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The Who's Who in Plastic Marine Pollution

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ABSTRACT

Plastic products are used widely in all industries and in our daily lives. This ubiquity of these degradation-resistant plastic products, however, has led to many environmental issues, including the serious impact on marine ecology.

Marine litter loads in sea compartments are an emergent issue due to their ecological and biological consequences. In fact, the pollution caused by microplastics (MPs) particles size <5 mm) in seas and fresh water is of growing environmental concern due to their slow degradability, biological ingestion by fish and other aquatic living organisms, that impact the food chains and potentially cause humans serious health problems.

This study aims to assess and quantify the microplastics in sea water, by doing a characterization study in the LU laboratories of water samples from the Mediterranean sea. Finally, suggest a solution by modeling a simulation on ASPEN PLUS of a pyrolysis to convert collected household plastic into fuel oil and gas.

KEYWORDS: Plastics, Microplastics, Characterization, Pyrolysis, Fuel oil , Gas

RESUME

Les produits en plastique sont largement utilisés dans toutes les industries et dans notre vie quotidienne. Cette ubiquité de ces produits en plastique résistant à la dégradation, cependant, a conduit à de nombreux problèmes environnementaux, y compris l'impact sérieux sur l'écologie marine.

Les charges de déchets marins dans les compartiments marins sont un problème émergent en raison de leurs conséquences écologiques et biologiques. En fait, la pollution causée par les particules de micro-plastiques dans les mers et l'eau douce est une préoccupation croissante de l'environnement en raison de leur dégradabilité lente, l'ingestion biologique par les poissons et autres organismes aquatiques vivants, qui influent sur les chaînes alimentaires et potentiellement causer des problèmes graves sur la santé des humains.

Cette étude vise à évaluer et quantifier les micro-plastiques dans l'eau de mer, en faisant une étude de caractérisation dans les laboratoires de LU des échantillons d'eau de la mer Méditerranée. Enfin, proposer une solution en modélisant une simulation sur ASPEN PLUS d'une pyrolyse pour convertir le plastique ménager collecté en fioul et gaz.

KEYWORDS: Plastique, Micro-plastiques, Caractérisations, Pyrolyse, Fioule , Gaz

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LISTE OF ABBREVIATIONS

AOP	Advanced Oxydation Processes
ATR	Attenuated Total Reflectance
Barg	Bar Gauge
BTX	Benzene, Toluene, Xylene
CDU	Crude Distillation Unit
FCC	Fluid Catalytic Cracking
FTIR	Fourier-transform Infrared
GC	Gas Chromatography
HDPE	High Density Polyethylene
IR	Infrared
LDPE	Low Density Polyethylene
LPG	Liquefied Petroleum Gas
MP	Microplastic
MPSS	Microplastic Sediment Separator
MS	Mass Spectroscopy
MTBE	Methyl Tertiary-Butyl Ether
NGL	Natural Gas Liquid
PA	Polyamide
PAH	Polycyclic Aromatic Hydrocarbon
PCB	Polychlorinated Biphenyl
PE	Polyethylene
PET	Polyethylene Terephthalate
POP	Persistent organic pollutant
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl Chloride
SBR	Styrene Butadiene Rubber
US	Ultra Sound
UV	Ultra Violet
UV-VIS	Ultra Violet - Visible
VGO	Vacuum Gas Oil

LISTE OF SYMBOLES

C	Carbon
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
C ₃	Propane
C ₄	Butane
C ₅	Pentane
C ₆	Hexane
C ₄ =	Butylene(Butene)
C ₅ =	Pentene
H	Hydrogen Atomic
H ₂	Hydrogen
H ₂ O ₂	Hydrogen Peroxide
H ₂ S	Hydrogen Sulfide
HNO ₃	Nitric Acid
N	Nitrogen Atomic
N ₂	Nitrogen
O	Oxygen Atomic
O ₂	Oxygen
O ₃	Ozone
S	Sulfur
μm	Micrometer
λ	Wave Length

INTRODUCTION

Plastic is a generic term for man-made polymers that are most often prepared by polymerization of monomers from oil or gas. When not made from oil and gas, the polymer can be manufactured from coal, natural gas, cellulose or latex from trees.

The molecular backbone of a plastic polymer is typically composed of hydrocarbons and other naturally occurring compounds. Other chemicals, additives, are also added to the polymer to provide desirable properties, such as plasticizers that are added to improve the malleability of certain polymers.

We now live in “a plastic world” where almost everything surrounding us is made of plastic, and it is hard to imagine a world free of this material. Plastic production has increased dramatically worldwide over the last 60 years, and is still increasing, with current production at around 300 million tons yearly. Polyethylene (PE) is the most common plastic type produced followed by polypropylene (PP) and polyvinyl chloride (PVC).

Despite the many advantages of plastic, plastic litter can pose a serious threat to the environment. Around 50% of the plastic produced is used in low value products designed for disposable single-use. The chemically inert nature of plastic makes it highly durable, a property that is often desirable. However, at the same time this becomes a challenge when plastic products are not properly disposed of or recycled and end up as litter. Exactly how long plastic can remain in nature is difficult to predict as there has been insufficient time to evaluate its true persistence.

Major impacts of plastic waste to marine biota results from ingestion and entanglement in large debris. More recently, large numbers of small plastic fragments, fibers and granules are present in the marine environment. These particles are currently treated as a class of pollutants separate to large marine debris pollutants, and have been informally identified as particles with size small than 5 mm.

Microplastics are broadly classified as primary and secondary microplastics. Primary microplastics are plastic particles that are deliberately manufactured to be in the sub-visible size range. These particles include pelletised raw materials for manufacture of plastic products and plastic beads destined for use in processes and applications such as air-blasting, medicinal vector and cosmetics. Secondary microplastics are created by the physical, chemical and biological degradation of larger plastic debris. Photo-oxidation of marine plastic debris weakens polymer bonds and makes it brittle and subject to cracking, which in abrasive environments facilitates fragmentation and breakdown into increasingly smaller particles.

The full implications of physical and chemical interactions of plastic debris with marine biota are unclear. Presently, it is known that plastic ingested by wildlife can pass through or accumulate in the intestinal tract for several months, block the intestinal tract, reduce feeding stimulus

or migrate from the digestive cavity into tissues and cells. Microplastics have been found in the digestive content of a wide range of wildlife including fish.

Furthermore, ingestion of marine plastic has been implicated in the mortality of organisms including sea birds, cetaceans, and manatees.

Organisms exposed to plastic litter are not only exposed to polymers but also the additives that they contain, which can leach from the plastic over time.

Additives have the potential to leach out into the environment as the littered plastic becomes more brittle and exposed to abiotic factors such as UV-radiation and mechanical forces, and thereby act as a source of pollutants. Plastics can also accumulate Persistent Organic Pollutants (POPs) and other pollutants.

Three fundamental origins of microplastic chemical toxicity to wildlife have been described, all of which require ingestion by the organism to exert toxicity: 1) Leaching: plasticisers, UV stabilisers and other chemicals added to polymers during production leach into the organism post-ingestion; 2) Sorption: pollutants such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), metals and pesticides adsorb onto microplastics from the surrounding environment and can be released internally post-ingestion; or 3) Trophic flow : accumulated can be bio-accumulated through the food chain¹.

CHAPTER I : LITERATURE REVIEW

I.1. THE REFINING OF CRUDE OIL

The objective of refining, petrochemical and gas industries is to transform the crude oil and gas, into final commercial products such as gasoline , diesel, plastics or natural gas to deliver to the consumers. This segment is also called the “downstream” segment of the oil and gas industry.

In crude-oil, you can find naturally 4 types of Hydrocarbon.

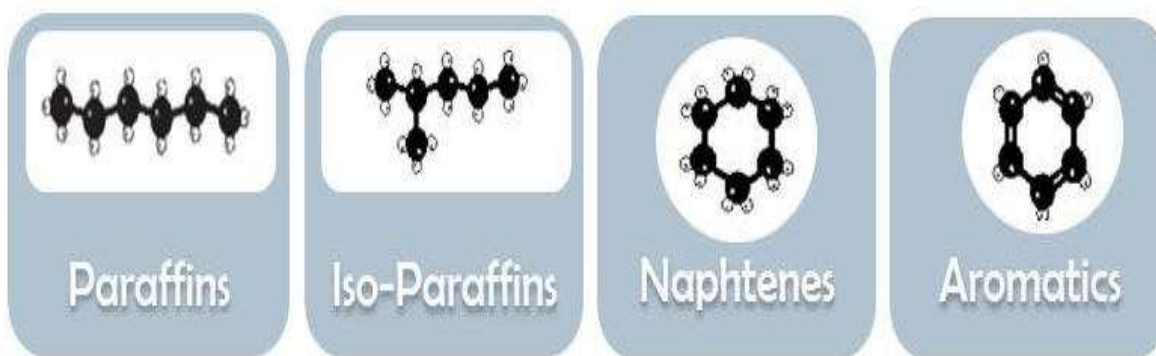


Figure 1.1: Types of hydrocarbons

- ✓ Paraffins are linear hydrocarbons made up of Carbon and Hydrogen atoms. Long linear paraffins are also called waxes.
- ✓ Iso-paraffins, which are non-linear paraffins, with one or multiple small groups of carbon and hydrogen, attached to them.
- ✓ Naphthene family. These hydrocarbons are composed of carbon and hydrogen, linked together in a ring shape.
- ✓ Aromatics are also hydrocarbons composed of rings of carbon and hydrogen, but, with double bonds between the carbon elements. Compared to Naphthenes, aromatics have, for a same number of carbons, less Hydrogen. The first Aromatic is called benzene with six atoms of carbon. It is an important compound for petrochemical and chemical industries.

In conclusion, a crude-oil is characterized by its Paraffin, Iso-Paraffin, Naphthene and Aromatic content.

It is important to know the type of hydrocarbon you have in crude, because these molecules will directly influence the quality of the different products, you will obtain from this crude-oil².

I.1.a. CRUDE DISTILLATION UNIT

The first unit of a refinery is called the Crude Distillation Unit or CDU. This unit is operated at high temperatures, around 360 °C at the bottom, and at a pressure of 2 barg. This first unit divides the crude oil into different smaller petroleum cuts, used as bases for everyday commercial products.

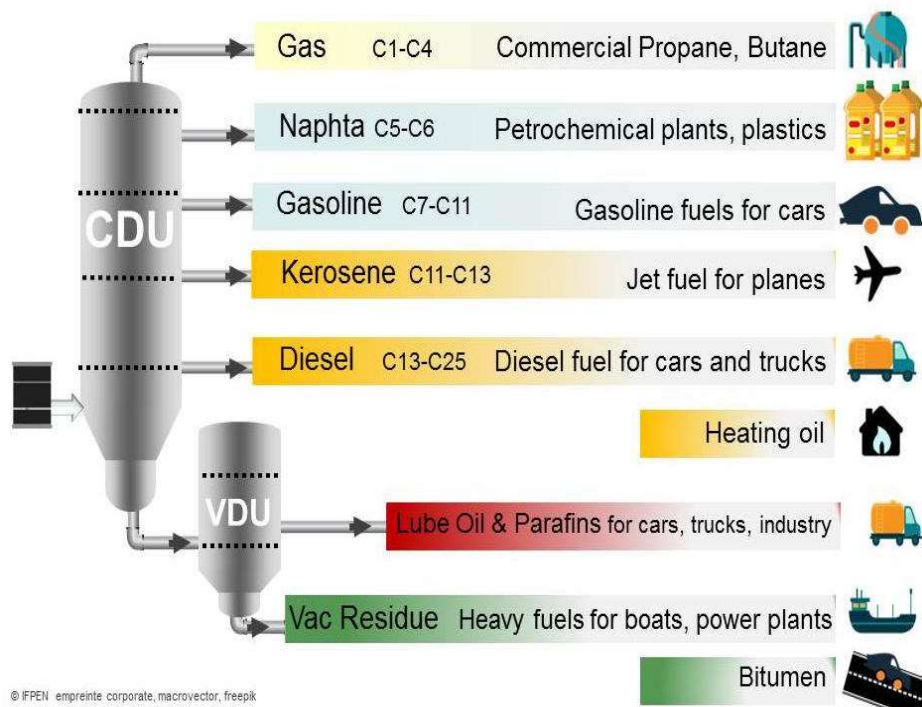


Figure 1.2 : Cuts of crude oil

The most important cut to this study is the Naphta cut because it is the raw material used in the petrochemical industry, to produce different types of plastics with different properties².

I.1.b. CATALYTIC REFORMING UNIT

Catalytic reforming is the process of transforming hydrocarbons ($C_6 - C_{10}$) with low octane numbers to aromatics and isoparaffins which have high octane numbers. It is a highly endothermic process requiring large amounts of energy.

In this process a special catalyst (platinum metal supported on silica or silica base alumina) is used to restructure naphtha fraction ($C_6 - C_{10}$) into aromatics and isoparaffins. The produced naphtha reformate has a much higher octane number than the feed. This reformate is used in gasoline formulation, and as a feedstock for aromatic production (benzene–toluene–xylene, BTX). Aromatics are really important bases for the petrochemical industry^{2,3}.

I.1.c. FLUIDISED CATALYTIC CRACKING (FCC)

The fluidised catalytic cracking (FCC) unit is the heart of the refinery and is where heavy low-value petroleum stream such as vacuum gas oil (VGO) is upgraded into higher value products, mainly gasoline and C₃/C₄ olefins like propylene. This molecule is really reactive, and it is an important base for the petrochemical industry for the manufacturing of plastics.

The role of the FCC is to take heavy desulphurised feedstock and crack it into lighter, mainly high octane gasoline. In a typical refinery, a FCC is installed mainly to produce gasoline. The FCC also produces olefins (C₄= and C₅=) and LPG. Olefins can be utilised for alkylation and MTBE production. In fact, some FCC units can be dedicated for the production of petrochemicals, as in the UOP petro-FCC process.

In conclusion we obtain, at the outlet of the FCC, a combination of different types of shorter molecules, mainly composed of aromatics and olefins^{2,3}.

I.2. THE DERIVATIVES OF PLASTICS FROM THE REFINERY

It is amazing how many products of our everyday life are made from oil and gas, and very few people from the general public are actually aware of it. It is in fact a fairly recent industry that has made it possible to produce all these goods: this is the petrochemical industry.

The petrochemical industry is actually a major sector of the large-scale chemical industry. Oil refineries and natural gas processing units produce streams that can be upgraded into petrochemical plants to make higher-end products. These products are first chemical intermediates, also called base chemicals. They are at the origin of a very important international trading activity.

Base chemicals are the precursors of an extraordinary large variety of more complex molecules that are used to make consumer products, including plastics and resins, synthetic rubbers, synthetic textiles, paints, cosmetics, medicines and so on. The profusion of petrochemical-sourced consumer products is just amazing and keeps increasing day by day. Just look around you and you will realize that they are a part of your everyday life.

Petrochemicals are at the heart of an extended value chain. The related industry covers the production of base chemicals and the manufacturing of raw plastics and resins. As their name infers, petrochemicals come basically from petroleum, that is to say crude oil, but also from natural gas, and, to a much less extent, from coal and biomass. The feedstocks used by the petrochemical industry are made of mixed hydrocarbons, which are molecules consisting mostly of carbon and hydrogen atoms. The hydrocarbon streams used are either specific oil cuts from refineries or condensable products from natural gas processing units⁴.

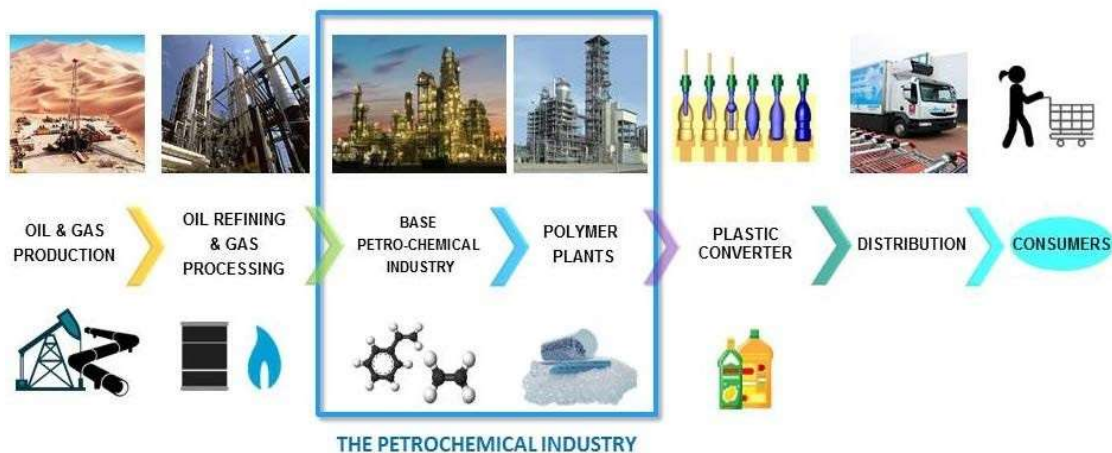


Figure 1.3 : The Petrochemical Industry

I.2.a. FROM FEEDSTOCKS TO PLASTICS

We have seen that petrochemicals are mainly sourced from oil and gas and that their production is energy-intensive. The fraction of oil and gas effectively consumed by the petrochemical industry remains, however, modest compared to the fraction used for transportation fuels and residential heating: less than 10 % of crude oil and 3 % of natural gas consumed annually is used to manufacture petrochemicals.

The main basic feedstocks of petrochemical platforms are:

- ✓ Natural Gas Liquids (NGL) consisting of ethane, propane and butane coming from natural gas processing units.
- ✓ By-product cuts of oil refineries such as naphtha, and mixed butane & propane, also called liquefied petroleum gas (or LPG).

The petrochemical platforms convert these feedstocks first into the so-called olefin and aromatic intermediates.

- ✓ **Ethylene** is the major petrochemical intermediate. This is the smallest building block. Ethylene represents over half of the total base chemical production volumes.
- ✓ **Propylene** is often a side product of ethylene production.
- ✓ **Aromatics** form the second main group of building-blocks in volume. They consist basically of BTX (Benzene, Toluene and Xylene)⁴.

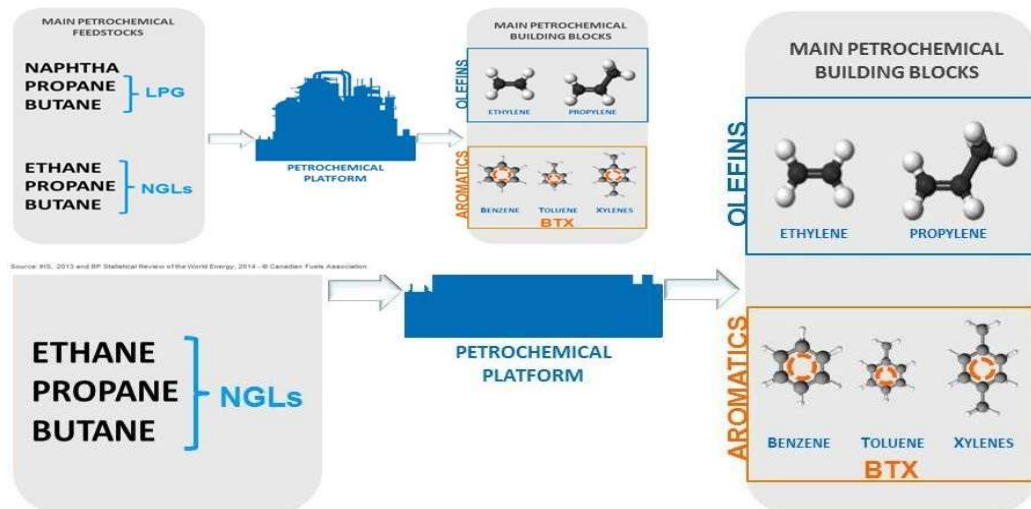


Figure 1.4 : The petrochemical intermediates

The final purpose of all these petrochemical intermediates is mostly to manufacture large commodity plastics and resins, as shown by their respective annual production tonnages.

Ethylene can afterwards be converted into lightweight plastics called **polyethylenes**, or it can be chemically transformed, after further steps, into polyvinyl chloride (PVC), a plastic material encountered in the building industry. In the same way, **propylene** can be used to make polypropylene, a versatile plastic.

Aromatic intermediates require further chemical modifications so as to be, in turn, possibly converted into useful plastics and resins. One of these plastics, polyethylene terephthalate (PET), is often the material of choice to make water and carbonated beverage bottles. In the same way, some aromatic-sourced plastics, such as polystyrene, are used to make dairy food packagings, building insulation boards or consumer electronic casings⁴.

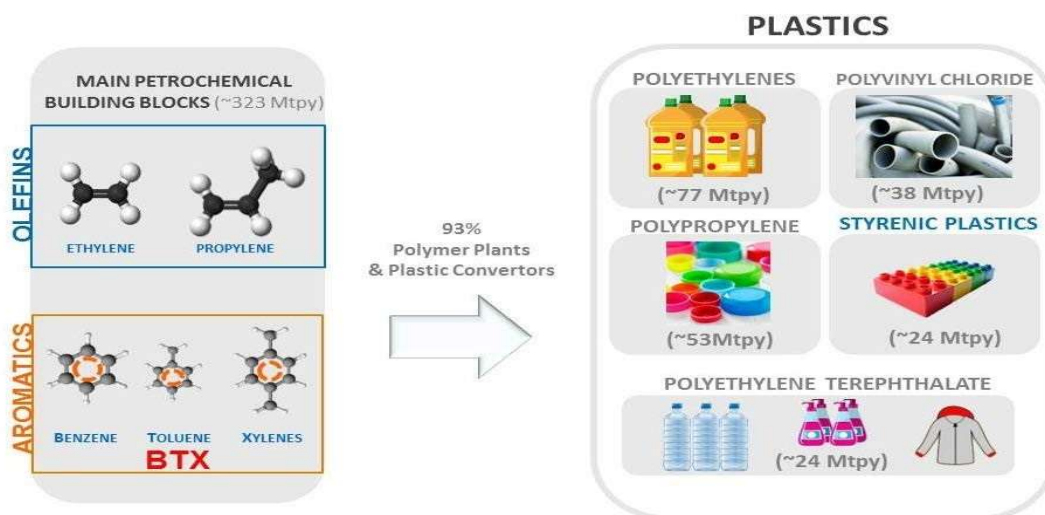


Figure 1.5 : From intermediates to plastics

I.2.b. THE INTERMEDIATES

The most important petrochemical intermediates are olefins and aromatics.

- ✓ OLEFINS are intrinsically reactive molecules thanks to their double bond. The smallest of them, namely ethylene and propylene, are the largest-volume intermediates of the industry, with 130 million tons of ethylene and 80 million tons of propylene produced per year.

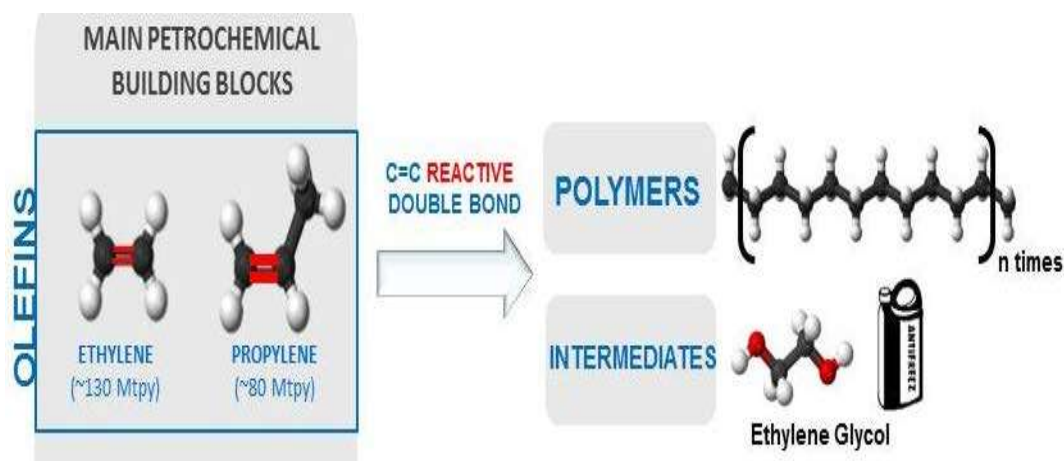


Figure 1.6: Olefins to polymers and intermediates

They are both reactive enough to be the direct precursors of long-chain molecules called polymers that are the base component of plastics and resins. They are also the precursors of other chemical intermediates like, for instance, ethylene glycol used as antifreeze for cars. Both are highly flammable gases. That is why they are difficult to transport. They are actually mostly transported onshore through gas pipelines and overseas in gas tankers.

- ✓ The 2nd family of intermediates is the AROMATICS Benzene, Toluene and Xylene, together abbreviated as BTX. They are characterized by a single 6-carbon aromatic ring⁵.

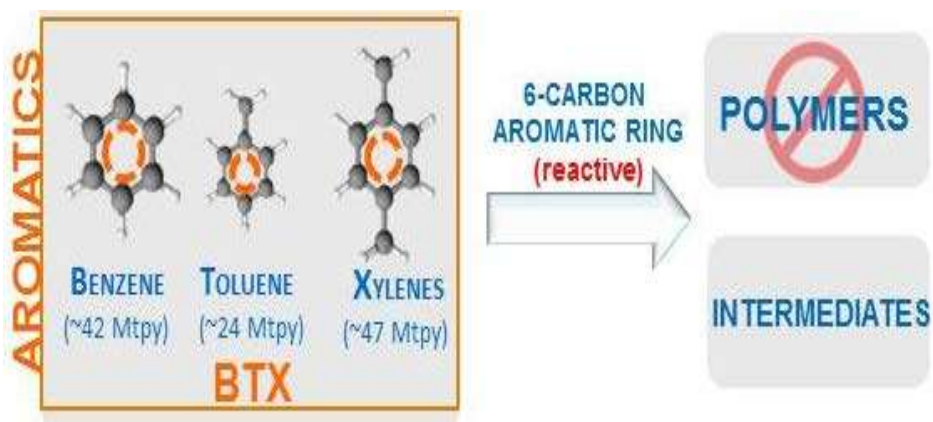


Figure 1.7 : Aromatics to Intermediates

BTX are liquid intermediates that cannot be readily converted into plastic polymers. For this purpose, they need to be chemically modified further on into more reactive molecules. As liquids, they can be easily transported by any means and are subject to overseas trading. All together, they represent currently an average yearly production tonnage of over 110 million tons⁵.

I.2.c. THE PETROCHEMICAL FEEDSTOCKS

Petrochemical intermediates come mostly from processed gas and refined oil. To be more precise, petrochemical platforms consume predominantly as feedstocks:

- Ethane and LPG from processed natural gas.
- Naphtha cuts, a mixture of C5 to C6 hydrocarbons, from the atmospheric distillation of crude oil.

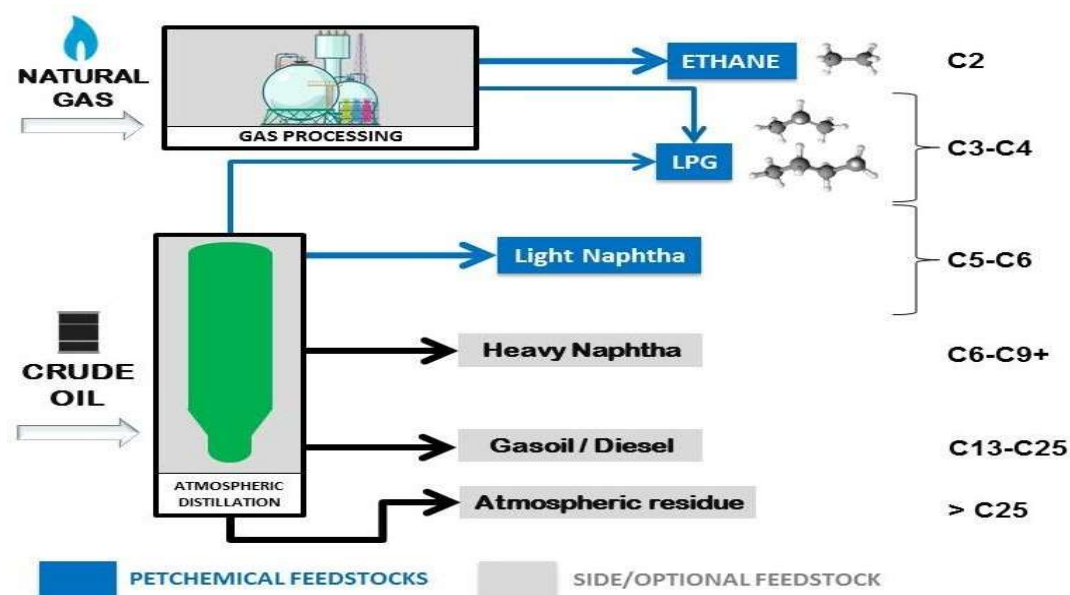


Figure 1.8 : The Petrochemical Feedstocks

Heavier refining cuts such as heavy naphtha, diesel oil or atmospheric residues from crude oil distillation can also be used as petrochemical feedstock.

All these products from refineries and natural gas plants are made of fairly stable hydrocarbons⁵.

I.2.d. GETTING THE BUILDINGS-BLOCKS

How can we convert these fairly stable feedstock molecules into the desired petrochemical intermediates which are olefins and aromatics? By **steam-cracking**. In this reaction, heavier hydrocarbons are broken down into shorter and more reactive molecules. In practice, hydrocarbon feedstocks are diluted with steam and then briefly heated in a very hot furnace at 800 °C or even higher in the absence of oxygen.

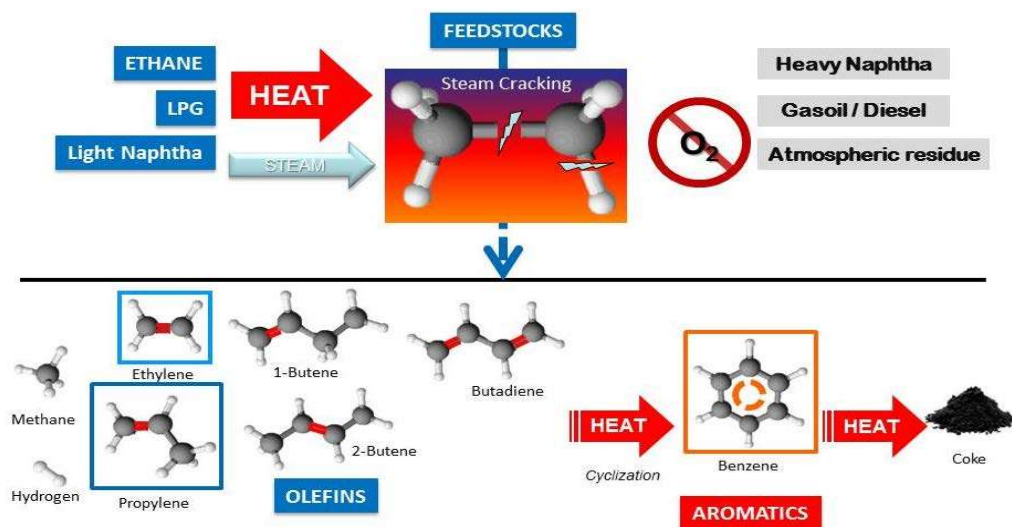


Figure 1.9: Steam Cracking of light HC

These specific conditions promote the high yield production of desired light olefins, such as ethylene and propylene, but also some heavier olefins like butenes. Butadiene, another C₄ molecule with 2 double bonds, is also produced. Methane and hydrogen are side-products. Under more severe conditions, for instance at higher temperatures, side cyclization reactions occur, yielding light aromatics. Benzene is the major aromatic produced this way. Further side reactions generally lead to the formation of carbon deposits, called coke.

As can be seen on this chart, figure 1.10, the feedstock used largely determines the composition of the products. Much larger proportions of ethylene compared to other products are formed from ethane and LPG steam-cracking. Ethylene is especially the sole product that can be valorized from ethane cracking. On the contrary, pyrolysis gasoline can only be produced by cracking heavier feedstocks such as naphtha or diesel oil⁵.

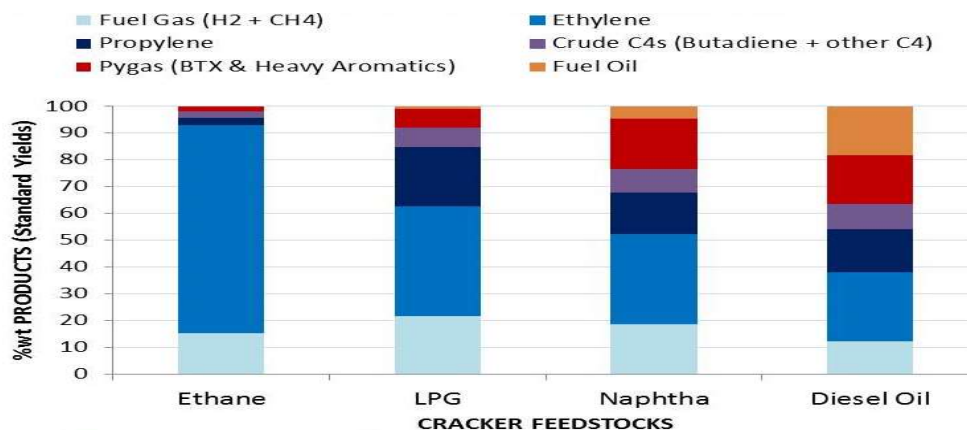


Figure 1.10: Feedstocks Versus Product Composition

I.2.e. OLEFINS AND AROMATICS FROM STEAM CRACKING

To summarize, steam crackers are core units of the petrochemical industry allowing us to produce mostly ethylene, and possibly propylene, C_4 s, and aromatic-rich pyrolysis gasoline, depending on the feedstock used.

Steam-crackers are some of the most technically complex and energy intensive plants in the chemical industry. Modern crackers are mega-units producing often 1 to 2 million tons of olefins.

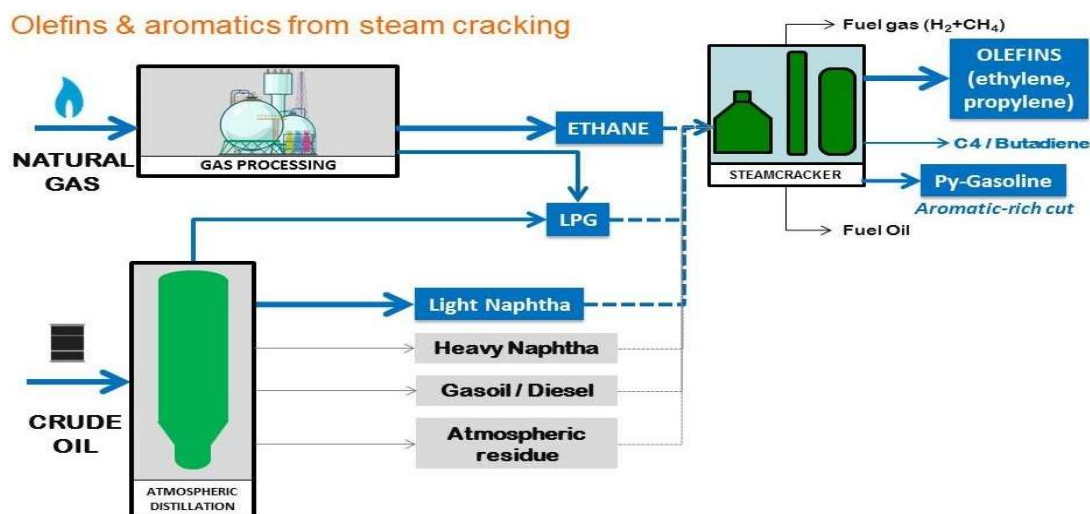


Figure 1.11: Olefins and Aromatics From Steam Cracking

We have just seen that propylene is only a co-product of ethylene production from naphtha crackers. Its demand has however largely outpaced the demand for ethylene, especially because of the great success of polypropylene plastics.

As seen previously a partial solution to the world propylene supply gap is “Refinery Propylene”, that is to say propylene from Fluid Catalytic Cracking⁵.

1.2.f. AROMATICS FROM CATALYTIC REFORMER

Naphtha crackers produce some pyrolysis gasoline which contains a lot of benzene, some toluene and a small fraction of xylenes.

This aromatics-rich cut can feed an aromatic complex, also called a BTX unit that separates the required aromatic intermediates, namely benzene, toluene and xylenes. As for propylene, pyrolysis gasoline remains a side-product of olefin production in naphtha crackers. Additionally, xylene production from steam-crackers is not sufficient to meet the demand: one of the xylenes, named para-xylene, is indeed highly demanded to make polyester plastics and fibers⁵.

For that reason, the main additional source of BTX aromatics is to be found in refineries equipped with a conversion unit called catalytic reformer.

Reformates can indeed be deviated from the gasoline pool to feed an aromatic complex and produce commercial-grade benzene, toluene and xylenes.

These two alternative supplies from refineries, namely refinery propylene and BTX from reformates, illustrate some of the synergies that can be drawn by associating a petrochemical platform to a refinery.

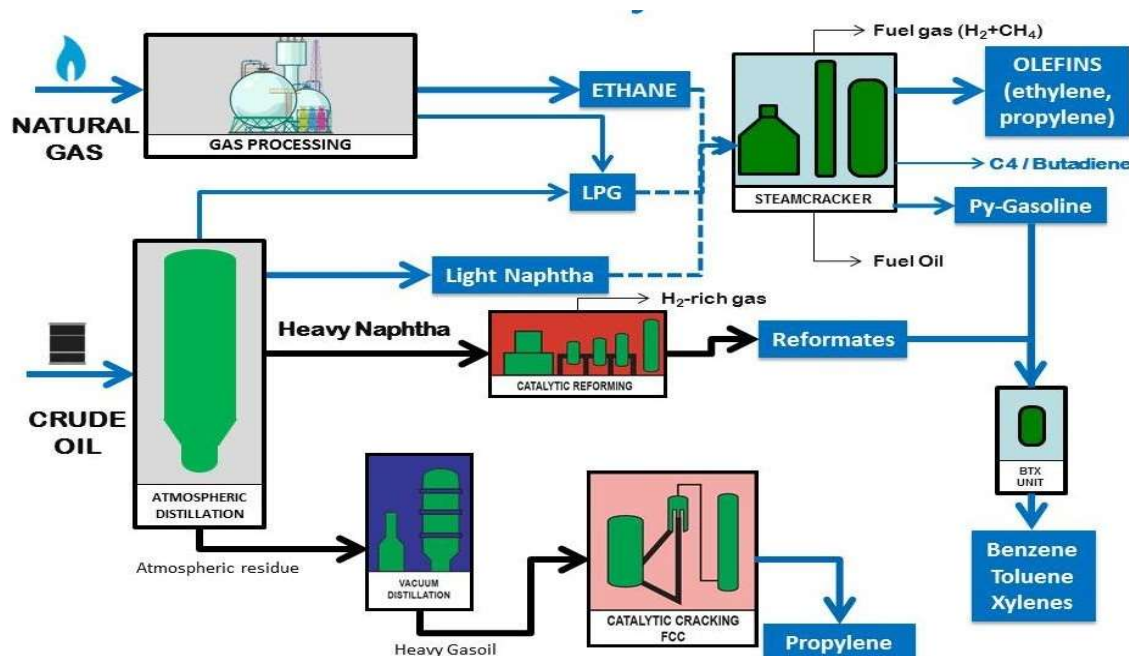


Figure 1.12: Olefins And Aromatics from The Refinery

To conclude, all these processes lead to small reactive molecules that can be used to make long-chain products by what we call “polymerization reactions”. These products, which are called “polymers”, are the base materials of an incredibly wide variety of plastics⁵.

I.3. DIVERSITY OF PLASTICS

Around 300 Mt of plastics are consumed each year worldwide. In Europe, only 46.3 Mt are needed to meet that demand. They are now everywhere in our lives, since their discovery a few decades ago. A huge amount is used in the packaging sector, to protect the final product after manufacturing and during transport to the supermarket and finally to the customer. In Europe, in 2013, this sector covered 40% of the plastics manufactured. The second most important application is for building and construction (almost 20%)⁶.

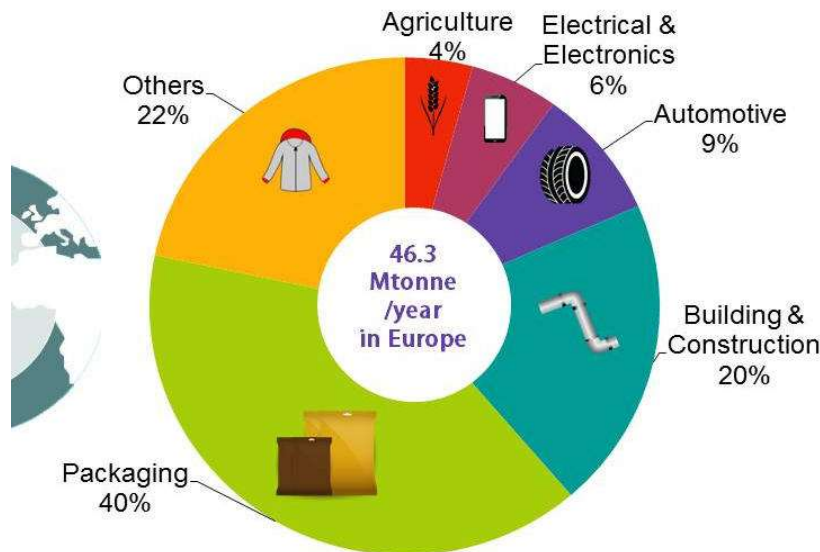


Figure 1.13: Diversity of plastics

We, as consumers, may recognize some plastics thanks to an identification code, quite common worldwide now. However, it is not compulsory for the plastic manufacturers to stamp it on their products. Several codes exist as shown here.



Figure 1.14: Worldwide identification code of different plastic

What are plastics? Well, first, let us introduce some vocabulary. Remember the reforming, FCC and steam-cracker units. They produce some molecules, the petrochemical intermediates, such as olefins and aromatics. The next step is to add them together (the so-called polymerization step) in order to build a very long chain, with a successive arrangement of repeating units, called a polymer⁶.

Then, some additives, bringing resistance to oxygen, or to UVs, may be added to polymers. After this step, we obtain mixtures called plastic compounds, most often available in pellet form.

They have now to be converted to the final object. This is known as plastic material processing.

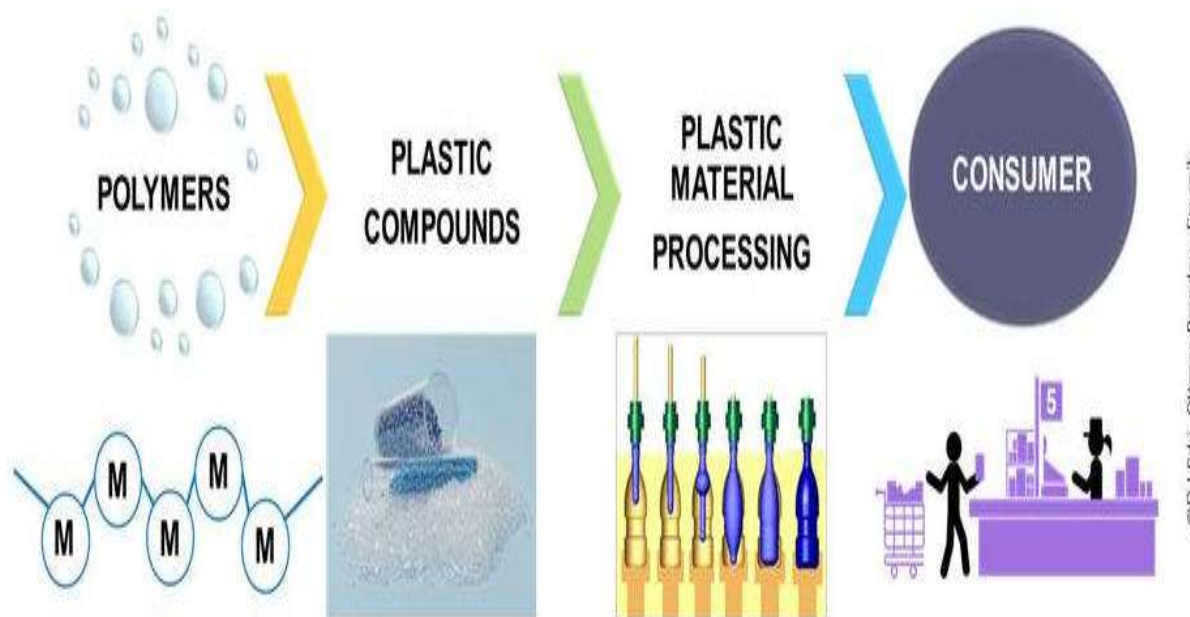


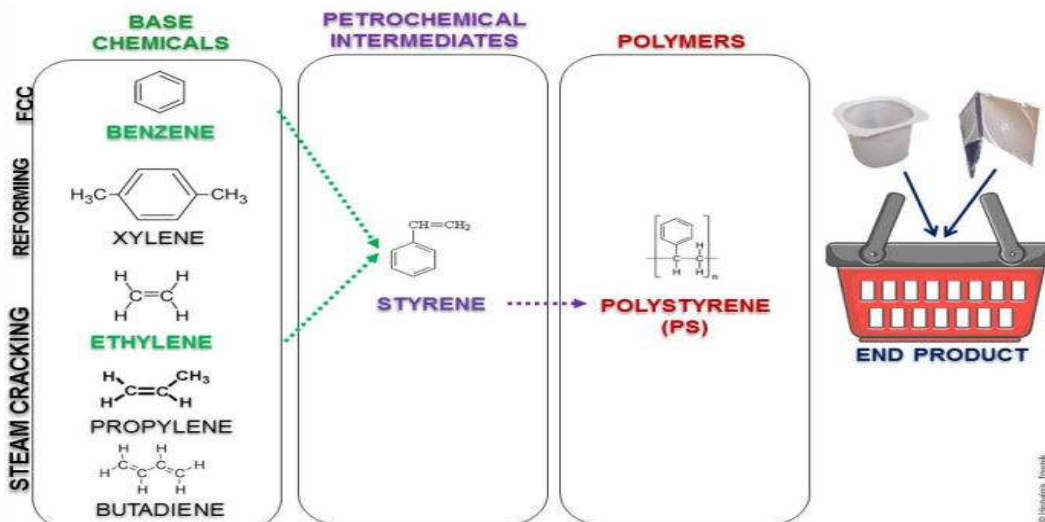
Figure 1.15: Plastic Material Processing

And last, after being filled with soap, water, food, etc., the end product is sold to the customer. Since we are able to combine different types of base chemicals, we can manufacture almost as many polymers and plastics as we want⁶.

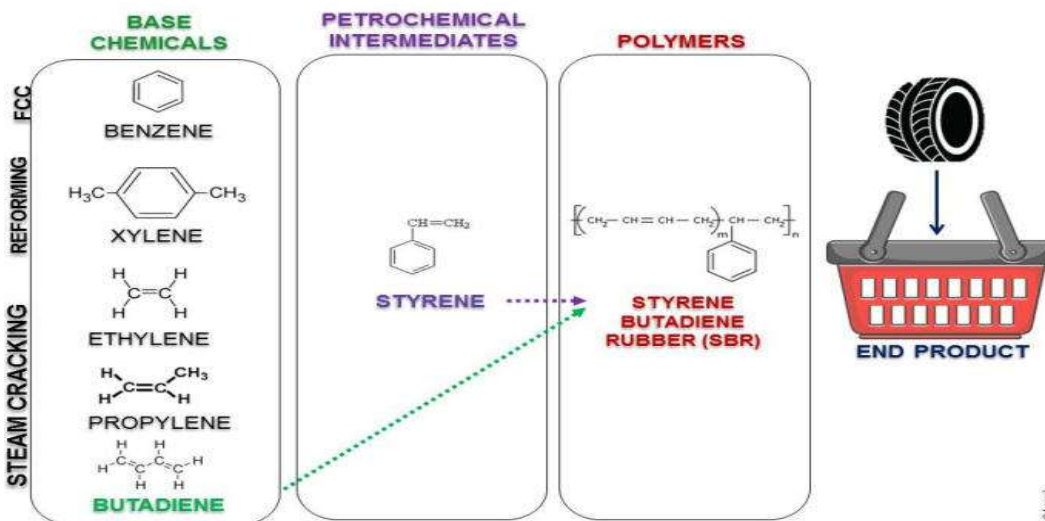
I.3.a. FROM BASE CHEMICALS TO POLYMERS

Let's remember first the simplest base chemicals from the reforming, steam-cracking and FCC units. These olefins and aromatics can be in the liquid state, like benzene and xylene, or in the gaseous state, like ethylene, propylene and butadiene.

As shown in figure 1.16, ethylene and benzene can react together to give styrene, a petrochemical intermediate. Then, in a last step, styrene can be polymerized with itself to give polystyrene, so-called PS, used to manufacture yogurt pots, casing for CDs, and insulation for houses etc⁶.



Starting from styrene again, instead of polymerizing it alone, we can make it react with butadiene, resulting in a polymer called Styrene Butadiene Rubber (so-called SBR), used for tyres.



Let's come back to ethylene. This base chemical can be chemically modified into a petrochemical intermediate, called ethylene glycol.

The chemical reaction between ethylene glycol and xylene will produce the polymer we call Poly Ethylene Terephthalate (PET) widely used for soft drink and fruit juice bottles (Figure 1.18). But the same polymer can be converted to another form, to produce polyester fibers, used for clothing⁶.

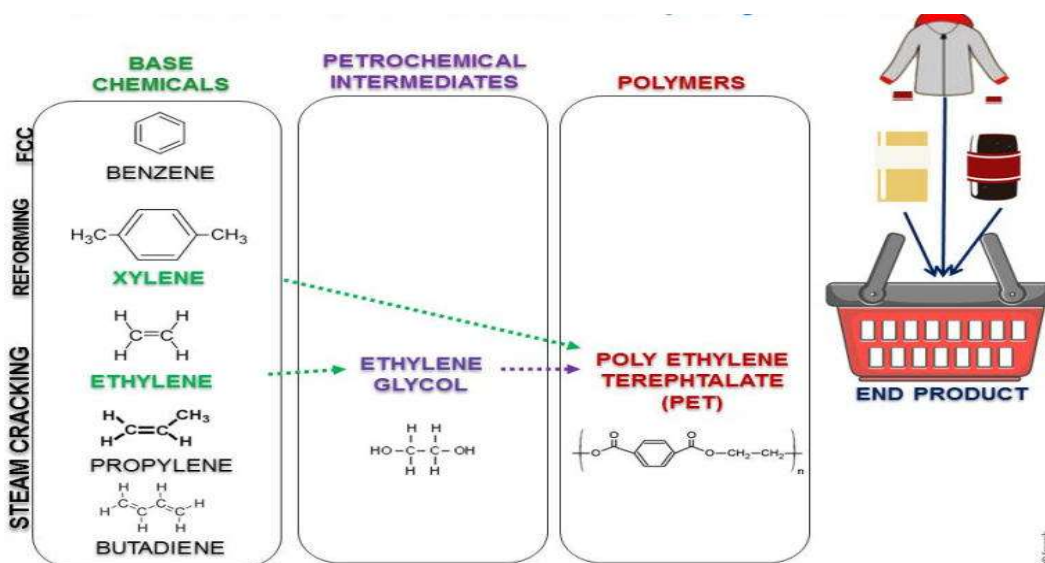


Figure 1.18: End product form PET

Going back to ethylene again, it can react with chlorine extracted from salt, to produce vinyl chloride. Polymerized with itself, it can be used to manufacture Poly Vinyl Chloride (PVC), widely used in the building and construction sector, for window frames and water pipes.

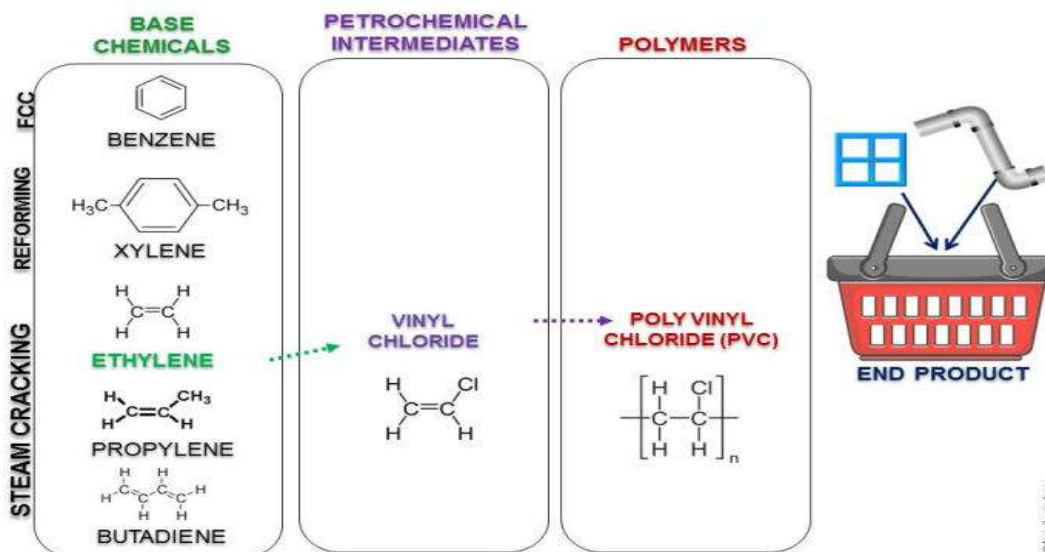


Figure 1.19: End product from PVC

Ethylene can be polymerized with itself. Depending on the reaction conditions, final polymers can be Low Density Polyethylene, LDPE, or High Density Polyethylene, HDPE. They do not have the same purpose (Figure 1.20). On the one hand, LDPE is used for transparent, flexible packaging for water bottle packs or bags. On the other hand, HDPE is used for milk bottles, cleaning agent bottles, shampoo containers etc⁶.

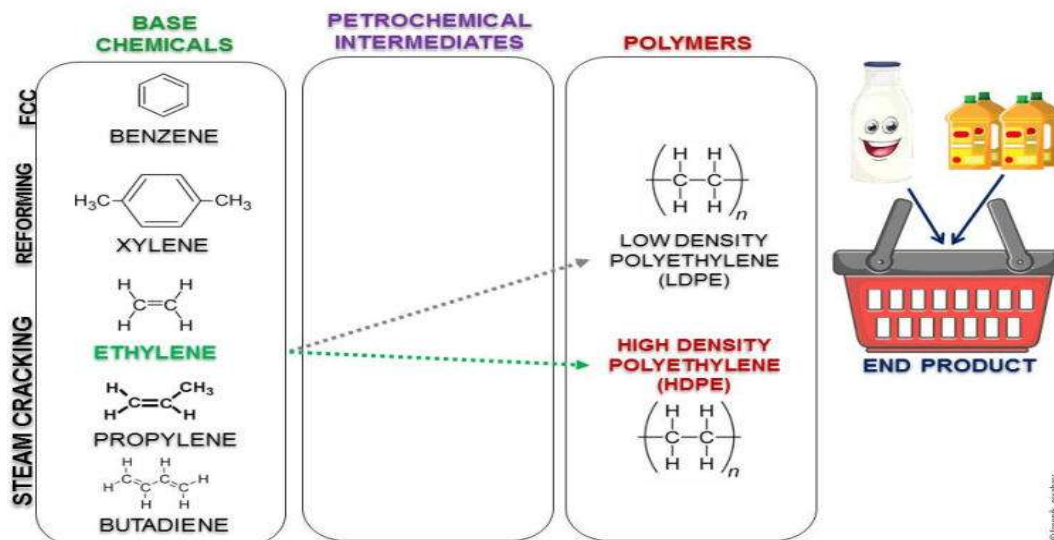


Figure 1.20 : End product from PE

Propylene can also be polymerized with itself, resulting in a polymer called Polypropylene, used for car bumpers, but also for take-away food containers and lunch boxes⁶.

I.3.b. FROM POLYMERS TO PLASTICS

Basically all the plastic compounds are in solid form and will flow, like honey, when you increase the temperature. During the processing step, the polymer will pass through the equipment. Once you reach the desirable shape, the product is cooled down to keep the right shape.

One example of processing is the thermoforming process where a hot plug punches a heated plastic sheet into a mould. Once the mould is released, while cooling, the plastic keeps the desired form. This is the case for PS meat packaging.

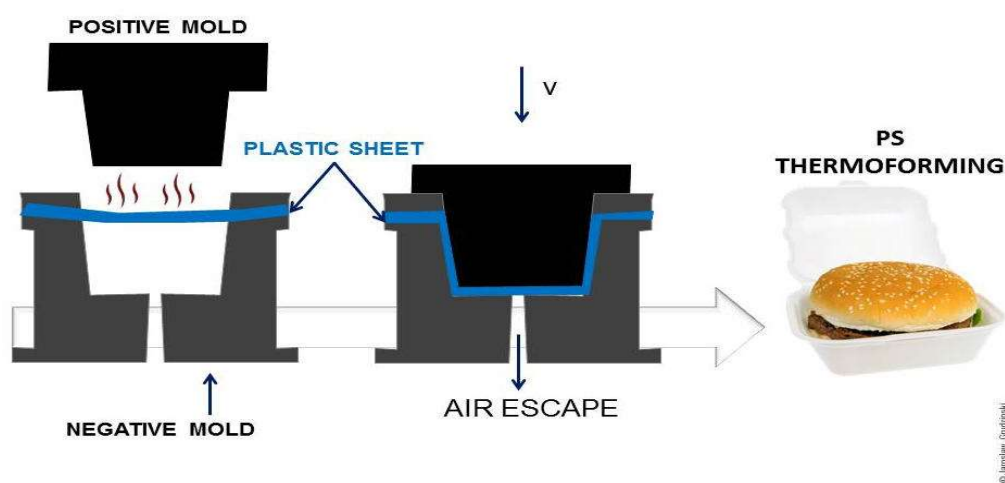


Figure 1.21: Thermoforming process

A second example of packaging is injection blow moulding, for water bottles. An initial piece of plastic, called a pre-form, is introduced into a mould. It is then heated and air is blown into this plastic pre-form, which grows until it reaches the walls of the mould. Then the mould opens to release the plastic.

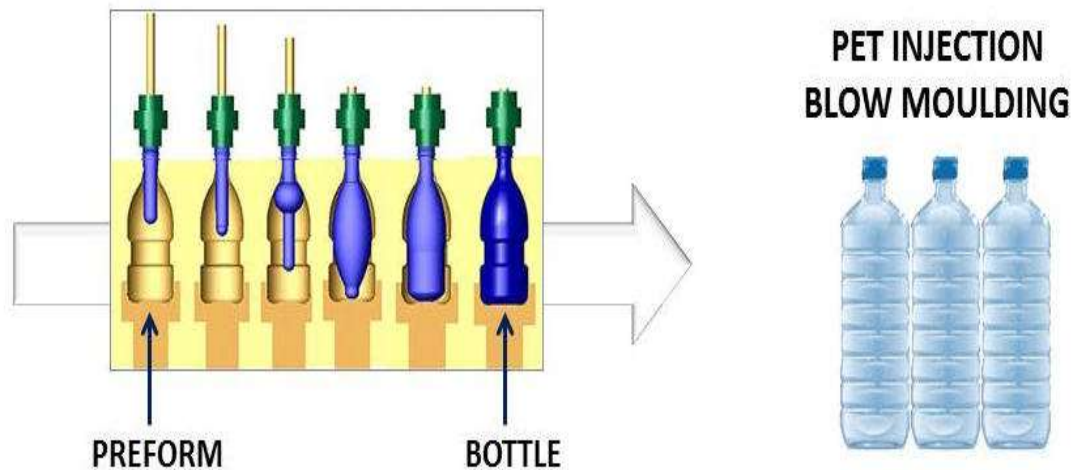


Figure 1.22: Injection blow moulding

Of course the choice of the process depends on what the final product will be used for, and on the properties you want to obtain.

If we focus on packaging properties, we first need our plastic to resist shocks. We thus have to assess a high mechanical resistance, which is possible with PET and HDPE.

PP is also used, for example in caps, which have to be opened and closed very often. On the reverse, for some applications, we prefer the plastic to break easily, like for the yogurt family pack manufactured with PS.

Another kind of property is the ability of the plastic to resist UVs, milk bottles for example. In this application, there are successively 3 layers, an outer white one in HDPE that brings mechanical strength, one dark one to resist UVs, and the third white one (the inner one) that forms a lining because the customer does not like to see a black color inside the bottle when he pours milk for breakfast.

Lastly, for packaging, some optical properties can be desired: the product looks more tasty, or luxurious if the plastic is highly transparent, like PET, or even glossy, like PP. Good examples are fruit juice bottles, or individual yogurt pots that can be more attractive for a customer than a classical and inexpensive yogurt family pack⁶.

I.4. THE KIND OF PLASTICS

Practically stated, a plastic is an organic polymer, available in some resin form or some form derived from the basic polymerized resin. These forms can be liquid or paste like resins for embedding, coating, and adhesive bonding, or they can be molded, laminated, or formed shapes, including sheet, film, or larger-mass bulk shapes.

Although there are numerous minor classification schemes for polymers, depending on how one wishes to categorize them, nearly all polymers can be placed in one of two major classifications - thermosetting materials (or thermosets) and thermoplastic materials. Likewise, foams, adhesives, embedding resins, elastomers, and so on, can be subdivided into thermoplastic and thermosetting classifications⁷.

I.4.a. THERMOPLASTICS

The material that softens when heated above the glass transition temperature or melting temperature and becomes hard after cooling is called thermoplastics. Thermoplastics can be reversibly melted by heating and solidified by cooling in limited number of cycles without affecting the mechanical properties. On increasing the number of recycling of thermoplastics may result in color degradation, thereby affecting their appearance and properties. In the molten state, they are liquids, and in the mushy state they are glassy or partially crystalline. The Molecules are joined end-to-end into a series of long chains, each chain being independent of the other. Above the melting temperature, all crystalline structure disappears and the long chain becomes randomly scattered.

The molecular structure of thermoplastic (figure 1.23) has an influence on the chemical resistance and resistance against environmental effects like UV radiation. The properties may also vary from optical transparency to opaque, depending on the molecular structure. The important properties of the thermoplastics are high strength and toughness, better hardness, chemical resistance, durability, self lubrication, transparency and water proofing.

With the application of heat, thermoplastic softens and it can be molded into desired shapes. Some thermoplastics can be joined with the application of heat and pressure. There are several techniques available for the joining of thermoplastics such as mechanical fastening, fusion bonding, hot gas welding, solvent bonding, ultrasonic welding, induction welding, and dielectric welding.

The different types of thermoplastic are: Acrylonitrile Butadiene Styrene (ABS), Acetals, Acrylics, Fluorocarbons, Polyamides, Polycarbonates, Polyethylene (PE), Polypropylenes (PP), Polystyrenes, Polyvinyl Chloride (PVC), Liquid Crystal Polymers (LCP) and Vinyls.

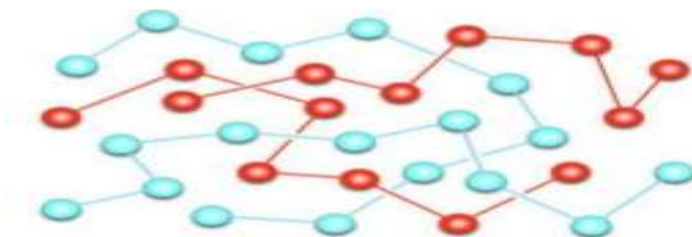


Figure 1.23: Molecular structure of thermoplastics

Thermoplastics can be used to manufacture the dashboards and car trims, toys, phones, handles, electrical products, bearings, gears, rope, hinges and catches, glass frames, cables, hoses, sheet, and windows, etc⁷.

I.4.b. THERMOSETS

The property of material becoming permanently hard and rigid after cooling when heated above the melting temperature is called thermosets. The solidification process of plastics is known as curing. The transformation from the liquid state to the solid state is irreversible process, further heating of thermosets result only in the chemical decomposition. It means that the thermosets can't be recycled. During curing, the small molecules are chemically linked together to form complex inter-connected network structures (figure 1.24). This cross-linking prevents the slippage of individual chains. Therefore, the mechanical properties (tensile strength, compressive strength, and hardness) are not temperature dependent, as compared to thermoplastics. Hence, thermosets are generally stronger than the thermoplastics.

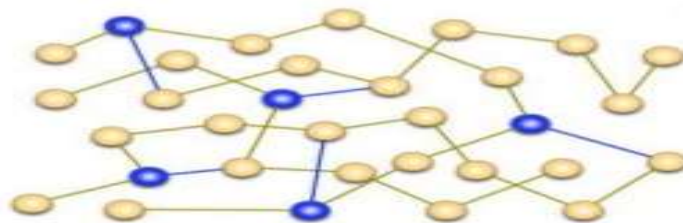


Figure 1.24: Molecular structure of thermosets

The joining of thermosets by thermal processes like ultrasonic welding, laser welding, and gas welding is not possible, but mechanical fastening and adhesive bonding may be used for low strength applications.

The different types of thermosets are Alkyds, Amine, Bakelite, Epoxy, Phenolic (PF), Polyester, Silicone, Polyurethane (PUR), and Vinyl Ester.

Thermosets are commonly used for high temperature applications. Some of the common products are electrical equipments, motor brush holders, printed circuit boards, circuit breakers, encapsulation, kitchen utensils, handles and knobs, and spectacle lenses⁷.

I.4.c. TYPES OF PLASTICS

The Society of the Plastics Industry (SPI) established a classification system in 1988 to allow consumers and recyclers to identify different types of plastic. Manufacturers place an SPI code, or number, on each plastic product, usually molded into the bottom. Table 1.1 provides a basic outline of the different plastic types associated with each code number.

Category of product	Description
PET	PET sometimes absorbs odors and flavors from foods and drinks that are stored in them. Items made from this plastic are commonly recycled. PET plastic is used to make many common household items like beverage bottles, medicine jars, rope, clothing and carpet fiber.
HDPE	High-Density Polyethylene products are very safe and are not known to transmit any chemicals into foods or drinks. HDPE products are commonly recycled. Items made from this plastic include containers for milk, motor oil, shampoos and conditioners, soap bottles, detergents, and bleaches. It is NEVER safe to reuse an HDPE bottle as a food or drink container if it didn't originally contain food or drink
PVC	Polyvinyl Chloride is sometimes recycled. PVC is used for all kinds of pipes and tiles, but is most commonly found in plumbing pipes. This kind of plastic should not come in contact with food items as it can be harmful if ingested.
LDPE	Low-Density Polyethylene is sometimes recycled. It is a very healthy plastic that tends to be both durable and flexible. Items such as cling-film, sandwich bags, squeezable bottles, and plastic grocery bags are made from LDPE.
PP	Polypropylene is occasionally recycled. PP is strong and can usually withstand higher temperatures. It is used to make lunch boxes, margarine containers, yogurt pots, syrup bottles, prescription bottles. Plastic bottle caps are often made from PP.
PS	Polystyrene is commonly recycled, but is difficult to do. Items such as disposable coffee cups, plastic food boxes, plastic cutlery and packing foam are made from PS.
Other	Polycarbonate is included in this category. This type of plastics is difficult to recycle. it is used in baby bottles, compact discs, and medical storage containers.

Table 1.1: Different types of plastics and their classification

I.5. THE NATURE AND CLASSIFICATION OF PLASTICS

Plastics are synthetic organic polymers, which are derived from the polymerisation of monomers extracted from oil or gas. Whilst the societal benefits of plastic are far-reaching, this valuable commodity has been the subject of increasing environmental concern. Primarily, the durability of plastic that makes it such an attractive material to use also makes it highly resistant to degradation, thus disposing of plastic waste is problematic. The proportion of plastic contributing to municipal waste constitutes 10% of waste generated worldwide. While some plastic waste is recycled, the majority ends up in landfill where it may take centuries for such material to breakdown and decompose.

In recent years, there has been increasing environmental concern about 'microplastics': tiny plastic granules used as scrubbers in cosmetics and air-blasting, and small plastic fragments derived from the breakdown of macro-plastics⁸.

I.5.a. MICROPLASTICS

Whilst macro-plastic debris has been the focus of environmental concern for some time, it is only since the turn of the century that tiny plastic fragments, fibers and granules, collectively termed "microplastics", have been considered as a pollutant in their own right. Microplastics have been attributed with numerous size-ranges, varying from study to study, with diameters of <10 mm, <5 mm, 2–6 mm, <2 mm and <1 mm.

This inconsistency is particularly problematic when comparing data referring to microplastics, making it increasingly important to create a scientific standard. Recently, the term "mesoplastics" is used as a scientific nomenclature, to differentiate between small plastics visible to the human eye, and those only discernible with use of microscopy⁸.

I.5.a.1. PRIMARY MICROPLASTICS

Plastics that are manufactured to be of a microscopic size are defined as primary microplastics. These plastics are typically used in facial-cleansers and cosmetics, or as air-blasting media. Under the broader size definitions of a microplastic, virgin plastic production pellets (typically 2-5 mm in diameter) can also be considered as primary microplastics, although their inclusion within this category has been criticised. Microplastic "scrubbers", used in exfoliating hand cleansers and facial scrubs, have replaced traditionally used natural ingredients, including ground almonds, oatmeal and pumice. Since the patenting of microplastic scrubbers within cosmetics in the 1980s, the use of exfoliating cleansers containing plastics has risen dramatically. Typically marketed as "micro-beads" or "micro-exfoliates", these plastics can vary in shape, size and composition depending upon the product. For example, the presence of polyethylene and polypropylene granules (<5 mm) and polystyrene spheres (<2 mm) in one cosmetic product.

Primary microplastics have also been produced for use in air-blasting technology. This process involves blasting acrylic, melamine or polyester microplastic scrubbers at machinery, engines and boat hulls to remove rust and paint⁸.

1.5.a.2. SECONDARY MICROPLASTICS

Secondary microplastics describe tiny plastic fragments derived from the breakdown of larger plastic debris, both at sea and on land. Over time a culmination of physical, biological and chemical processes can reduce the structural integrity of plastic debris, resulting in fragmentation.

Over prolonged periods, exposure to sunlight can result in photo-degradation of plastics; ultraviolet (UV) radiation in sunlight causes oxidation of the polymer matrix, leading to bond cleavage. Such degradation may result in additives, designed to enhance durability and corrosion resistance, leaching out of the plastics.

The cold, haline conditions of the marine environment are likely to prohibit this photo-oxidation; plastic debris on beaches, however, have high oxygen availability and direct exposure to sunlight so will degrade rapidly, in time turning brittle, forming cracks and "yellowing". With a loss of structural integrity, these plastics are increasingly susceptible to fragmentation resulting from abrasion, wave-action and turbulence. This process is ongoing, with fragments becoming smaller over time until they become microplastic in size. It is considered that microplastics might further degrade to be nanoplastic in size, although the smallest micro-particle reportedly detected in the oceans at present is 1.6 micrometer in diameter.

The development of biodegradable plastics is often seen as a viable replacement for traditional plastics. However, they too may be a source of microplastics. Biodegradable plastics are typically composites of synthetic polymers and starch, vegetable oils or specialist chemicals designed to accelerate degradation times that, if disposed of appropriately, will decompose in industrial composting plants under hot, humid and well-aerated conditions⁸.

1.6. THE SOURCE OF SUCH POLLUTANTS

Plastics are synthetic organic polymers (i.e. they contain carbon as an essential element along their chains), which are long and high molecular-weight molecules consisting of repeating units called monomers. It is estimated that around 4% of the world's annual petroleum production is converted to plastics while a similar amount of petroleum is used to provide the energy for plastic manufacturing. The annual global production of plastics highly increased since the development of synthetic polymers in the middle of the 20th century and has doubled in the last 15 years⁹.

Plastics are ideally suited for a variety of applications in transport, telecommunications, clothing and packaging because of light weight, low cost, strong and potentially transparent material.

Packaging represents more than a third of European plastic consumption and consists of products which have a very short life span. Several broad classes of plastics are used in packaging, including polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET) and polyvinyl chloride (PVC).

Plastic Class	Specific Gravity	Products and typical origin
Low-density polyethylene (LDPE LLDPE)	0.91 - 0.93	Plastic bags, six-pack rings, bottles, netting, drinking straws
High-density polyethylene (HDPE)	0.94	Milk and juice jugs
Polypropylene (PE)	0.83 - 0.85	Rope, bottle caps, netting
Polystyrene (PS)	1.05	Plastic utensils, food containers
Foamed Polystyrene	-	Floats, bait boxes, foam cups
Nylon (PA)	-	Netting and traps
Polyethylene terephthalate (PET)	1.37	Plastic beverage bottles
Polyvinyl chloride (PVC)	1.38	Plastic film, bottles, cups
Cellulose Acetate (CA)	-	Cigarette filters

Table 1.2: Classes of plastics that are commonly encountered in the marine environment

Generally, the plastic polymers are mixed with various additives to improve performance, such as carbon and silica to reinforce the material, plasticizers to render the material pliable, thermal and UV stabilizers, flame retardants and coloring.

Some additive chemicals are potentially toxic and there is a particular concern about the extent to which additives released in the environment from plastic products of high production volume and wide usage (e.g. phthalates, Bisphenol A (BPA), bromine flame retardants, UV screens and anti-microbial agents) have adverse effects on animal or human populations, while a recent study estimated that the direct ingestion of microplastics by some aquatic species is a negligible pathway for exposure to BPA⁹.

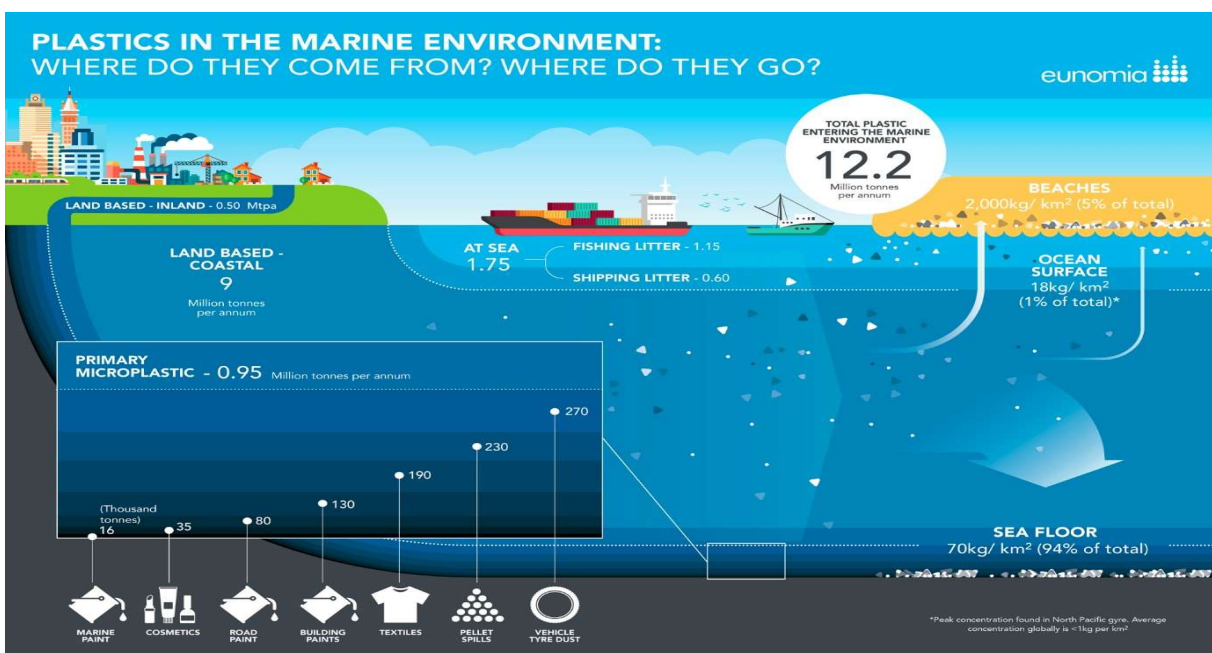


Figure 1.25: Schematic drawing showing the main sources and movement pathways for plastics debris in the oceans

Although limited in terms of mass compared to the other plastic sources, the wide use of microplastic scrub beads (especially polyethylene and polypropylene particles; as abrasives in personal care products (e.g. facial cleaners and some toothpastes) has been only recently identified as potential contributor to marine pollution.

However, these microplastic particles that are generally smaller than 1 millimeter in size may be a major source of microplastic pollution for aquatic environments, because they are designed to be washed down the drain and they are usually not captured by treatment screens in wastewater plants (generally larger than 1 to 6 mm). As a result, the worldwide use of microplastic-containing products directly releases huge amounts of micro-beads via sewage discharge into the aquatic environment. These insoluble particles can be ingested by planktonic and filter-feeding organisms at the base of the aquatic food chain.

The United Nations Environment Program (UNEP) and the European Commission define marine litter as “any persistent, manufactured or processed solid material discarded, disposed of or abandoned in the marine and coastal environment”. The average proportion of plastics varies between 60 to 80% of total marine debris and can reach as much as 90 to 95% of the total amount of marine litter. Table 1.2 shows the main classes of plastics that are commonly encountered in the marine environment during the 2012 International Coastal Cleanup, the world’s largest volunteer effort to collect information on the amounts and types of marine debris.

Many of the most commonly found pieces of trash include items we use every day from food wrappers and beverage containers to plastic bags⁹.

I.7. IMPACTS OF PLASTIC ON MARINE ORGANISMS

Marine plastic debris has major direct and indirect harmful effects on the marine biota and wildlife. Problems associated with absorption and entanglement of plastic debris include ingestion of specific plastic items by animals that mistake plastic waste for prey, and to a lesser extent consumption of pelagic fish and other prey that have microplastic particles in their guts. Accumulation of plastic debris in the marine environment can result in habitat degradation. Finally, plastics contain toxic substances that were added to the polymers during the production process. Marine plastics accumulate toxic pollutants present at the sea surface and serve as a potential transport vector for chemical contaminants of concern⁹.

I.7.a. THE PHYSICAL EFFECTS OF PLASTIC INGESTION

There are two major concerns associated with the ingestion of plastic by marine animals: Entanglement and ingestion of plastics. Potentially leading to suffocation or intestinal blockage, entanglement is largely underestimated as most victims are undiscovered over vast ocean areas when sunk or eaten by predators. The second concern is the increasing exposure of marine organisms to toxic materials through ingestion of plastics and consequently entrance of hazardous pollutants into the food chain, either originating from the material itself (plastic additives) or from the chemical pollutants that adsorb to it from polluted surrounding waters. The ingestion of plastic debris does not only concern predatory organisms (e.g. birds, turtles, seals, whales or dolphins) but also smaller invertebrate organisms.

Animals can get entangled by plastic floating at the sea surface, and in particular by derelict and lost fishing gear (or fishing nets, ropes, monofilament lines, trawl and gill nets) made of synthetic fibers that are resistant to degradation. These so called ghost nets continue to indiscriminately entangle and trap fishes and non-target organisms while they drift in the ocean⁹.



Figure 1.26 : Entangling of marine animals

Although the entanglement of marine species due to marine litter has been frequently described as a serious mortality factor, only a small numbers of entanglements are recorded and the impact of suffocation on marine populations specifically due to plastic litter is difficult to estimate.

The ingestion of plastic items by marine species has been widely reported, including for sea birds, turtles, fish, mussels, crustaceans and marine mammals. There is evidence that some birds and marine species mistake plastic particles waste for potential prey items, and select specific plastic shapes and colors. Plastics as part of the animal's diet reduce actual food uptake and cause internal injury and death following blockage of intestinal tract. Sea turtles also often consume plastic debris and semi-inflated floating plastic bags drifting in ocean currents which look similar to their favorite natural prey, jellyfish.



Figure 1.27 : Ingestion of Plastics by animals

As a consequence, some obstructions caused by ingested plastics can prevent organisms from taking in food and this phenomenon can lead to malnutrition, starvation, suffocation and death with some effects being nonetheless specific to certain species⁹.

I.7.b. CHEMICALS ASSOCIATED WITH PLASTIC DEBRIS

There is a growing concern about the negative health effects of some additives (added to the polymers during the manufacturing process) to which most people are exposed, such as phthalates or BPA because they are not chemically bound to the plastic matrix and they can easily leach into their surrounding environment; especially when plastics breakdown in smaller pieces and more surface area is exposed to degradation. Experiments furthermore demonstrate that hard plastic trash discarded in the oceans leaches BPA at an accelerated rate when exposed to the salts in seawater and that biodegradation of plastic polymers by bacteria introduces BPA into seawater.

Another major concern for marine organisms is that floating plastics in the ocean can serve as transport vectors for persistent organic pollutants (POPs) that accumulate on their surface

(adsorption) during their long residence time in polluted surface water. POPs are persistent synthetic organic compounds with a hydrophobic nature, chemically stable and not easily degraded in the environment.

It is however important to note that the concentration of chemicals associated with plastic debris via environmental sorption is primarily controlled by the pollution of the surrounding waters and therefore by transport pathways, conversely to the concentration of chemicals associated to the manufacturing process (plastic additives).

Plastic pellets are the industrial raw material that is used to manufacture plastic products and that are shipped to factories all over the world to make plastic bottles, caps, bags and packaging. Some plastic pellets have been introduced through accidental releases into the ocean where they accumulate POPs, with PCBs concentration up to million times higher than in the surrounding seawater.

POPs are highly toxic chemicals which can trigger a wide range of chronic effects, including endocrine disruption and cancer-causing mutations but it is yet unknown how these pollutants that are absorbed into the organisms through the ingestion of microplastics accumulate up in the food chain.

Some marine zooplankton contains high concentration of fluorescent microplastics by the ingestion of micrometer polystyrene (PS) beads, and then the transfer of microplastics particles via planktonic organisms from one trophic level (meso-zooplankton) to a higher level (macro-zooplankton) as shown in figure 1.28.

The ingestion of contaminated microplastics by different marine organisms (lugworm and fish) can transfer pollutants and additives to their tissues at concentrations sufficient to disrupt eco-physiological functions linked to health and biodiversity⁹.

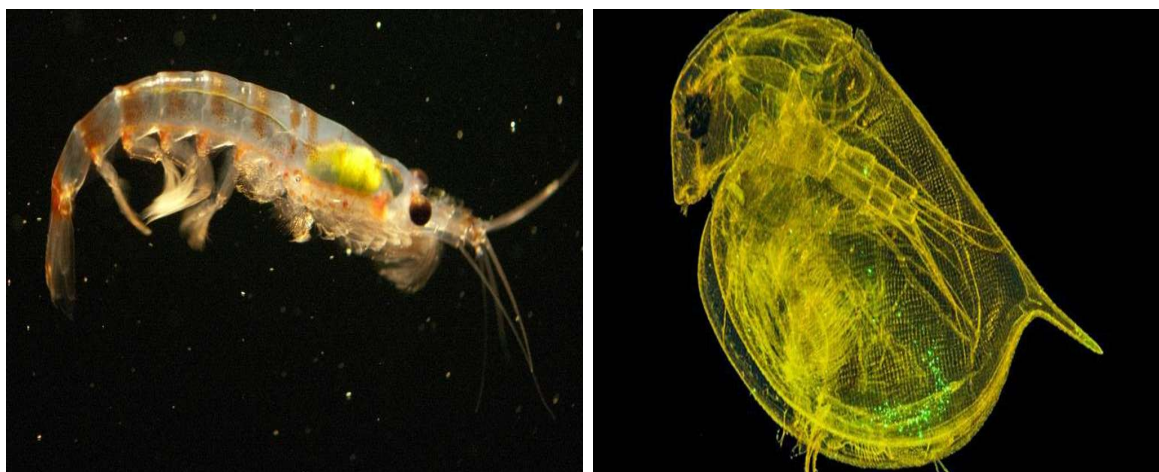


Figure 1.28 : Bio-imaging technique (fluorescence microscopy) showing the ingestion of microplastics.

I.8. PLASTICS AND HUMAN HEALTH

The quantity of microplastics in the environment is likely to increase due to the legacy of plastic items that contaminate the planet. Given the evidence suggesting human exposure to microplastics and their associated pollutants is possible, it is important to assess the risk they pose to human health.

Given the prevalence of microplastics in the marine environment, an anticipated route of human exposure is via seafood, which forms an essential dietary component. It is one of the most important food commodities consumed globally; however, it can also be a source of environmental contaminants such as polychlorinated biphenyls (PCBs) and dioxins. If seafood were to exceed regulatory levels of contaminants, there could be negative health impacts following consumption.

In addition to seafood, potential microplastics have been reported in other foods. The presence of synthetic microfibers (minimum 40 μm in length) and fragments (mostly 10–20 μm in size) was reported in honey and sugar. The contamination of honey suggests synthetic microplastics are airborne. If airborne, microplastics may be deposited on flowers and foliage, where they could become incorporated with pollen and transported by bees to the hive.

Microplastics have recently been identified in sea salt. PET was the most common type of plastic found, followed by PE. It is likely that the coastal waters used to produce sea salt were the source of contamination. Clearly, microplastics currently contaminate food destined for human consumption, the impacts of which are unknown.

Plastic consists of a synthetic organic polymer to which chemical additives are incorporated during manufacture. The continuous fragmentation of microplastics will constantly expose new surfaces, facilitating the migration of additives from the core to the surface of the particle.

If microplastics are capable of accumulating, they present a source of chemicals to tissues and fluids. This is of concern as many chemical additives and monomers have known human health effects, including reproductive toxicity (e.g. BPA), carcinogenicity (e.g., vinyl chloride and butadiene), and mutagenicity (e.g., benzene and phenol). Some of the most harmful additives include brominated flame retardants, phthalate plasticizers, and lead heat stabilizers.

In addition to chemical additives, plastic can also leach hazardous unreacted residual monomers. Polyurethanes, PVC, epoxy resins, and styrenic polymers have been identified as plastics of the greatest concern in terms of environmental and health effects, as their monomers are classified as carcinogenic, mutagenic, or both¹⁰.

I.9. MINIMIZING WATER POLLUTION

The need for better microplastic removal from wastewater streams is clear to prevent potential harm the microplastic may cause to the marine life. The development of effective technologies is therefore the effective way to treat and remove these pollutants.

Several physical techniques like coagulation, flocculation, filtration, adsorption on the activated carbon, and chemical methods like photo-oxidation, adsorption, have been used to reduce these pollutants from waste water. But During the last few years a series of new methods for water and wastewater purification, called advanced oxidation processes (AOP), have received increasing attention.

AOPs refer to a set of oxidative water treatments that can be used to treat toxic effluents at industrial level, hospitals and wastewater treatment plants. AOPs are successful to transform toxic organic compounds into biodegradable substances.

Advanced oxidation was recently also used as quaternary treatment or a polishing step to remove micro-pollutants from the effluents of municipal wastewater treatment plants and for the disinfection of water. The combination of several AOPs is an efficient way to increase pollutant removal and reduce costs.

The concept of “AOP” was established by Glaze et al. (1987). AOP were defined as the oxidation processes, which generate hydroxyl radicals in sufficient quantity to affect water treatment¹¹.

Many systems are qualified under this broad definition of AOP. Most of these systems use a combination of strong oxidants, like O₃ and H₂O₂, catalyst, like transition metal ions or photo catalyst, and irradiation, like ultraviolet (UV), ultrasound (US), or electron beam. Table 1.3 lists typical AOP systems¹².

Non-photochemical	Photochemical
O ₃ /OH ⁻	H ₂ O ₂ /UV
O ₃ /H ₂ O ₂	O ₃ /UV
O ₃ /US	O ₃ / H ₂ O ₂ /UV
Fe ²⁺ /H ₂ O ₂	H ₂ O ₂ / Fe ²⁺ (Photo-Fenton)
Electro-Fenton	UV/TiO ₂
Electron Beam Radiation	H ₂ O ₂ /TiO ₂ /UV
US	O ₂ /TiO ₂ /UV
H ₂ O ₂ /US	UV/US

Table 1.3 : List of typical AOP systems

The main advantages of these methods are high rates of pollutant oxidation, flexibility concerning water quality variations, and small dimension of the equipment. The main disadvantages are relatively high treatment costs and special safety requirements because of the use of very reactive chemicals (ozone, hydrogen peroxide), etc. and high-energy sources (UV lamps, electron beams, radioactive sources).¹³

Advanced oxidation involves several steps schematised in the figure below and explained as follows:

1. Formation of strong oxidants (e.g. hydroxyl radicals).
2. Reaction of these oxidants with organic compounds in the water producing biodegradable intermediates.
3. Reaction of biodegradable intermediates with oxidants referred to as mineralisation (i.e. production of water, carbon dioxide and inorganic salts)¹⁴.

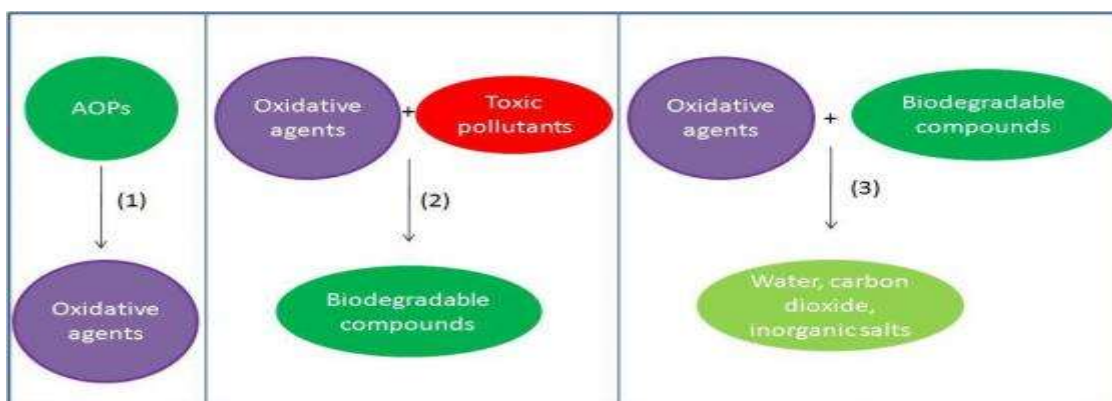


Figure 1.29: Main steps involved in an AOPs treatment of wastewater containing toxic organic compounds.

AOPs have gained popularity for the treatment of industrial effluents because of their many advantages over the traditional methods such as:

- Destroys toxic organic compounds without pollution transfer to another phase
- Very efficient to treat almost all organic pollutants and remove some toxic metals
- Do not produce sludge as in the case of physical, chemical, or biological processes
- High degradation efficiency
- Cheap to install

- Cost effective
- Adaptable to small scales in developing countries

I.10. DIFFERENT METHODS OF DETECTION AND CHARACTERISATION OF MICROPLASTICS IN WATER

In this part, we will critically review the methodology presently used for assessing the concentration of microplastics in the marine environment. We will focus on the most convenient techniques and approaches recently applied for the identification of microplastics. After an overview of non-selective sampling approaches and sample processing in the laboratory, we will introduce the reader to currently applied detection techniques for microplastics.

I.10.a. SAMPLING FOR MICROPLASTICS

Today, synthetic polymers are omnipresent and daily life without plastics is inconceivable. As a consequence, even microplastic sampling, preparation and analysis procedures themselves are affected by the ubiquity of synthetic polymers in the environment. Hence, a multitude of contamination sources from sampling equipment through clothes or airborne particles can compromise the analysis of microplastics in the environment. This can lead to a great overestimation of concentrations of microplastics in samples. Because of their ability to hover in air, especially fibers have a high contamination potential and can cause problems during microplastic analysis. Thus, a special focus should be laid on the prevention of contamination. Potential sources of contamination should be avoided by replacing plastic devices or laboratory ware by non-plastic material and the strict use of control samples is highly recommended. Analysis of control samples facilitates the identification of the source in case a contamination has occurred^{15,16,17,18}.

I.10.a.1. WATER SAMPLES

Because of their relatively low concentrations in the environment sampling of microplastic particles generally requires large sample volumes. Thus, samples from the open water are usually taken with plankton nets of different mesh sizes. The sea surface is sampled for floating microplastics by manta trawls or neuston nets. The volume filtered by a net is usually recorded by a flow-meter mounted at the net opening, enabling the normalization to the filtered water volume and thus a calculation of concentrations of microplastics (items/grams) per unit water volume. The water column can be sampled for suspended microplastics by trawling with different plankton nets. Besides common net sampling, other techniques are occasionally used for assessing microplastic concentrations in the water column: bulk sampling with subsequent filtration, screening Continuous Plankton Recorder (CPR) samples or using direct in situ filtration^{18,19,20}.

I.10.a.2. SEDIMENT SAMPLES

Microplastics in sediments or beaches are currently more frequently analyzed than microplastics in the water column. Sampling approaches depend on the sampling location i.e. sampling sediments directly on beaches or sampling subtidal sediments from a ship¹⁵.

I.10.a.2.a. BEACHES

Sampling beaches for microplastics is relatively easy and requires nothing more than a non-plastic sampling tool (tablespoon, trowel or small shovel), a frame or a corer to specify the sampling area and a container (if possible non-plastic) to store the sample. The positioning of the sample location on the beach is still a matter of scientific debate as the distribution of microplastic particles is as dynamic as the beach itself. Commonly applied sampling strategies include random sampling at several locations on the beach, on transects perpendicular or parallel to the water or in single squares. Another point of concern is the sampling depth. If corers are used for sampling, different depth layers can be sampled so that microplastic concentrations can be related to sediment depth and eventually to the age of the corresponding sediment layer¹⁵.

I.10.a.2.b. SUBTIDAL SEDIMENTS

Subtidal sediments can be sampled from vessels with grabs, or corers of different design. Grabs tend to disturb the sediment and are suited for surface or bulk sampling, whereas undisturbed core samples enable the simultaneous sampling of surface and depth layers but yield smaller sample volumes. The size of the instrument applied as well as the time needed for its retrieval depends strongly on the water depth at the sampling location. The use of corers enables sampling to a water depth of more than 5000 m. Sediment samples are usually stored frozen or dried and kept in the dark until further analysis²¹.

I.10.a.3. BIOTA

Laboratory studies on the ingestion of microplastics by marine biota frequently use microscopic plastic beads of known polymer origin, which can be easily recognized and counted under the microscope. In this context, the use of fluorescent particles facilitates the recovery and enumeration of the particles.

The target for sampling is the content of the digestive tract or the excretions of an organism. Larger organisms that are directly sampled for microplastics are mainly fish, which are usually sampled by nets or traps.

Stranded carcasses (e.g. birds, seals, cetaceans) can be collected and examined for ingested microplastics. After dissection, the gut content or the entire digestive tract has to be conserved

or frozen for later analysis. Smaller invertebrate organisms such as worms, mussels and snails can be directly collected in the field with nets or traps and are best frozen as a whole until analyzed. Biological samples can be conserved by using plastic-friendly fixatives (e.g. formalin) or best be frozen or dried and kept dark until analysis^{22,23}.

I.10.b. LABORATORY PREPERATION OF SAMPLES

I.10.b.1. EXTRACTION OF MICROPLASTICS

The densities of common consumer-plastic polymers range between 0.8 (silicone) and 1.4 g.cm⁻³ (e.g. polyethylene terephthalate (PET), polyvinyl chloride (PVC)) while expanded plastic foams have only a fraction of the densities of the original polymer (e.g. expanded polystyrene (EPS) < 0.05 g.cm⁻³). Microplastic particles can thus be separated from matrices with higher densities, such as sediments (2.65 g.cm⁻³), by flotation with saturated salt solutions of high density. The dried sediment sample is mixed with the concentrated salt solution and agitated (e.g. by stirring, shaking, aeration) for a certain amount of time. Plastic particles float to the surface or stay in suspension while heavy particles such as sand grains settle quickly. Subsequently, microplastics are recovered by removing the supernatant. Depending on the solution used, different fractions of the range of consumer polymers are targeted, the higher the density of the solution the more polymer types can be extracted. Often a saturated NaCl solution is used for the extraction of microplastics. Although being an inexpensive and environment-friendly approach, not all common polymers are extracted (e.g. PVC, PET, polycarbonate (PC), polyurethane (PUR)) because of the relatively low density of the solution ($\cong 1.2$ g.cm⁻³). Other solutions used include sodium polytungstate solution (1.4 g.cm⁻³), zinc chloride solution (1.5 - 1.7 g.cm⁻³) or sodium iodine solution (1.8 g.cm⁻³). These high-density solutions are suitable for the extraction of most of the common user plastics. For financial/environmental reasons the use of zinc chloride and the recycling of the saturated solution by pressure filtration is highly recommended.

There is great variability in the extraction techniques applied. The approaches range from simply stirring the sediment sample in a saturated salt solution (classical setup) to the use of an elutriation/fluidisation with subsequent flotation or the extraction with a novel instrument, the “Microplastic Sediment Separator” (MPSS). The extraction efficiencies vary between the techniques used but also depend on the particle shape, size and the polymer origin of the model particles used during recovery experiments. The classic extraction setup reaches recoveries of 80–100 % but recovers small microplastics insufficiently (mean recovery rate 40 %, mean particle size 40–309 μ m) whereas new approaches achieve high recovery rates of 68 - 99 %, 96 - 100 % and 98 - 100 %. Small particles (<500 μ m) are more difficult to extract from sediments. Therefore, time-consuming repeated extraction steps are recommended to maximize recovery. Only the MPSS showed a recovery rate of 96 % for small microplastics in a single extraction step^{16,23,24}.

I.10.b.2. SIZE FRACTIONATION

Irrespective of the technique used for later identification of microplastics the fractionation of samples (water, sediment, biota) into (at least) two size classes, e.g. $> 500 \mu\text{m}$ and $< 500 \mu\text{m}$, is reasonable. Water samples can be fractionated easily by sieving. If large amounts of biological matrix (e.g. gut contents, tissue, large plankton) clog the sieve a purification step prior to sieving can be helpful. Microplastics from sediment samples are easily size-fractionated after extraction. If the sediment sample matrix consists mainly of smaller grains ($< 500 \mu\text{m}$) it can be sieved after drying (or wet) to reduce the volume for later extraction. In this case, the sample must be handled with care during sieving to avoid the mechanical generation of additional microplastic particles from larger, brittle plastic material. A $500 \mu\text{m}$ sieve, ideally made of steel, can be used for size separation. The use of a sieve cascade of different mesh sizes allows for size separation and quantification of different size classes of microplastics.

Microplastic particles $> 500 \mu\text{m}$ can be sorted out manually under a stereomicroscope using forceps and subsequently analyzed (visually, spectroscopically, other techniques). The effort involved in the manual sorting of particles increases for the fraction $< 500 \mu\text{m}$ owing to difficulties in handling small particles. Furthermore, an increasing amount of background matrix particles of different organic or inorganic origin may impede a proper separation. Therefore, this fraction should be purified and concentrated on filters for further analysis by, e.g. spectroscopy. The suggested size separation ($> 500 \mu\text{m}$; $< 500 \mu\text{m}$) is accounted for by the techniques that can be used for later identification^{15,25}.

I.10.b.3. SAMPLE PURIFICATION

The purification of microplastic samples is obligatory, especially, for instrumental analyses (FTIR/Raman spectroscopy, pyrolysis-GC/MS). Bio-films and other organic and inorganic adherents have to be removed from the microplastic particles to avoid artifacts that impede a proper identification. Furthermore, the purification step is necessary to minimize the non-plastic filter residue on filters on which the microplastic fraction $< 500 \mu\text{m}$ is concentrated. The gentlest way to clean plastic samples is stirring and rinsing with freshwater. The use of ultrasonic cleaning should be carefully considered because aged and brittle plastic material might break during treatment resulting in the artificial generation of secondary microplastics. A treatment with 30 % hydrogen peroxide of the dried sediment sample, the sample filter or the microplastic particles themselves removes large amounts of natural organic debris. We can use mineral acids to disintegrate organic impurities in samples. Hot acid digestion with HNO_3 resulted in the best purification results. However, several plastic polymers (e.g. polyamide, polyoxymethylene, and polycarbonate) react to strong acidic or alkaline solutions, which limit the applicability of these reagents. More promising is the use of a sequential enzymatic digestion as a plastic-friendly purification step^{16,24,25}.

I.10.c. IDENTIFICATION OF MICROPLASTICS

I.10.c.1. VISUAL IDENTIFICATION

Visual sorting to separate potential microplastics from other organic or inorganic material in the sample residues is an obligatory step for the identification of microplastics. If large microplastics are the target of a study this can be done by visual inspection whereas smaller microplastic particles should generally be sorted out under a dissection microscope. Generally, if no more accurate methods (e.g. FTIR or Raman spectroscopy) are used to verify synthetic polymer origin of potential microplastic particles the visual identification should not be applied to particles < 500 µm as the probability of a misidentification is very high. The selection of particles according to standardized criteria in connection with a strict and conservative examination reduces the possibility of misidentification. General aspects that are used to describe visually sorted microplastics are source, type, shape, degradation stage, and color of the particles.

It is strongly recommended to subsequently analyze sorted particles by techniques that facilitate a proper identification of plastics because the quality of the data produced by visual sorting depends strongly on (1) the counting person, (2) the quality and magnification of the microscope and (3) the sample matrix (e.g. plankton, sediment, gut content).

Another fundamental drawback of visual sorting is the size limitation, i.e. particles below a certain size cannot be discriminated visually from other material or be sorted because they are unmanageable because of their minuteness. Furthermore, visual sorting is extremely time-consuming. In summary, even an experienced person cannot discriminate all potential microplastic particles unambiguously from sand grains, chitin fragments, diatom frustules fragments, etc^{15,18}.

I.10.c.2. IDENTIFICATION OF MICROPLASTICS BY THEIR CHEMICAL COMPOSITION

The repetitive fingerprint-like molecular composition of plastic polymers allows for a clear assignment of a sample to a certain polymer origin. In the following we will give a short overview of methods applied for polymer identification with a focus on the nowadays frequently used FTIR and Raman analyses of microplastics.

I.10.c.2.a. DENSITY SEPERATION WITH SUBSEQUENT C:H:N ANALYSIS

The specific densities of particles are used to identify the polymer origin of visually sorted microplastics. For this purpose, the sample was placed in distilled water and, depending on the density of the sample, either ethanol or concentrated solutions of calcium or strontium chloride were added until the sample was neutrally buoyant. The density of the particle was indirectly

assessed by weighing a certain volume of the solution. This facilitated the determination of the density with high precision. Different groups of polymers possess a characteristic elemental composition, which was used to identify the plastic origin of a particle by a subsequent C:H:N analysis.

By comparison with the densities and C:H:N ratios of virgin-polymer samples the particle could be assessed as either plastic or not and assigned to a group of potential polymers. This approach represents an approximation to the identification of microplastic particles by narrowing the search for the potential polymer type but not a rigorous chemical analysis. Further drawbacks are the relatively high time effort, which hampers a high sample throughput and that this technique is not applicable to smaller particles²⁶.

I.10.c.2.b. PYROLYSIS-GC/MS

Pyrolysis-gas chromatography (GC) in combination with mass spectrometry (MS) can be used to assess the chemical composition of potential microplastic particles by analyzing their thermal degradation products. The pyrolysis of plastic polymers results in characteristic pyrograms, which facilitate an identification of the polymer type. This analytical approach is already used after extraction and visual sorting of microplastics from sediments. The polymer origin of particles is then identified by comparing their characteristic combustion products with reference pyrograms of known virgin-polymer samples. If a thermal desorption step precedes the final pyrolysis organic plastic additives can be analyzed simultaneously during pyrolysis-GC/MS runs. Although the pyrolysis-GC/MS approach allows for a relatively good assignment of potential microplastics to polymer type it has the disadvantage that particles have to be manually placed into the pyrolysis tube. Since only particles of a certain minimum size can be manipulated manually this results in a lower size limitation of particles that can be analyzed. Furthermore, the technique allows only for the analysis of one particle per run and is thus not suitable for processing large sample quantities, which are collected during sampling campaigns or routine monitoring programs^{16,27}.

I.10.c.2.c. RAMAN SPECTROSCOPY

Raman spectroscopy is a straightforward technique that has been successfully used to identify microplastic particles in different environmental samples with high reliability. During the analysis with Raman spectroscopy the sample is irradiated with a monochromatic laser source. The laser depends on the system used: available laser wavelengths usually range between 500 and 800 nm. The interaction of the laser light with the molecules and atoms of the sample (vibrational, rotational, and other low-frequency interactions) results in differences in the frequency of the backscattered light when compared to the irradiating laser frequency. This so called Raman shift can be detected and leads to substance-specific Raman spectra. Since plastic polymers possess characteristic Raman spectra the technique can be applied to identify plastic polymers within minutes by comparison with reference spectra. Raman spectroscopy is a “surface technique”, thus large, visually sorted microplastic particles can be analyzed and the

technique can also be coupled with microscopy. Accordingly, micro-Raman spectroscopy allows for the identification of a broad range of size classes down to very small plastic particles of sizes below 1 μm . If Raman microscopy is combined with Raman spectral imaging it is possible to generate spatial chemical images based on the Raman spectra of a sample. Micro-Raman imaging theoretically allows for the spectral analysis of whole membrane filters at a spatial resolution below 1 μm . One drawback of Raman spectroscopy is that fluorescent samples excited by the laser (e.g. residues of biological origin from samples) cannot be measured as they prevent the generation of interpretable Raman spectra. Generally, lower laser wave lengths, which transfer a high energy result in high signal intensity but also in a high fluorescence. The fluorescence can be minimized by using lasers with higher wave lengths (>1,000 nm). However, the lower energy of the laser results in a lower signal of the polymer sample. Generally, a purification step of samples to prevent fluorescence is thus recommended prior to measurements for a clear identification of the polymer type of microplastic particles with Raman spectroscopy^{21,22}.

I.10.c.2.d. IR SPECTROSCOPY

Similar to Raman spectroscopy, infrared (IR) or Fourier-transform infrared (FTIR) spectroscopy offers the possibility of accurate identification of plastic polymer particles according to their characteristic IR spectra. FTIR and Raman spectroscopy are complementary techniques. Molecular vibrations, which are Raman inactive are IR active and vice versa and can thus provide complementary information on microplastic samples. IR spectroscopy takes advantage of the fact that infrared radiation excites molecular vibrations when interacting with a sample. The excitable vibrations depend on the composition and molecular structure of a substance and are wave-length specific. The energy of the IR radiation that excites a specific vibration will - depending on the wave length - be absorbed to a certain amount, which enables the measurement of characteristic IR spectra. Plastic polymers possess highly specific IR spectra with distinct band patterns making IR spectroscopy an optimal technique for the identification of microplastics. FTIR spectroscopy can provide further information on physico-chemical weathering of sampled plastic particles by detecting the intensity of oxidation.

As for Raman spectroscopy the comparison with reference spectra is necessary for polymer identification. Large particles can be easily analyzed by a FTIR surface technique - “attenuated total reflectance” (ATR) FTIR spectroscopy - at high accuracy in less than one minute. A step forward with respect to the characterization of small-sized particles is the application of FTIR microscopy. In this context, the use of two measuring modes is feasible: reflectance and transmittance. The reflectance mode bears the disadvantage that measurements of irregularly-shaped microplastics may result in non-interpretable spectra due to refractive error. The transmittance mode needs IR transparent filters (e.g. aluminium oxide) and is, owing to total absorption patterns, limited by a certain thickness of the microplastics sample. However, the additional use of micro-ATR objectives in combination with microscopy can circumvent this as IR spectra are collected at the surface of a particle enabling the direct measurement on the sample filter without the need for manual handling of particles. Thus, an approach combining transmittance measurements with micro-ATR measurement of particles that show total

absorption could be a promising solution for the measurement of particles < 500 µm collected on filters. Although micro-FTIR mapping, i.e. the sequential measurement of IR spectra at spatially separated, user-defined points on the sample surface, has been successfully applied for microplastics identification this technique is still extremely time-consuming when targeting the whole sample filter surface at a high spatial resolution because it uses only a single detector element^{28,29}.

I.11. PLASTICS TO FUEL

Plastics are organic compounds having long chained hydrocarbon synthesized from petroleum products. Because of its own special features, plastic had acquired wide popularity in short time. Plastic production and consumption rate increased exponentially due to its low cost, non-degradable nature, easy availability and management, wide range of usage and application³⁰.

The increasing demand of plastic products also increases the accumulation of plastic waste that endangers the environment because of their disposal problems.

There is a number of technologies offered as commercial propositions for the conversion of plastic to oil products, but, despite differences in the detail of the equipment and the operating conditions, these all fall within two categories. Within these two categories, there is a number of subcategories, as shown in table 1.4³¹.

Depolymerisation processes	Gasification processes
Pyrolysis	Gasification and conversion to diesel
Catalytic depolymerisation	Gasification and conversion to gasoline
	Gasification and conversion to ethanol

Table 1.4 : Plastic to oil conversion technologies³²

I.11.a. PYROLYSIS

Pyrolysis is the thermal degradation of organic materials at temperatures between 400 °C and 1000 °C in the absence of oxygen.

Pyrolysis produces gas, liquid and solid char, the relative proportions of which depend upon the method of pyrolysis and the operating conditions of the pyrolysis reactor, chiefly the rate of heating, the operating temperature and residence time within the pyrolysis reactor. Long residence times and low heating rates are typical of processes such as charcoal manufacture, effectively converting the majority of the carbon present in the feedstock into elemental carbon. As residence time reduces and heating rate increases, the proportion of liquid produced increases as there is sufficient heat in the system to boil off any compounds formed by the breaking of polymer chains. Very short residence times and high temperatures give conditions very similar to those encountered in the gasification process, and consequently produce more

gas. For the purposes of conversion of plastic into oil products, maximisation of liquids production is desirable, as this will give a material which can be easily transported and refined. This is achieved by so-called 'fast' pyrolysis, with residence times of less than 2 seconds, rapid heating and temperatures of around 500 °C³².

Process	Slow pyrolysis	Fast pyrolysis	Flash pyrolysis
Feed size	< 200 mm	< 1 mm	< 1 mm
Moisture	< 15 %	< 10 %	< 10 %
Res. time	10-60 min	0.5-5 s	< 1 s
Temp.(°C)	450-600	550-650	450-900
Pressure	1 Atm.	1 Atm.	1 Atm.
Products	gas, oil, char	gas, oil	gas, oil

Table 1.5: Pyrolysis processes³³

I.11.b. GAZIFICATION

Gasification is a thermal degradation process working under a controlled atmosphere at temperatures between 800 - 1000 °C³⁴.

The process involves direct heating, allowing a limited amount of oxygen to react with carbon in order to achieve a partial combustion³⁵.

This results in the total decomposition of the feedstock into a mixture of gases known as 'syngas', including carbon monoxide, carbon dioxide, hydrogen, water and methane. The decomposition reaction also produces a carbon char, which is oxidized in situ thereby providing the heat required achieving the high operating temperature. This incomplete oxidation also leads to the formation of tars, which need to be removed from the syn-gas as they foul catalyst surfaces used for subsequent processing into oil products. The relative quantities of carbon monoxide, hydrogen and methane are determined by the composition of the feedstock and the operating temperature of the gasification reactor³².

Output	Proportion of total output
Syngas	93% wt
Tars	6% wt
Char	1% wt

Table 1.6: Typical outputs from a waste gasification process

Thermal gasification proceeds generally in three major steps. First, the remaining moisture in the material is evaporated; secondly the material is converted into char and condensable gases (water and tars). Finally char is converted into gaseous products and gas phase reactions take place³⁶.

CHAPTER II: EXPERIMENTAL STUDY

The aim of the experimental study was to evaluate the applicability of FTIR for the identification of microplastic particles in environmental samples. we tested this technique on samples from sea water taken from three locations on the beach.

II.1. SAMPLING

Sea water is sampled at three stations along the beach, from " Al Mina - Tripoli " at 1 : 15 PM, from " Anfeh " at 2 : 00 PM on September 11 / 2018, and from " Ramlet AL Baida - Beirut " at 11 : 40 PM on September 18 / 2018.

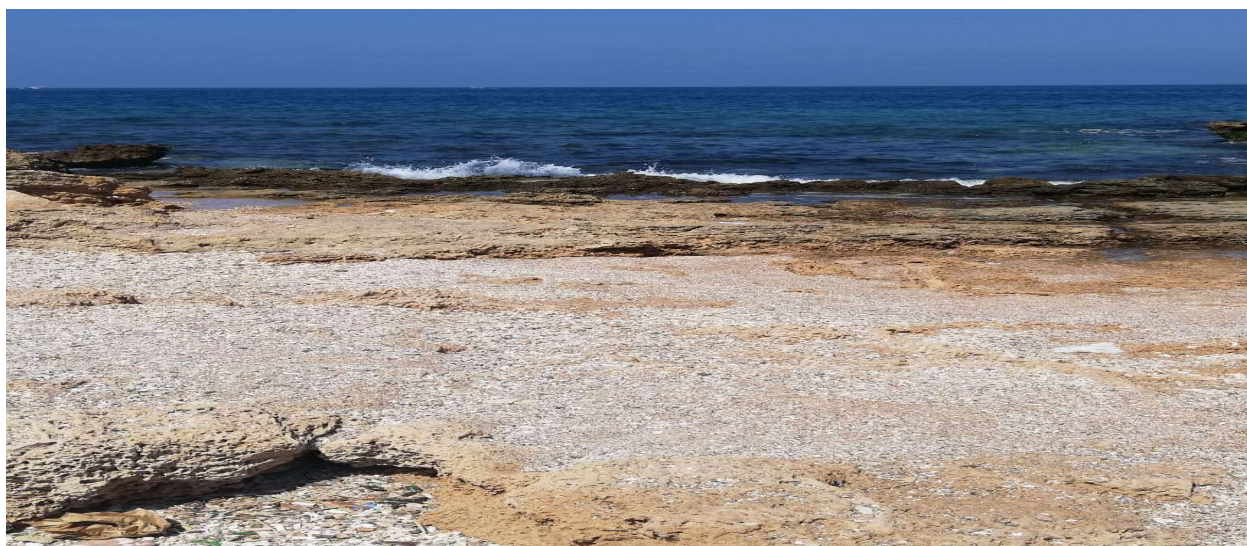


Figure 2.1: Sample from Tripoli



Figure 2.2: Sample from Anfeh



Figure 2.3: Sample from Beirut

Straight line or air distance between Tripoli and Anfeh is approximately 12.57 Km, and between Anfeh and Beirut is approximately 57.61 Km.



Figure 2.4: Site map of the three locations

No plastic equipment was used during sampling and all samples were stored in glass bottles until further processing.



Figure 2.5: Sea water samples

Samples were stored in a moderate environment away from sunlight to avoid any further degradation of microplastics.

II.2. IDENTIFICATION OF MICROPLASTICS

For the samples from Tripoli and Anfeh, the identification of microplastics was done after two days of sampling, exactly on September 13 / 2018, and for the sample from Beirut, the identification was done on September 24 / 2018, in the Platform for Research and Analysis in Environmental Sciences "PRASE", which located in "HADATH" campus.

The platform established new materials, device structures for chemical and physical analysis as well as for molecular and cellular biology. It serves research in most disciplines (biology, geology and engineering).

The platform is dotted with sophisticated instruments such as FTIR, UV-VIS, GC-MS and other equipments.

Microplastics identification of the samples was determined using FTIR because it is one of the most common and robust analytical techniques to identify and characterize synthetic polymers, as it is fast, relatively cheap, and highly selective. In normal case, IR spectra of unknown polymer samples were evaluated by comparing these to a library of known reference polymer spectra to find matches. But in our case, IR spectra of the sea water samples was evaluated by comparing these to an IR spectra of a prepared salt water identical to purified sea water.

II.3. RESULTS AND INTERPRETATION

II.3.a. FTIR

Spectral data were accumulated for 64 scans at 4 cm^{-1} resolution under a transmittance mode with a wave number range of $400 - 4000\text{ cm}^{-1}$.

Transmittance is the inverse of absorbance. A clear, colorless pane of glass has near 100% transmittance of visible light. A piece of colored glass will have 100% transmittance at certain frequencies, while less transmittance (i.e. strong absorbance) at other frequencies. When we graph transmittance versus wavelength we obtain an appearance which is “flipped” in relation to a typical UV spectrum. The baseline is at the top, and “absorbance peaks” point towards the bottom, depending on the strength.

Wavenumber is the inverse of wavelength ($1/\lambda$): it corresponds to the number of cycles in a given unit of length, and is thus a measure of frequency. The left-hand region of the spectrum (at 4000 cm^{-1}) is high-frequency; the right-hand region (at about 400 cm^{-1}) is low frequency.

Now let's look at the IR spectrum of the samples.

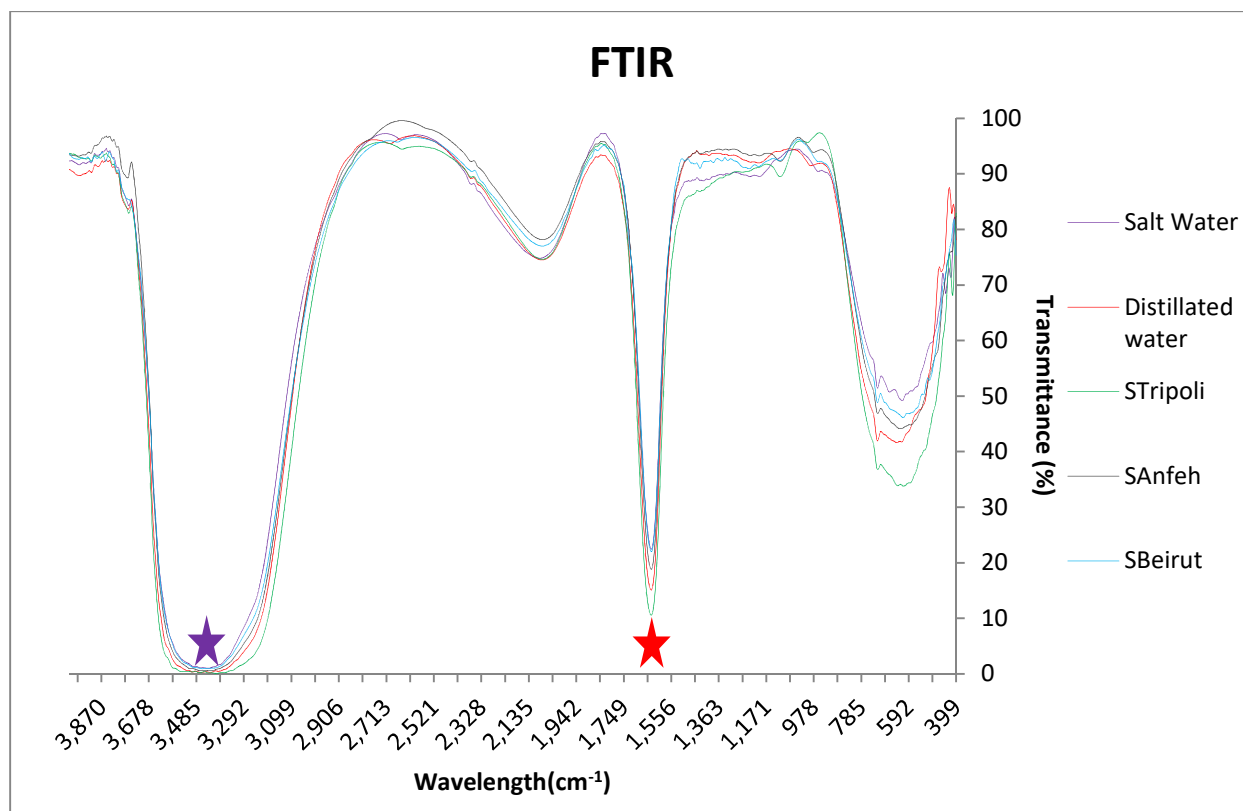


Figure 2.6: FTIR Spectrum of samples

A few things to note:

- ❖ The region on the left (toward 4000 cm^{-1}) corresponds to high frequency and short wavelength; the region on the right (toward 400 cm^{-1}) corresponds to low frequency and long wavelength.
- ❖ The major "peaks" for water are at about $3200 - 3600\text{ cm}^{-1}$ (very broad and strong), 1650 cm^{-1} (relatively sharp) and then another peak around 650 cm^{-1} that is also quite broad.
- ❖ See that peak around 2100 cm^{-1} that is weak and broad and somewhat undefined. That's the kind of peak we typically ignore.

The most important thing to note is that each of these peaks corresponds to the vibration of a chemical bond in the sample which is being promoted by infrared light.

Hence, a different way of looking at it is that each molecule will give a characteristic "IR fingerprint" corresponding to the bonds present in the molecule.

Note that, as shown in figure 2.6, the purple star which was at $3200 - 3600\text{ cm}^{-1}$ corresponds to the frequency of vibration of an O-H bond. It's also another O-H vibration which is indicated by the red star at 1650 cm^{-1} . There is no wavelength corresponds to the frequency of vibration of a C-H bond.

Since the shape of the spectrums obtained is similar to the spectrum of water, and since we got the same peaks (at the same wavelength), we can conclude that we could not detect microplastics in these samples.

It's important to keep in mind that the samples are taken from the surface of the water on the beach, not at certain depth where the microplastics may exists, where the samples are diluted and not contain any microplastics particles. For a better result, the samples must be taken away from the shore and at a certain depth where it is possible to have microplastics.

Table 2.1 shows the transmittance of the samples at some wave number.

Wave Number(cm^{-1})	Salt Water	Distillated Water	STripoli	SAnfeh	SBeirut
650.8576	51.216	41.8818	34.6899	44.9233	47.3584
1650.7677	25.3601	17.4388	12.6772	21.5051	24.6517
3400.8513	1.50968	0.512106	0.0674435	0.865187	1.15081
3500.1675	1.37155	0.346935	0.367518	0.971363	1.20509

Table 2.1 : Transmittance(%T) of samples from the FTIR for a specified range of wave number

CHAPTER III : WASTE PLASTIC PYROLYSIS SIMULATION PROCESS

In this chapter, an ASPEN Plus simulation of the pyrolysis process is presented. Within the simulation, the pyrolysis reaction is carried out with basic assumptions: steady state kinetic free model, isothermal system, and ash is assumed as pure carbon to reduce complexity.

Pyrolysis is carried out by reacting waste plastic in a no-oxygen environment. Heat produced from the combustion of fuel maintains the reactor temperature to carry out the endothermic reactions inside it. The pyrolysis processes can be divided into four physic-chemical processes as shown in Figure 3.1. The simulation is modeled for a 1000 Kg per hour capacity of waste plastic.

The pyrolysis reactor has been modeled in four stages. In the first stage before using the pyrolysis reactor, the moisture content of the waste plastic is reduced by drying. In the second stage, the waste plastics are decomposed into conventional components because waste plastic are considered as a non-conventional material in ASPEN Plus. In the third stage the pyrolysis reaction is conducted by minimizing the Gibbs energy. The gaseous product is condensed using a water cooler to produce the pyrolytic oil. Table 3.1 shows the models used in the simulation.

Aspen Plus ID	Block ID	Description
RStoic	DRY-REAC	Moisture content of waste plastic reduction
RYield	DECOMP	Conversion of Non-conventional materials (Plastics) to conventional components using FORTRAN Statement
RGibbs	PYROLYS	Calculation of the product composition by minimizing Gibbs free energy
SSplit	ASH-SEP	Separation of the gaseous products from ash by specifying split ratio
Heater	COOLER(CONDEN)	Condensation of the gases to produce pyrolytic oil
Flash	OIL-SEP	Separation of the oil from non-condensable gases

Table 3.1: ASPEN Plus unit operation model description

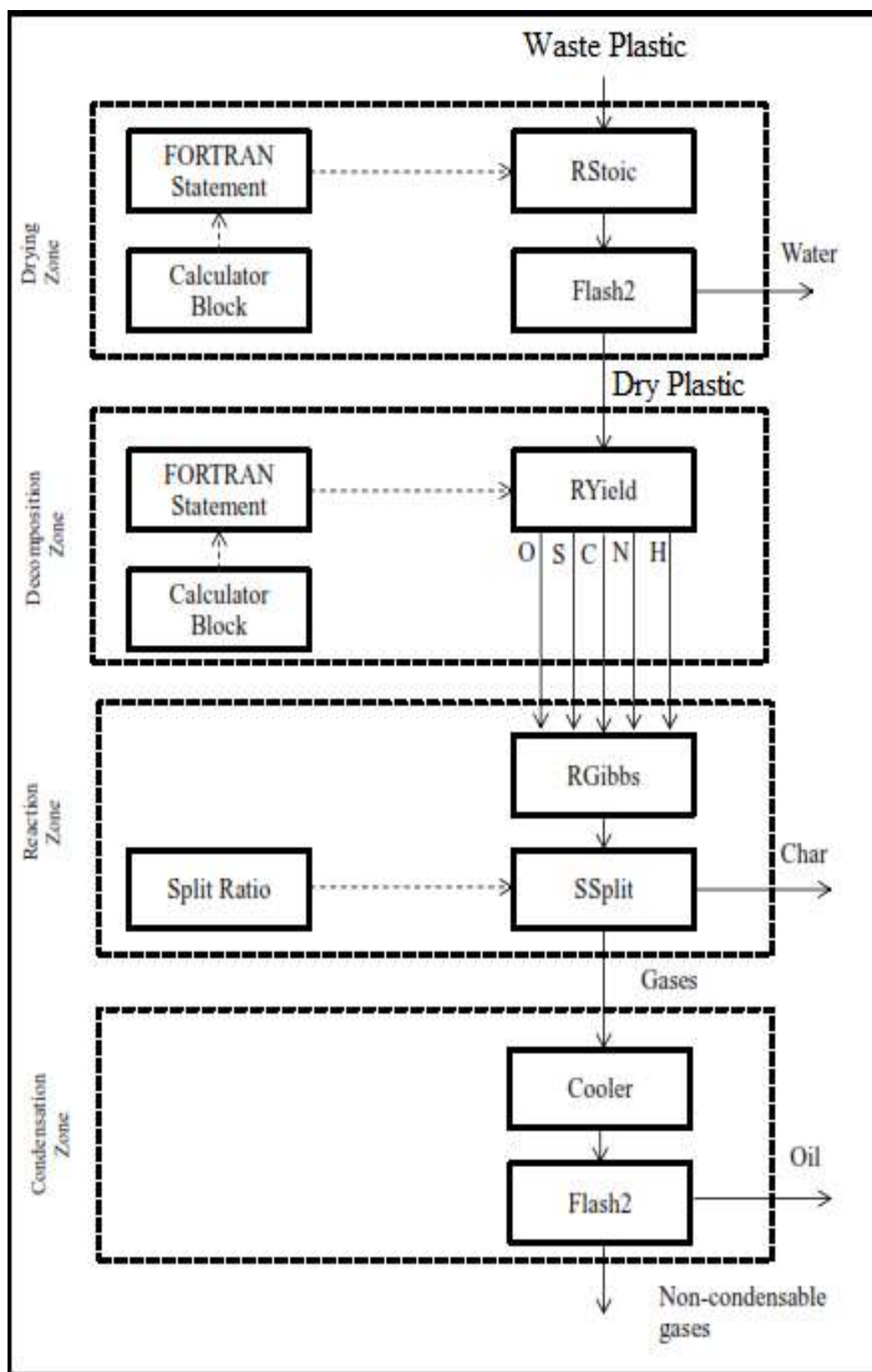


Figure 3.1: ASPEN Plus calculation procedure

III.1. PROCESS DESCRIPTION

III.1.a. PHYSICAL PROPERTY METHOD

In order to estimate the physical properties of the conventional components in the pyrolysis process, the Peng-Robinson with Boston-Mathias alpha function equation of state (PR BM) was used. Alpha is a temperature dependent parameter that improves the pure component vapor pressure correlation at very high temperatures. For this reason, PR-BM is suitable for the pyrolysis process since it is carried out at relatively high temperatures. The density and enthalpy models for waste plastic and ash are DCOALIGT and HCOALGEN.

III.1.b. PYROLYSIS MODEL DESCRIPTION

As mentioned earlier, the pyrolysis process converts waste plastic to oil, non-condensable gases and ash byproduct. The ASPEN Plus flowsheet of the process is presented in Figure 3.2. As illustrated in Figure 3.1, four blocks have been used to simulate the pyrolysis process. Waste plastic are considered as a non-conventional material which is modeled in the simulation by using the proximate and ultimate analysis that is presented in Table 3.2³⁷.

Proximate Analysis wt %	
Moisture	0.02
Fixed Carbon FC	0
Volatile Material VM	99.85
Ash	0.15
Ultimate Analysis wt %	
C	85.81
H	13.86
N	0.12
O	0
S	0.06
Ash	0.15

Table 3.2: Proximate and Ultimate analysis of the waste plastic used in this study

III.1.b.1. DRYER

The RStoic block (DRY-REAC) is used to model the drying process of waste plastic where a FORTRAN statement in the calculator block is used to control the operation. Although plastic drying is not normally considered a chemical reaction, RStoic block is used to convert a portion of the plastic to form water. The dry waste plastics are fed to the next stage.

III.1.b.2. DECOMPOSITION

The RYield block (DECOMP) is used to decompose waste plastic (non-conventional material) into its elements (H, C, O, N, S). This step is conducted by using RYield block connected with calculations based on components yield specifications where the total yield of the volatiles is assumed to be equal to volatile content in the proximate analysis of the waste plastic. The waste plastic yield distribution into its elements was specified by using a FORTRAN statement in a calculator block. The statement evaluates the mass flow rate of the elements in the outlet stream from the RYield block.

III.1.b.3. PYROLYSER AND SEPERATORS

The RGibbs block (PYROLYS) is used to model the pyrolysis of waste plastic where it evaluates the chemical equilibrium composition of the product by minimizing the Gibbs free energy. The decomposed waste plastics enter the reactor where the pyrolysis reaction takes place at 450 °C under atmospheric pressure. The products from the RGibbs reactor pass through a unit operation model SSplit (ASH-SEP) where the ash is separated from the gases based on a specific split ratio.

Then, the gaseous stream leaving SSplit enters a water cooler (CONDENSE) where the gasses are condensed to form a liquid fraction. The final stage in the simulation is the Flash block (OIL-SEP) where the liquid is separated from the non-condensable gases. The liquid fraction then leaves the pyrolysis plant as the pyrolytic oil product.

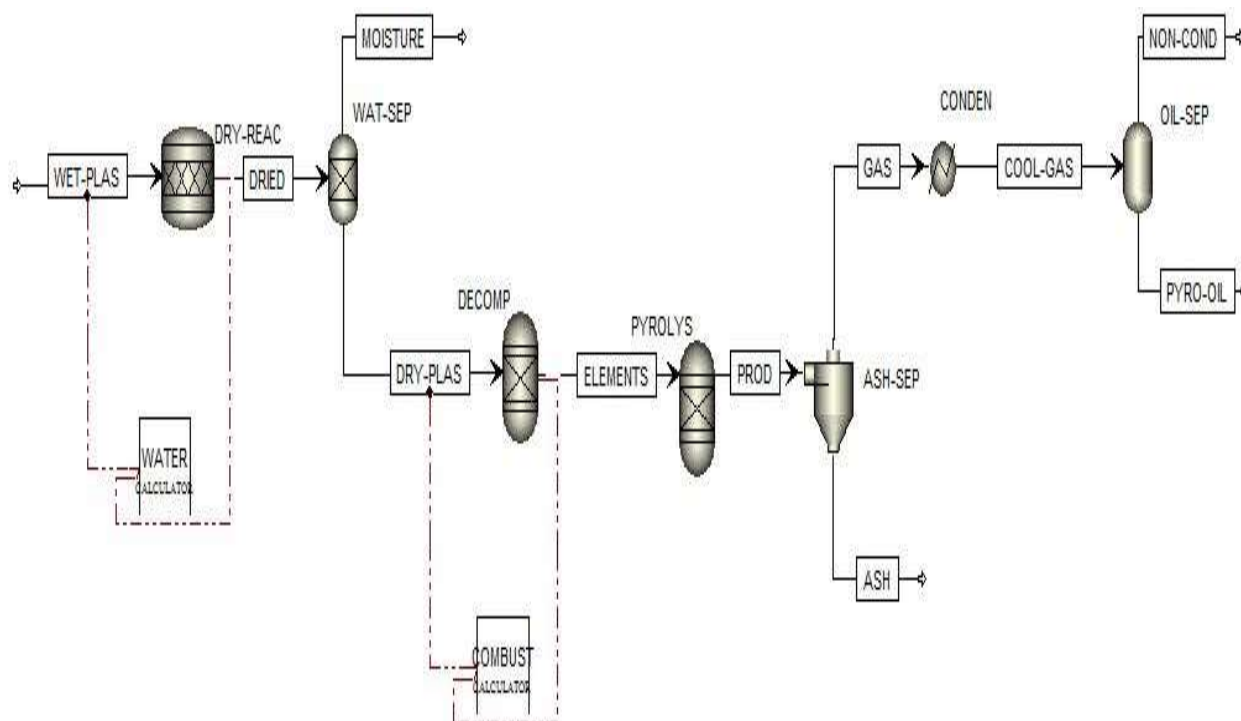


Figure 3.2 : ASPEN Plus model of pyrolysis process

III.2. RESULTS AND DESCUSSION

The basic process was modeled in specific operation conditions (i.e. 450 °c and atmospheric pressure with the assumption of no pressure drop).

Table 3.3 shows the Composition of components produced from pyrolysis process at 450°C.

Component	Composition(%wt/wt)
Water	7.88986×10^{-5}
CO ₂	6.1763×10^{-9}
CO	1.6897×10^{-6}
H ₂ S	6.3759×10^{-4}
N ₂	1.199×10^{-3}
H ₂	0.0294
Methane	0.4341
Ethane	9.8753×10^{-6}
Propane	1.1018×10^{-9}
Ethylene	1.3395×10^{-8}
Propylene	2.1216×10^{-11}
N-Butane	1.0716×10^{-13}
I-Butane	8.046×10^{-14}
N-Pentane	8.6185×10^{-18}
Benzene	1.8265×10^{-16}
Toluene	3.9545×10^{-19}
Styrene	5.0389×10^{-25}
Carbon(Ash)	0.5343

Table 3.3 : Composition of components produced from pyrolysis process at 450 °C

Due to the diversity of components of pyrolytic oil, it is difficult to quantify and measure them. The concentrations of the light components (i.e. hydrocarbon gases C₁ - C₅, olefins, carbon monoxide and carbon dioxide) are significantly different from the results of other studies. The main reason for these inconsistent results is the Gibbs model used in the simulation where the product compositions were calculated by minimizing Gibbs free energy. In order to develop reliable results, a kinetic reaction model based on reaction mechanisms needs to be established to predict the pyrolysis products with respect to feedstock composition and reaction operating conditions. Then, the produced pyrolytic oil yield and component composition can be evaluated with a high level of detail.

III.3. SENSITIVITY ANALYSIS

A sensitivity analysis was carried out by studying the effect of temperature on component composition. The temperature of the pyrolysis reactor (RGibbs block) was varied from 400 °C to 900 °C at every 50 °C. The effect of temperature on the pyrolytic oil yield is represented in Figure 3.3. As illustrated, the highest oil yield evaluated was 7.84 % at 400 °C which is significantly different from other studies where the pyrolytic oil yield reaches up to 50% at the same temperature range. At relatively low temperature (i.e. 400 °C), the carbon content in waste plastics is not converted completely, so the oil yield will be low but it will increase with increasing temperature.

Regarding the products yield, Figure 3.3 shows that there is an obvious trend where the yield of liquid decreases with temperature and the maximum amount was produced at 400 °C. However in other studies, liquid yield increases to a certain level and reaches its maximum around 450 °C; then it decreases as the temperature increases. For gases, the trend is consistent with the results of other studies as the yield increases with temperature due to rapid cracking of waste plastics at higher temperatures. However, the percentage of gases is significantly different from the results of other studies which explained by the failure of simulation model to represent pyrolysis reaction.

The Ash consists mainly of carbon black, solid hydrocarbons and additives, and for this, it is not expected to have a significant loss or change in Ash yield with temperature.

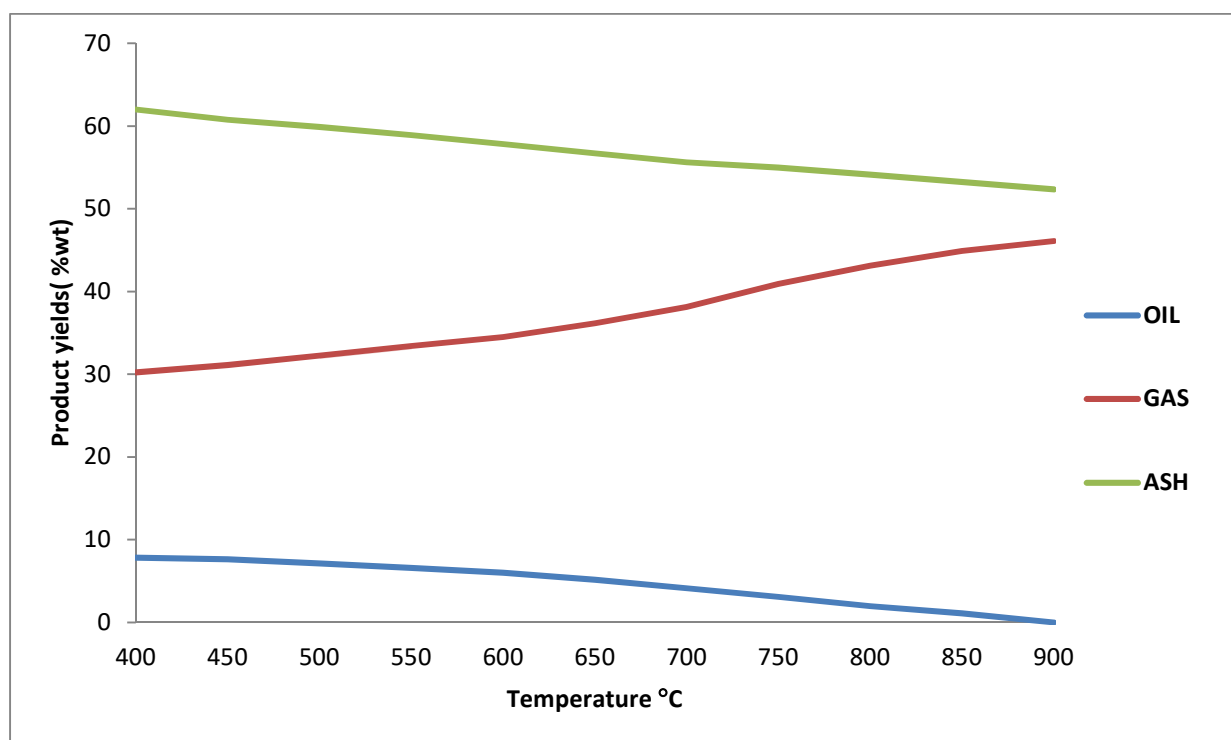


Figure 3.3: Effect of temperature on product yields

CONCLUSIONS AND RECOMMENDATIONS

It's evident that microplastic pieces now contaminate marine habitats worldwide. They are found in the water column, sediments and marine organisms. The source of these microplastics is the direct release of microplastic particles, primarily used in personal care products and plastic manufacturing as well as the breakdown of larger plastic objects and the shedding of fibers from synthetic materials.

Organisms are known to ingest microplastic particles, including many commercially important marine species. Ingestion of microplastics is well known and the digestive system is often examined when looking for the presence of microplastic.

Plastic contains additives, chemicals added to improve the desirable properties of the plastic product. Many of these additives are known hazardous substances and can leach from the plastic surface. While only a limited number of classes of chemicals (e.g. POPs) have been assessed in plastic particles until now, plastics are likely to be able to sorb a wide range of chemicals. Chemical additives present in microplastics have the potential to be released upon discharge of these polymeric particles into the marine environment. There are concerns about the physical and toxicological harm that ingesting this debris might cause.

Plastic pollution in the marine environment is now recognized as a real threat with a global-scale distribution and adverse effects spanning from molecular level, physiological performance and organisms health. Due to the long-life of plastics on marine ecosystems, harm to marine life would continue for many decades even if the production and disposal of plastics suddenly stopped.

To solve plastic pollution, we need to better understand marine plastic sources and transport in order to develop mitigation strategies and targeted clean up options that must be efficient on a long-term perspective.

Public awareness should be raised to reduce single plastic use (e.g. plastic bags and plastic bottles) and encourage people to re-use and recycle plastic waste. Sufficient litter and recycling bins must be placed on beaches and in coastal areas. Commercial, municipal (household waste) and agricultural (packaging and construction materials) wastes must be collected from residential areas, streets, parks and waste dumps.

Concerning marine areas, shipping, fishing and tourism industries should be informed about the necessity to prohibit throwing plastic wastes into the sea. Traditional fishing gears could be replaced by eco-friendly products. Fishermen and the public should be encouraged to participate to the monitoring and collection of marine litter.

Burning plastics with other wastes in incinerators should be preferred over dumping in landfills or littering, while this process can produce energy; but open-air combustion of plastics

release hazardous chemicals to air, surface waters and soils from where they can enter the food-chain and be of concern to living organisms and human health.

Recycling or valorization (pyrolysis and gasification) of plastic materials are the most important actions available for reducing the environmental impacts of open landfills and open-air burning that are often practiced in developing countries to manage domestic wastes.

In this study, the waste plastics pyrolysis process was conducted. A steady state equilibrium model in computer aided software (ASPEN Plus 8.4) was developed where the pyrolysis process was simulated at 450 °C and atmospheric pressure. Then, a sensitivity analysis was conducted to study the effect of temperature on the yield of the pyrolytic oil. It was concluded that the effect of temperature on the pyrolysis product follows a certain pattern where the optimum temperature to produce highest pyrolytic oil yield was around 450 - 550 °C. Then, as the temperature increases, the yield of pyrolytic oil decreases. However, the model results are not consistent with the results of other studies. Therefore, the results require further study in order to improve the representation of the pyrolysis reactions in the simulation and create a model that succeeds in predicting the performance of the pyrolysis reactor.

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