

# **INCREASE THE USAGE OF BIOPOLYMERS AND BIODEGRADABLE POLYMERS FOR SUS- TAINABLE ENVIRONMENT**

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<p><b>Abstract:</b></p> <p>The research has been performed to understand the problem of pollution caused by non- degradable polymers in various parts of India, which is responsible for several environmental problems and health diseases. The research is providing a sustainable way to solve this problem with the help of existing biopolymers and cost effective ways to produce the eco-friendly plastics from the industrial food waste in order to obtain polysaccharides and sugars, instead of contributing to the global food crisis. The biotechnology, Mutagenesis, has excellent solutions involving synthetic biology for the synthesis of genetically modified strains that has been grown on renewable feedstock for improving the production of PHAs and extraction of lignin from cellulose in suitable ways. The motive of this research is to aware people of the hazards of using plastics and to inspire them into opting to use the sustainable way, with the utilization of eco-friendly plastics to maintain nature's balance. The process of biodegradation and composting has been briefly explained to acquire deep knowledge about end of life options for biodegradable polymers in suitable environments without leaving toxic residue behind. The idea of using aerobic and anaerobic digesters for bio-waste and biopolymers is one of the best options to reuse the biomass in energy conversion techniques rather than to end up in landfill. In addition, various experiments/methods have been discussed that enable the efficient use of biopolymers as this could be the best approach to solve the problem of marine pollution.</p>	
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# CONTENTS

<b>List of abbreviations, acronyms .....</b>	<b>8</b>
<b>1 Introduction.....</b>	<b>11</b>
1.1 Origin of Plastic .....	11
1.2 Plastic and its Applications.....	12
1.3 Main Objectives of the study .....	13
<b>2 Literature review .....</b>	<b>14</b>
2.1 Marine pollution .....	16
2.2 Climate variability .....	16
2.3 Chemical pollution from plastics.....	17
2.4 News regarding initiatives against plastics pollution .....	18
<b>3 Sustainability .....</b>	<b>19</b>
3.1 Plastic waste in India .....	20
3.2 Method of Recycling plastics in India .....	21
3.3 3 R's – reduce, reuse and recycle.....	22
3.4 Worldwide Conservation and Environmental Organizations .....	23
<b>4 An alternative to synthetic polymer materials.....</b>	<b>25</b>
4.1 Some Important Definitions .....	27
4.2 Types of Biopolymers.....	29
4.3 Cost effective methods of producing biopolymers .....	40
4.3.1 <i>Biotechnology in biopolymer production.....</i>	<i>42</i>
4.4 Biomass energy conversion .....	52
4.4.1 <i>Thermochemical Conversion.....</i>	<i>53</i>
4.4.2 <i>Biochemical Conversion.....</i>	<i>56</i>
4.4.3 <i>Utilizing biogas into fuel cell .....</i>	<i>62</i>
<b>5 Biodegradation process.....</b>	<b>63</b>
5.1 Enzymatic degradation .....	65
5.1.1 <i>Degradation site of plastic material .....</i>	<i>68</i>
5.1.2 <i>Abiotic methods of degradation.....</i>	<i>70</i>
5.2 Factors that affect biodegradability .....	72
5.3 Biological Methods of Degradation.....	74

5.4	The process of industrial composting (EN 13432) .....	77
5.4.1	<i>Factors affecting the composting process</i> .....	78
<b>6</b>	<b>Standard, Certification and Labels .....</b>	<b>79</b>
<b>7</b>	<b>Results .....</b>	<b>83</b>
<b>8</b>	<b>Discussions .....</b>	<b>85</b>
<b>9</b>	<b>Conclusions .....</b>	<b>86</b>
<b>10</b>	<b>References.....</b>	<b>87</b>

## Figures/Graphs

Figure 1. Energy requirement for synthetic polymers compared to biopolymers (Piemonte, 2011) .....	13
Figure 2. Flow chart of the Harmful effects of plastic pollution.....	15
Figure 3. Late summer Arctic sea Ice Extent [Visualization by Author, Data source. (Brown, 2015)] .....	17
Figure 4. Harmful gases emits from the Open burning and landfill fires in Mumbai (Ranjith, 2012).....	18
Figure 5. Basic concepts of a sustainable product design (Edwards, 2010).....	20
Figure 6. Depicts the ban of plastic bags in California and US subsequently increases from the year 2007-2015[Visualization by Author, data source (Brown, 2015)] .....	24
Figure 7. Basic idea of research.....	26
Figure 8. The process of Biological degradation of biodegradable polymers (Šprajcar, 2012).....	27
Figure 9. Understanding the three different categories of bioplastics (Novamont, 2016) .....	28
Figure 10. Types of EPS microbial polysaccharides with their chemical structure (Öner, 2013).....	32
Figure 11. Chemical structure of all biodegradable aliphatic polyesters (Scott, 2002)..	36
Figure 12. The process of converting biomass into ethanol with the help of genetically modified strains (Ha, 2011).....	46
Figure 13. Method of extraction of pectin with hot water from the orange residues (K. Rezzadori, 2012).....	48
Figure 14. The flow chart representing the production of Bio-oil with the process of pyrolysis (K. Rezzadori, 2012).....	49
Figure 15. Method of extraction the polysaccharides from tomato and lemon industrial waste (Preedy, 2008) .....	50
Figure 16. Carbon dioxide emissions from energy consumption in coal and natural gas (EPA, 2016). .....	53
Figure 17. The processes in thermochemical conversion of biomass (Mckendry, 2002) .....	54

Figure 18. Generation of three energy products from the process of pyrolysis. (Mckendry, 2002) .....	55
Figure 19. Steps involved in biochemical conversion of biomass (council, 2009) .....	56
Figure 20. Mechanism of Saccharification done by three enzymes EG (endoglucanases), CBH (exo glucanases) and BG ( $\beta$ -glucosidase) (French, 2009) .....	58
Figure 21. Conversion of lignocellulose into simple monomers (Kumar, 2009) .....	58
Figure 22. Illustration the process of Organosolv pretreatment of lignocellulosic biomass (Clifford, 2015) .....	59
Figure 23. The Bioprocesses steps in Biogas production within anaerobic digestion (Nayono, 2009) .....	61
Figure 24. Illustration the process of producing purified hydrogen gas from the biomass feedstock (Ballard, 2013) .....	63
Figure 25. The first step of fragmentation in the process of degrading plastics (BPI, 2003-2016) .....	64
Figure 26. Illustrate the second step of biodegradability of the polymers (BPI, 2003-2016) .....	65
Figure 27. Mechanism of degradation via Hydrolysis (Smith, 2005) .....	66
Figure 28. Mechanism of hydrolysis within polymer (Chhaya Engineer, 2010) .....	67
Figure 29. Criteria of degradation in Bulk Erosion and Surface Erosion (Gajjar, 2014) .....	69
Figure 30. Abiotic degradation processes of Biopolymers (Grabowska, 2010) .....	70
Figure 31. Schematic representation of Norrish II type reaction for photo degradation of PLA (Niaounakis, 2015) .....	71
Figure 32. The color lightning within 6-12 weeks on PHB and PHBV by photo degradation method (Fechine, 2011) .....	71
Figure 33. The rate of biodegradation in terms of melting temperature (Tokiwa, 2009) .....	73
Figure 34. Aerobic and Anaerobic Environments for biodegradation of plastics (Bastioli, 2005) .....	74
Figure 35. Test environments for Biological degradation of biopolymers (Wilde, 2013) .....	75
Figure 36. End of life options for biodegradable plastics (J. H. Song, 2009) .....	76
Figure 37. Disintegration of Biopolymer sample within 90 days in industrial composting (Wilde, 2011) .....	78

Figure 38. Results of the experiment performed to check the level of biodegradability (Kershaw, 2015) .....	84
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## Tables

Table 1. Classification of biopolymers (Niaounakis, 2013).....	29
Table 2 Methods of extraction of microbial polysaccharides from Biomass of Food waste (Öner, 2013) .....	41
Table 3 Methods of extraction of microbial polysaccharides from Biomass of Food waste (Öner, 2013) .....	42
Table 4. Most commonly used microorganisms (GMMs) for the process of gene transfer methods (Han, 2004) .....	43
Table 5. Synthetic modified strains for the production of PHA from cheap renewable resources (Chee, 2010) .....	44
Table 6. Consuming ethanol from biomass by Synthetic biology of yeast ( <i>saccharomyces cerevisiae</i> ) (Giese, 2015).....	45
Table 7. Extraction techniques for obtaining polysaccharides from industrial food waste (Poli, 2011) .....	47
Table 8. Content of cellulose, hemicellulose and lignin in the discarded lignocellulose waste (Teixeira, 2010) .....	54
Table 9. Certification institutes in the field of biodegradability (Wilde, 2013) .....	83

## LIST OF ABBREVIATIONS, ACRONYMS

ASTM -American society for testing and materials

AD- Anaerobic digestion

BPA- Bisphenol- A

BC-Bacterial cellulose

C/N or C: N- Carbon Nitrogen ratio

DDT- Dichlorodiphenyltrichloroethane

EPS- Exopolysaccharides substances

GMMs- Genetically modified microorganism

HDPE-High density polyethylene

LDPE-Low density polyethylene

PAHs- Polyaromatic hydrocarbons

PCBs-Polychlorinated biphenyls

PCDFs- Poly dibenzofurans

PCDDs- Polychlorinated dibenzodioxins

PE-Polyethylene

PP-Polypropylene

PS-Polystyrene

PET-Polyethylene terephthalate

PGA-Poly glycolic acid

PLA-Poly lactic acid

PCL-Polycaprolactone

PHA- Polyhydroxyalkanoate



PHB-Polyhydroxybutyrate  
PHV- Poly Oxy Valerate  
PHBV-Poly (3-hydroxybutyrate-co-3-hydroxyvalerate)  
PADCs-Poly (alkylenedicarboxylates)  
PBA-Poly (butylene adipate)  
PBS-Poly (butylene succinate)  
PBSE- Poly (butylene sebacate)  
PVOH/PVA-Polyvinyl alcohol  
PDL- Poly ( $\epsilon$ -decalactone)  
PVL- Poly (valerolactone)  
PDO- Poly (para-dioxanone)  
PMLA- Poly ( $\beta$ -malic acid)  
PPL – Poly ( $\beta$ - propiolactone)  
PESE- Poly (ethylene sebacate)  
PEDe- Poly (ethylene decamethylate)  
PEA- Poly (ethylene adipate)  
PEAz- Poly (ethylene azelate)  
PESu- Poly (ethylene suberate)  
SB- Synthetic biology  
SFF- Solid state fermentation  
MMC- Mixed Microbial Cultures  
FDCA- 2-5 Furandicarboxylic acid  
TFA- Trifluoroacetic acid

## **FOREWORD**

I would like to thank my advisor, Mr. Jyrki Ant- Wuorinen, Chairman of Plastex Oy who has been suggesting the topic of biopolymers. I would like to acknowledge further to Merja Koskinen, Director of Ecovid who has motivating and teaching me a lot of new things regarding establishing a business and providing me deep knowledge about the product development. I am grateful to have Mirja Andersson as my supervisor and co-advisor for providing me some useful comments and advices during my research. Thanks to my family for always being there as a source of inspiration and support.

# 1 INTRODUCTION

## 1.1 Origin of Plastic

A commonly used plastic bag is made from Polyethylene polymer which is originated from petroleum product. Petroleum is a naturally occurring, complex mixture of carbon and hydrogen compounds which contains sulphur and other elements like nickel, vanadium in it. Due to its high concentration of heavy metals and chlorinated hydrocarbons like DDT and PCB, petroleum is quite toxic for plants and animals when release to the environment. (Jensen, 2013)

Drilling → Separation → Conversion → Upgrading

In the process of petroleum extraction, crude petroleum has been drilled from the area where the organic sedimentary are buried for several years and shipped by tanker to refineries for further three steps. The first step is separation/fractionating, the process in which hydrocarbons are being separated by the process of evaporation/condensation at different temperatures. Following the process, the next step is generally cracking where the molecular weight and shape of the compounds is changed by catalysts like platinum with the presence of heat, pressure. Refined petroleum serves as fuel to various industries and factories for making plastic products and fertilizers. (Jensen, 2013) The ethylene is formed from this refining process in order to make plastic products. It is moderately dangerous, toxic carrying carcinogenic substance, have greatest risk to the workers due to inflammable and explosive nature (Assaff, 1984).

During the refining process several type of toxic gases are emitted to the environment carrying harmful elements like hydrocarbons, particulates, nitrous oxide, carbon-monoxide and Sulphur dioxide, which remain in the petroleum after the process of fractionating. These harmful gases can cause acidification in ecosystem which results in harmful acid rain.

### *Oil pollution*

According to researchers approximately 706 million gallons of waste oils are drained into bodies of water each year (Embach, 2007). There are several activities that are re-

sponsible for this pollution such as offshore drilling, production operations and spills, and oil leaks from storage tanks and large gallons while transporting oil, which goes straight into oceans. The oil in the sea acts as a poison to aquatic life with its toxic substances, sometimes leading to death and interruption of the food chain. Due to these accidents, several environment conservation conscious organizations are taking initiatives to prevent the oil spills within the oceans. There are various agreements introduced to overcome this problem, for example in one agreement, the aim is to encourage the tanker owner to clean up oil spills. (Anyanova, 2012) Oil spills in the oceans actually account for a small fraction of ocean pollution, the majority of the ocean pollution comes from other sources like trash on land, sewage, industrial waste, agricultural runoff, garbage dumping and harmful chemical spills. Pollution from burning forests and coal factories releases toxic gases in the air and is also absorbed by the ocean resulting in biomagnification (excess amount of chemicals) for the aquatic life present in the ocean (Dijl, 2015)

## **1.2 Plastic and its Applications**

Plastic has become a useful and versatile material that is used in several applications like product packaging, household products, garden applications, vehicles as well in aerospace. The large plastics market comprises of easily available, cheap, flexible, durable, and lightweight products. Plastics are of two types: Thermoplastics, a plastic which can be melted and recycled, and Thermoset. For example, common Thermoplastics include PP, PE, Polyamide, PS and PET. Thermoset, as the name indicates, is a plastic that stays permanently and cannot be melted by heating because its polymer chains are bonded firmly with meshed crosslinks like polyurethane, epoxy resin, and unsaturated polyester (Jain, 2014) . The conventional plastic does not undergo degradation and thus produces pollution. The alternative for this problem is to enhance the use of biodegradable plastics as they take less time to decompose or breakdown after being discarded or with the process of composting they mix with soil and degrade in it by microbes and bacteria which actually increase the fertility level of the soil. The life of biodegradable plastic starts from the renewable resources such as starch, cellulose and polysaccharides and ends in cleaner atmosphere as compared to petroleum based plastic, which actually pollutes the environment during manufacturing and disposing activities.

During the production of biodegradable plastic, only half of the energy is used, that means it is possible to make twice the amount of biodegradable products using the same amount of energy as described in Figure 1. The process of recycling is also much easier with the biodegradable plastic. Furthermore, they cause no harm to the environment, as there are no toxins or chemicals residue produced as a byproduct. (Musa, n.d.)

Type of plastic	Energy requirement, MJ/kg	Global warming, kg CO <sub>2</sub> eq/kg
From non-renewable sources		
HDPE	80.0	4.84
LDPE	80.6	5.04
Nylon 6	120.0	7.64
PET	77.0	4.93
PS	87.0	5.98
PVOH	102.0	2.70
PCL	83.0	3.10
From renewable sources		
TPS	25.4	1.14
TPS + 15% PVOH	24.9	1.73
TPS + 60% PCL	52.3	3.60
PLA	57.0	3.84
PHA	57.0	Not Available

Figure 1. Energy requirement for synthetic polymers compared to biopolymers (Piemonte, 2011)

### 1.3 Main Objectives of the study

The aim of this research is:

- To aware people about the concerns regarding environment, limited fossil fuel sources, climate change, greenhouse gas abatement and global warming.
- Due to inappropriate disposal and burning waste in open spaces causes environmental problems.
- The motive of this thesis to gather all researches regarding new biotechnology related biopolymer production and finding solution for expanding clean and wildlife friendly renewable energy (Bio-fuel, Bio-diesel).
- To acquire the deep knowledge about the basic properties of different kind of biopolymers, with their renewable resources and applications.

- Achieving the brief knowledge about the cost effective methods for biopolymer production from cheap renewable resources.
- Understanding the biological degradation process of biopolymers that ends up in suitable & healthy environment with the help of composting.

## **2 LITERATURE REVIEW**

Plastic pollution in India: The production and consumption of plastics products is increasing day by day due to its inexpensive, extremely efficient and excellent mechanical properties. The additives inside plastic are not chemically bound with the polymeric chain hence they migrate from plastic into the soil. The leachates that come from plastic waste in the landfills are causing various diseases. The most common chemicals that are found in soil are petroleum hydrocarbons, heavy metals, pesticides and solvents. (Rajesh kumar Mishra, 2016) According to plastic EU 2015, almost 8 million tons of plastics entered landfills every year, where it may take decades to decompose completely (Europe, 2015). The pollutants leaked from the plastic debris have harmful effects that are shown in Figure 2 below.

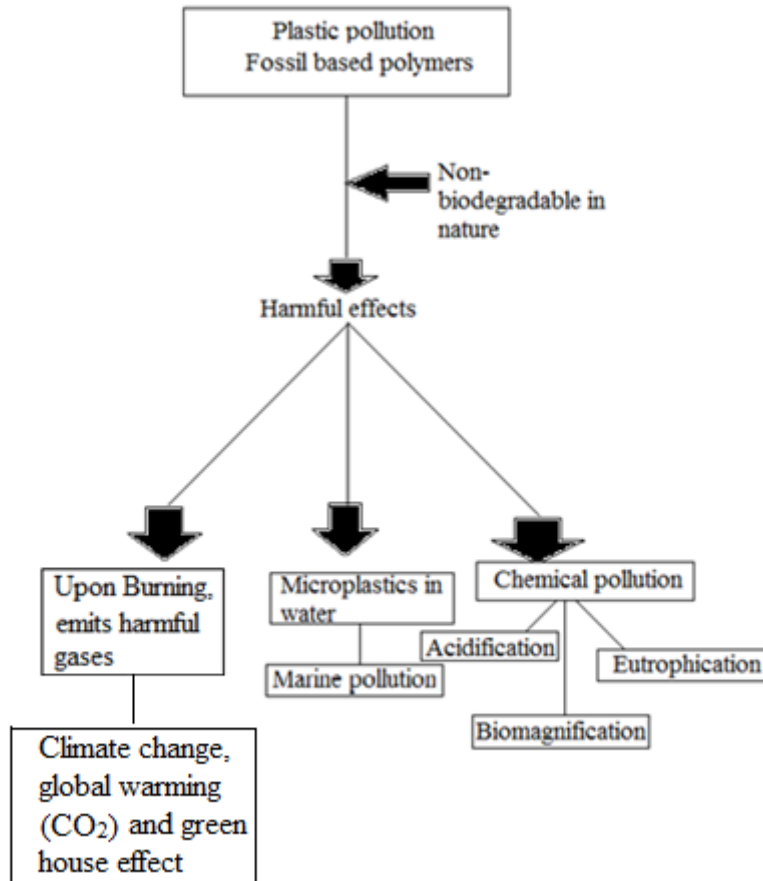


Figure 2. Flow chart of the Harmful effects of plastic pollution

Most of the plastics have been used for packaging. Lots of waste is found littered on streets, corners, cities and towns in India. Stray animals are ingesting the waste mistakenly for food, which often results in death. The waste management system is relatively poor in the country, due to lack of financial resources, inefficient institutional arrangement, inappropriate technology, and weak legislative measures. It seems rather difficult to overcome this problem. (Vijay Kumar, 2013) In the year 2012, the government banned all kinds of plastics bags under The Environment Protection Act and impose penalty amounting to around 1 lakh rupees along with a prison sentence of 7 months. According to a survey, even after the ban, majority of the people are manufacturing the plastic bags illegally, in which 62% of vendors and 78% consumers are still using plastic carry bags for different activities. There is a great need for proper maintenance and public awareness to solve this problem (Mahesh, 2014). The waste from plastic has af-

affected many other areas including marine, coastal and climate issues are discussed below in sections 2.1, 2.2 & 2.3.

## **2.1 Marine pollution**

The term Biomagnification stands for the increasing contaminated chemicals which affects simultaneously food chains. According to the several surveys, up to 80% of waste enters in the marine and coastal shorelines from which 10% is microplastics. In addition, around 267 species including turtles have eaten this waste mistakenly for food and water. It has been noticed that human activity is responsible for extinction of species. (Lynne Eagle, 2016) The micro plastic in the oceans disturbing the natural food chain, due to its small size the tiniest organisms like plankton ingesting the plastic, which further causes problems for the larger animals that swallow them as food. In this way whole chain is being disrupted and is dying with this poison. In 2010, according to a study there were 4.8 million- 12.7 million tons of micro plastic washed into the sea which was later found in the stomach of sharks. (Forster 1) Researchers say that this problem leads to increasing the mortality rate of the endangered species like perch by stunting their growth and appearing to change behaviour. Animals higher up the food chain such as seals can have contamination levels which are millions of times higher than the water in which they live. Polar bears for example, which feed on seals, can have contamination levels up to 3 billion times higher than their environment. People become contaminated either directly from household products or by eating contaminated seafood and animal fats. Evidence is mounting that a number of man-made chemicals can cause serious health problems - including cancer, damage to the immune system, behavioural problems, and reduced fertility. (Gunther, 2016)

## **2.2 Climate variability**

Plastic pollution and climate change are linked together in a way that both of them have their roots with fossil fuels. Many other factors such as production of plastic, burning of fossil fuels, greenhouse effect, deforestation, and industrial pollution are disturbing the environment with the increasing effect of gases in the air like methane, nitrous oxide,



and  $\text{SO}_2$  are increasing the level of carbon dioxide in ecosystem. The summers are getting hotter and winters colder. The production of ice in glaciers is decreasing significantly every year due to change in climate. Figure 3 shows the progressively higher temperatures caused by global warming have led to greater summer melting that diminishing the snowfall due to late winters and early springs, resulting in imbalance in natural climate pattern. Animals like polar bears, penguins are dying with this problem. The ice melting from the glaciers causes a rise in the sea level, which can result in devastating disasters like floods in the low-lying areas. (Glazner, 2015)

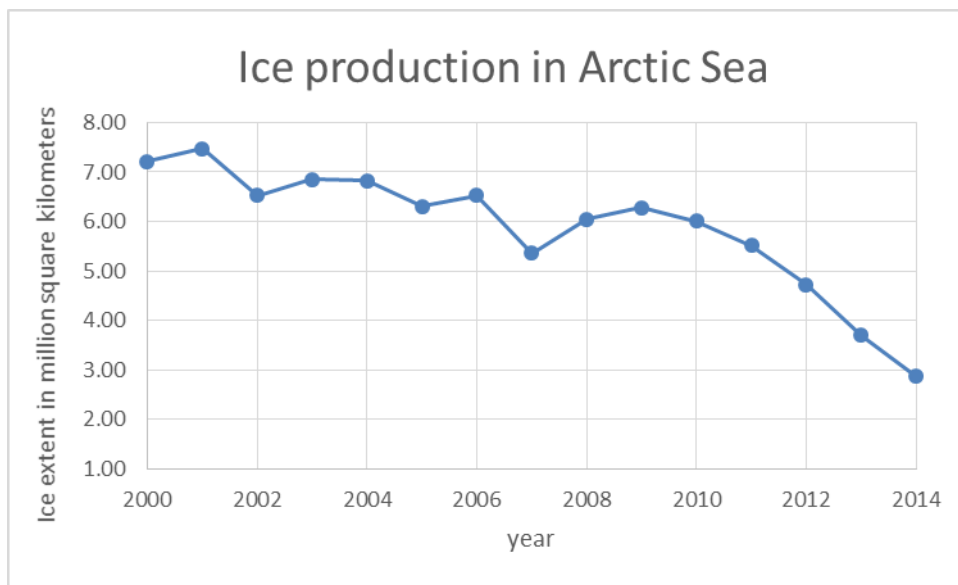


Figure 3. Late summer Arctic sea Ice Extent [Visualization by Author, Data source. (Brown, 2015)]

## 2.3 Chemical pollution from plastics

Chemical pollution including global warming, acidification, aquatic and terrestrial eutrophication and carcinogenic substances are caused by energy generation while mining of coal, during the processing of uranium, huge amounts of harmful gases are emitted to the atmosphere. The factors influencing the increase of pollution includes growing technology, high population, great consumption of energy, transportation and other industrial activities worsening the situation of urban areas. The burning of plastics in an open areas emits various harmful gases in the atmosphere including alkanes, alkenes, chlorinated and aromatic hydrocarbons (PAHs, PCDDs, and PCDFs). As shown in Figure 4, several tons of harmful gases are accumulated in the ecosystem (Ranjith, 2012). Smog

forms from chemicals like carbon monoxide, nitrogen oxide and volatile particulates. In the manufacturing extrusion process when the melting temperature reaches at 150-300°, various chemical compounds are released to the environment due to ageing, long thermal exposure, intrinsic sensitivity and the attraction between polymers and additives. (He, 2015)

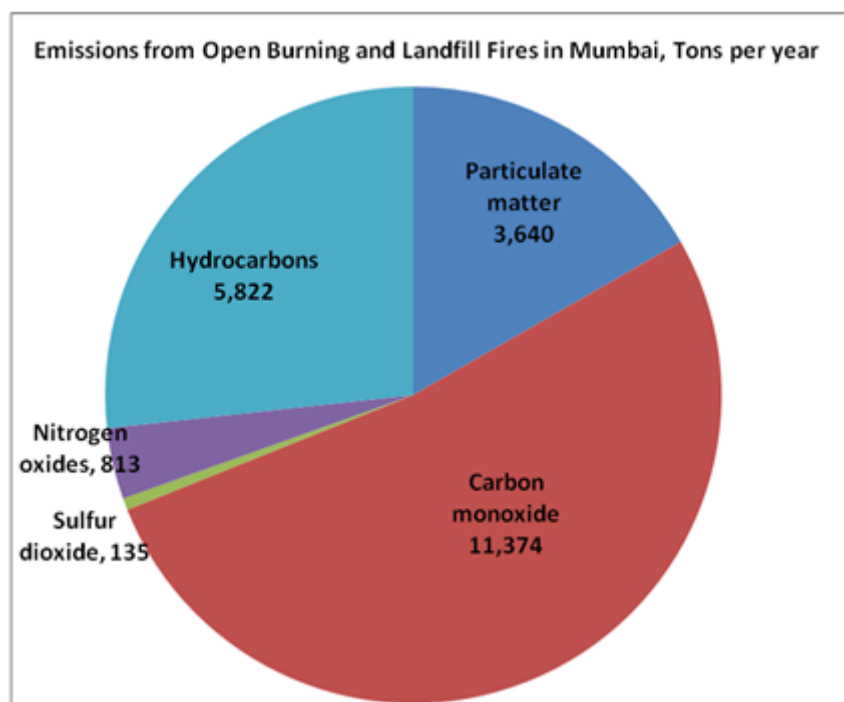


Figure 4. Harmful gases emits from the Open burning and landfill fires in Mumbai (Ranjith, 2012)

## 2.4 News regarding initiatives against plastics pollution

In the news people who are aware from the negative impacts of using plastics for daily purposes started to distributed cloth bags made from natural fibre and same time convincing people not to use plastic bags from market for daily basis. (Kumar, 2016)

United Kingdom became the first country to ban the use of micro-plastic in cosmetics and personal care products. The Department of Environment, food and Rural Affairs (Defra) announced plans to ban the micro-plastic pollution since it is more hazardous than big plastic pieces, because small size is more likely eaten by animals that disturbs the food chain. (MP, 2016)

Replacing the PET bottle into algae bottle, a student in Iceland named Jonsson invented new bottle for a sustainable environment by mixing powdered agar with water. Accord-

ing to him, people can even chew this bottle to taste agar which is often used in desserts. (Dockrill, 2016)

The direction of ministry in Sri Lanka and commerce Rished Bathiudeen are enforcing plastic producers to add standard on the plastic bottles. There are so many unknown local brands in market without any proper description about the product. (Desk, 2016)

The place named Thiruvananthapuram is the capital of largest city in India is now known as plastic-free place. They started a project called 'Ente Nagaram Sundara Nagaram' meaning 'my city beautiful city'. In this project they are seizing all plastic bags from the city and final dates has been announced to the shops to clear all plastic bags. (Service, 2016)

### **3 SUSTAINABILITY**

In the plastic, chemical substances like additives are commonly used to enhance the properties but at the same time it has negative impacts to the environment. A sustainable way to manufacture the plastic is to decrease the chemical diversity in it. The micro particles of the plastics are generally scattered in the ecosystem with natural activities like wind, water, birds or by organisms. Sometimes they clog up in the gutter and drains causing water and sewage problems. Extensive littering in the atmosphere is responsible for so many health related issues which lead to deaths and injuries of the organisms due to swallowing micro particles mistakenly for food. To decrease its extent of negative effects, for instance, it can be done by using recyclable bags made from natural fibres or using low- quality and single use articles. (Markus Klar, 2014)

The idea of sustainability which fulfils some basic encouraging concepts with non-toxic behaviour and safest to the environment. The toxic inputs in the product can cause so many serious problems such as poor air quality and poor surroundings of workstations. A proper sustainable product should meet the requirement of healthy atmosphere for the consumers (Edwards, 2010). Figure 5 outline the all major aspects needed for a sustainable design of the product. In case of bioplastic, farmers grows the plants and then it is polymerized and converted into final product by manufacturers, further continuing the process the product transports to the retailer and wholesalers that is how the consumers have it. The end of life options are composting, recycling without leaving any toxins behind that maintains the nature's balance for sustainability.

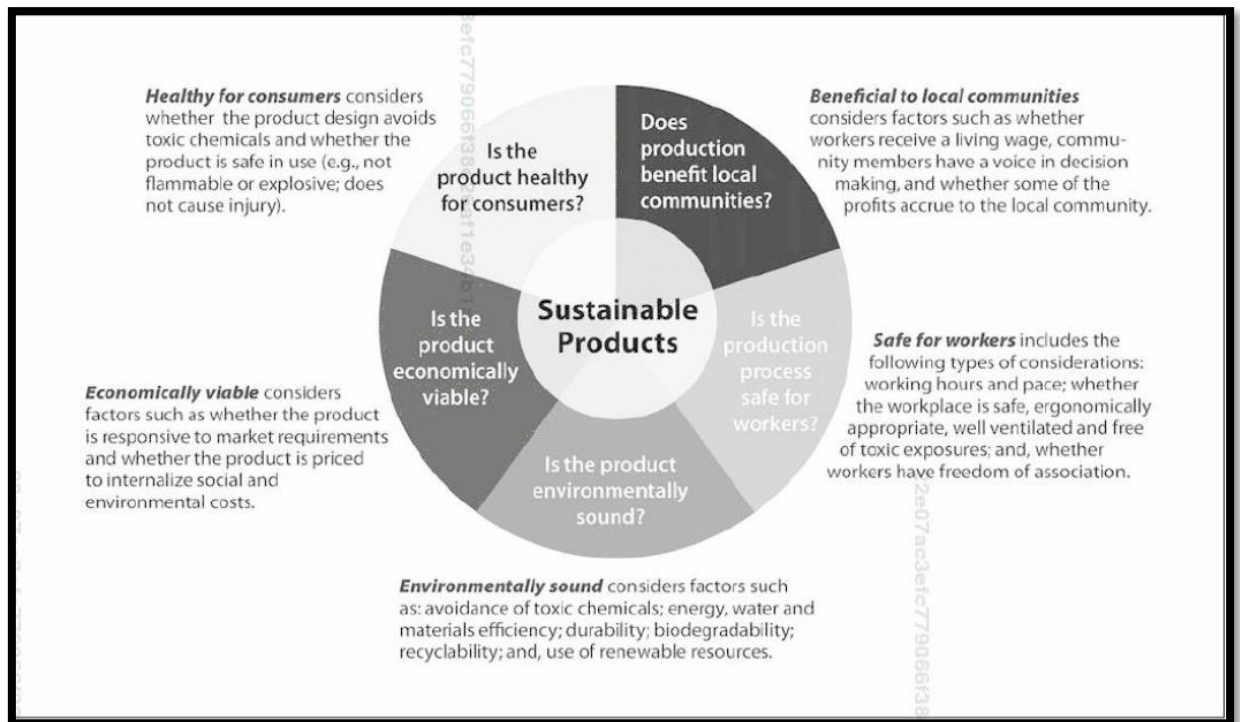


Figure 5. Basic concepts of a sustainable product design (Edwards, 2010)

### 3.1 Plastic waste in India

Due to the large population the country produced millions of tons of plastics waste every year since it is third largest polymer production country in the world. The plastic waste generated by per person is around 4.38 pounds. The disposal of plastic become a major problem due to its non-biodegradability behaviour. The method to recycling the plastics at large scale is relatively an expensive option due to several factors such as collecting, sorting, transportation, cleaning and processing as well as time consuming process. All the waste goes straight into landfills for accumulation and fill up landfills spaces and interacts with water to form hazardous chemicals. Waste from PET bottles are dramatically increased in India because it is non-returnable beverages due to the reason of 80% of people are selling their own local brands. (Markus Klar, 2014)

According to the Swedish society of nature conservation research, most of the plastic bottles have traces of BPA (Bisphenol) which can cause health issues like cancer and uterine infections. Over 50% of pollution in India is caused by polyethylene bags that are responsible for spreading waterborne diseases like malaria during rainy season when

the water remains in PE bags for longer time. Street animals like cows and bulls ingest the plastic from the roadsides and garbage which leads to constipation and finally death. Studies have found that around 30-60 kg plastic waste has been found in stomach of cows and other street animals. Mumbai, one of the largest metropolitan cities of India, has discarded 3 billion polyethylene bags every year and in 2005 there was an incidence of flood and the reason behind was the choking of plastic bags in the drainage system. (Markus Klar, 2014)

### **3.2 Method of Recycling plastics in India**

There are commonly three ways to discard the plastic waste in India, recycling, incineration and littering. The recycling sectors are not well developed, most of them are not registered themselves legally to evade rules and regulation such as tax laws, minimum wages laws and workplace safety. Children are working in these conditions which is unethical and illegal. Most of these recycling sectors are manual and done on the basis of experience over the years. During recycling the plastic, the first step is to wash the plastic products in soap water for removing all dirt, after using numerous times the soap water goes straight into drainage system without any prior treatment of high polluted water which further cause several waterborne diseases. The water needs to be treated properly before being discarded to open drainage system.

Impacts of recycling: The process of recycling done by small sectors with unorganized system. In most of the places work is done by small child, women and other illiterate people who need a source of money for their basic necessities. There is a great need of safety measures in these areas, people are doing work with bare hands, for sorting and segregation of the plastics. During recycling, the extrusion process takes place in an enclosed room where recycled pellets generate a lot of dust which cause respiratory problems for the workers due to poor ventilation system within the room. India is one of the warmest country where temperature reaches up to 50 degrees during summer, to work in this high temperature with the dangerous, explosive and hazardous chemicals can causes serious problems for an example due to constant exposure of carbon black die inhaled by workers during extraction get deposited inside lungs which later causes lung cancer. There is great need for enforcement of proper rules and regulations by the government

and to aware people about safety measures and environmental hazards. (Markus Klar, 2014)

### **3.3 3 R's – reduce, reuse and recycle**

According to the research a single plastic bottle will take more than 450 years to completely breakdown (Schmitt, 2005). It is really important to reuse the plastic into other useful activities for example the use of empty water bottle in flowering pots inside the home, as a holder for pencil and toothbrushes. Pollution can be minimized at some point by reusing and reducing plastic products. Instead of using PE bags, buyers must carry their own reusable fabric cloth from home for shopping. The poly bags are single use plastic carrier bags and often reused for some other household purposes.

To recycle the plastic is easy within industries and factories, for example when large amount of products are produced from the machine also with some defected parts due to temperature, heat and pressure. At the same time shredders are used to recycle those parts back into granules hence to reuse.

The discarded plastic waste in municipal waste are collected in mixed waste and further crushed to generate electricity [Vantaa Energia plant].

Process: In the waste bunker, waste cranes mix the waste into a mass of uniform quality at least for one week before the waste is fed into the incineration boiler. In the boiler, the waste converted into energy with the help of combustion process. The fly ash left behind from the waste has been recovered several times. The gas emits during the burning to waste “flue gas” reacts with lime to absorb harmful gases like Sulphur dioxide and activated carbon. The heat recovered from the flue gases is transferred into the district heating water knows as recycled heat to produce steam at temperature around 320°C.

### 3.4 Worldwide Conservation and Environmental Organizations

Following are the organizations who are contributing in cleaning eco-system from plastic wastes.

*Ocean conservancy (international coastal clean-up)*: It has been reported that in the year 2014 about 16 million pounds of trash been removed from 13,000 miles of beaches and different inland waterways. There are total 560,000 volunteers in 91 countries who are taking care of this responsibility. The funding provided to this organizations through governmental agencies, foundations and cooperations. Ever increasing ocean trash, plastic waste have worse impact on global crises for ocean waters, marine wildlife and habitat, human health and safety. Several countries who are participating in cleaning the oceans are USA, Philippines, Canada, Hong Kong, Peru, Ecuador, Mexico, Japan, Puerto Rico, India, Dominican Republic, Jamaica, Taiwan, Chile and United Kingdom. The items collected during the cleaning are most of them made from plastics such as bottle caps, cigarettes butts, straws, stirrers, food wrapper and beverage bottles. (Merkl, 2016)

*UNEP (United Nations environment programme)*: The aim of this community is to promote the wise use and sustainable development of the global environment. The organization taking care of marine environmental and land based activities.

*Greenpeace*: An international organization puts step towards for saving the arctic, forests, fighting global warming, protecting oceans, and promoting toxic-free sustainable food for living organism.

*Californians against waste*: It has been reported as about 8 metric tons of plastic debris enters the oceans every year. Reporters says that the amount of plastic waste will be more than the number of fishes in the lake by 2050, if there would be no control on throwing waste in oceans. Due of accumulation of plastic waste in sea, the aquatic life are ingesting microplastics, up to 90% of seabirds already eaten it. This is the reason why plastic bags banned in US and California, one reason related with cleaning the trash of plastic bags that is much more costly than the production of bags, hundreds of dollars costs annually to clean up the plastic pollution every year. Figure 6 representing,

that the total number of population in US and California has been charged for using the plastic bags and there is sudden increase after the year 2014. (waste, 2015)

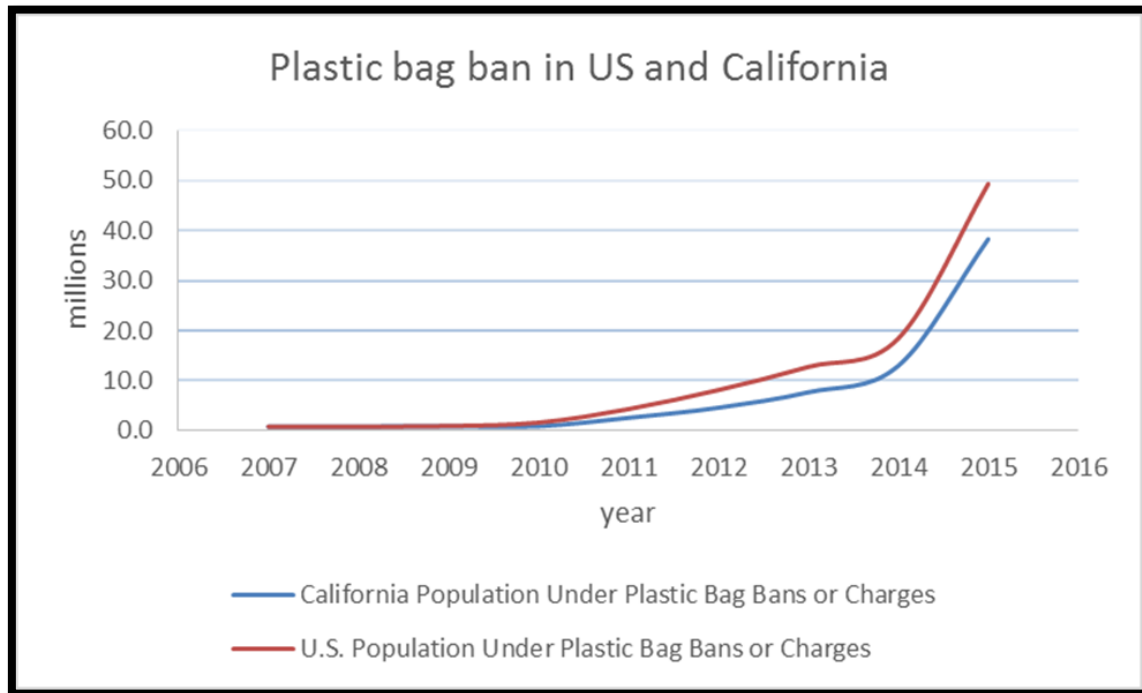


Figure 6. Depicts the ban of plastic bags in California and US subsequently increases from the year 2007-2015[Visualization by Author, data source (Brown, 2015)]

**National wildlife federation:** The organization helps in various sectors to save the wildlife, one of sector is related to reduce the carbon pollution and to minimize the limit of greenhouse gas emissions from power plants. According to the survey, to generate the electricity emits 41 percent of carbon dioxide (CO<sub>2</sub>) from the power plant. The aim of this organization is to ensure all countries to rapidly cut carbon pollution so that they can protect their citizens and wildlife from the impact of climate change. (O'Mara, 2015)

**Rainforest Action Network:** The public property has been sold to the companies for private fossil fuels extraction. Companies are benefited from these lands for digging the fossil fuels like coal mining, onshore & offshore oil and gas drilling, which gives the company millions of dollars per year. At the same time, people are not aware of damaging the environment while gaining the profit. Scientists agreed that instead of digging the earth for obtaining fossil fuels, it is easier to deal with the problem of global warming, because the CO<sub>2</sub> produced from coal, gas and oil are much more responsible for



carbon emissions in the environment. America's public lands and waters are being given away to some of the wealthiest energy companies in the world for as low as \$2 an acre. These companies have long track records of corruption, violation of Indigenous sacred sites, severe health impacts on communities, environmental destruction, evading payments, and jeopardizing the future of our climate. (Network, 2015)

*Tree people:* This organization believes in growing more and more trees, because more trees means more carbon dioxide (CO<sub>2</sub>) can be consumed by them hence, it is one of the sustainable way to decrease the global warming at some point. (Zucker, 2016)

*WWF global:* According to the organization over 80% of marine pollution comes from land-based activities. From plastic bags to pesticides, most of the waste produced on land eventually reaches the oceans, either through deliberate dumping, wind activity or from run-off through drains and rivers. Oil spills cause huge damage to the marine environment, but in fact are responsible for only around 12% of the oil entering the seas each year. According to a study by the US National Research Council, 36% of sewage waste runoff from cities and industries are entering into water bodies. Fertilizers and pesticides runoff from farms and lawns is a huge problem for coastal areas. The extra nutrients cause eutrophication flourishing of algal blooms that deplete the water's dissolved oxygen and suffocate other marine life. Eutrophication has created enormous dead zones in several parts of the world, including the Gulf of Mexico and the Baltic Sea. Solid garbage also makes its way to the ocean such as plastic bags, balloons, glass bottles, shoes, and packaging material. The garbage may come back to shore side to pollute beaches and other coastal habitats. In many parts of the world, 80% of urban sewage discharged into the Mediterranean Sea is untreated that give rise to eutrophication which is responsible for various diseases and finally leads to beach closures. (Gunther, 2016)

## **4 AN ALTERNATIVE TO SYNTHETIC POLYMER 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 this research (Fig. 7) 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<sub>2</sub>) and water and composting done by without leaving any toxic residue. However there applications are limited to some extent due to its high cost synthesis. (Narayan, 1993)

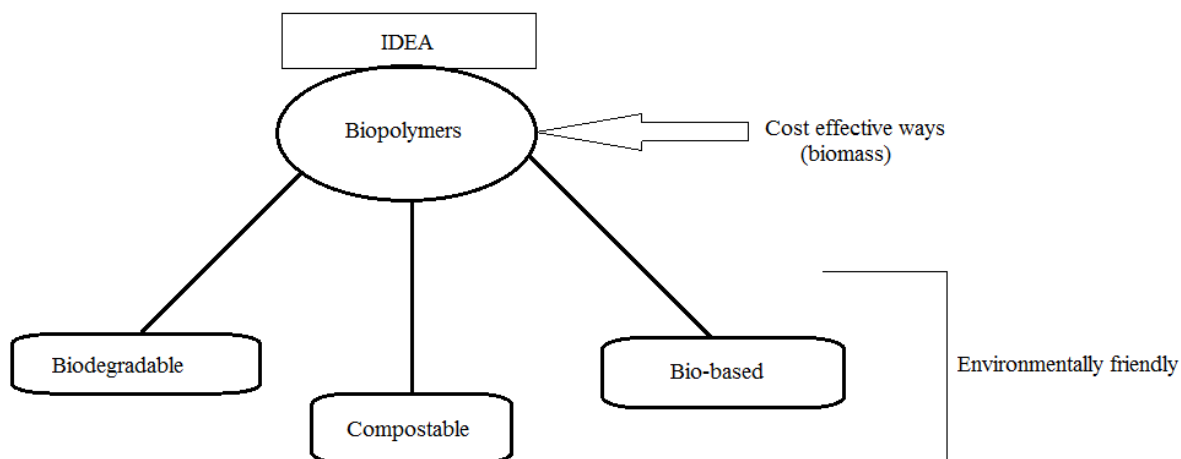


Figure 7. Basic idea of research

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 (CO<sub>2</sub>), 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. (Systems, 2012)

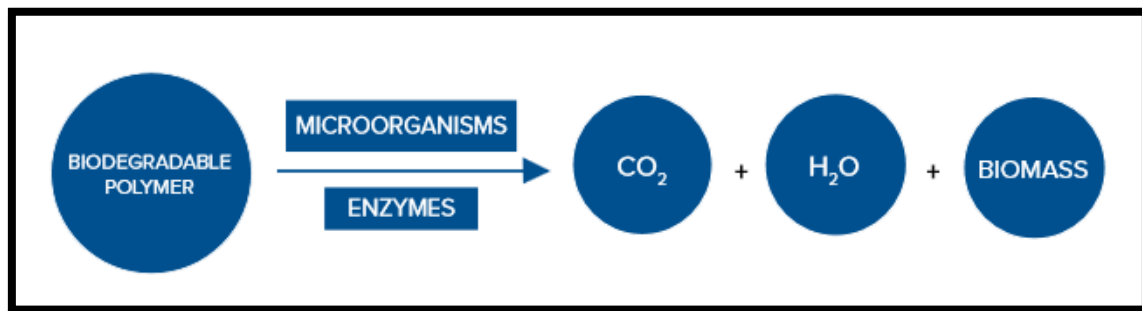


Figure 8. The process of Biological degradation of biodegradable polymers (Šprajcar, 2012)

## 4.1 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 degrade the polymer depends upon the thickness and composition of the material. (Jane Gilbert, 2015)

**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). (Kershaw, 2015)

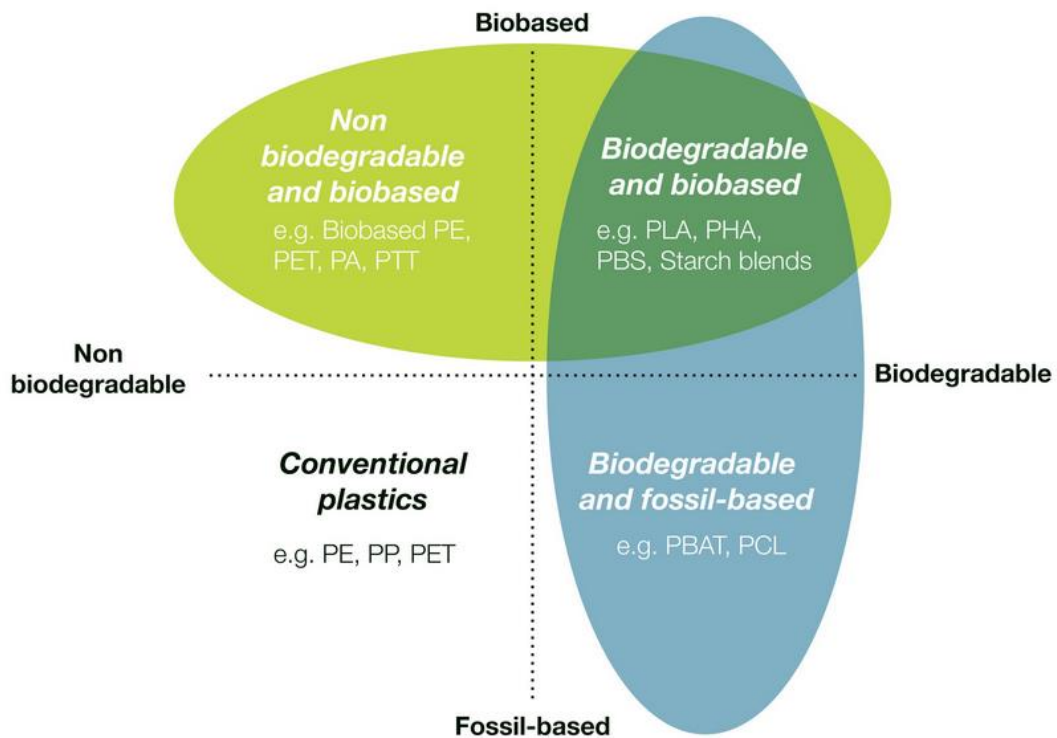


Figure 9. Understanding the three different categories of bioplastics (Novamont, 2016)

**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. (Jane Gilbert, 2015)

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

## 4.2 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 (Niaounakis, 2013)

Biodegradable				Nonbiodegradable
Bio-based			Fossil-based	Bio-based
Plants	Microorganisms	Animals		
Cellulose and its derivatives <sup>1</sup> (polysaccharide)	PHAs (e.g., P3HB, P4HB, PHBHV, PHBHH <sub>x</sub> )	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( $\epsilon$ -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, poly(hydroxyalkanoate); PHBHH<sub>x</sub>, poly(3-hydroxybutyrate-co-3-hydroxyhexanoate); PHBHV, poly(3-hydroxybutyrate-co-3-hydroxyvalerate); PHF, poly(hydroxy 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).

<sup>1</sup>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.

*In the first category consists of natural occurring biopolymers:*

**Polysaccharides:** They may be homo-polysaccharides composed of a single monosaccharides or can be hetero- polysaccharides containing two or more sugars. Homo-polysaccharides consists linear chains polysaccharides like pullulan, levan, curdlan or bacterial cellulose whereas hetero comprises with multiple copies of oligosaccharides, such as gellan and xanthan. (Prof. Dr. Zhen Fang, 2013) Other elements such as acyl groups, amino acids and inorganic residue may be attached. Polysaccharides offers a very wide variety of glycosidically linked structures based on 40 different monosaccharides. Mostly formed from hexoses and pentoses by prokaryotes some of sugars can be found. Some material properties such as water absorbance and biocompatibility and reinforcing effects have been found in polyglucoside acrylates. Following are some important structural polysaccharides which plays an important role in the production of biopolymers.

**Cellulose:** It is one of the highly polar, main structural component of flax and hemp fibres which are available at low cost and are biodegradable in nature, having strong mechanical properties. It has a very long molecular chain, which often converted into derivatives to increase solubility that increases adhesion within matrix. (M. Kolybaba, 2003) Bacterial synthesized cellulose has great potential within the packaging industry. Acetic acid bacteria can synthesize almost same kind of cellulose which extract from plants. The main source for cellulose is wood and cotton. Cellulose fibres are used to mix in various other components to improve their mechanical properties, gas permeability and water resistance. (Šprajcar, 2012)

**Chitin and Chitosan:** Found in marine invertebrates such as crabs, lobsters, shrimps, insects, fungi and yeasts. It is a modified polysaccharides that contains  $\beta$  (1-4) polymer of N-acetyl-D-glucosamine. It has been widely used for making artificial skin, absorbable sutures, cosmetics, wound treatment and drug carriers (Smith, 2005). Chitosan is obtained from chitin by removal of acetyl groups. They are eco-friendly and non-toxic, cheap renewable biopolymers with excellent biocompatibility that they have no antigenic properties, and are insoluble in water (hydrophobic in nature) due to intermolecular hydrogen bonds. (Cheba, 2011)

**Starch:** Starch is an agricultural feedstock hydrocolloid biopolymer found in variety of plants including wheat, corn, rice and potatoes. Starch is usually utilized in the form of granules, and is actually formed by one branched and one linear polymer. Amylose, the linear polymer, comprises approximately 20% of starch while amylopectin, the branched polymer, constitutes the remainder. Starch can be used in a gelatinized form. Upon heating the starch in extrusion or injection moulding processes there is a formation of thermoplastic material that further deforms during blending. To allow further bonding, extra heat is provided to the starch above to its transition temperature then for softening the material normally plasticizers added in the starch. The starch became plasticized starch after the addition of plasticizer in it. (M. Kolybaba, 2003)

**Pectin:** A naturally occurring polysaccharides commercially extracted from citrus peels contains 10-15% of pectin and apple pomace 20-30% of pectin under some acidic conditions, it can be found in plant middle lamella. The chemical structure of pectin consists of D-galacturonic acid (GalA) units joined in chains by means of (1-4) glycosidic linkage.

It has ability to form gel hence it is used to make fruit jelly. The formation of gel depends upon its molecular size and degree of esterification. Pectin is water soluble biopolymer but some factors that affect solubility like increase in gel formation which increases viscosity. Dissolved pectin can be decomposed with the process of deesterification and depolymerization. The important use of pectin is in pharmaceutical areas in variety of drugs, ionotropic gelation and gel coating. (Sriamornsak, 2003)

**EPS:** Defined as extracellular polymeric substances or exopolysaccharides substances. They can be produced by eukaryotic (phytoplankton, fungi, and algae) and prokaryotes (eubacteria and archaeobacteria). They are organic homopolysaccharides, composed of one type of monosaccharide, or heteropolysaccharides composed of different sugars are illustrated in Figure 10. The production of EPS depends upon several factors such as medium composition (C/N ratio), co-cultures, presence of casein hydrolysate and the amount of glucose (sugar). It has been noticed that 10:1 C/N ratio is most favourable for the high yield of EPS. Due to the reason, industrial production of the polysaccharides is much better option to control the fermentation conditions by using high level strains. (Singha, 2012)

Microbial EPS have versatile applications in medical and food industry include xanthan gum, scleroglucan, polysaccharides from *Alcaligenes* sp., gellan gum, curdlan, bacterial alginate, dextran, pullulan, and baker's yeast glycan, 6-deoxy-hexose containing polysaccharides and BC. (Bernd H.A, 2009)

EPS	Monomers	Charge	Characteristics of chemical structure	Organism
<b>Bacteria</b>				
Alginate	Guluronic acid Mannuronic acid	Anionic	Blocks of $\beta$ -1,4-linked D-mannuronic residues, blocks of $\alpha$ -1,4-linked L-guluronic acid residues, and blocks with these uronic acids in random or alternating order	<i>Pseudomonas aeruginosa</i> <i>Azotobacter vinelandii</i>
Cellulose	Glucose	Neutral	$\beta$ -1,4-D-glucan	<i>Gluconacetobacter xylinus</i>
Curdlan	Glucose	Neutral	$\beta$ -1,3-D-glucan	<i>Alcaligenes faecalis</i> <i>Cellulomonas flauigena</i>
Dextran	Glucose	Neutral	$\alpha$ -D-glucan linked by $\alpha$ -1,6-glycosidic bonds; some 1,2-, 1,3-, or 1,4-bonds are also present in some dextrans	<i>Leuconostoc mesenteroides</i>
Gellan	Glucose Rhamnose Glucuronic acid	Anionic	Partially O-acetylated polymer of D-glucose-1,4- $\beta$ -D-glucuronic acid-1,4- $\beta$ -D-glucose-1,4- $\beta$ -L-rhamnose tetrasaccharide units connected by $\alpha$ -1,3-glycosidic bonds	<i>Sphingomonas paucimobilis</i>
Hyaluronan	Glucuronic acid Acetylglucosamine	Anionic	Repeating units of $\beta$ -1,4-linked disaccharides of $\beta$ -D-N-Acetylglucosamine- $\beta$ -1,3-D-Glucuronic acid	<i>Pseudomonas aeruginosa</i> <i>Pasteurella multocida</i>
Levan	Fructose	Neutral	$\beta$ -2,6-D-fructan	<i>Bacillus subtilis</i> <i>Zymomonas mobilis</i> <i>Halomonas</i> sp.
Xanthan	Glucose Mannose Glucuronic acid	Anionic	$\beta$ -1,4-D-glucan with $\beta$ -D-mannose-1,4- $\beta$ -D-glucuronic acid-1,2- $\alpha$ -D-mannose sidechain. Approximately 50 % of terminal mannose residues are pyruvated and the internal mannose residue is acetylated at C-6	<i>Xanthomonas campestris</i>
<b>Fungi</b>				
Pullulan	Glucose	Neutral	$\alpha$ -1,6-linked $\alpha$ -1,4-D-triglucoside maltotriose units	<i>Aureobasidium pullulans</i>
Scleroglucan	Glucose	Neutral	$\beta$ -1,3-D-glucan with $\beta$ -1,6-D-glucose linked to every third unit	<i>Sclerotium glutanicum</i>

Figure 10. Types of EPS microbial polysaccharides with their chemical structure (Öner, 2013)

**Pullulan:** The polysaccharide first discovered in 1958 by Bernier, obtained with the fermentation of black yeast *Aureobasidium pullulans* which forms black pigment, melanin. Pullulan is used as a food ingredients and in medical areas in japan. It is highly soluble in water and starts to decompose at the temperature around 250°C and then converted into chars at 280°C. It is biodegradable polymer having low viscosity which is not affected by heat, change in pH and sodium chloride. (Kumar, 2012)

**Xanthan:** A natural hetero-polysaccharide which was discovered in 1950s in the laboratory of US department of agriculture, is produced by bacteria *Xanthomonas campestris*. The chemical structure is identical to that of cellulose. In the production of xanthan gum starting from the culture to the growth of the microorganism where the bacte-



ria need proper nutrients like carbon and nitrogen in proper amount of 2-4% of concentration and with the help of important factors like type of bioreactor used, mode of operation, composition in the medium, and culture conditions such as temperature of 25-34°C, pH value should be close to 5 and oxygen in dissolved state. (F. Garcí-Ochoa, 2000)

**Curdlan:** It is a homogenous polysaccharide produced by alkaline tolerant mesophilic pathogen *Alcaligenes faecalis*, also by *Cellulomonas flavigena* as an extracellular storage polymer (Prof. Dr. Zhen Fang, 2013). It is insoluble in water due to its regular ordered structure. It can be dissolved by increasing pH values which helps in ionized the OH-groups and for obtaining the single standard structure.

**Alginates:** They are natural hetero-polysaccharides made up from blocks of mannuronic acid (M block) and guluronic acid (G block), which contains 30-60% of brown algae as a calcium, magnesium and sodium salts of alginic acid. Calcium alginates is insoluble in water which has been used in medical areas for dressing the wounds. (Piskin, 2001) The physical properties of the alginates depends upon some factors like, if the proportion of calcium ions and G blocks are in the large amount then there would be more gel strength whereas solubility depends upon the proportion of both MG blocks. (McHugh, 1987)

**Bacterial cellulose (BC):** Bacterial cellulose is another alternative to produce biopolymers and with its unique properties that has successfully replace the plant cellulose. The cellulose is produced by aerobic bacteria (*Acetobacter xylinum*) in synthetic and nonsynthetic medium with the help of fermentation. The bacterial cellulose has various properties like high water holding capacity, high degree of polymerization, high mechanical strength and crystallinity. During the production, the bacteria actively fermented at pH of 3-7 and the temperature around 23-30°C. The process is quite expensive to produce BC for high yield production, more research needed in this area for cost-effective carbon sources. BC has been used in various fields like food industry, medical areas and in electrical instruments. (Faezah Esa, 2014)

**Polypeptides (Proteins):** Protein based bioplastics has been proved to have antibacterial properties.

**Collagen and gelatin:** Gelatin is a mixture of peptides and protein that synthesized from collagen with the process of hydrolysis. The collagen usually found in animal parts such as skin, bones from cattle, chicken and pigs. It is used as an additive for foods in different ways. (Lausund, 2014)

**Casein:** It is also called milk protein have four main fractions ( $\alpha S1$ ,  $\alpha S2$ ,  $\beta$ ,  $\kappa$ ). These fractions are organized within the casein micelle according to their behaviour with water. Its molecular weight comes between 1000 to 20,000  $\text{g.mol}^{-1}$ . It has heat stable properties with the pH of  $>6.5$ . It is used in great number of fields such as adhesives, controlled releases and biomedical applications (Pollet, 2012). In the market, a film used to wrap a food which is quite similar to plastic wrap but actually eatable. This film is made from milk casein which is mixed with citrus pectin and salts. The film is quite strong and moist resistance which proves 500 times better than petro based plastic film at keeping oxygen away from food. (Antonio, 2016)

**Albumin:** It is widely used in medical areas with an attractive macromolecular carrier. It is biodegradable, non-toxic and non-immunogenicity protein. (Dutta, 2013)

**Zein:** The zein is rich in Glutamic acid, leucine, proline and alanine, which makes biodegradable polymer extracted as a by-product of the corn wet- milling industry. It is not water soluble in nature, about 60-95% content of aqueous ethanol has been used as a solvent which enhances the solubility. (Kim, 2010)

### ***Others***

**Lignin, Shellac:** Lignin is extracted from plant cell walls and it is formed by three phenolic alcohols such as monolignols, p-coumaryl and sinapyl alcohols. It has ability to replace plastic with its wonderful strength. Lignin is biodegradable, burnable, dark brown coloured with amorphous structure. The major use of lignin is in paper-pulp industries, agriculture and construction purposes. (Sabu, 2013)

**Natural rubber:** Natural rubber also called polyisoprenoids is used as biopolymer which is currently produced from two important resources *Hevea brasiliensis* (the Brazilian rubber tree) and *Parthenium argentatum* Gray (guayule). The purified form of rubber is *cis-polyisoprene*, having linear long-chain polymer of repeating units of iso-

prene (2-methyl-1, 3-diene). It is soft, sticky and thermoplastic with the properties of low tensile strength and elasticity. It is used in many areas from household to industrial applications. (Dr. Norimasa Ohya, 2005)

*In the second category the biopolymers are those chemical synthesized from bio-derived monomers and are biodegradable*

*Poly lactic acid (PLA):* The most widely used biodegradable aliphatic polyester family described in Figure 11 with their chemical structure. Lactic acid is produced from the fermentation of glucose, which is extract from sources like sugar, potatoes, sugarcane etc. It is the first polymer from renewable resources to be produced on an industrial level. Applications for this polymer are currently in use to make cups, bowls, and most of packaging films and foils in agricultural purposes and cutlery. It has good mechanical properties similar to PET and PP. The degradation of the PLA is non-enzymatic hydrolysis process consists several enzymes like *Proteinase K*, *pronase* and bromelain. PLA products are suitable for composting and 90% of the degradation was achieved in 90 days in case of industrial composting. (Doble, 2005)

*Poly glycolic acid (PGA):* PGA is biocompatible, low cost, tough fibre polymer having highly crystalline material, high melting point with superior barrier properties, high mechanical strength and toughness. It has a glass transition temperature between 35-40° and melting point around 224-227°C. It is obtained from the process of polycondensation in which two principal equilibrium exists, dehydration equilibrium and ring chain equilibrium. (Tiwari, 2010) It can be easily extruded and injection moulded in the combination with variety of other polymers making a wide range of packaging and industrial applications, pharmacy product enhancements and new developments. (Jeff Sherry, 2010)

Polymer and acronym	Structure
Poly(glycolic acid) (PGA)	$[-O-CH_2-CO-]_n^-$
Poly(lactic acid) (PLA)	$[-O-\overset{*}{\underset{\text{CH}_3}{\text{CH}}}-CO-]_n^-$
Poly( $\epsilon$ -caprolactone) (PCL)	$[-O-(CH_2)_5-CO-]_n^-$
Poly(valerolactone) (PVL)	$[-O-(CH_2)_4-CO-]_n^-$
Poly( $\epsilon$ -decalactone) (PDL)	$[-O-\overset{*}{\underset{(CH_2)_3CH_3}{\text{CH}}}-CO-]_n^-$
Poly(1,4-dioxane-2,3-one)	$[-O-(CH_2)_2-O-CO-CO-]_n^-$
Poly(1,3-dioxane-2-one)	$[-O-(CH_2)_3-O-CO-]_n^-$
Poly( <i>para</i> -dioxanone) (PDO)	$[-O-(CH_2)_2-O-CH_2-CO-]_n^-$
Poly(hydroxybutyrate) (PHB)	$[-O-\overset{*}{\underset{\text{CH}_3}{\text{CH}}}-CH_2-CO-]_n^-$
Poly(hydroxyvalerate) (PHV)	$[-O-\overset{*}{\underset{CH_2-CH_3}{\text{CH}}}-CH_2-CO-]_n^-$
Poly( $\beta$ -malic acid) (PMLA)	$[-O-\overset{*}{\underset{COOH}{\text{CH}}}-CH_2-CO-]_n^-$

Figure 11. Chemical structure of all biodegradable aliphatic polyesters (Scott, 2002)

*In tissue engineering:* Biodegradable synthetic polymers such as PGA and PLA and their copolymers have been used successfully in clinical use as sutures, their use in fixation devices or replacement implants in musculoskeletal tissues are considered safe. The major applications include resorbable sutures, drug delivery systems and orthopaedic fixation devices such as pins, rods and screws. The degradation of both polymers generally involves random hydrolysis of their ester bonds. PLA degrades to form lactic acid which is normally present in the body. The rate of degradation is determined by the factors like configurational structure, copolymer ratio, crystallinity, molecular weight, morphology, stresses, and amount of residual monomer, porosity and site of implantation. (Adhikari, 2003)

*In the third category the biopolymers produced by microorganisms or genetically modified bacteria*

**Polyhydroxyalkanoates (PHA):** PHAs are having family of polyesters of 3, 4, 5 and 6- hydroxyl acids. They are natural aliphatic polyesters which are synthesized through the fermentation process of sugar, alkanes, alkenes and lipids with the help of different type of bacteria including *Bacillus* sp., *Pseudomonas* sp., *Azotobacter* sp. and many other strains. (Sukan, 2015) They are biodegradable and the process takes place in the presence of enzymes. In the production of PHA, the bacteria are grown in suitable medium by supplying all essential nutrients to it and monitored in specific way for increasing the growth rate. When the bacteria reaches at desired size, then the composition of nutrients has been change that encourages bacteria to synthesize PHA (Katarzyna Leja, 2009). It is highly contributed in the sustainability of an environmental conditions, due to its high biocompatibility. It has relatively similar properties to conventional polymers because of high blending of PHA acquiring new materials with desired properties. (Šprajcar, 2012)

**Polyhydroxybutyrate (PHB):** They are natural macromolecules having semi- crystalline behaviour and high melting temperature with brittle and stiff properties extracted from bacteria (*Bacillus megaterium*). The polyester is expensive due to its thermally unstable behaviour, during processing the viscosity and molar masses decreases gradually. It is synthesized by large number of bacteria as a storage material. The amount of bacteria for manufacturing PHB is about 1 up to 30% under controlled fermentation conditions. It is fully biodegradable polyester with optical activity and having excellent barrier properties. PHB is insoluble in water has low permeable properties for oxygen, hydrogen and carbon dioxide. This biopolymer is used in various applications related with pharmacology such as material for cell and tablet packaging, also in food industry for example, bottles, laminated and agricultural foils and many more. (Katarzyna Leja, 2009)

**Poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV):** PHBV is a copolymer of PHB which is produced to improve the properties for industrial applications by the fermentation processes. It is obtained by the addition of propionate to the growing of *A. eutrophus* culture, because it is more flexible than PHB, due to this reason the propio-

nate is always having different amount in the culture to obtain various degree of flexibility. The applications of this biopolymer are mainly in production of disposable materials, packaging, medicines, and automobile industry products and so on. (Brunel, 2014)

*The last category consists fossil based biodegradable polymers*

**Polycaprolactone (PCL):** It is a semi-crystalline aliphatic polyester derived from a ring opening polymerization of caprolactone, with a relatively low melting point of 60°C with the glass transition temperature of -60°C. PCL is one of cheaper biodegradable polymer, can be completely biodegraded by microorganisms in marine, sludge, soil, sewage and composting system within 2 years (Katarzyna Leja, 2009). It is studied that PCL can be degraded in anaerobic and aerobic microorganisms in the ecosystem by lipases and esterases, enzyme *Cutinases* obtained from fungal phytopathogens (Doble, 2005). PCL can be degraded by auto catalysed bulk hydrolysis, the rate of degradation depends upon its molecular weight and degree of crystallinity (Mulla, 2013). The biodegradability of PCL can be increased by copolymerization with aliphatic polyesters. (Yutaka Tokiwa, 2009)

**Poly (alkylene dicarboxylates) (PADCs):** These are aliphatic homopolyesters prepared from diols and diacids. They show good biodegradability due to having poor water and gas barrier capabilities compared to polyolefin. Some of the examples are poly (butylene adipate) (PBA) and poly (butylene succinate) (PBS), they are synthesized through polycondensation of succinic or adipic acid and 1, 4 butanediol. The monomers used in polycondensation process are basically from petrochemical sources, but there is another possibility to produce succinic acid from bio-based resources in large amount in green and sustainable polymeric materials. (Kathuria, 2007) The degradation of poly (alkylene dicarboxylate) can be done by enzymatic degradation process, with the help of microorganisms in the soil is much faster whereas in case of hydrolysis degradation the process is little slow (Sanjay Kumar Sharma, 2011).

**Aliphatic-Aromatic polyesters:** The aliphatic-aromatic polyesters comprise an important class of biodegradable polyesters with same properties as PP, PE but the thermal and mechanical properties are relatively low in these polyesters. They are water soluble and degrades within water and carbon dioxide (CO<sub>2</sub>) in the soil. The major applications

for these polyesters are used to make beverages bottles, diapers, trash bags and in cosmetic areas. (Smith, 2005)

*Polyvinyl alcohol (PVOH):* PVOH or PVA is produced from polyvinyl acetate monomer with the help of polymerization and partial hydrolysis in the year 1924 by Hermann and Haehnel by hydrolysing in ethanol with potassium hydroxide. The linkage of carbon-carbon in PVA are similar to conventional plastics such as polyethylene, polystyrene (Doble, 2005). It is odourless, tasteless and translucent, white colour powder granules which is soluble in water having a melting point around 180-190°C. It is used in food industry for coating purposes and paper making and for textiles. (S.K.Saxena, 2004) It can be degraded by enzymatic dehydrogenase by the action of hydrolase or aldolase enzymes (Doble, 2005).

*Modified polyolefin:* Olefins like polypropylene obtained from waste agricultural raw materials with the help of gasification reaction of the lignocellulosic materials which is ending up with the formation of methanol and transformed into polypropylene. The by products from this reaction are ethylene and butylene. According to the ASTM D6866-12 standard, this bio based polyolefin are 100% carbon from renewable natural resources. (Niaounakis, 2015)

#### *Category of biopolymers that are bio-based but non-biodegradable in nature*

*PE from bioethanol:* Braskem producing green Polyethylene from the fermentation of sugarcane. This is one of the sustainable way to produce bio-based polymer that helps in reducing the greenhouse gas emission. The green PE product is non-biodegradable but are recyclable with the same properties as in fossil based polymers. Braskem I'm green polyethylene is certified by Vincotte in a reference of renewable source. (Braskem, 2016)

Some other examples are green PVC from bioethanol currently used to make credit debit cards, Bio-PET (consists 70% of terephthalic acid and 30% of monoethylene glycol MEG), PDO from glycerol and polyamides from essential oils (Elnashar, 2011).

### 4.3 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 (Piemonte, 2011). 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 and 3. (Öner, 2013)

*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. (Thomas, 2013)



Table 2 Methods of extraction of microbial polysaccharides from Biomass of Food waste (Öner, 2013)

EPS	Microorganism	Biomass	Pretreatment	Yield (Time)
Curdlan	<i>Agrobacterium</i> sp. ATCC 31749	CCS	Clarification by filtration	7.72 g/L (120 h)
Dextran	<i>L. mesenteroides</i> NRRL B512	Carob extract	Milling	8.56 g/L (12 h)
Dextran	<i>L. mesenteroides</i> NRRL B512	Aqueous extraction Carob extract and cheese whey	Deproteinization of whey	7.23 g/L (12 h)
Dextran	<i>L. mesenteroides</i> V-2317D	Sugar beet M	No treatment	50 g/L (9 days)
Gellan	<i>S. paucimobilis</i> ATCC-31461	Sugarcane M	Dilution	13.81 g/L (48 h)
Gellan	<i>S. paucimobilis</i> ATCC 31461	Cheese whey Heat treatment	Neutralization	7.9 g/L (100 h)
Levan	<i>Halomonas</i> sp. AAD6 Sugar beet M	Starch M pH adjustment Acid hydrolysis TCP treatment AC treatment	Clarification by centrifugation	12.4 g/L (210 h)
Levan	<i>Paenibacillus polymyxa</i> NRRL B-18475	Sugar beet M  Gel filtration chromatography Anion exchange chromatography	Dilution	38.0 g/L (5 days)
Levan	<i>P. polymyxa</i> NRRL B-18475	Sugarcane syrup	Clarification by filtration	19.6 g/L (5 days)
Levan	<i>Zymomonas mobilis</i> ATCC 31821	Sugarcane M	Clarification by centrifugation and filtration	2.53 g/L (24 h)
Levan	<i>Z. mobilis</i> ATCC 31821	Sugarcane syrup Filtration	Clarification by centrifugation	15.5 g/L (24 h)
Pullulan	<i>Aureobasidium</i> sp. NRRL Y	CCS	Clarification by centrifugation	4.5 g/L (9 days)
Pullulan	<i>A. pullulans</i> SU-M18	Carob extracts	Aqueous extraction	6.5 g/L (3 days)
Pullulan	<i>A. pullulans</i>	OMW	Clarification by filtration	8 g/L
Pullulan	<i>A. pullulans</i> NRRLY-6220	OMW	No treatment	10.7 g/L (7 days)
Pullulan	<i>A. pullulans</i> NRRLY-6220	Grape pomace	Aqueous extraction	22.3 g/L (7 days)
Pullulan	<i>A. pullulans</i> NRRLY-6220	Sugar beet M	Dilution	6.0 g/L (7 days)
Pullulan	<i>A. pullulans</i>	Sugar beet M	Acid hydrolysis	32.0 g/L

Table 3 Methods of extraction of microbial polysaccharides from Biomass of Food waste (Öner, 2013)

EPS	Microorganism	Biomass	Pretreatment	Yield (Time)
Pullulan	<i>A. pullulans</i> P 56	Sugar beet M AC treatment	Acid hydrolysis	24 g/L (144 h)
Pullulan	<i>A. pullulans</i> P56	Sugar beet M K <sub>3</sub> [Fe(CN) <sub>6</sub> ] treatment AC treatment	Acid hydrolysis	35 g/L (96 h)
Scleroglucan	<i>Sclerotium rolfii</i> MTCC 2156	Sugarcane juice	Dilution	23.87 g/L (72 h)
Scleroglucan	<i>S. rolfii</i> MTCC 2156	Sugarcane M	Dilution	19.21 g/L (72 h)
Scleroglucan	<i>S. rolfii</i> MTCC 2156	Coconut water	Dilution	12.58 g/L (72 h)
Scleroglucan	<i>S. rolfii</i> MT-6	Waste loquat kernel Acid Hydrolysis Detoxification	Milling	12.08 g/L (72 h)
Scleroglucan	<i>S. glucanicum</i> NRRL 3006	CCS	Dilution	14.8 g/L (144 h)
Xanthan	<i>X. campestris</i>	Carob extracts Pressing Heat treatment	Aqueous extraction	0.126 g/L/h
Xanthan	<i>X. campestris</i> PD 656	Apple pomace Alkaline treatment	Drying and crushing	52.1 g/L (6 days)
Xanthan	<i>X. campestris</i>	Grape pomace Alkaline treatment	Drying and crushing	10 g/L (6 days)
Xanthan	<i>X. campestris</i> PD 656	Tangerine peels	Alkaline treatment	32.9 g/L (6 days)
Xanthan	<i>X. campestris</i> NRRL B-1459	Sugar beet pulp	No pretreatment	1.19 g/L (4 days)
Xanthan	<i>X. campestris</i> NRRL B-1459	OMW	Clarification	4 g/L (5 days)
Xanthan	<i>X. campestris</i> T646	OMW	Clarification	7.7 g/L (5 days)
Xanthan	<i>X. campestris</i> ATCC 1395	Sugar beet M	No pretreatment	53 g/L (24 h)
Xanthan	<i>X. campestris</i> EBK-4	Ram horn hydrolysate Heat treatment Clarification by filtration	Acid hydrolysis	25.6 g/L (48h)
Xanthan	<i>X. campestris</i> 1182	Cheese whey	No pretreatment	26.35 g/L (72 h)
β-Glucan	<i>Botryosphaeria rhodina</i>	OMW	Clarification by centrifugation	17.2 g/L (120 h)
EPS	<i>Paenibacillus jamilae</i> CECT 5266	OMW	Clarification by filtration	2.5 g/L (100 h)
EPS	<i>P. jamilae</i> CP-38	OMW	Clarification by filtration	5 g/L (72 h)
EPS	<i>Halomonas</i> sp. AAD6	Sugar beet pulp	Drying and milling	2.22 g/L (3 days)

#### 4.3.1 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. (Wibowo, 2010). 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. (Han, 2004)

Table 4. Most commonly used microorganisms (GMMs) for the process of gene transfer methods (Han, 2004)

Type of Organism	Industrial Applications	Gene Transfer Methods
<i>Aspergillus</i>	Food fermentations	Protoplast transformation Electroporation Biolistic transformation
<i>Yeasts</i>	Food and beverage fermentations	Protoplast transformation Electroporation
<i>Bacillus</i>	Industrial enzymes Fine chemicals Antibiotics Insecticides	Transformation of competent cells Protoplast transformation Electroporation
<i>Corynebacterium</i>	Amino acids	Protoplast transformation Conjugation Electroporation
<i>Escherichia coli</i>	Therapeutic protein production Biodegradable plastics	Transformation of competent cells
<i>Lactic acid bacteria</i>	Food fermentations Organic acids	Electroporation Protoplast transformation
<i>Pseudomonas</i>	Plant biological control agents Bioremediation	Electroporation Conjugation
<i>Streptomyces</i>	Antibiotics, antitumor and antiparasitic agents Herbicides	Protoplast transformation Electroporation Conjugation

**PHA:** The high production cost of PHA is a major drawback to compete it with petro based polymers. The major production cost of PHA is the cost of substrate using as a carbon source whereas it can be produced from biomass sugar and fatty acids as cost effective way. An alternative to produce high yield with the help of genetically modified strains like *P. putida* was formed from suicide plasmid bearing beta- oxidation genes *fadA* and *FadB*. It is concluded that genetically modified strains have high production capacity compared to natural strains, *E.coli*. (Lei Pei, 2011).

These genetically modified strains can produce PHA from inexpensive renewable resources very efficiently by encoding the selected genes into the host body. Plant oils such as soybean oil, palm oil, corn oil contains higher carbon contents per weight to the sugars, having high yield efficiency for biomass and PHA production. For example, the bacteria used in converting plant oils into PHA are *Burkholderia cepacia* and *Comamonas testosterone* are clearly explained in Table 5 with more examples. (Chee, 2010). It has been concluded from the results, that the use of waste substrate as a carbon source in the production of PHA from both pure and mixed microbial cultures (MMC) shows significant results with very good properties. After the process of extraction of PHA by using modified strains, certain methods of separation has been applied to filter the PHA

subsequently by using centrifugation method. The final process of “recovery procedure” clarifies the amorphous, crystalline structure of the PHA that is applied to avoid the decreasing of molecular weight and consequential detrimental effect on material properties. (Martino, 2014)

Table 5. Synthetic modified strains for the production of PHA from cheap renewable resources (Chee, 2010)

Strains	PHA type	Substrates	PHA content (wt %)
<i>Alcaligenes latus</i> DSM 1124	P(3HB)	Soya waste, malt waste	33, 71
<i>Bacillus megaterium</i>	P(3HB)	Beet molasses, date syrup	~50
<i>Burkholderia sp.</i> USM (JCM 15050)	P(3HB)	Palm oil derivatives, fatty acids, glycerol	22- 70
<i>Comamonas testosteroni</i>	MCL-PHA	Castor oil, coconut oil, mustard oil, cottonseed oil, groundnut oil, olive oil, sesame oil	79-88
<i>Cupriavidus necator</i>	P(3HB)	Bagasse hydrolysates	54
<i>Cupriavidus necator</i> H16	P(3HB-co-3HV)	Crude palm kernel oil, olive oil, sunflower oil, palm kernel oil, cooking oil, palm olein, crude palm oil, coconut oil + sodium propionate	65-90
<i>Cupriavidus necator</i> DSM 545	P(3HB)	Waste glycerol	50
Recombinant <i>Cupriavidus necator</i>	P(3HB-co-3HHx)	Palm kernel oil, palm olein, crude palm oil, palm acid oil	40-90
Recombinant <i>Escherichia coli</i>	P(3HB-co-3HHx-co-3HO)	Soybean oil	6
<i>Pseudomonas aeruginosa</i> IFO3924	mcl PHA	Palm oil	39
<i>Pseudomonas aeruginosa</i> NCIB 40045	mcl PHA	Waste frying oil	29
<i>Pseudomonas guezennetii</i> biovar. <i>tikehau</i>	mcl PHA	Coprah oil	63
<i>Thermus thermophilus</i> HB8	P(3HV-co-3HHp-co-3HN-co-3HU)	Whey	36

**Cellulose:** To deal with the problems of an expensive pre-treatments and difficulty in cellulose extraction, genetically modified microbial enzymes (SB) are used to obtain the cellulose from biomass with the help of enzymatic or nonenzymatic hydrolysis process. Some of the typical examples of the enzymes are *endoglucanases*, *exoglucanases* and  $\beta$ -*glucosidase*. (Chee, 2010). Reports has been describing the expression of fungal cellu-

lases in *saccharomyces cerevisiae* for producing yeast strain with the fermentation process of cellulose into ethanol. As it shows in Table 6, the first example to generate the recombinant strain of *saccharomyces cerevisiae*, the enzyme *T. reesei* endoglucanase II and cellobiohydrolase II including aspergillus  $\beta$ -glucosidase, the recombinant strains has produced 3 g l<sup>-1</sup> ethanol form amorphous cellulose rather than crystalline cellulose. (French, 2009)

Table 6. Consuming ethanol from biomass by Synthetic biology of yeast (*saccharomyces cerevisiae*) (Giese, 2015)

Enzymes	Substrate	Result	References
<i>T. reesei</i> EG II and CBH II, <i>Aspergillus</i> $\beta$ -glucosidase (secreted)	Amorphous cellulose	3 g/l ethanol	Fujita et al. (2004)
<i>T. reesei</i> EG I, <i>Saccharomycopsis</i> $\beta$ -glucosidase (secreted)	PASC	1 g/l ethanol, growth achieved (with peptone, yeast extract)	Den Haan et al. (2007)
<i>Clostridium</i> endoglucanase, <i>Saccharomycopsis</i> $\beta$ -glucosidase (secreted)	CMC	11 g/l ethanol	Jeon et al. (2009)
<i>Thermobifida</i> processive endoglucanase Cel9A with or without <i>T. reesei</i> EG I, EG II, CBH I, CBH II	Amorphous cellulose	growth achieved (with peptone, yeast extract)	van Wyk et al.(2010)
<i>T. reesei</i> EG II and CBH II, <i>Aspergillus</i> $\beta$ -glucosidase (surface display)	Acid-swollen Avicel	1.04 g/l ethanol	Apiwatanapiwat et al. (2011)
<i>T. reesei</i> EG II and CBH II, $\beta$ -glucosidase 'cocktail $\delta$ -integration' (see main text)	PASC, rice straw	7.6 g/l ethanol, 7.5 g/l ethanol	Yamada et al.(2011)
Mini-cellulosome (cellulases expressed in <i>E. coli</i> )	PASC	3.5 g/l ethanol	Tsai et al.(2009)
Mini-cellulosome (enzymes expressed endogenously)	PASC, Avicel	1.8 g/l ethanol, 0.4 g/l ethanol	Wen et al. (2010)

### Gene transfer method

By transporting the fungal cellulases (multiple copies of bifunctional endo/exoglucanase of *Bacillus sp.* DO4 and  $\beta$ - glucosidase of *Bacillus circulans*) into the chromosomal DNA of yeast *saccharomyces cerevisiae*. It has been noticed that all three transporters enables the growth of cello oligosaccharides which further responsible for high yield of ethanol. (Ha, 2011)

In strain *Saccharomyces cerevisiae* there is a lack of cellobiose transporters (cdt-1 & gh1-1) therefore the use of *N. crassa* actually solved this problem. The process described below in the Figure 12, the strain *Neurospora crassa* has been modified to express three transporters (cdt-1, cdt-2 and Ncu 00809) were introduced in engineered *Saccharomyces cerevisiae* to secrete  $\beta$ -glucosidase (gh1-1). This method shows the better production of ethanol by using strain *N. crassa*. In the results, it is concluded that *cdt-1* (cellodextrin transporter) and *gh1-1* ( $\beta$ -glucosidase) in *Saccharomyces cerevisiae* are the fastest cellulose fermenting transporters. (Ha, 2011)

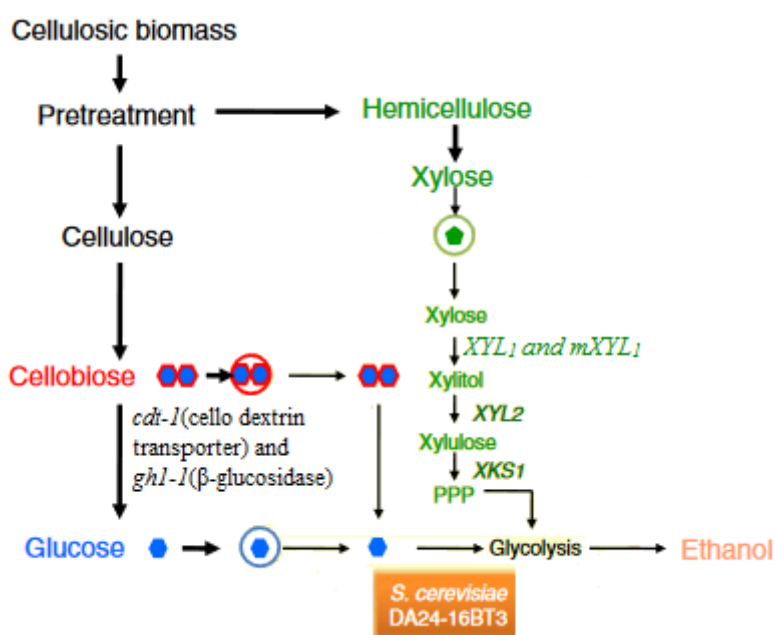


Figure 12. The process of converting biomass into ethanol with the help of genetically modified strains (Ha, 2011)

**Polysaccharides from industrial vegetable waste:** Biomass from industrial vegetable waste is the best option to utilize it as a source of biopolymer. A normal food industry generates residue around 30-50% of the feedstock thus takes a lot of cost to vanish in the environment due to its high organic matter content. The waste goes to landfill causes high amount of carbon dioxide and ammonia production which harms the environment. The sustainable way to use that waste in source of value added chemicals such as polysaccharides for the economical way to produce biopolymers. Table 7 illustrates the processes of extraction of polysaccharides with their composition (monosaccharides) from different types of industrial food waste. (Lei Pei, 2011)



Table 7. Extraction techniques for obtaining polysaccharides from industrial food waste (Poli, 2011)

Waste source	Extraction technique	Total Yield (%)	Molecular Weight (KDa)	Monosaccharide Composition (% molar ratio or mg/g dry weight)	Reference
Apple pomace	EtOH (85%) at 70 °C; oxalic acid-ammonium oxalate (pH 4.6) at 85°C	7.7	233.4	GalA/Ara/ Gal / Glc/ Rha/Xyl (853.5/37.3/23.3/16.9/9.6/7.3) (mg/g dry weight)	Min et al., 2011
Apple pomace	Mixing in H <sub>2</sub> O; homogenization; autoclave at 121 °C; $\beta$ -glucanase (Viscozyme® L)	4.6	231.7	GalA/Ara/ Gal / Rha/Glc/ Xyl (693.2/78.04/26.2/ 15.47/14.8/13.2) (mg/g dry weight)	Min et al., 2011
Apple pomace	Phenol/acetic acid/H <sub>2</sub> O; CDTA chlorbutol; 1M KOH; 4 M KOH	4.1	N.D.	Fuc/ Ara/Xyl/Man/Gal/Glc/UronicA (5.6/1.2/25.3/6.9/12/46.2/2.8) (% molar ratio)	Watt et al., 1999
Orange peels	Microwave pre-treatment; drying at 60 °C; 0.5M HCl at 80 °C	18	64	GalA (665) (mg/g dry weight)	Kratchanova et al., 2004
Citrus peels	Enzyme extraction (protease, cellulase)	12.6	180	Rha/Fuc/ Ara/Xyl/Man/Gal/Glc/GalA (10/2/71/7/10/34/12/756) (mg/g dry weight)	Zykwinska et al. 2008
Citrus peels	Sequential Extraction: EtOH/H <sub>2</sub> O	3.6 - 8.6	N.D.	Identified as pectin according to Yu & Love, (1996)	Wang et al., 2008
Bergamot peels ( <i>Citrus bergamia</i> Risso)	Sequential Extraction: EtOH/H <sub>2</sub> O (EtOH insoluble fraction)	45.2	N.D.	Glc/GalA/ Ara/Gal/Xyl/Man/Rha/Fuc (217.1/216.6/66.2/48.1/29.7/24.6/7.8/5.1) (mg/g dry weight)	Mandalari et al., 2006
Bergamot peels ( <i>Citrus bergamia</i> Risso)	Sequential Extraction: EtOH/H <sub>2</sub> O (EtOH soluble fraction)	29.8	N.D.	Glc/ Ara/Rha/Man/GalA/Gal/Xyl/Fuc (328.6/43.7/36.4/24.3/19.2/4.7/2.8/2.2) (mg/g dry weight)	Mandalari et al., 2006
Banana peels	Sequential Extraction: H <sub>2</sub> O/ Chelating agent/ Acid solution	21.7	573-249	GalA/Rha/ Ara/Xyl/Man/Glc/Gal (69.1/ 0.5/1.7/ 0.5/ 1.2/ 4.3/ 1.0) (% molar ratio)	Happi Emaga et al., 2008
Plantain peels	Sequential Extraction: H <sub>2</sub> O/ Chelating agent/ Acid solution	14.6	570-129	GalA/Rha/ Ara/Xyl/Man/Glc/Gal (48.3/0.5/9.0/6.5/2.7/6.6/4.0) (% molar ratio)	Happi Emaga et al., 2008
Peanut cakes	EtOH extraction	25.8	N.D.	Gal (main component)	Song et al., 2011
Agro-waste materials	Distilled H <sub>2</sub> O, pH 11 under stirring	8.1 - 54.8	N.D.	Cellulose, hemicelluloses, galactans, arabans, pentosans	Kuan & Liong, 2008
Soy hull	0.1 M HCl at 95°C; precipitation with 2-propanol, pH 3.5	28	N.D.	GalA (720) (mg/g dry weight)	Kalapathy & Proctor, 2001

**Methods of extraction:** There are several ways to extract polysaccharides from the food waste such as solid liquid extraction, soxhlet extraction, ultrasound- assisted, microwave- assisted, hot water treatment, acid and alkaline extraction, ethanol water treatment, sequential extraction and enzyme-assisted extraction. Researches said that the pretreatment of waste with microwaves proves to be an ideal option for high yield pec-

tin because with the microwaves it is easy to diminish the plant tissue which increases the porosity that results in the high water absorption capacity. (Poli, 2011)

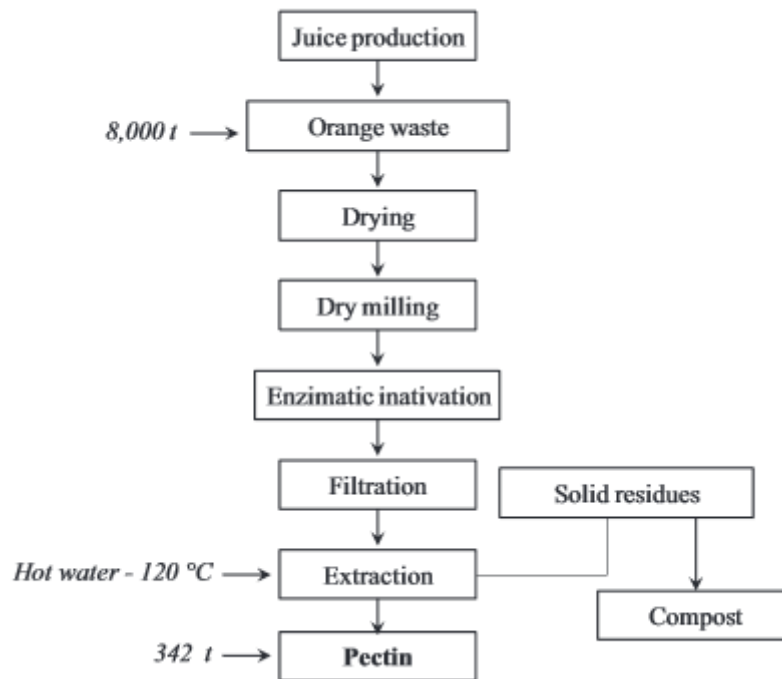


Figure 13. Method of extraction of pectin with hot water from the orange residues (K. Rezzadori, 2012)

Figure 13 describes the process of extraction of pectin from industrial orange peel waste from juice production treated with hot water. In the process the remaining residue can further useful to make compost for plant fertility in an environmentally friendly way. Studies says that the organic food waste have so many applications to replace the petrochemical products. The production of bio-oil from food waste with the process of pyrolysis that can be used for transport fuel can be seen in Figure 14. (K. Rezzadori, 2012)



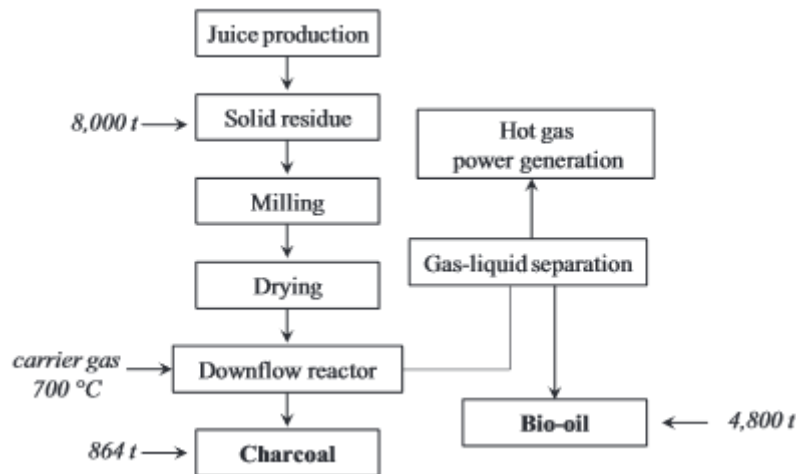


Figure 14. The flow chart representing the production of Bio-oil with the process of pyrolysis (K. Rezzadori, 2012)

The waste of tomato, granadilla and lemon kept at certain freezing point to dry them up and further treated with KOH with different extraction times. A method of centrifugation were used in order to separate the solid residues from waste. The liquid form of waste then treated with ethanol at -20°C overnight. After that the small particles collected from the centrifugal method has been dissolved with warm water and dialyzed against running water for 3 days to obtain dried polysaccharides as described in Figure 15. (Preedy, 2008)

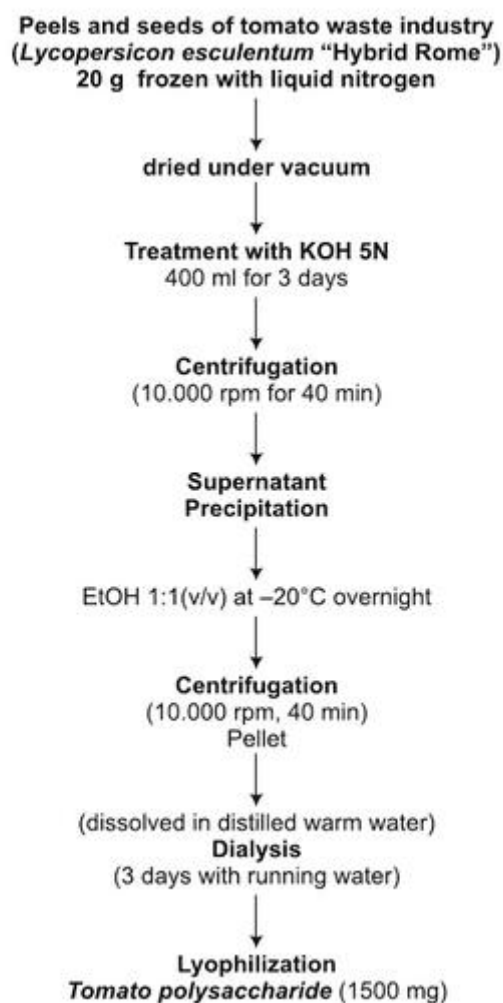


Figure 15. Method of extraction the polysaccharides from tomato and lemon industrial waste (Preedy, 2008)

The most suitable method for obtaining high yield of polysaccharides with the use of enzyme- assisted extraction, enzymes such as cellulases (to degrade cellulose) and proteases (to degrade proteins) (Poli, 2011). The enzymes hydrolyzed the cell wall of biomass that increases the permeability to obtained compounds like carbohydrates, cellulose, natural oils, pigments etc. The current barrier for this method to obtain large volume industrial scale biopolymers is such a difficult challenge for enzymes because they react differently with change in environmental conditions such as pH, temperature, humidity and nutrient variability. (Baiano, 2014)

**Shrimp:** Shrilk (fibroin protein from silk and from chitin): An insect cuticle made from discarded shrimp and proteins derived from silk. It was developed in 2011 at the Wyss

Institute for Biologically Inspired Engineering, at Harvard University by the Spanish materials scientist Javier G. Fernandez. This low cost, biodegradable and biocompatible shrilk has specific characteristics features with respect to strength, toughness which is similar to aluminium alloy but not similar to the weight.

The polysaccharide is environmentally safe, biodegradable and can be used to make trash bags, packaging and diapers that degrade quickly. Medical use: it can be used as sutures that actually bear high loads. (Mowatt, 2011)

*Algal Biopolymer:* One project name SPLASH including 20 partners worked on a project to produce sustainable polymers from algae sugars and hydrocarbons and exopolysaccharides from the algal species *Botryococcus braunii*. The project is funded by European Union. Genetically altered algae is required to produce biopolymer in large scale for industrial use. (Vogt, 2016)

*Root of spinach* an Italian researcher develops turning the waste materials of industrial agriculture into renewable plastic by mixing it with Trifluoroacetic acid (TFA) which resulting in extracting the cellulose from the spinach roots, hence it has so many properties similar to synthetic ones in strength, from rigid to soft and stretchy. The process is fastest and less expensive. To manufacture a biopolymer from agricultural waste also beneficial to produce cost effective biopolymer. This process can work with various other wastes like cocoa pod husks, rice hulls and parsley. (Silverberg, 2014)

*Stanford Scientists Make Plastic from Carbon dioxide (CO<sub>2</sub>) and Grass:* Anandeeta Banerjee, a chemistry graduate student at Stanford and Matthew Kanan discovered an achievement to produce plastic by mixing together furoic acid (derivative of a compound made from agricultural waste called furfural), carbonate and CO<sub>2</sub> and then heating up to create a form of molten salt. After that the molten salt had been converted to a compound called 2-5 Furandicarboxylic acid or FDCA, which is a key component in making plastic. The aim of this invention to reduce the amount of CO<sub>2</sub>, a greenhouse gas that contributes to a global warming. So this low cost method is quite helpful to manufacture plastic. (Albarazi, 2016)

*Turning Urban Waste into Bioplastic* (the Synpol project funded by EU): The process is done by using certain type of bacteria in fermenting gases in the waste like municipal and chemical waste that contain a lot of reusable carbon that bacteria can digest and converted into biopolymers like PHAs (polyhydroxyalkanoates) in acetogenic bacteria. It is an alternate to produce cost effective PHA biopolymer, also this process helps in sustainability in environment by eradicating municipal waste. (Synpol, 2012)

*Using chicken features as a source of biopolymers (keratin)*: One of the best way to use the waste of dead chicken feathers from the poultry farms for manufacturing biopolymers. The feathers consists 91% of keratin protein, fat 1.3% and water 7.7% and different kind of amino acids as well. Various groups like hydroxyl group, carboxyl groups, amino group, thiol and aromatic groups are linked with each amino acids. (Ayutthaya, 2015)

*Avocado seeds*: The Mexican Company “Biofase” produces the resins from discarded avocado seeds from industrial food wastes. This is one of an efficient way to produce raw material in cost effective way by utilizing the waste. The avocado seeds industrial waste coming from avocado processing factories for reusing them in some aspect that contains no carbon radicals. The product have similar properties as PE, PP and PS and are capable for injection molded products, hence suitable for sustainable environment. (Monterrey, 2013)

#### **4.4 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 16. According to the surveys the future energy sources would come up with CO<sub>2</sub> neutral ener-

gy including solar and wind energy, bioenergy, nuclear fission and fusion, and fossil fuels with carbon capture technology (Thunman, 2007).

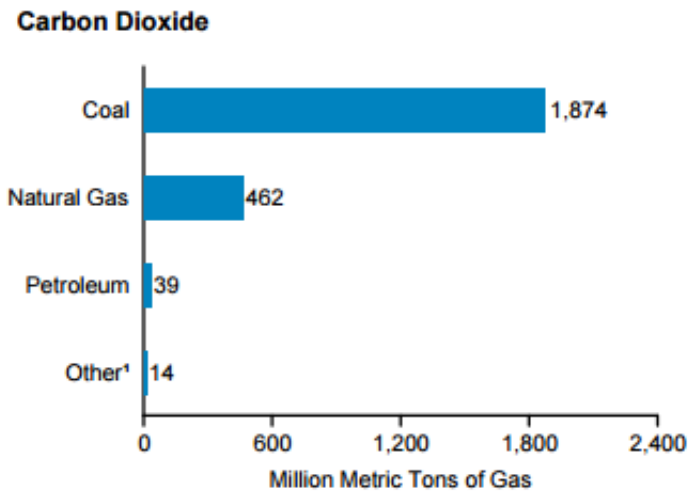


Figure 16. Carbon dioxide emissions from energy consumption in coal and natural gas (EPA, 2016).

The process consists two main steps are thermochemical and biochemical conversion, also mechanical extraction can be used during the production of energy from biomass. (Mckendry, 2002)

#### 4.4.1 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 8. (Teixeira, 2010)

Table 8. Content of cellulose, hemicellulose and lignin in the discarded lignocellulose waste (Teixeira, 2010)

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 shows that there is a possibility to produce biopolymer from the agro-industrial waste as it consists cellulose in it (Ballinas-Casarrubias, 2016). The thermochemical process can be done in four major steps including, combustion, pyrolysis, gasification and liquefaction are shown below in Figure 17. 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. (Goyal, 2008)

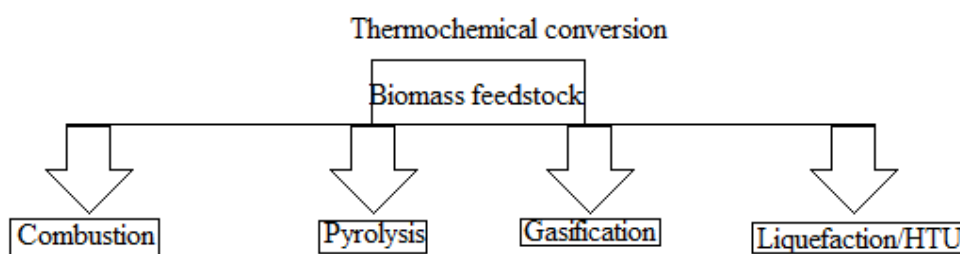


Figure 17. The processes in thermochemical conversion of biomass (Mckendry, 2002)

**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. (Mckendry, 2002)

**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. (Mckendry, 2002)

**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 18. 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. (Brownsort, 2009)

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. (Mckendry, 2002)

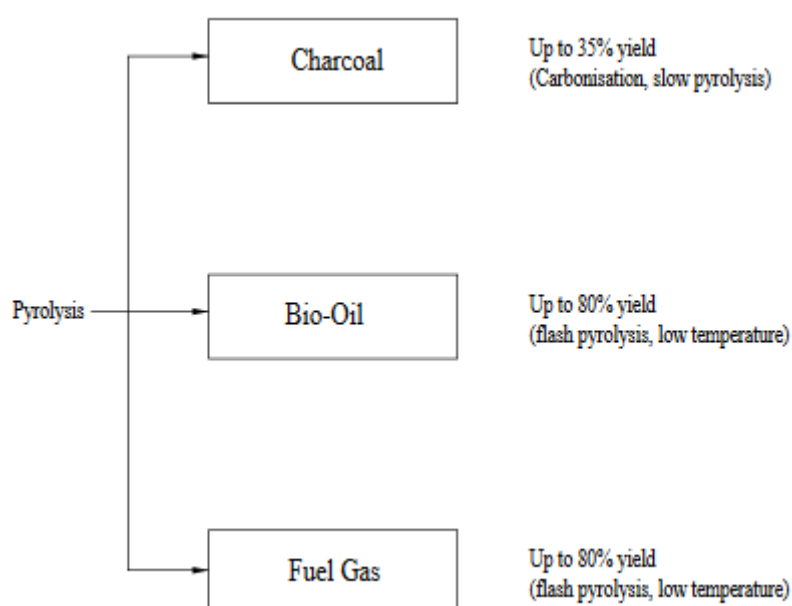


Figure 18. Generation of three energy products from the process of pyrolysis. (Mckendry, 2002)

**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. (Mckendry, 2002)

#### 4.4.2 Biochemical Conversion

The biochemical process mainly consists pre-treatment, saccharification /hydrolysis, fermentation as shown below in Figure 19. Anaerobic digestion (AD) is another way to convert organic matter into CO<sub>2</sub>, methane with the help of microbial activity, the process follows 4 steps as hydrolysis, acidogenesis, acetogenesis and methanogenesis (Appels, 2008).

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 ligno-cellulosic material is more complex into simple form, thus biomass undergoes the process of hydrolysis in two different ways, chemically with acids (H<sub>2</sub>SO<sub>4</sub>, 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.* (Kitani, 1999)

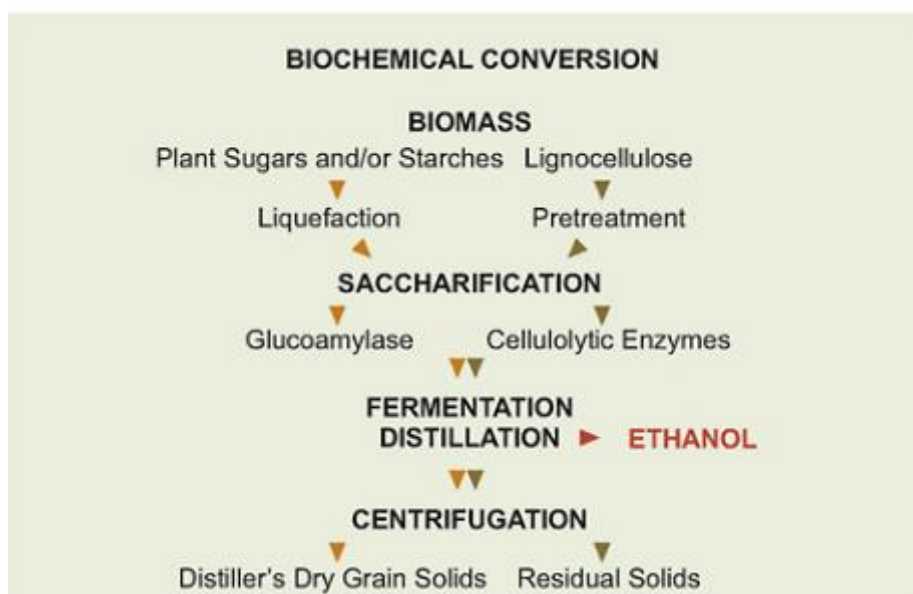


Figure 19. Steps involved in biochemical conversion of biomass (council, 2009)

**Pre-treatment processes:** The aim of the pre-treatment method is to remove the content of lignin and hemicellulose as much as possible while maintaining the cellulose content in the residue that undergoes saccharification and fermentation processes. (Ballinas-Casarrubias, 2016)



*Acid hydrolysis:* The presence of lignin in lignocellulosic biomass such as wood and grass are having long-chain polysaccharides which requires dilute acid, concentrated acid and enzymatic hydrolysis for the conversion into simpler monomers sugars (Kumar, 2009). The process breaks down the lignin protection and crystalline cellulose structure, leaving the brown paste which creates sulphur dioxide in air. In case of dilute acid the reaction occur at high temperature and high pressure that cause glucose degradation but on the other hand the use of  $H_2SO_4$  at moderate temperature is more preferable to achieve high yield for depolymerisation of structural plant cell wall. However acid produces large amount of by-products which further inhibit the microbial activity. (Dussan, 2014)

*Saccharification/ enzymatic hydrolysis:* The breaking down carbon chains with the help of enzymes called cellulolytic enzymes are of three types as presented in Figure 20, endoglucanases (cleaves internal glycosidic bonds), cellobiohydrolases/ exoglucanases (cleaves the cellobiose especially from chain ends),  $\beta$ -glucosidases (cleaves the glucose units from cello-oligosaccharides) (council, 2009). As it discussed above, the hydrolysis process with the help of dilute acid has so many drawbacks such as it inhibits the whole process of converting sugars into ethanol at the same time in case of enzymatic hydrolysis, due to its mild conditions the furfural components are totally negligible. (Moe, 2012). The acid hydrolysis process needed non-corrosive materials that gave the colour and salty affect to the content, further requires more energy and therefore the whole process is difficult to handle (Chaplin, 2004)

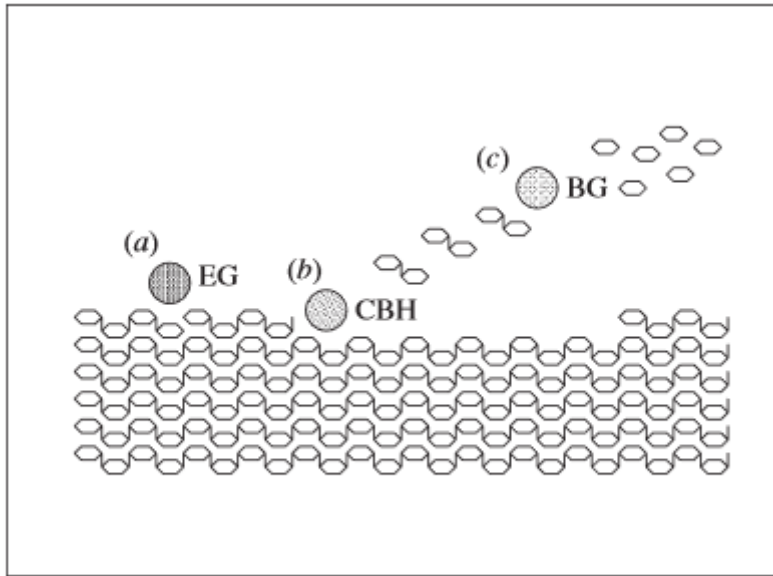


Figure 20. Mechanism of Saccharification done by three enzymes EG (endoglucanases), CBH (exo glucanases) and BG ( $\beta$ -glucosidase) (French, 2009)

### Other processes

The *steam explosion* method for the extraction of lignin protection is one of the environmental suitable way to treat the biomass with hot steam around 180- 240°C and under pressure of 1- 3.5MPa that results in rupturing the biomass fibres rigid structure (Fig.21). The major drawback of this method is incomplete disruption of lignin from carbohydrate matrix. (Stelte, 2011)

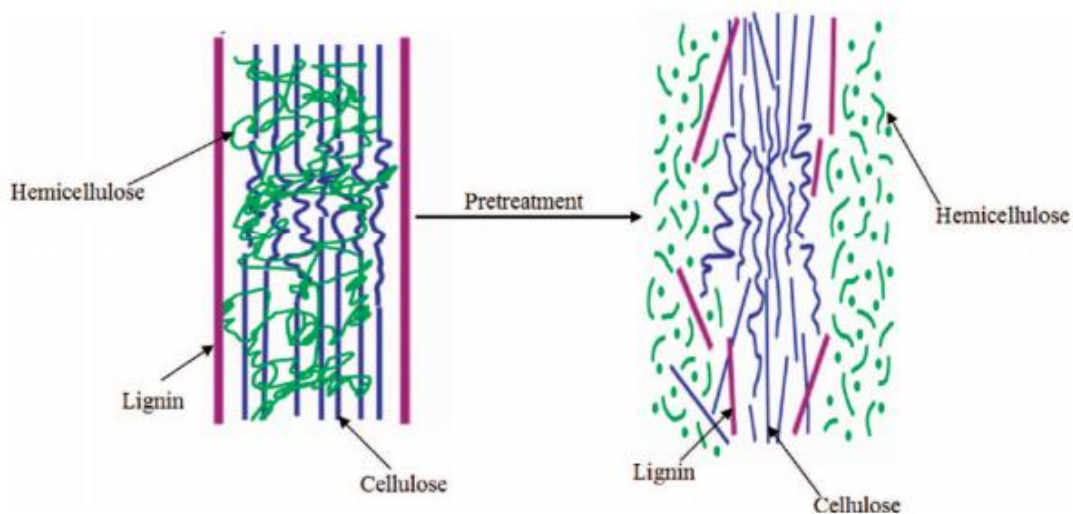


Figure 21. Conversion of lignocellulose into simple monomers (Kumar, 2009)

The use of *Bacterial cellulose* in separation of entangled lignin from cellulose in plants are another alternative to obtain hemicellulose from plants. Due to its ultra-fine reticulated structure, BC is used in many applications such as in paper, textile, food industries, cosmetics and pharmacy. The method itself is expensive due to the use of bacteria in this process. (Almasi, 2013)

*Organosolv process* is used to extract the lignin with the organic solvents (ethanol and methanol) or aqueous solvents from pulp in paper manufacturing factories (Ballinas-Casarrubias, 2016). Due to the use of aqueous ethanol in this process, it is one of the safest method. The catalyst (hydrochloric acid, sulphuric acid and phosphoric acid) are combined with organic solvent to break the bonds of lignin and cellulose are explained in Figure 22. The catalyst increased the delignification and higher yield of xylose formed from it. The process is difficult to handle due to the need of draining the solvents from reactor that undergo evaporated, condensed, recycled and not easily industrially scalable. (Xuebing Zhao, 2009)

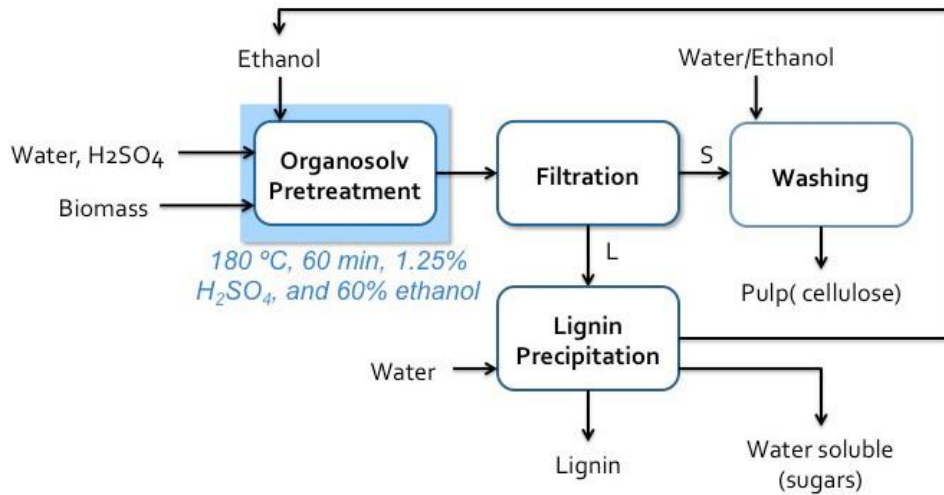


Figure 22. Illustration the process of Organosolv pretreatment of lignocellulosic biomass (Clifford, 2015)

**Fermentation process:** An anaerobic process that converts (biomass) sugar into ethanol. The glucose break down into alcohol or acid with the help of yeast and other bacteria. The ethanol produced from this process distilled and dehydrated for higher concentration of alcohol then further use as fuel for automotive purposes. The residue from this process can be used for cattle-feed and the bagasse as a fuel for boilers. (Mckendry, 2002)

**Solid- state fermentation systems:** *SSF*, the process of fermentation of enzymes on the moist solid material in the absence of free flowing water is one of the new technology by using natural and inert substrates (nutrients) as solid supports. The rot fungi such as *Phanerochaete chrysosporium* and *Ceriporiopsis subvermispota*, are commonly used by providing low moist. The process is time taking and there is threat yield loss with fungus attacks the polysaccharides that is why instead of using microorganism scientists are more interested in enzymes such as lignin peroxidase complex produced by some fungi like *Phanerochaete chrysosporium* are suitable for the extraction process. (Ballinas-Casarrubias, 2016) The other enzymes used in the process are  $\alpha$ -amylase, cellulase, xylanase, protease, fructosyl transferase, chitinase and pectinase produced by various bacterial and fungal strains. The substrate materials for enzymes are available through lignocellulose wastes for example, rice straw, rice bran, red gram husk, jowar straw and many more. (Teixeira, 2010)

**Anaerobic digestion (biogas formation):** It is a biological process of breaking down biomass in the absence of oxygen under controlled atmosphere. The process occurs in three stages, hydrolysis/liquefaction, acidogenesis and methanogenesis are described in Figure 23. (Siebert-Raths, 2011). In the first phase the polymeric material converted into monomers and oligomers such as glucose, amino acids and long chain fatty acids by extracellular enzymatic reactions following the process, bacterial (anaerobes) acidification of the substances are degraded to organic acids like acetic acid, propionic acid and butyric acid, low alcohols, aldehydes, hydrogen and gases like carbon dioxide, hydrogen sulfide. In the stage of acetogenesis, the low molecular weight substances are converted into further acetate and hydrogen (Cavinato, 2011). In the last stage of methanogenesis, methane is produced by methanogens in typically two different ways: either from acetate with the help of aceticlastic methanogenic bacteria or by reduction of car-

bon dioxide (CO<sub>2</sub>) with hydrogen by hydrogen philic methanogenic bacteria. The methanogenic bacteria includes *methanobacterium*, *methanobacillus*, *methanococcus* and *methanosarcina* are helpful in this process. (Shefali, 2002) The end products such as (biogas) methane and carbon dioxide captured by AD inside the tank and further used to produce electricity and heat. The residual products during separation process from anaerobic digesters are typically used as bio fertilizers for the growth of crops. (Nayono, 2009)

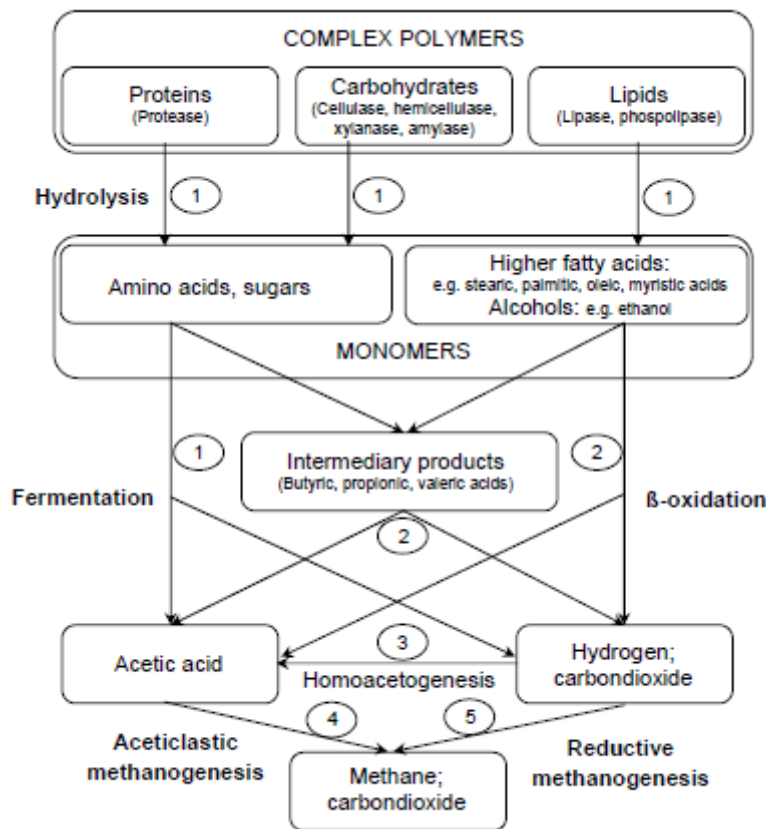


Figure 23. The Bioprocesses steps in Biogas production within anaerobic digestion (Nayono, 2009)

*Important operating parameters in this AD process are as follows*

**Temperature:** The temperature for psychrophilic, mesophilic and thermophilic micro-organisms varies from 10°C, 20-45°C and less than 50°C. (Muzenda, 2014) It is noticed that higher temperature in the thermophilic range reduce the retention time. (Shefali, 2002)

**pH value:** pH plays an important role in the process, which should lie between 7 -7.5, there are several biogas plant using the pH value of 8 which is not affecting system be-

cause once methane production is stabilized, the pH level stays between 7.2 and 8.2. (Shefali, 2002)

*Carbon and Nitrogen ratio:* C/N ratio needed for metabolic activity of methanogenic bacteria is approximately 8-20, but in case of anaerobic digesters the ratio is 20-30. A high ratio results in lower gas production whereas the lower C/N ratio cause ammonia accumulation by rapid increase of pH value at the scale of 8.5 which is act like a poison to methanogenic bacteria.

*Retention time:* The retention time for this process varies with substrate composition, digestion system configuration and temperature. For thermophilic digestion the retention time is about 14 days, whereas in mesophilic it varies from 15-40 days and for hydraulic usually between 10-25 days (Muzenda, 2014).

*Particle size:* According to EU regulation the particle size is about 12mm.

#### **4.4.3 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 (Islam, 2008). During anaerobic digestion, the mixture of gases (biogas) formed at different percentage such as 50-75% methane and 25-45% carbon dioxide (Prashanth, 2016) whereas in the thermochemical process of gasification and pyrolysis converted 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 24. The purified hydrogen is used in low cost fuel cell PEM (polymer electrolyte membrane) for generating heat and power. (Ballard, 2013) 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. (Meng Ni, 2005)

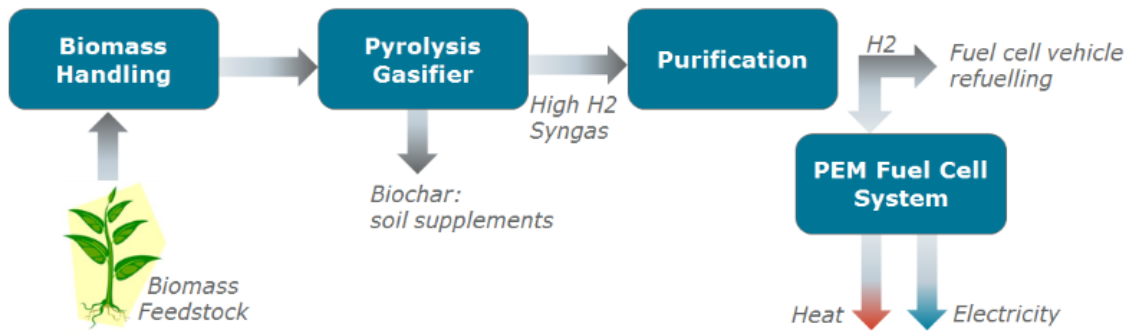


Figure 24. Illustration the process of producing purified hydrogen gas from the biomass feedstock (Ballard, 2013)

## 5 BIODEGRADATION PROCESS

There are several ways to degrade the polymers, one of them with the help of microorganisms such as fungi, bacteria, yeasts are secreting the enzymes and other by-products like acids and peroxides. The process includes two different steps: a) the initial step is Depolymerization/ Disintegration/ Fragmentation or chain cleavage step, this step occurs outside the organism depending on the size of the polymer chain but in case of extracellular organisms, the process can take place including both factors exogenous which includes (temperature, humidity, pH, availability of oxygen and enzymatic activity) or endogenous (as molecular weight, crystallinity, flexibility of molecules) (Piemonte, 2011). In the mechanism, the microorganism attacks the polymer chain resulting in breaking down the chemical structure of the polymer with the help of heat, moisture, microbial enzymes or with different environmental conditions which deterioration in physical properties such as discoloration, embrittlement, and fragmentation are shown in Figure 25. (BPI, 2003-2016) (S. Hemjinda, 2007)

### Step 1: Fragmentation

- Typically 2 step process
  - **Degradation/Fragmentation:** Heat, moisture, oxygen, sunlight and/or enzymes shorten & weaken polymer chains, resulting in fragmentation

#### Degradation/Fragmentation →

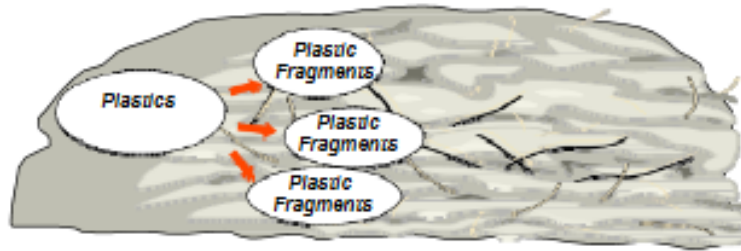


Figure 25. The first step of fragmentation in the process of degrading plastics (BPI, 2003-2016)

b) In the second step of Biodegradation/Mineralization the polymer come after the conversion into small fragments (in the depolymerization process) where cell derives metabolic energy from the mineralization process is represented in Figure 26. The carbon chains are converted as a food for microorganism and energy sources like  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2$ ,  $\text{H}_2$  water, salts, minerals and biomass in the case of anaerobic conditions. (Bastioli, 2005)



## Step 2: Biodegradation

- Typically 2 step process
  - **Degradation/Fragmentation:** Heat, moisture, oxygen, sunlight and/or enzymes shorten & weaken polymer chains, resulting in fragmentation
  - **Biodegradation:** Fragments consumed by microorganisms as a food & energy source and converted to carbon dioxide at an acceptable RATE.

### Biodegradation

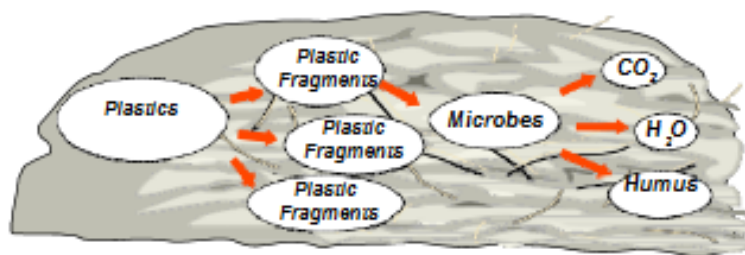


Figure 26. Illustrate the second step of biodegradability of the polymers (BPI, 2003-2016)

## 5.1 Enzymatic degradation

Different enzymes have different mechanism of catalysis. Some enzymes convert their substrate directly into free radical while some use chemical routes. The mechanism of physical deterioration with the help of liquid fluid in form of glue “slime” secreted by enzymes enters in the porous structure of the polymers which further changes the physical composition of the polymer by changing its moisture level. The function of the slime is to protect the microorganism from the unfavourable conditions. Most of the aliphatic polyester family polymers are degraded by the process of enzymatic degradation. (Lucas, 2008)

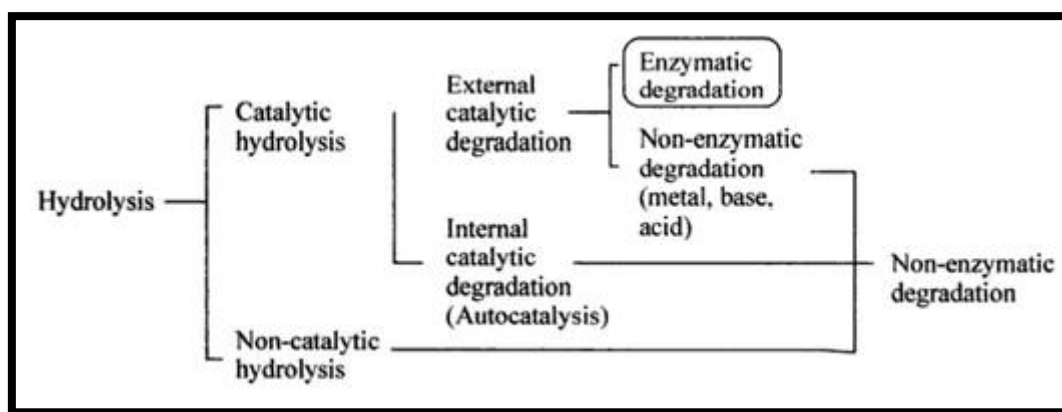


Figure 27. Mechanism of degradation via Hydrolysis (Smith, 2005)

Therefore the mechanism of polymer degradation described in Figure 27 where the hydrolysis process divided into two types, catalytic hydrolysis and non-catalytic hydrolysis. In further the catalytic hydrolysis are of two types a) external catalytic degradation which includes (enzymatic and non- enzymatic degradation), b) internal catalytic includes (autocatalysis, non-enzymatic degradation) (Smith, 2005).

The accumulation of microorganism in specific polymer for the bio deterioration depends upon the several parameters such as humidity, weather and atmospheric pollutants, studies shows that the environment pollutants are attractive source of nutrients for the growth of microorganism to form a colony called “biofilm”. (Lucas, 2008)

**Simple hydrolysis/ non-enzymatic:** Most of the naturally occurring polysaccharides biopolymers undergoes simple hydrolysis method. To interact with water, the polymer should contain some hydrolysable covalent bonds in groups such as ester, ether, anhydride, amide, ester amide and so on. The polymer with no hydrolysable bonds and strong covalent bond took a lot of time to degrade (Azevedo, 2004, pp. 177-180). The process can be catalysed by acids, bases, salts and enzymes, they can react with polymer and increase the rate of degradation. The water enters into the polymer breaking down covalent bonds, initiate the process of hydrolysis, to convert the polymers into (simplest form) oligomers by adding  $-OH$  and  $-H$  groups and finally into monomers within the matrix. The production of pores in the system resulting into releasing of oligomers and monomers from the polymer as described in Figure 28 (Lucas, 2008).

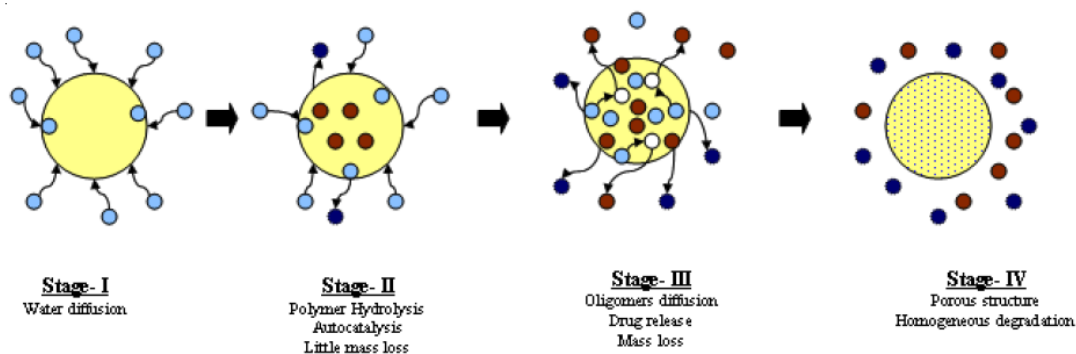


Figure 28. Mechanism of hydrolysis within polymer (Chhaya Engineer, 2010)

**Enzymatic hydrolysis:** Hydrolysis reactions may be catalysed by enzymes known as hydrolases, which include *proteases*, *esterases*, *glycosidases* and *phosphatases*. It is expected that some of the enzymes plays an important role in the degradation of biomaterials by catalysing their hydrolysis. (Azevedo, 2004, pp. 177-180)

During the enzymatic degradation the microorganism secretes extracellular depolymerases that attacks the polymer to start the enzymatic hydrolysis by increasing the polymer water solubility to breakdown it completely into oligomers and further into small monomers. (Averous, 2016)

**Proteases enzymes** catalyse the hydrolysis of peptides bonds and ester linkages. Proteases are generally obtained from bacteria genera *Bacillus* with proteases *B.alcalophilus* and *B. licheniformis*. They are divided into four groups:-

The serine proteases

The cysteine proteases

The metal containing proteases

The aspartic proteases

**Esterases enzymes:** In the process the ester linkage is separated by addition of water. The enzyme also suitable for non-degradable polymers such as polyesters, PU, PP, PS and PVC (Niaounakis, 2013) Lipases catalysts comes under this category, it acts as lipid water interface and have very little activity on soluble substrates. Lipases are helpful in catalysing hydrolysis in triglycerides  $\rightarrow$  diglycerides  $\rightarrow$  monoglycerides  $\rightarrow$  glycerol and fatty acids. (Bastioli, 2005)

*Glycosidases enzymes:* These enzymes splits the natural occurring polysaccharides like starch, insulin, cutin and cellulose and their derivatives. The most important types are amylase, cellulose and cutinases (Bastioli, 2005)

*Enzymatic oxidation:* The process of enzymatic oxidation is catalysed by enzymes called oxidoreductases. The oxidation process applied, when it is difficult to breaking down the chemical bonds in such reactions like amorphous, hydrophobic zones and steric hindrances. Enzymes like peroxidases and laccases are used to catalyse with one or two oxygen atoms to form alcohol and hydrogen peroxide for simple fragmentation. (Convents, 2000) The enzyme incorporated with oxygen called oxygenase, generally they are of two types, monooxygenase and dioxygenase. In the process of oxidation several superoxide for example hydrogen peroxide, nitric oxide, and hypochlorous acid may cause polymer chain scission and contribute to their degradation. According to Lee and Chu, these super oxides helping in degrading sutures and they found that superoxide could accelerate the degradation of aliphatic polyesters by the cleavage of ester bonds via nucleophilic attack of superoxide. (Azevedo, 2004) The degradation method is used for non-hydrolysable polymers such as polyolefin, natural rubber, lignin and polyurethanes (Smith, 2005).

### **5.1.1 Degradation site of plastic material**

The process of breaking down the polymer with the help of water by cleaving long chain into monomeric acids. Polymer erosion refers to processes like degradation, swelling, dissolution and diffusion of oligomers and monomers, and morphological changes. The two different mechanism of bio deterioration of plastic material i.e. bulk erosion and surface erosion. (Chhaya Engineer, 2010) (Smith, 2005)

*Bulk erosion:* The process of rapid penetration of water into the matrix of polymers structure leading to hydrolysis with the help of chemicals like  $H_2O$ , acids, bases, transition metals and radicals resulting into the change in molecular weight of the polymer. In the beginning of the process some cracks and curves occurs which results in the subsequent mass loss of the material. The rate of diffusion of the chemicals into material is much higher than the rate of hydrolysis which leads to rapid crumble of the material see

(b) Figure 29 (Buddy D. Ratner, 2004). Polyesters like PLA and PGA can be degraded with hydrolysis process.

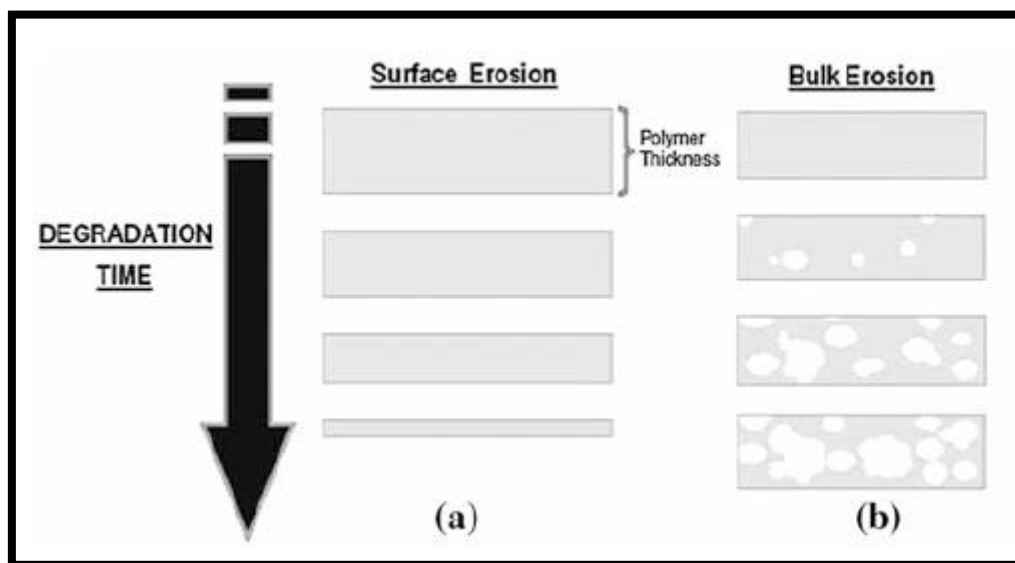


Figure 29. Criteria of degradation in Bulk Erosion and Surface Erosion (Gajjar, 2014)

**Surface erosion:** In this process the material eroded from the surface, see (a) in Figure 29. The process is faster than the bulk erosion, with the decreasing thickness of the material also referred as device thinner. In this case rate of hydrolysis is higher than the rate of diffusion of chemicals. Surface eroding polymers are ideal candidate for drug delivery devices. (Gajjar, 2014) The mechanism surface erosion of PHB and aliphatic-aromatic copolymers are described by various authors (Lucas, 2008).

The initial step of chemical degradation of the polymer is hydrolysis, in this process the molecular size of polymer decreases, which allows them to diffuse from the bulk material to the surface and then to the solution, causing significant weight loss. Whereas in the second step of surface erosion mechanism is done by loss of material from the surface only. The enzyme catalysed degradation of polymeric biomaterials may follow the surface erosion mechanism, especially for the highly crystalline and hydrophobic homopolymers. The factors on the enzymatic degradation are chemical composition, degree of homogeneity and processing techniques. (Azevedo, 2004, p. 190)

### 5.1.2 Abiotic methods of degradation

The term abiotic degradation refers to the chemical breakdown of substance into small fragments by abiotic means such as hydrolysis, photolysis, and oxidation by exposing the polymeric material to outdoor conditions such as weather, ageing and burying that significantly weakens the substances in undesirable conditions as shown in Figure 30. The synthetic polymers have potential to undergo abiotic degradation (Lucas, 2008).

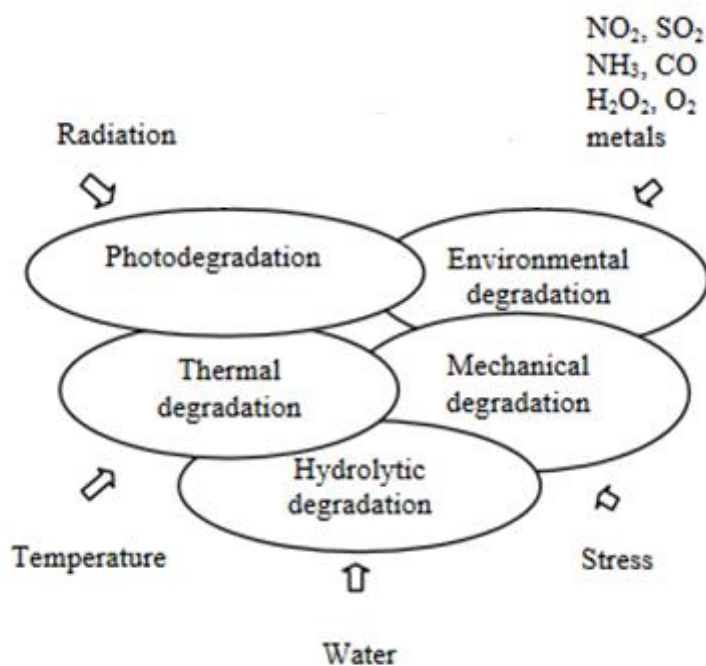


Figure 30. Abiotic degradation processes of Biopolymers (Grabowska, 2010)

**Photodegradation:** In this process, the additives called photo-sensitive additives are used to added in the polymer (the photosensitive molecular structure) has been introduced by addition and copolymerization process to make it possible to degrade the polymer by intensity of light. When the polymer exposed to sunlight (UV rays) it starts to emit free radicals which actually attack and breaking down the polymeric bonds into small fragments in anaerobic conditions. (S. Hemjinda, 2007)

The photodegradation mechanism of PLA and PCL has been carried out via Norrish II-type reaction (Fig. 31), by chain scission with the formation of C=C double bonds and O-H hydroperoxide. (Niaounakis, 2015)

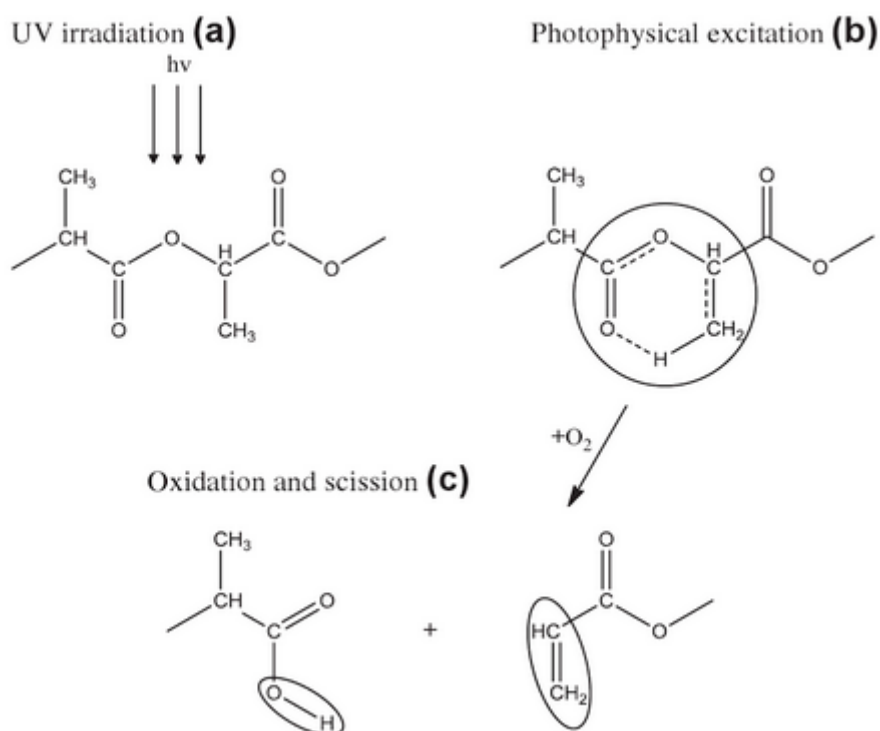


Figure 31. Schematic representation of Norrish II type reaction for photo degradation of PLA (Niaounakis, 2015)

Fechine and his co-workers concluded the effect of UV radiation photodegradation behaviour on appearance, morphology and mechanical properties of PHB and PHBV biopolymers. During experiment, the UV radiation light exposed to both samples with the UV-A fluorescent lamps. It was clearly visible in Figure 32, the effect of UV radiation from the surfaces of the both samples with the change of brown colour into white due to cracks formed on the surface further increased the roughness shows colour lightning within 6-12 weeks of time period. (Fechine, 2011)

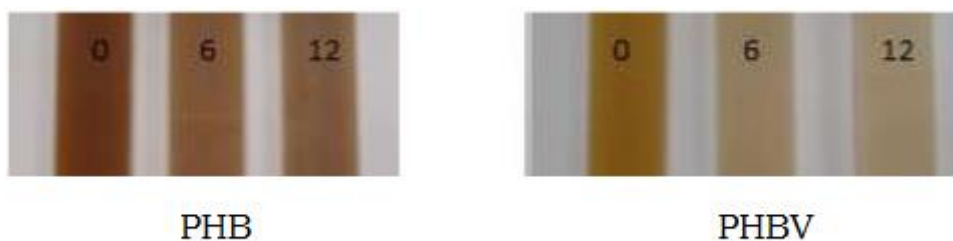


Figure 32. The color lightning within 6-12 weeks on PHB and PHBV by photo degradation method (Fechine, 2011)

**Mechanical degradation:** Mechanical degradation takes place due to shear forces, tensions, and compression. The processes like agitation, grinding and extrusion are used in

this process. With the help of powerful shearing forces the polymer break down into low molecular weight polymer. The environmental parameters such as UV exposure, temperature and humidity are helpful to see the transformation of the polymeric material. (Lucas, 2008).

**Thermal degradation:** This process is carried out by increasing the thermal temperatures, where the polymer change its state from solid to liquid with the help of high temperature. Due to high temperature the long chain backbone in the polymer can be separated by molecular scission. Thermal degradation can be investigated by using techniques like thermogravimetric and differential scanning calorimetry. Above 200°C, PLA degraded with inter- and intramolecular ester exchange, cis- elimination, radical and concerted non- radical reactions with the end product of CO, CO<sub>2</sub>, acetaldehyde and methyl ketene. (Niaounakis, 2013). Thermal degradation of aliphatic polyesters PHA has been carried out by the mechanism of  $\alpha$ - $\beta$  hydrogen bond scission (Lucas, 2008).

## 5.2 Factors that affect biodegradability

There are several factors that affect process of biodegradability among polymers some of them are as using right microbe, molecular structure, morphology and molecular weight of the polymer. Both chemical and physical properties such as surface area, hydrophobic and hydrophilic nature of polymers and chemical structure, high molecular weight, glass transition temperature, melting temperature, modulus of elasticity all of them have great influence on biodegradation. (Tokiwa, 2009)

The rate of degradation decreases with the increase of crystallinity of the polymer. Since the microbes generally attacks amorphous region in most cases due to its loosely packed molecules compared to crystalline part which tends to more resistant to the degradation. (Bastioli, 2005) High Melting temperature ( $T_m$ ) of the polymer decreases its biodegradability as shown below in Figure 33, the polymer PEA having low melting point around 60°C, with low mechanical strength shows excellent biodegradability by enzyme *R. arrhizus* lipase. The amount of microorganisms in PBS are relatively lower than other polymers like PCL, PHB due to presence of PBS copolymers containing aromatic, amide or urethane units which increases rigidity of the PBS. In some cases IDA (Imide



dihydric acid) has been added to decrease the degree of crystallinity by breaking out regular chains of the polymer. (Tokiwa, 2009)

Other factors in enzymatic degradation are important such as chemical linkage in the polymer, the pendant groups, their positions and end groups with chemical activity all of them have great influence on enzymatic degradation. (Bastioli, 2005)

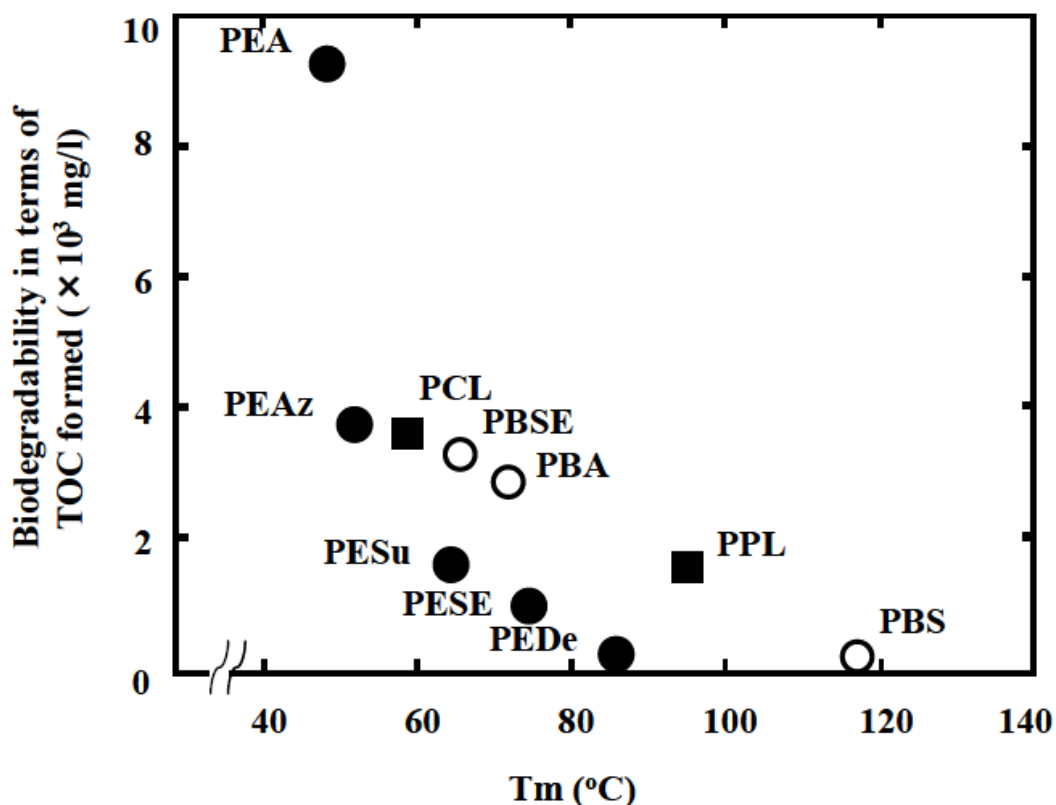


Figure 33. The rate of biodegradation in terms of melting temperature (Tokiwa, 2009)

The Substituents like hydroxyl, carboxyl, methyl and phenyl groups also affecting the biodegradability. In case of synthetic polymers because of the high crystallinity, the degradation rate is relatively low, whereas monomers and oligomers degrade at faster rates which means the rate of degradability of the polymer increases with lowering the molecular weight. In case of natural polymers, the enzymatic reactions decreases the molecular weight, hence it degrades within the cell. (Smith, 2005)

### 5.3 Biological Methods of Degradation

Biological degradation can be done in aerobic and anaerobic conditions. The aerobic biodegradation occurs in the presence of oxygen where the organic matter converted into CO<sub>2</sub>, H<sub>2</sub>O, biomass and other residuals. On the other hand in case of anaerobic biodegradation, there is no oxygen consumed and the carbon matter converted into carbon-dioxide CO<sub>2</sub>, methane (CH<sub>4</sub>), biomass and other residuals. The various environments of aerobic and anaerobic biodegradation are described in Figure 34.

	<i>aquatic</i>	<i>high solids</i>
<i>aerobic</i>	<ul style="list-style-type: none"><li>• aerobic waste water treatment plants</li><li>• surface waters, e.g., lakes and rivers</li><li>• marine environments</li></ul>	<ul style="list-style-type: none"><li>• surface soils</li><li>• organic waste composting plants</li><li>• littering</li></ul>
<i>anaerobic</i>	<ul style="list-style-type: none"><li>• anaerobic waste water treatment plants</li><li>• rumen of herbivores</li></ul>	<ul style="list-style-type: none"><li>• deep sea sediments</li><li>• anaerobic sludge</li><li>• anaerobic digestion/ biogasification</li><li>• landfill</li></ul>

Figure 34. Aerobic and Anaerobic Environments for biodegradation of plastics (Bastioli, 2005)

The method takes place in natural and man-made habitats such as landfills, septic tanks, anaerobic digesters for waste water treatment and sludge. The different test method have their own level of biodegradability depending upon parameters like temperature, moisture and amount of microorganisms.

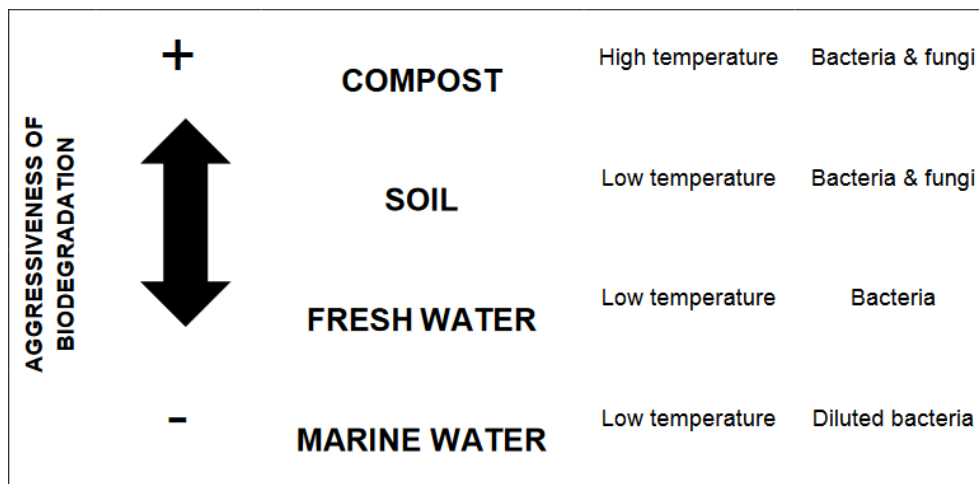


Figure 35. Test environments for Biological degradation of biopolymers (Wilde, 2013)

The bioplastics are designed to discard in mixed waste enters into landfill and composting areas where the waste degraded under microbial activities. The dissolution of biopolymers can be rapid or slow by mixing with chemical and aqueous solutions. The rate of biological degradation in different environments such as lakes, rivers, salt water, in laboratory tests have significant low- high degradation level compared to soil and compost due to the amount of microbial activity within the system can be seen in Figure 35. (Muller, 2005)

**Landfill:** The biopolymers degrade anaerobically in the landfills thus converted into methane and carbon dioxide (CO<sub>2</sub>) gases. These gases can be collected and then utilized as an energy source. But this is least desirable option which is not suitable for biopolymers due to the concern with global warming. Bio waste like garden waste, house waste when goes straight to the landfill producing high amount of CO<sub>2</sub>, NH<sub>3</sub> gases, responsible for global warming (J. H. Song, 2009)

**Composting:** It is one of the suitable method that accelerate the degradation of the wastes in a controlled manner, within the scope of the biological carbon cycle and the constraints of the ecosystem. In this process the organic matter degraded by mixed microbial population in a moist, warm, aerobic environment under controlled conditions.

This non-toxic process of degrading biomass is helpful to generate carbon-rich soil (humic material), which increases fertility, nutrient retention, level of the soil and also act like a food for future crops by reducing chemical inputs and suppress plant diseases. The carbon dioxide (CO<sub>2</sub>) produced from this process cannot accounted in increasing the greenhouse effect due to a part of carbon cycle. A material is compostable, if it is capable of undergoing biological decomposition in a compost site as illustrated in Figure 36. (Systems, 2012)

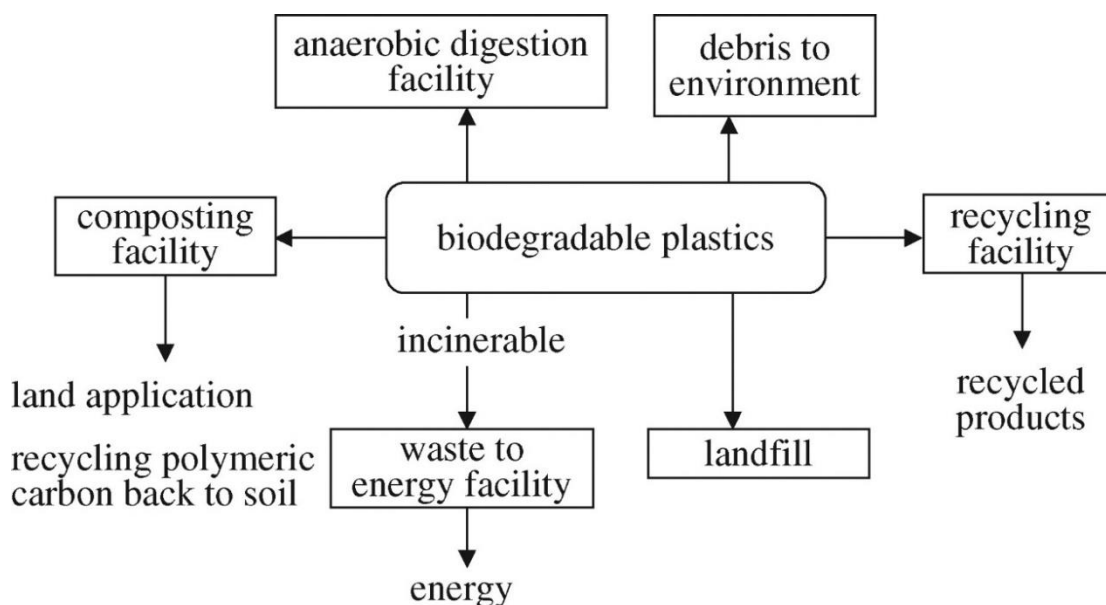


Figure 36. End of life options for biodegradable plastics (J. H. Song, 2009)

**Composting** are of two types, one is domestic composting, also known as home composting which includes kitchen waste, biodegradable polymer waste and garden waste. The other type of composting is industrial composting which is actually done in proper atmosphere under controlled conditions. In the course of industrial composting biomass is generally mixed with oxygen, moisture content with required temperature. The process requires separation, collection and transport to an industrial composting plant. The amount to CO<sub>2</sub> generates in this process is equivalent to the amount of CO<sub>2</sub> in the process incineration, thus this process is more suitable for biodegradable polymers (Siebert-Raths, 2011). Composting provides the much-needed organic matter in soil, and in combination with conventional soil conservation methods by providing an answer to the major environmental and agricultural problem of soil erosion. The benefits of compost-amended soil includes increasing organic carbon, improving water and nutrient reten-

tion, reducing the need for additional chemical inputs, suppressing plant disease, increase earthworm and microorganism biomass in the soil (Narayan, 1992).

## **5.4 The process of industrial composting (EN 13432)**

In laboratory scale under controlled composting test biodegradation is determined with the addition of mature compost or activated vermiculite with the help of thermophilic microorganism obtained from compost (Kapanen, 2012). The sample of the raw material reduced to powder form and mixed with mature compost as a source of nutrients for microorganism by maintaining the moisture content and constant temperature of 58°C free from vapours. The organic matter mixed with the inoculum and introduced into a static composting vessel providing all controlled conditions. The carbon dioxide produced in the process are monitored. The four essential requirements for this process are chemical characteristics, biodegradation, disintegration and eco toxicity.

In chemical characteristics, the product must contain 50% of organic matter, heavy metals and fluorine vary between different standards. In the process of biodegradation the organic matter C converts into CO<sub>2</sub> under the action of microorganism can be considered as chemical composition under simulating composting conditions. The product should biodegrade at least 90% in time period of six months. Biodegradation is determined by the measuring the amount of CO<sub>2</sub> over the period of time. Third step of disintegration deals with the physical appearance of product in which breaking of whole product into small fragments within 12 months in controlled conditions can be seen in Figure 37. The disintegration rate generally decreases with the increase in thickness of the sample.

The last process of eco-toxicity checks the fertility level of the soil residue from the composting process. In other words eco-toxicity assessment provides tools to conduct risk assessment of chemicals. The Australian standard also requires the evaluation of toxicity on the earthworms. The plant toxicity is required in European, international American and Brazilian standards to check if the material is containing any toxic substances that significantly inhibit the plant growth or the survival of soil fauna. (Wilde, 2014) Active biodegradation of polymers in soil give negative effects to the plants with

the high microbial activity can lead to anaerobic conditions in the soil. High amount of methane in the residual also have adverse impact on plant growth. In order to decrease the amount of toxic compounds in the residue, addition of proper amount of organic matter and heavy metals should be taken into account. (Kapanen, 2012)



Figure 37. Disintegration of Biopolymer sample within 90 days in industrial composting (Wilde, 2011)

#### 5.4.1 Factors affecting the composting process

The factors includes C: N ratio, moisture content, pH value, particle size, oxygen supply and temperature. Heavy metals contents like Cd, Cr, Cu, Hg, Ni and Pb with the help of bacteria *Salmonella* and *E.coli* as well as other nutrients like P and K used to analyse by laboratory using standard of EN 13432 Test method. (Barrena, 2014)

**C: N ratio:** C stands for carbon and N for nitrogen are essential elements for composting. The ratio must be around 25:1 suitable for the process, if the C: N ratio is above 40 it results in slowing down the process with the increasing amount of nitrogen in it, on the other hand if it is less than the required value, the excess amount of nitrogen might start to produce ammonia which cause odour and other environmental problems. The carbon is generally important for the growth of the microorganisms whereas nitrogen is for protein synthesis.

**Moisture content:** The balanced moisture content is also one of the major factor of industrial composting, which can be done during mixing different types of waste. The average range is from 45% to 55%. Below 40% the compost is too dry for the microorganisms and if it exceeds 65% then the process turned into anaerobic process with the in-

creasing amount of water in pores which further create odour and slowing down the decomposition method. The humidity lies between 30% and 35%.

*Oxygen content:* The oxygen content which lies between 16- 18.5% for stable conditions. The organic waste must contain at least 30% of free air space to proper aeration within the process.

*Temperature:* According to the International Standard ISO 16929, the temperature for composting should lie above 60°C for the beginning of the process (a week). The exact temperature must be around 58°C for the decomposition of organic matter. By increasing temperature above 75°C, actually kills the microorganism in the system which further cause barrier to the whole process.

*Particle size:* Smaller particle size an ideal option for the industrial composting as it provides higher surface to volume ratio. More porous material is suitable for the process for the good aeration in it. On the other hand, larger parts can actually cause anaerobic digestion with the loss of porosity. (Wilde, 2014)

## **6 STANDARD, CERTIFICATION AND LABELS**

The product is Biodegradable, if it is certified legally by any of the International Standards like ISO 17088:2012 (International), EN13432:2000 (European), EN 14995:2006, ASTM D6400-12 (USA), according to all them the product is capable of undergoing decomposition into carbon dioxide, methane, water and other inorganic compounds like biomass with the help of micro-organisms. (Kershaw, 2015). Compostable products are defined by ASTM D6002-92(2002), to the polymers that have ability to undergoing biological decomposition in a compost site. For compostable plastics the international standard is ASTM D6400-12 and for compostable packaging ASTM D6868-11.

In Europe the two most important certification organizations are Vincotte, and DIN CERTCO. These companies performed biodegradability and compostability laboratory tests accordance to standard ASTM D6866, schemes and granted the certifications to the companies by providing the proof of material conformity to the standard requirement. (Martino, 2014)

The labels and symbols play a vital role in the product's biodegradable and compostable behaviour. They represent the level of toxicity, eco-friendly, non-chemical nature to the customers. Some of European labels are described below.

### 1. *Blue Angel/Der Blaue Engel*



The German logo 1988 represents the environmentally friendly products satisfying low toxicity to aquatic life, saving resources, water-saving, climate friendly and health conscious. The label is supported by four institutes: the environmental label jury, federal ministry for the environment, nature conservation, building and nuclear safety, Umwelt Bundesamt and RAL gGmbH. (Angel, 2016)

### 2. *Nordic ecolabel or swan*



The label demonstrates the environmental friendly products in Nordic countries including Sweden, Norway, Finland, Iceland and Denmark. It is the first internationally accepted labelling program that developed in the year 1989 by the Nordic council of ministers for sustainable environment. There are total 64 product groups of different countries who have this labelling in the market. (Ecolabelling, 2016)

### 3. *EU Ecolabel*





The label minimized the use of hazardous substances in the environment, it also implies the use of biodegradable products that has least impacts to aquatic environment and waste water system.

#### 4. DIN- Certo

Based in Berlin, Germany, this certification of composability and bio-based are managed by DIN-Certo which signifies the product have capability to undergo composting. The standards used in laboratory scale are EN13432 and ASTM D6400-99 as well as DIN V 54900.



#### 5. BPI

Biodegradable product institute, an American institute who promotes the use of sustainable and recyclable polymeric materials and providing the approval to completely biodegradable and compostable products.



#### 6. Vincotte logos



The logo provided by Vincotte to different companies who are producing bio-based products that are partially or completely from natural resources. This signifies that the product has the potential to reduce carbon footprints. The classification is symbolized in number of stars that shows the bio based carbon content in the product. (Vincotte, 2012)

One star	★	$20\% \leq \text{BCC} < 40\%$
Two stars	★★	$40\% \leq \text{BCC} < 60\%$
Three stars	★★★	$60\% \leq \text{BCC} < 80\%$
Four stars	★★★★	$80\% \leq \text{BCC}$

The OK compost logo from Vincotte deals with only industrial composting (EN13432) and does not covers all types of composting such as domestic, biodegradation in soil, water also suitable for recycling whereas OK compost home is suitable for only home. (Vincotte, 2012)



Vincotte is providing different types of logos of biodegradable related to different environment such as soil, water and marine, for example OK biodegradable logo in water clearly indicating the ability to degrade the polymer into water bodies. To have this logo the product should meet specific requirements such as solubility or dispersibility, Eco toxicity and other chemical characteristics. (B. De Wilde, 2013)

The normalisation institutes who are certifying the biodegradable, compostable products for the industries are shown in Table 9.

Table 9. Certification institutes in the field of biodegradability (Wilde, 2013)

<b>Environment</b>	<b>Certification body</b>
Industrial compostability	European Bioplastics (Europe) Vinçotte (Belgium) DIN CERTCO (Germany) Biodegradable Products Institute (USA) Cedar Grove (USA) Japanese BioPlastics Association (Japan) Australasian BioPlastics Association (Australia & New Zealand) Consorzio Italiano Compostatori (Italy) SP Technical Research Institute (Sweden) Catalonian government (Catalonia, Spain)
Home compostability	Vinçotte (Belgium) DIN CERTCO (Germany) Australasian BioPlastics Association (Australia & New Zealand) Organics Recycling Group – Renewable Energy Association (UK)
Biodegradability in other environments	Vinçotte (Belgium) SP Technical Research Institute (Sweden)
Oxo-degradation	Emirates Authority for Standardization and Metrology (UAE) Oxo-biodegradable Plastics Association (UK) SP Technical Research Institute (Sweden) Biosystems America (USA) Singapore Environment Council (Singapore)

## 7 RESULTS

The purpose of this research is to increase awareness about the benefits of biopolymers and their important role in sustainability. The increasing effect of global warming arises a lot of issues regarding climate change, acidification and biomagnification. The use of synthetic plastic disrupting the life of flora and fauna with their hydrophobic nature as can they migrate into water and other surfaces of the ecosystem. Apart from production of biopolymers, there are several other cost effective approaches for manufacturing high yield biopolymers. The use of municipal waste in the formation of bioenergy (bioetha-

nol & biodiesel) is another opportunity to utilize it an efficient way. Nevertheless, the scientists are inventing new biotechnological ways to develop bacterial strains (SB) by using recombinant strains to produce bioplastics from the food waste biomass for a sustainable carbon source. Most of them have complex structures biomass such as wood waste, for extraction the cellulose content which is mixed with lignin, different strategies have been discussed to obtain the cheap renewable resource for the profitable production of biopolymers. The use of aerobic and anaerobic digestion of municipal waste enables the energy recovery in the near future. Several researches that depicts the use of biomass in the production of PHA has been successfully achieved with good properties. A number of experiments has been performed to check the biodegradable nature of biopolymers in sea to insure that they are not polluting the water bodies. Three samples were used during the experiment, conventional HDPE, PE (Oxo-degradable) and PBAT/Starch blend mater bi (biodegradable). All three samples were placed in sea for 49 days. The results in weight losses in case of HDPE and PE were negligible whereas the weight loss in meter bi was ranges from 4.5-8.5% can be seen in Figure 38. (Kershaw, 2015)

POLYMER TYPE	POLYMER SOURCE	WEIGHT LOSS AFTER 49 DAYS
HDPE	Shopping carrier bag	negligible
Oxo-degradable	Shopping carrier bag – PE with pro-oxidant (d2w™ technology)	negligible
Biodegradable	Shopping carrier bag – starch-based Mater-Bi™ from BioBag®	Green turtle 8.5% Loggerhead turtle 4.5 %

Figure 38. Results of the experiment performed to check the level of biodegradability (Kershaw, 2015)

Rutkowska and co-workers observed the complete de-fragmentation of PCL in a sea water with the help of hydrolysis and enzymatic degradation at temperature around 9°C-21°C within 8 weeks of time period. (Muller, 2005)

Another approach with the copolymer of PHAs (PHBV)/ starch blend and pure form of PHBV in the tropical coastal waters at temperature 25-32°C .It is observed that the degradation rate by weight loss and deterioration of tensile properties pure PHBV was quite slower than PHBV/ starch blends that fully degraded within 140 days. (Muller, 2005)

It was concluded by Ohura and co-workers that the degradation rate of PHBV fibres samples (213µm and 493µm) were much higher in sweetwater compared to seawater. During the lab test, the natural water and mineral salts has been added to increase the microbial activity to see the complete degradation of both samples. A complete degradation rate of PHBV sample (213µm) were obtained from Sweetwater within 2 weeks of time period and the integration of sample (493µm) within 4 weeks of time period as twice from the sea water. (Muller, 2005)

Above all experiments shows that there is a possibility to control the marine pollution by increasing usage of biopolymers for daily purposes.

## **8 DISCUSSIONS**

The current barriers for the production of biopolymers generally related with cost, public awareness and lack of market and policy incentives for eco-friendly materials. Most of the articles and journals are related with plenty of issues regarding marine pollution, increasing CO<sub>2</sub> emissions in the air and finding new inventions to stopping them but nobody talks about the root of this problem that is coal and petroleum. If the use of coal reaches to minimum level then there is a solution for sustainable environment. The end of life option for biodegradable polymers are environmental friendly in a way the CO<sub>2</sub> produced during composting process are absorbed by plants without harming the surroundings. Results from various other experiments clearly signifies the solution for sustainable environment to control the marine pollution by increasing the use of microbial biopolymers such as PHA, PHB. The PHA plastic fermented by GMMs under sterile conditions are more feasible for industrial use due to their mechanical properties similar to fossil based plastic. It is observed that by improving pre-treatment methods and enzymatic production at low cost significantly increase the production of biopolymers

from biomass. The use of enzymes proves to be best method to extract the polymers from the biomass with safe eco- friendly ways but the method is efficient only at low volume production. There is a great need of further research in finding out the suitable ways how to keep the right amount of parameters and environmental conditions during enzymatic extraction methods to produce biopolymers at high volume industrial scale.

## **9 CONCLUSIONS**

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 CO<sub>2</sub> and NH<sub>3</sub>. Since the waste contains large amount of sugars, carbohydrates and cellulose in them, to utilize them in eco-friendly 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 thesis was discussed and excellent results has been achieved during the research that there is a possibility to control marine pollution with the increasing use of biopolymers for the green economy.

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