand, liquefaction converts the biomass into stable liquid hydrocarbon at low temperature and high hydrogen pressure. [20]

Biochemical Conversion:

The biochemical process mainly consists pre-treatment, saccharification /hydrolysis, fermentation as shown below in Figure 7. Anaerobic digestion (AD) is another way to convert organic matter into CO2, methane with the help of microbial activity, the process follows 4 steps as hydrolysis, acidogenesis, acetogenesis and methanogenesis [25]. The plants are the main feedstock such as sugar crops and starch based crops are fermented by yeast and fungi that converts the sugar into ethanol. The conversion of lignocellulosic material is more complex into simple form; thus, biomass undergoes the process of hydrolysis in two different ways, chemically with acids (H2SO4, HCl, Dilute acid) also known as acid hydrolysis and enzymatically into sugars, proteins with the help of enzymes and bacteria like Bacteroides spp. and Clostridium spp. [26]

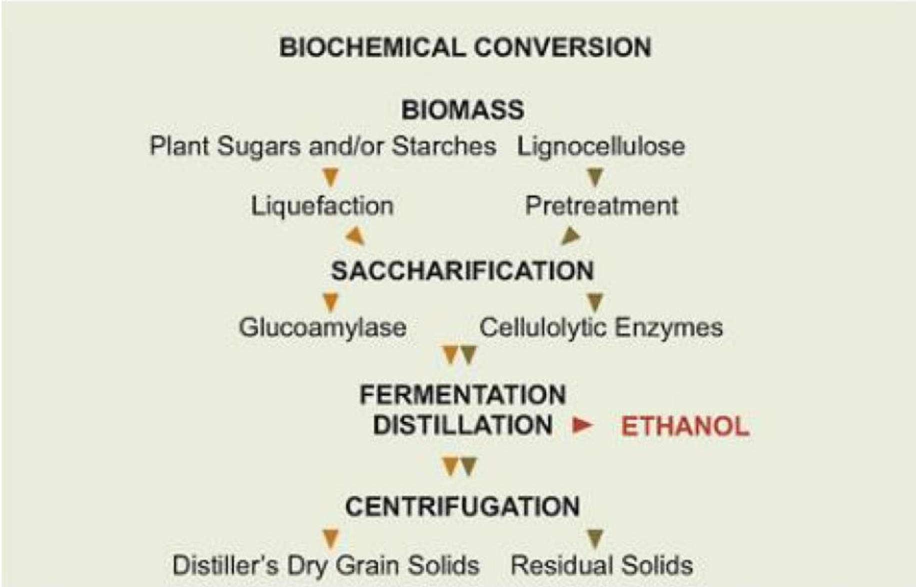

Figure 7. *Steps involved in biochemical conversion of biomass* [27]

Utilizing biogas into fuel cell:

Hydrogen is light weight, simple and most abundant chemical element in the planet. Fuel alcohol can be obtained from biomass containing forestry, agricultural resources, industrial processing residues, and municipal wastes are fully renewable source which helps in reducing greenhouse gas emissions [28] (Islam, 2008). During anaerobic digestion, the mixture of gases (biogas) formed at different percentage such as 50-75% methane and 25-45% carbon dioxide [29] whereas in the thermochemical process of gasification and pyrolysis c;onverted biomass into gaseous state with the production of syngas hydrogen which contains 65% of hydrogen, 30% carbon dioxide and 5% of other elements which are further purified/separate for obtaining high purity hydrogen by elimination of other residues as shown in Figure 8. The purified hydrogen is used in low cost fuel cell PEM (polymer electrolyte membrane) for generating heat and power. [30] Both processes are suitable for obtaining biogas hydrogen, but the process of gasification is more suitable hence it is mainly deal with gases. The production of carbon dioxide in this process are environmentally safe because it came from biomass, thus this process is sustainable and economically feasible. [31]

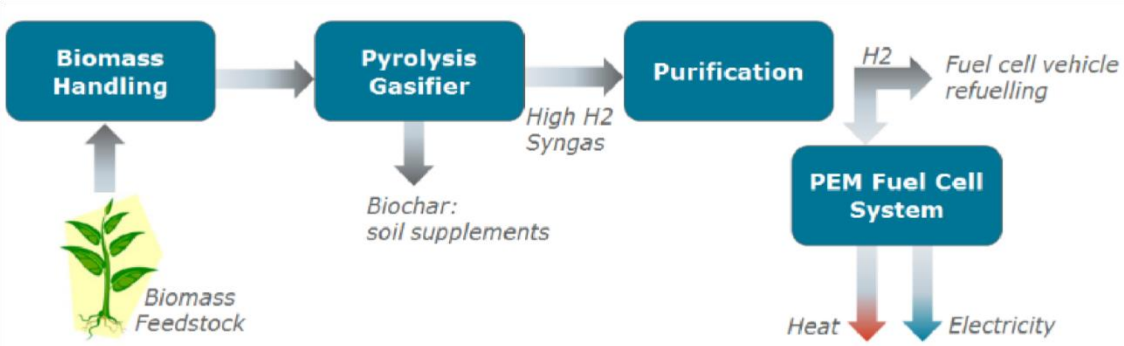

Figure 8. Illustration the process of producing purified hydrogen gas from the biomass feedstock [30]

Conclusion:

It is concluded from the report that the use of petro based polymers have numerous adverse impact on atmosphere. Most of the plastic waste ended up in the landfill creates pollution with the accumulation of chemicals, only 10% of plastics has been recycled. On the other hand, biopolymers converted into biomass with the help of living organisms which later use as manure in plants. Disposal of bio-waste in landfill creates environmental problems, due to the huge production of CO2 and NH3. Since the waste contains large amount of sugars, carbohydrates and cellulose in them, to utilize them in ecofriendly way for industrial use with the help of bacterial fermentation in a cost-effective way is the best approach. Biomass can be converted into biofuel, biogas and bio-oil in eco-friendly way with the help of mutagenesis technique. The use of bioplastics over conventional plastics limits due to its high cost but there are several other options to produce bioplastics from the biomass feedstock in cost effective way. The future market for biopolymers are significantly increasing due to its sustainability. The biotechnology of microorganism gives a new hope to bioplastic production could significantly influence the production to compete with current barriers. The motive of the review was discussed, and excellent results would have achieved which is a way to control marine pollution with the increasing use of biopolymers for the green economy.

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