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# Mémoire

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# Master

**Filière** : Génie des Procédés

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# *Synthesis Methods of High Density Polyethylene (HDPE) ; Determination of Properties ; Quality Control Parameters and their Influence on Various Process Properties*

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# *Dedication*

# Dedications

*I dedicate this modest Master-Thesis*

*To my dearest Parents, **my Father** and **Mother**, who have always been a great source of love, tenderness, and encouragement, those who have patiently awaited the fruits of their good upbringing.*

*To my entire family, not forgetting those who have been by my side in every period of joy and happiness, in particular, my uncle **Salah***

*To my dear brothers **Yahia, Abderrahmane, Iskander, and Yousef***

*To all my dear friends and colleagues, especially*

***Khairo and Moumouh and Fate***

*And finally, to the entire Polymer Engineering Class of*

***2022/2023***

***Nouara Seif Eddine***

# *Dedications*

*I dedicate this modest work Master-Thesis*

*To my precious source of tenderness, who has constantly watched over me with her prayers, patience, and support:*

***My Dear Mother***

*To **My Father**, who has given me the will, affection, and courage necessary to persevere in the right direction*

*To my dear brother **Zakariya***

*To my dear sisters **Asma and Hadjer***

*To my brother's wife **Amina***

*To my nephews and nieces*

***Iskander,Djouri Rassil,Tadj Eddine,Djoud, and Maher***

*To my dear grandmother **Fatima,** my God protect her*

*To all my family*

*To all my dear friends and colleagues, especially*

***Asma***

*And finally, to the entire Polymer Engineering Class of*

***2022/2023***

***Beledjehem Amina***

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*Thanks to Almighty God who has*

*given me the courage, the will, and the strength to complete this*

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*I dedicate this modest Master-Thesis*

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*and tender care, shaping me into who I am today. I will always*

*be grateful to them.*

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***Alla Edine*** *To whom I owe all the love.*

*To my entire family, my grandmother, my aunts, my cousins, and*

*my cousins*

*To all my friends, especially*

***Amina***

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*To all my teachers.*

*And finally, to the entire Polymer Engineering Class of*

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| Abbreviations | Description |
|---|---|
| **ADM** | General Administration Department |
| **AF** | Family Allowances |
| **AIBN** | Azobiziso-butyronitrile |
| **$Al(C_2H_5)_3$** | Triethylaluminum |
| **$AlEt_3$** | Triethylaluminum chloride |
| **BAD** | Algerian Development Bank |
| **CNAS** | Caisse nationale des assurances sociales |
| **CNASAT** | Caisse Nationale d'Assurances Sociales, Agence de Tlemcen |
| **CNR** | Caisse nationale des retraites |
| **CP1K** | Skikda Petrochemical Complex 1 |
| **CP2K** | SKIKDA petrochemical complex 2 |
| **$Cr_2O_3$** | Chromium oxide |
| **ENIP** | ENIP National Company of Petrochemical Industries |
| **FIR** | Intervention and Reserve Force |
| **HDPE** | High-density polyethylene |
| **HRC** | Human Resources Committee |
| **HRD** | Human Resources Department |
| **HRM** | Human Resources Management. |
| **HSE** | Health, Safety, and Environment |
| **ICI** | Imperial Chemical Industries |
| **ISD** | Internal Security Department |

# List of Abbreviations

| | |
|---|---|
| **ITD** | IT Department |
| **LDPE** | Low-Density Polyethylene |
| **LLDPE** | Linear Low Density Polyethylene |
| **MAO** | Methylalumoxane |
| **MCS** | Manufacturing control sheets |
| **MFI** | Melt Flow Index |
| **$MgCl_2$** | Magnesium Chloride |
| **MI** | Melt Index |
| **MIP** | Mutuelle de l'Industrie du Pétrole |
| **MW** | Molecular weight |
| **PE** | Polyethylene |
| **PF** | Phillips Process |
| **PVC** | Polyvinyl chloride |
| **UHMWPE** | Ultra High Molecular Weight PolyEthylene |
| **SSC** | Single-Site Catalysts |
| **Ti** | Titanium |
| **$TiCl_4$** | Titanium Tetrachloride |
| **UV** | Ultraviolet |
| **Zr-C** | Zirconocene |

# *Introduction*

## General Introduction

During the second half of the 20th century, polymers attracted increasing interest from industrialists. The objective was to achieve the production and market introduction of materials that could replace metals and other substances while possessing good mechanical properties.

The importance of polymer materials is such that it has become difficult to imagine our environment without this material. The production and consumption of polymer materials have thus become a criterion for development. A race has long been underway to discover new processes that give rise to new grades and new materials.

Since 1950, global production has continued to increase, but it was from 1970 onwards that this increase became more significant and has continued to grow ever since. In 2010, the number of synthetic plastics produced was 265 million tonnes. Polyethylene alone accounted for a quarter of this production due to its low manufacturing cost and good physical and mechanical properties. Additionally, this polymer allows for generally easy shaping processes such as extrusion or injection. It also possesses excellent electrical insulation and impact resistance properties and exhibits high chemical and biological inertness (suitable for food contact). The demand for polyethylene is only increasing worldwide, and Algeria is no exception to this trend. Thus, to meet the domestic market demand, Algeria acquired the POLYMED unit located at CP2K in order to reduce its polyethylene imports and, on the contrary, attempt to export if there is a surplus.

This Master-Thesis is divided into three chapters. The first chapter provides an overview of polyethylene; the second chapter is dedicated to the presentation of the CP2K-Skikda Complex plant and the description of the high-density polyethylene (HDPE) production process. The third chapter will describe in detail the experimental study conducted at CP2K, along with the experimental results and their interpretations.

The general conclusion is presented in the last part.

# Chapter I
# Synthesis Methods of Polyethylene, Properties and Applications

# Chapter I    Synthesis Methods of Polyethylene, Properties and Applications

## I.1 Introduction

Polyethylene (PE) (sometimes known as polythene) was discovered in 1933 by Reginald Gibson and Eric Fawcett at the British industrial giant, Imperial Chemical Industries (ICI). Although it is more than 70 years since it was fi rst produced, it is still a very promising material. This widely used plastic is a polymer of ethylene, $CH_2 = CH_2$ , having the formula $(–CH_2-CH_2 –)n$ . It is produced at high pressures and temperatures in the presence of any one of several catalysts, depending on the desired properties of the end-use product. Other structures (leading to long and short branches) may be present, depending on the procedure used in the synthesis. PE is the largest volume polymer consumed in the world. It is a versatile material that offers high performance compared to other polymers and alternative materials such as glass, metal or paper**. [1]**

## I.2 Polyethylene

### I.2.1 Synthesis Methods of Polyethylene

Polyethylene is derived from the polymerization of the monomer ethylene alone to form a homopolymer, or in the presence of a comonomer such as a 1-alkene to form a copolymer. The two main pathways for producing high-density polyethylenes are catalyzed polymerization reactions using chromium oxide-based systems or Ziegler-Natta-type organometallic compounds. In recent years, a catalytic synthesis pathway based on so-called metallocene species has emerged, allowing for access to more homogeneous (**Figure I.1**). **[2]**

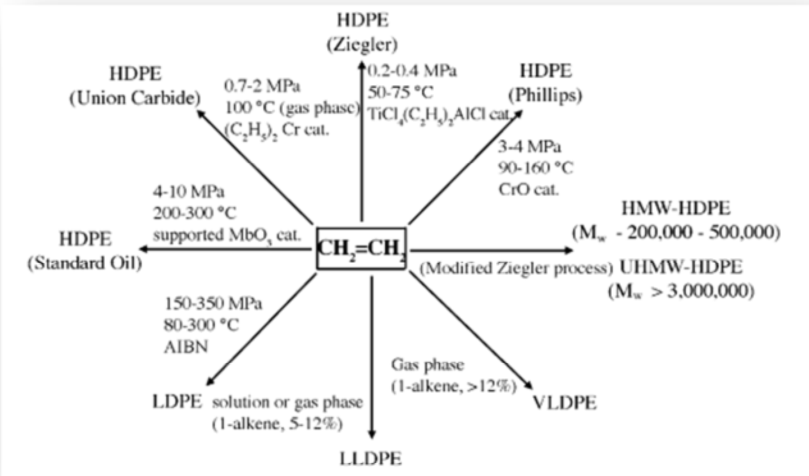


**Figure I.1** Different preparative routes for commercial PE. MW: Molecular Weight, AIBN: Azobiziso-butyronitrile

### I.2.2 Catalytic Polymerization with a metal oxide

This type of polymerization occurs under moderate temperature and pressure conditions. There are two processes that use metal oxides as catalysts: the Phillips process, which uses chromium oxide as a catalyst, and the Standard Oil process, also known as the Indiana process, which uses molybdenum oxide. The most commonly employed method comes from the Phillips process. Chromium oxides (**Figure I.2**) are the most widely used catalysts for the production of high-density polyethylene, accounting for slightly more than half of global production. They are supported by a porous silica or low-alumina Aluminosilicates support. **[2]**

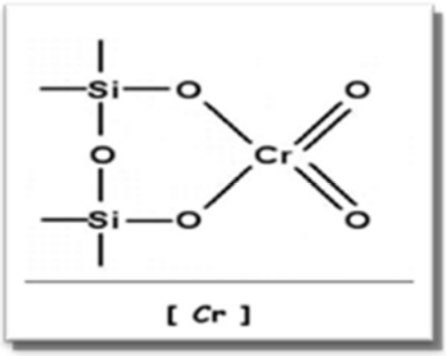


**Figure I.2** Structure of a metal oxide type catalyst.

A probable mechanism is proposed in (**Figure I.3**). The first step of the synthesis involves impregnating highly porous silica or Aluminosilicates support with an aqueous solution of chromic acid or chromium trioxide. After drying, the catalyst is activated by heating at 500-700°C in an oxidizing environment, leading to chromate species on the surface, precursors to active sites. In a high-temperature ethylene environment (in the reactor), a reduction of the valence state occurs (ranging from CrII to CrV depending on the mechanisms). Polymerization then takes place from the active site comprising a Cr-C bond that complexes an ethylene molecule. This molecule then inserts itself between the chrome and carbon atoms; the operation repeats to form the polymer chain. **[2]**

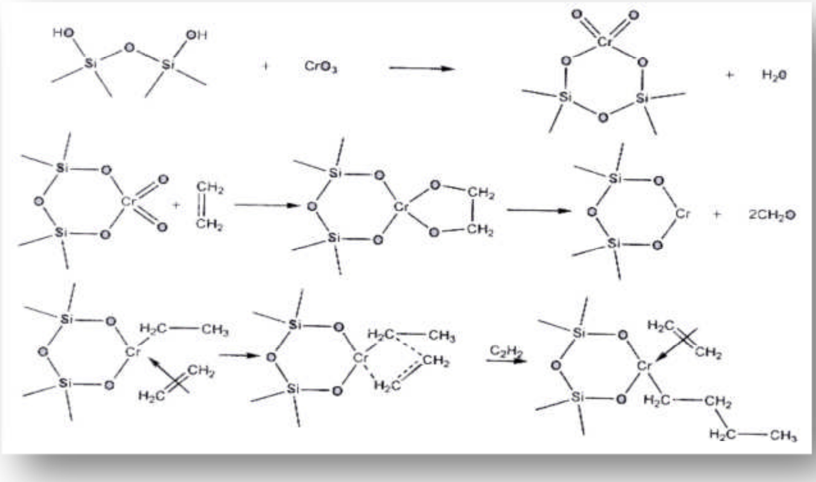

**Figure I.3** Polymerization mechanism by chromium oxide catalysis.

### I.2.3 Polymerization of the Ziegler-Natta

Type this synthesis route takes place under relatively low temperature and pressure conditions, slightly lower than the previous method. The variety of catalysts is immense. Generally, they consist of a complex between an organometallic compound (from group I-III) and a transition metal salt (group IV-VIII). The most typical example for the synthesis of HDPE, presented in **(Figure I.4)**, is the case of triethylaluminum chloride ($AlEt_3$) with titanium tetrachloride ($TiC_{l4}$). **[2].**

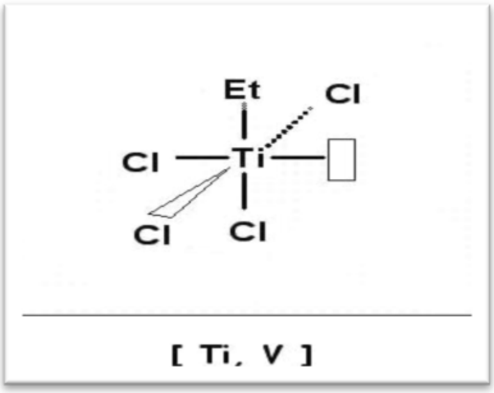


**Figure I.4** Structure of a Ziegler-Natta type catalyst.

The active site of this polymerization consists of a titanium atom complexed with 4 chlorine atoms and an alkyl group in an octahedral configuration, with a vacant site. The latter allows an ethylene molecule to complex with the titanium atom. In the next step, the ethylene molecule inserts itself between the metal and the alkyl group, creating a new vacant site and allowing the repetition of the operation that leads to a PE chain (**Figure I.5)**. **[2]**

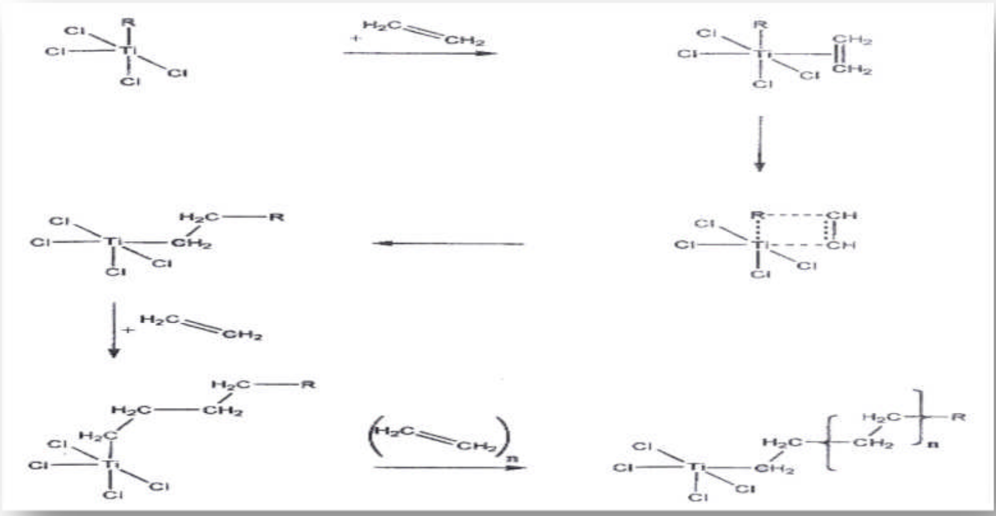

**Figure I.5** Ziegler-Natta polymerization mechanism.

### I.2.4 Metallocene-type Polymerization

This process is used to produce a range of ethylene-α-olefin copolymers that are less polydisperse than those obtained with the Ziegler-Natta process. To do this, metallocene-based catalysts are used, such as zirconocenes, **[3]** where each catalyst molecule contains a single type of active site that polymerizes the monomer in the same way. Metallocene catalysts are therefore commonly referred to as "single-site catalysts (SSC)"(**Figure I.6)**. **[2]**

The group IV metal atom is attached to two cyclopentadiene ligands, which can be linked together and more or less substituted. Metallocene catalysts can be supported on a silica support, and there is also the possibility of using a co-catalyst such as methylalumoxane (MAO), which acts as a ligand exchange agent and significantly increases the catalyst's activity. **[4]**

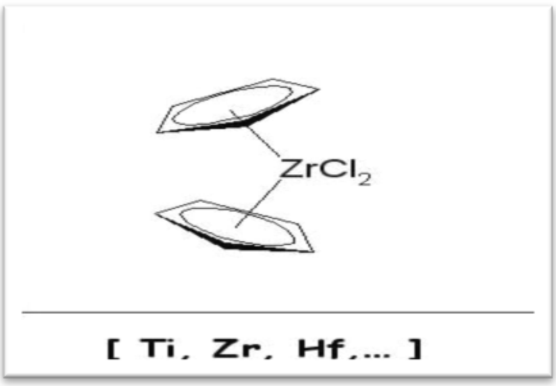


**Figure I.6** Structure of a Metallocene-type catalyst.

In the case of a synthesis using an MAO co-catalyst, **(Figure I.7)** illustrates, in the first step, the conversion of the catalyst after complexation into an active species with a free coordination position for the monomer. The latter then complexes with the zirconocene, and then inserts itself between the Zr-C bond, freeing up another coordination position to repeat the operation, thus forming the polymer chain in a very short time. **[4-6]**

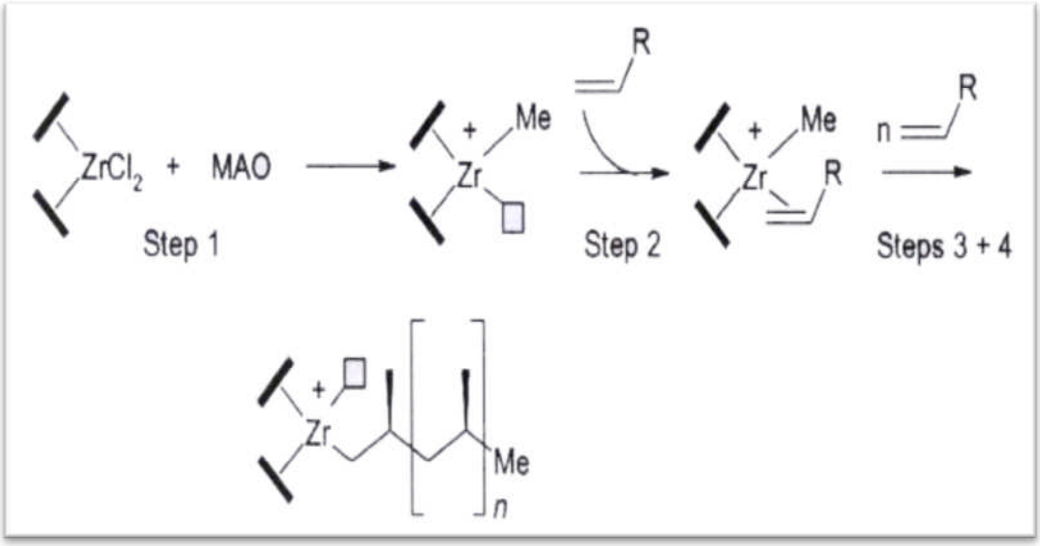


**Figure I.7** Metallocene Polymerization Mechanism.

## I.3 Chemical Structure of Polyethylene

Ethylene **(Figure I.8),** a colorless, flammable gas, is the basis of many plastic materials. This gas is obtained from many sources: natural gas, distillation of coal, petroleum cracking **(Figure I.9),**, and chemicals.**[7]**

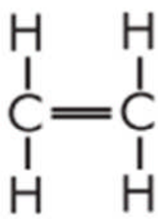


**Figure I.8** Chemical structure of ethylene monomer

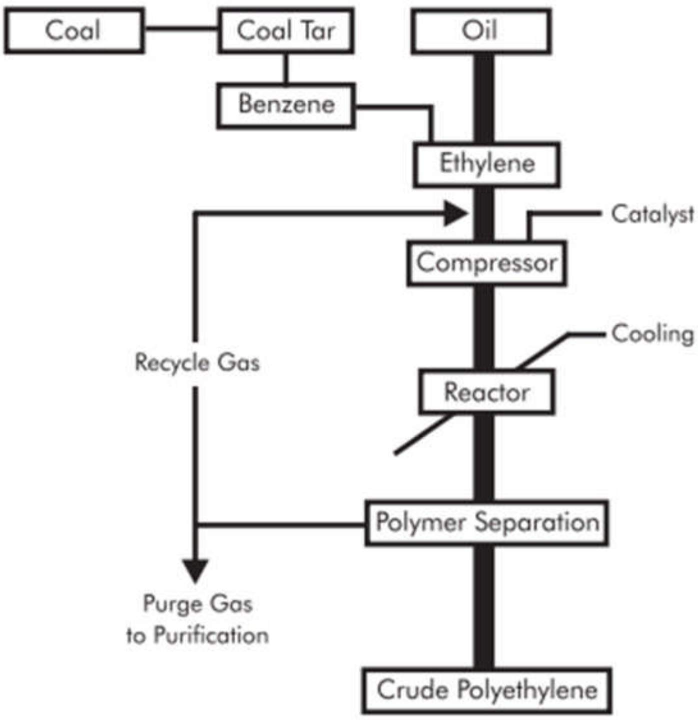


**Figure I.9** Process of crude Polyethylene

As compared to other plastic materials, which must go through many processes before actually arriving at a point where they are plastic materials, Polyethylene is derived directly by the polymerization of the ethylene gas in the presence of suitable catalysts. Free-radical catalysts, such as peroxides or other diluents, are used.

Polymerization is accomplished in a pressure chamber or autoclave and the type of Polyethylene produced is entirely dependent on the amounts of pressure, heat, and catalyst used. **(Figure I.10) [7]**

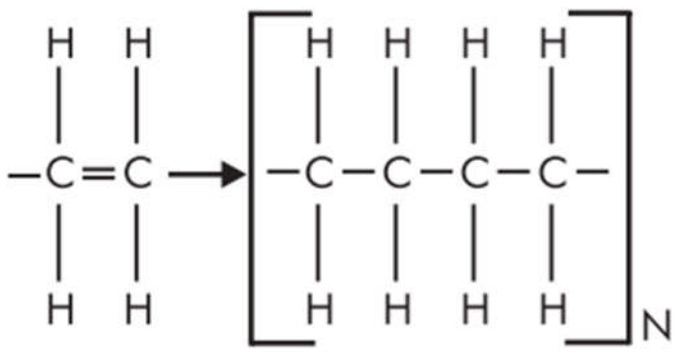

**Figure I.10** Polymerisation of the ethylene gas.

Polyethylene is generally referred to as being high, low, or medium density. By using high pressures and heat, a low-density material is formed. The molecular structure appears to be somewhat broken up and it is generally referred to as being “branched.” Polyethylene material of this type is soft, flexible, and tough**. (Figure I.11), [7]**

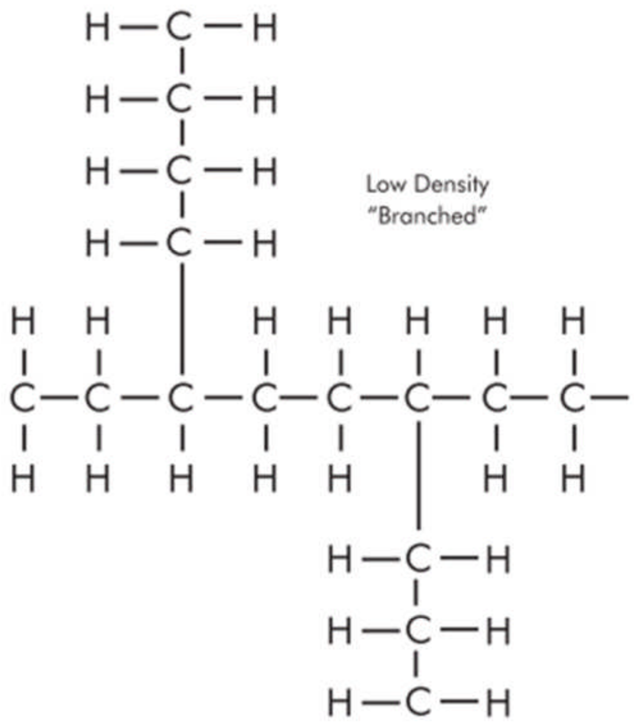


**Figure I.11** The molecular structure of low-density polyethylene for more flexible,and though

The high-density Polyethylenes are formed at relatively low pressures and are much stiffer, glossier, and more resistant to heat. This is because the molecules are distributed in a more orderly fashion**.[7]**

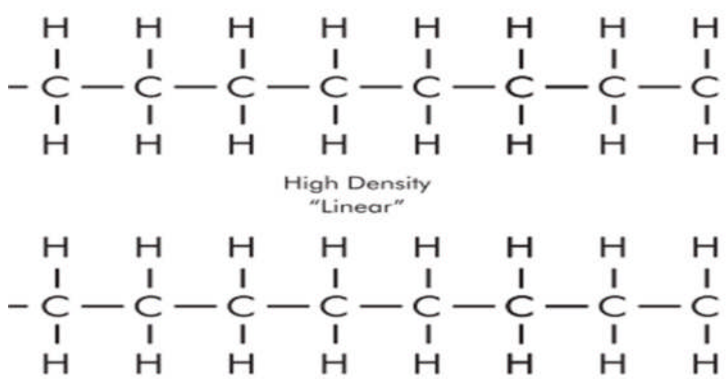


**Figure I.12** The way the molecules are distributed for more resistant to heat and glossier more.

To obtain a medium density material the same technique is used as to produce high-density material, only at a lesser pressure. Another method is to mix high- and low-density material in equal amounts.**[7]**

## I.4 Properties of Polyethylene

### I.4.1 Physical properties of Polyethylene

Polyethylene is a commonly used plastic material that has a range of physical properties, including:

1. Density: Polyethylene has a low density, ranging from 0.91 to 0.96 g/cm³. This makes it a lightweight material that is easy to handle and transport.
2. Melting point: The melting point of polyethylene varies depending on its molecular weight and density. Generally, it ranges from 115 to 135°C.
3. Tensile strength: Polyethylene has a high tensile strength, making it strong and durable. Its tensile strength can range from 8 MPa to 50 MPa, depending on the type of polyethylene.
4. Flexibility: Polyethylene is a flexible material that can be easily molded and shaped. It can withstand repeated bending and stretching without cracking or breaking.
5. Chemical resistance: Polyethylene is resistant to many chemicals, including acids, alkalis, and solvents. It is also resistant to water, making it ideal for use in pipes and other water-related applications.
6. Electrical insulation: Polyethylene is an excellent electrical insulator, which makes it a popular choice for wires and cables.
7. UV resistance: Polyethylene is resistant to UV radiation, which makes it a good material for outdoor applications. However, prolonged exposure to sunlight can cause it to degrade over time.

Overall, the physical properties of polyethylene make it a versatile material that is widely used in many industries, including packaging, construction, and automotive.**[8]**

### I.4.2 Chemical properties of Polyethylene

Polyethylene is a synthetic polymer that is commonly used in a variety of applications due to its advantageous properties. Some of the important chemical properties of polyethylene include:

1. Chemical Resistance: Polyethylene is highly resistant to most chemicals, including acids, bases, and organic solvents. This makes it an ideal material for use in chemical storage tanks, pipes, and fittings.

2. Thermal Stability: Polyethylene has excellent thermal stability and can withstand high temperatures without undergoing significant degradation. This makes it an ideal material for use in high-temperature applications such as hot water pipes.
3. Oxidation Resistance: Polyethylene is highly resistant to oxidation and does not degrade when exposed to ultraviolet (UV) light. This makes it an ideal material for use in outdoor applications.
4. Flammability: Polyethylene is a highly flammable material and can ignite easily when exposed to an open flame. However, it can be treated with flame retardants to reduce its flammability.
5. Water Resistance: Polyethylene is highly resistant to water and does not absorb moisture. This makes it an ideal material for use in applications where water resistance is important, such as in roofing materials and electrical insulation.
6. Biodegradability: Polyethylene is not biodegradable and can persist in the environment for many years. However, efforts are being made to develop biodegradable forms of polyethylene to reduce its impact on the environment**.[9]**

### I.4.3 Thermal properties of Polyethylene

Polyethylene has several thermal properties that make it a useful material in various applications:

1. Melting Point: The melting point of polyethylene varies depending on the type and molecular weight of the polymer. Generally, the melting point of polyethylene ranges from 110°C to 135°C.
2. Thermal Conductivity: Polyethylene has a relatively low thermal conductivity compared to other materials. This means that it is a good insulator and can be used in applications where heat transfer needs to be minimized.
3. Coefficient of Thermal Expansion: Polyethylene has a relatively low coefficient of thermal expansion, which means that it expands and contracts less than other materials when exposed to changes in temperature. This property makes it useful in applications where dimensional stability is important.
4. Heat Resistance: Polyethylene is resistant to heat and can withstand temperatures up to around 80-90°C without undergoing significant degradation. However, at higher temperatures, it can begin to soften and lose its mechanical properties.

5. Thermal Stability: Polyethylene is highly stable thermally and does not break down when exposed to heat or light. This makes it suitable for use in applications where long-term stability is important, such as in outdoor applications.

Overall, polyethylene's thermal properties make it a versatile material that can be used in a wide range of applications where temperature resistance and insulation properties are needed**.[10]**

### I.4.4 Mechanical properties of Polyethylene

Polyethylene is a widely used plastic material that has a range of mechanical properties, including:

1. Tensile strength: Polyethylene has a high tensile strength, which means it can resist pulling forces without breaking. The tensile strength of polyethylene can vary depending on the type of polyethylene, ranging from 8 MPa to 50 MPa.
2. Flexural strength: Polyethylene has a high flexural strength, which means it can resist bending forces without breaking. The flexural strength of polyethylene can vary depending on the type of polyethylene, ranging from 8 MPa to 50 MPa.
3. Impact strength: Polyethylene has a high impact strength, which means it can resist sudden forces or shock without breaking. The impact strength of polyethylene can vary depending on the type of polyethylene, ranging from 15 $kJ/m^2$ to 100 $kJ/m^2$.
4. Hardness: Polyethylene is a relatively soft material, which means it has a low hardness. The hardness of polyethylene can vary depending on the type of polyethylene, ranging from 20 Shore D to 70 Shore D.
5. Fatigue resistance: Polyethylene has a good fatigue resistance, which means it can withstand repeated cycles of stress without breaking.
6. Creep resistance: Polyethylene has a low creep rate, which means it can resist deformation under constant load over time.

Overall, the mechanical properties of polyethylene make it a versatile material that is widely used in many industries, including packaging, construction, and automotive**. [11]**

## I.5 Manufacturing of Polyethylene

Several types of reactors are used for ethylene polymerization reactions with transition metal catalysts **[10, 11]** Gas Phase Polymerization Technology: A gas-phase polymerization reactor is a large cylindrical tower with a height of up to 25 m with a length-to-diameter ratio of ~7. It usually operates at a pressure of 1.5 to 2.5 MPa (15 to 25 atm) and at a temperature from 70 to 100 °C. The reactor is half-filled with a bed of polymer particles, which is vigorously agitated and mixed by a high-velocity gas stream. The gas stream enters the reactor through a perforated distribution plate at the reactor's bottom; it fluidizes the bed of the polymer particles and removes the heat of polymerization. The stream includes ethylene, an -olefin (in copolymerization reactions), hydrogen, which is used for molecular weight control, and nitrogen (an inert component). The gas mixture exits the reactor at its top; it is compressed and cooled, its composition is reconstituted, and the gas is returned to the reactor. A solid catalyst in the form of small particles is continuously fed into the reactor. On average, these particles remain in a reactor for 2.5 to 4.0 hours. As soon as a catalyst particle enters a reactor, it starts polymerizing ethylene and, as a result, the size of an average polymer particle gradually increases 15 to 20 times compared to the diameter of the original catalyst particle. The particulate resin is continuously removed from the reactor. Solution Polymerization Technologies: Two types of high-temperature solution polymerization technology are used for LLDPE manufacture. Processes of the first type utilize hydrocarbon solvents and the processes of the second type are carried out in mixtures of supercritical ethylene and molten PE. Both solution processes usually operate at 130 to 180 °C, their reaction pressure varies from 3 to 20 MPa (30 to 200 atm), the ethylene content in the reactors ranges between 8 and 10%, and the residence time varies from 5 to 15 minutes. These processes can accommodate both particulate catalysts and soluble metallocene catalysts. The product stream containing up to 30–35 wt% of a molten polymer leaves the reactor and is discharged into a stripping vessel where the polymer is separated from unreacted monomers and the solvent and then pelletized. Slurry (Suspension) Polymerization Technology: Most slurry reactors for the production of HDPE and LLDPE resins are built as large folded loops containing vertically positioned long runs of pipe 0.5 to 1 m in diameter connected by short horizontal stretches of the same pipe. The loop reactors operate at a pressure of up to 3 MPa (30 atm) and at a temperature from 60 to 75 °C. The reactor is filled with a slurry of polymer particles suspended in a low-boiling solvent, usually isobutane or isopentane. An internal pump forces a high-speed circulation of the suspension through the loop. The concentration of polymer particles in the slurry is maintained at ~20 to 25 wt%. The residence time of polymer particles in the reactor ranges between 1.5 and 3 hours and the ethylene conversion in the process is usually very high, 97 to 98%.**[12]**

### I.5.1 Grades of HDPE produced at CP2K level

Since HDPE finds a good number of applications, such as the manufacture of pipes, plastic films for various uses, bottles, etc., different grades must be produced. Thus, the CP2K complex offers a whole range of HDPE comprising nine different grades. These are characterized by their melt flow index and density, which are reported in the following table.

**Table I.1**: The different grades of HDPE produced at the CP2K level and their uses

| Grade | Melt flow index (powder/granule) | Density | Use |
|---|---|---|---|
| **TR 402** | 0,11-0,19/0,08-0,14 | 0,9430-0,9460 | PIPE : (Tube Eau). |
| **TR 418** | - | - | Gas tub |
| **5502** | 0,55-0,70 /0,27-0,43 | 0,9530-0,9580 | Blow molding: bottles of small and large sizes |
| **TR 140** | 0,33-0,48/0,20-0,36 | 0,9430-0,9480 | FILM: General usage for all types of packaging. |
| **TR 144** | 0,25-0,38/0,14-0,24 | 0,9420-0,9470 | FILM: General usage for all types of packaging. |
| **6080** | 7,0-10,0/6,80-9,20 | 0,9420-0,9470 | Injection: Pallet, crate, drum, cap, crate, household items. |
| **6030** | 2,0-3,80/1,80-3,20 | 0,9590-0,9650 | Injection: Pallet, crate, drum, cap, crate, household items. |
| **6040** | 3,0-5,80/2,80-5,20 | 0,9590-0,9650 | Injection: Pallet, crate, drum, cap, crate, household items. |
| **6006L** | 0,80-1,15/0,47-0,73 | 0,9570 min | Blow molding: bottles of small and large sizes. |

## I.6 Major advantages of Polyethylene

Polyethylene has a range of advantages that make it a popular choice for many applications, including:

1. Low cost: Polyethylene is a low-cost material, making it an affordable option for many applications.

2. Lightweight: Polyethylene is a lightweight material, which makes it easy to handle and transport.
3. Chemical resistance: Polyethylene is resistant to many chemicals, including acids, alkalis, and solvents. This makes it ideal for use in packaging, where it can protect the contents from exposure to harmful substances.
4. Water resistance: Polyethylene is resistant to water, making it ideal for use in pipes and other water-related applications.
5. Durability: Polyethylene has a high tensile strength and impact strength, making it a durable material that can withstand repeated use without breaking or cracking.
6. Versatility: Polyethylene is a versatile material that can be used in many applications, including packaging, construction, and automotive.
7. Recyclable: Polyethylene is a recyclable material, which means it can be melted down and reused to make new products, reducing waste and conserving resources

Overall, the advantages of polyethylene make it a widely used material in many industries, and its versatility and affordability make it an attractive choice for many applications**.[13]**

## I.7 Drawbacks of Polyethylene

While polyethylene has many advantages, there are also some drawbacks to consider, including:

1. Environmental impact: Polyethylene is a non-biodegradable material that can take hundreds of years to decompose. This can lead to environmental issues, including pollution and harm to wildlife.
2. Heat sensitivity: Polyethylene can melt at relatively low temperatures, which means it is not suitable for high-temperature applications.
3. UV sensitivity: Polyethylene is sensitive to UV radiation and can degrade when exposed to sunlight over time.
4. Poor adhesion: Polyethylene has poor adhesion properties, which means it can be difficult to bond with other materials.
5. Flammability: Polyethylene is a flammable material and can ignite easily when exposed to fire.
6. Limited temperature range: Polyethylene has a limited temperature range, which means it is not suitable for use in extreme temperatures.

Overall, while polyethylene has many advantages, its drawbacks need to be considered when selecting it for a particular application. Efforts are being made to develop more sustainable and environmentally friendly alternatives to polyethylene to address some of its drawbacks**.[14]**

## I.8 Applications of Polyethylene grade in industrial fields

The applications of plastics in general and of PE, in particular, are innumerable. The consumption of LDPE at the European level is 4.7 million tonnes, of which film accounts for 60%. Co-extruded film permits a reduction in film thickness for the same mechanical resistance. LDPE is mainly used as film (59%), extrusion coating (17%), injection molding (6%), wire and cable (4%), adhesives and sealants (4%), sheets (2%), blow molding (1%), and miscellaneous, including pipe, conduit, and roto molding (7%). There are also increasing demands for PE use in the medical field (growing demand for sterile packaging), the automotive sector (HDPE automotive fuel tanks is a booming business), cosmetics (innovative packaging designs), liquid food packaging, and twin-sheet thermoformed HDPE pallets to replace wooden pallets. HDPE is also used in pipes for canalization (17%), injection molded products (20%), industrial containers, packaging, housewares, and so on. **[3]**

**HDPE**: Pipe and pipe fittings for water, and petroleum tanks, toys, bowls, buckets, milk bottles, crates, containers, films for packaging, blown bottles for food, food cutting boards, corrosion-resistant wall coverings, pipe flanges, lavatory partitions, inspection covers in chemical plants, radiation shielding, self-supporting containers, prosthetic devices (implants), yarns, chemical drums, jerry cans, carboys, toys, picnic ware, household and kitchenware, cable insulation, carrier bags, food wrapping material**. [3]**

**LDPE**: Chemically resistant fittings, chemical drums, tanks, and containers for storing water and most liquid fertilizers, pesticides, herbicides, insecticides, and fungicides, food storage containers, laboratory equipment, gas and water pipes, buckets, drinking glasses, insulation for wires and cables, core in UHF cables, disposable goods, gloves, kitchen tools, thermoformed products, corrosion-resistant work surfaces, vacuum formed end caps and tops, moisture barriers, liquid packaging, flexible and commercial packaging of photographic paper, extrusion coating grades, fittings and accessories, films or sheets for packaging, medical and hygiene shrink, shower curtains, unbreakable bottles, bowls, lids, gaskets, toys, packaging films, film liners, squeeze bottles, heat-seal films for metal laminates, squeeze bottles, toys, carrier bags, high-frequency electrical insulation, chemical tank linings, heavy duty sacks, general packaging. **[3]**

**LLDPE**: Packaging, particularly film for bags and sheets. Lower thickness (gauge) may be used compared to LDPE. Cable covering, toys, lids, buckets and containers, pipes**. [3]**

**UHMWPE** Unit conveying: chain guides, star wheels, feed screws. Mining: truckbeds, hoppers, and bunker liners. Pulp and paper: suction box covers, rollers, foil blades. Medical: orthopedic prostheses, knee, shoulder, and hip implants. Agricultural: food preparation surfaces. Automotive: lead–acid battery separators. Fibers: ballistic cloth, fishing lines, and nets. Recreational: snow ski soles, snowmobile bogie wheels. Others: filtration material**. [3]**

**EVA material** Deep-freeze bags, agricultural film, shoe soles, teats, handle grips, flexible tubing, record turntable mats, beer tubing, and vacuum cleaner housing**. [3]**

**Chlorinated PE** Modifier for polyvinyl chloride (PVC) or compounded with LDPE or HDPE fi lm to improve toughness; films are used as liners and for agricultural applications, flame retardant**. [3]**

**Wax emulsions, PE waxes (molecular weight ~ 2000)** Internal lubricants in PE (increase the melt flow index, do not increase the susceptibility to environmental stress cracking). **[3]**

## I.9 Conclusion

In conclusion, the synthesis of polyethylene, along with its diverse applications and distinct grades, underscores its crucial position in the realm of polymers, offering immense possibilities for various industries and contributing to the advancement of materials science.

# References

## Chapter I

### Synthesis Methods of Polyethylene, Properties and Applications


**[1]** Cornelia Vasile Mihaela Pascu: " Practical Guide to Polyethylene", Shropshire, **2005**.

**[2]** A.J. Peacock: "Handbook of Polyethylene: Structure, Properties, and Applications", New York: Marcel Dekker, **2001**.

**[3]** C.Vasile, M.Pascu: " Practical Guide to Polyethylene", Shropshire, **2005**.

**[4]** W. Kamminsky, A. Laban: "Metallocene catalysis, Applied catalysis A: General, **2001**, 222(1-2), p. 47-61.

**[5]** J. Scheirs, W. Kamminsky: "Metallocene-based polyolefins", vol 1, UK, Wiley, **2000**, 526 p.

**[6]** Manuel d'opération, CP2K, INTEDRA.

**[7]** , By Bill Fry Working with Polyethylene Society of Manufacturing Engineers Dearborn, Michigan,**1999** page 8.9.10.11

**[8]** Physical Properties of polyethylene ; by the following link ligne https://chat.openai.com/ (**30/04/2023**)

**[9]** Chemical of polyethylene ; by the following link ligne https://chat.openai.com/ (**30/04/2023**)

**[10]** Thermal of polyethylene ; by the following link ligne https://chat.openai.com/ (**30/04/2023**)

**[11]** Mechanical of polyethylene ; by the following link ligne https://chat.openai.com/ (**30/04/2023**)

**[12]** Edited by Mark Handbook of Industrial Polyethylene and Technology **2018** page25

**[13]** Major Advantages of Polyethylene; by the following link ligne https://chat.openai.com/ (**30/04/2023**)

**[14]** Major Drawbacks of Polyethylene; by the following link ligne https://chat.openai.com/ (**30/04/2023**)

# Chapter II



# Presentation of the CP2k Petrochemical Complex

## II.1 Introduction

Polyethylene is found every day in various products: plastic wrapping, layered sheets for packaging cartons, toys, and industrially molded products through injection molding, as well as products such as detergent bottles used for household tasks, molded through blow molding, cable coatings, and piping for the transport of gases and liquids, are just a few of the current applications of polyethylene. The factories that use the PHILLIPS PETROLEUM COMPANY process can produce a wide variety of polyethylene resins. Continuous research and accumulated experience over the years ensures the production of polymers with densities ranging from 0.92 to 0.96 g/cm$^3$. Thanks to the XPF catalyst, high molecular weight resins are obtained with flow indices of 70 or more. However, PHILLIPS PETROLEUM COMPANY is constantly researching the production of new resins, which will be passed on to process licensees at the time of their commercialization.

## II.2 Importance of polymer materials

The importance of polymer materials is such that it becomes difficult to imagine our environment without this material. The production and consumption of polymer materials have become a criterion for development. A race has long been launched to develop new processes giving birth to new grades and new materials.

Despite the rise in the production of new plastic materials, high-density polyethylene (HDPE) occupies a significant portion of global polymer production because it constitutes a basic material for the polymer and plastics processing industry. It has been able to replace a large number of materials with various uses during the past century and continues to do so today. The demand for polyethylene is only growing worldwide.

In 1933, scientists from Imperial Chemical Industries (ICI) succeeded in realizing the radical polymerization of ethylene by working at high pressures (150-300 MPa). The process opened the doors to global production in 1939. It is still used, with the polymerization initiated by either an organic peroxide or molecular oxygen at a temperature between 140 and 180°C. The resulting polymers are specifically named using the acronym LDPE, which stands for "low-density polyethylene." Polymerizations are obtained in continuous flow either in agitated reactors (autoclaves) with a volume of around 1 m$^3$ or less bulky tubular reactors (0.4 m$^3$) in which the pressure can be higher than in the autoclaves **[1].**

## II.3 Manufacturing processes of HDPE

The "Phillips" catalysts based on supported chromium oxide are still widely used to produce HDPE. However, the discovery of coordination catalysts by Ziegler in 1953 revolutionized the production of polyethylene. Indeed, catalytic systems based on titanium halides and aluminum alkyls offer several advantages in terms of processes (polymerization under moderate pressure) as well as the properties of the resulting polymers. The most commonly used catalytic systems are $TiCl_4$ and Al $(C_2 H_5)_3$, and the product of the reaction is supported on $MgCl_2$. They provide extremely high outputs (up to 500kg of polyethylene per gram of Ti), which allows for the elimination of the "scavenger", a necessary phase to remove catalytic residues. A wide variety of techniques are used for coordination polymerization: high pressure, solution in an aliphatic hydrocarbon, "gas phase" process, and suspension in a diluent. Each of these techniques should be adapted for the production of the polymer in large quantities. Molecular weights are controlled by transfer to molecular hydrogen. Metallocenes are capable of initiating the polymerization of ethylene and its copolymerization with other α-olefins to produce copolymers. The efficiency of these catalysts is close to unity. They allow for very high outputs, which provide these catalytic systems with a promising future (**Figure II.1). [1]**

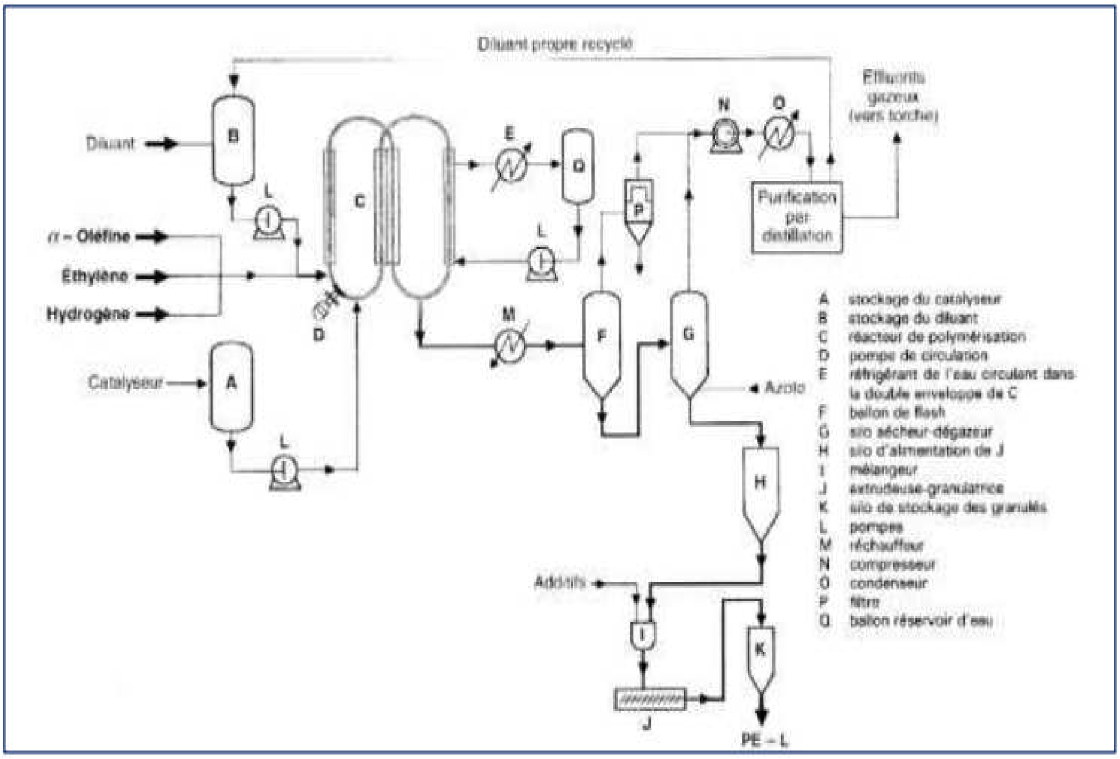


**Figure II.1:** HDPE suspension production process. **[2]**

## II.4 History

The CP2K complex was established in the industrial area of Skikda in January 2004 after the project to build a high-density polyethylene unit was signed in April 1991 between ENIP (National Company of Petrochemical Industries) and Repsol Quimica (a subsidiary of Repsol) as part of the Algerian-Spanish industrial cooperation. The joint unit was then called POLYMED (Mediterranean Polymers). The unit's capital was held by ENIP at 64%, REPSOL at 23%, and BAD (Algerian Development Bank) at 13%. Subsequently, ENIP decided to buy back the shares of REPSOL and BAD after they decided to withdraw. Today, Sonatrach has taken over the unit, which is now called CP2K.

## II.5 Location

The CP2K complex, which includes the HDPE unit, is located within the industrial zone of Skikda. Covering an area of approximately 17 hectares (166,800 m²), of which 10% is built, the CP2K complex is located on the coast, 6 km east of the capital of the Skikda province, and at an average altitude of about 6 m above sea level **(Figure II.2).**

Its geographical location is shown in the figure below. It is limited as follows:

-To the North: by the Mediterranean Sea

-To the South: by the main road of the industrial zone.

-To the East: by the FIR (Intervention and Reserve Force).

-To the West: by CP1K (Skikda Petrochemical Complex 1).

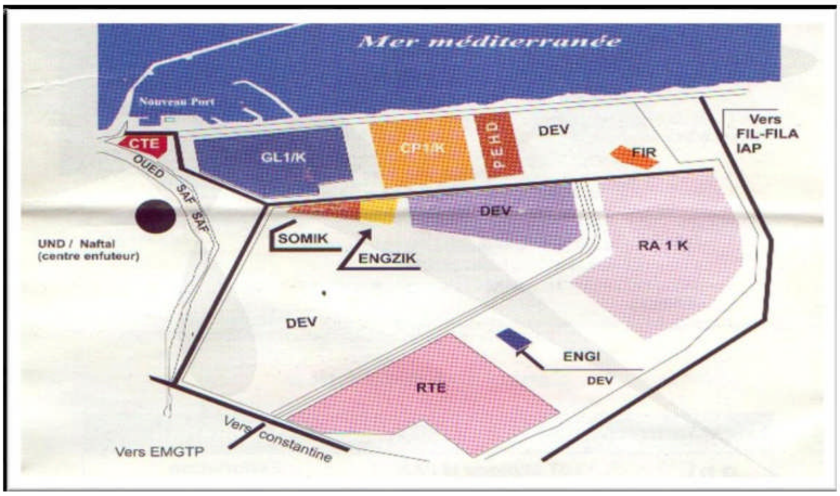


**Figure II.2:** Implementation of the CP2K (PEHD) complex.

## II.6 Description of the plant

CP2k aims to produce a high-density polyethylene production unit with a capacity of 130,000 tons per year. The raw materials used are:

- Ethylene from the nearby CPIK;
- Isobutane from the also nearby GLIK.

The complex is designed for the production of high-density base polyethylene (HDPE) and is intended to supply the national plastic processing industry and export any excess.

### II.6.1 Site Layout

The CP2K complex consists of 5 important zones, which are:

**a) Off-site area**

Utilities (boilers, nitrogen, desalinated water, fire water, potable water, and gas expansion)

- Flare;
- Isobutane and hexene storage;
- Wastewater treatment;
- Catalyst activation.

**B) Wet area**

- Reactors.
- Compressors.
- Capacities.

**c) Dry area**

- Extruder.
- Blowers.
- Storage silos for finished products (powder and granules).
- Bagging.

**d) Building area**

• ADM and finance block.

• Canteen and changing rooms.

• Security and medical block.

• Spare parts store, workshops, and technical block.

• High and low voltage substations.

• Process control room and laboratory.

**E) Storage area**

• Ethylene storage tanks.

• Ethylene vaporizer;

• Loading/unloading section

**II.6.2 Organization of CP2K**

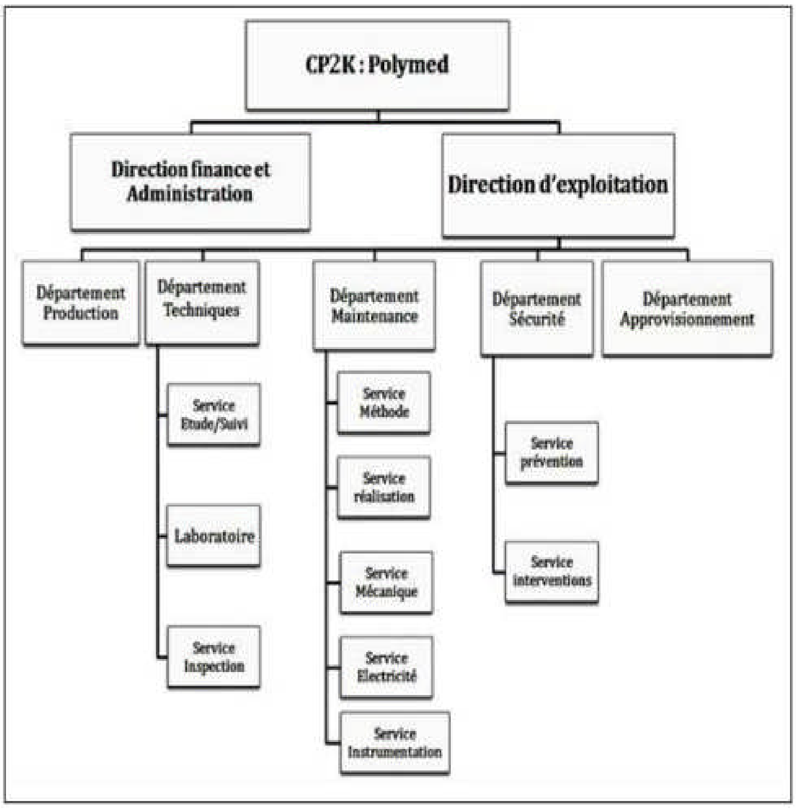


**Figure II.3**: Organization chart of CP2K.

"The complex is composed of two departments:

• Finance and Administration department

• Operations department which is divided into 5 departments"

**II.6.2.1 Production Department**

It includes the three areas of the complex mentioned earlier (off-site area, wet area, and dry area), which are grouped into two types of facilities:

**a.Main plant facilities**

• Raw material preparation and processing unit.

• Reactor where HDPE polymerization and powder recovery takes place.

• Extruder that transforms the powder into pellets.

• Intermediate storage (capacity 3500 tons). • Packaging unit.

**b. Auxiliary facilities**

• Steam, electricity, air production, etc;

• Wastewater treatment;

• Raw materials, utilities, and additives storage (water, hydrogen, hexene, isobutane);

• Finished product storage warehouse with an area of 18,000 $m^2$ and a capacity of 12,000 tons.

**II.6.2.2 Technical Department**

This is a very important department that works in parallel with the other departments. It consists of three services:

• Study/Follow-up service: whose work is focused on studying problems that may arise in the various departments and making necessary modifications. New project studies are also carried out at this service level.

• Inspection service: whose role is to validate equipment and installations through programmed systems.

• Laboratory service: whose task is to continuously analyze the raw material, catalyst, and finished product.

The different laboratory tests and analyses carried out are:

- Analysis of the purity of the raw material;
- Activation of the catalyst on a laboratory scale;
- Production of pellets and films using a laboratory-scale blown film extruder and plates using a press.

Mechanical and physical tests such as stress cracking (resistance to cracking), torsion resistance, rupture resistance, tear resistance of films, opacity, softening point, degradation time (service life), density, and melt flow index (MFI).

### II.6.2.3 Maintenance Department

This department is responsible for the maintenance and upkeep of equipment. It consists of five services:

• Methods service: divided into two sections, planning section and preparation section.

• Implementation service

• Mechanical service

• Electrical service

• Instrumentation service

The work of this department is divided into two parts: periodic work scheduled for each piece equipment and work carried out in response to requests from the production department in case of breakdowns. In this second case, the work is first planned, then prepared and finally sent to the relevant service, which always depends on the maintenance department.

### II.6.2.4 Safety Department

The CP2K complex, like all factories, has an HSE (Health, Safety, and Environment) department, which in turn contains two services:

• Prevention service

• Intervention service

#### II.6.2.5 Internal Security Department (ISD)

It is responsible for protecting the company's human and material assets and implementing security measures such as controlling and recording all entry and exit movements of complex personnel and foreign personnel (visitors, contractors). It handles all requests for administrative investigations concerning new recruits, interns, and foreign missionaries and ensures their protection. It manages access authorizations for vehicles (complex personnel and subcontractors).

#### II.6.2.6 IT Department (ITD)

Its main missions are the development of all necessary programs, applications, or software for the operation of the complex's structures, maintenance and repair of computer equipment, and IT assistance.

#### II.6.2.7 Human Resources Department (HRD)

The development strategy of a company depends on certain pillars, among which is Human Resources Management. HRM covers many areas, intervening at all stages of the worker's "life" in the organization: recruitment, career management, training, performance evaluation, conflict management, social consultation, staff motivation and involvement, communication, job satisfaction, and working conditions.

"Forecasting, organizing, commanding, coordinating, controlling and analyzing" are the imperatives of a good mastery of human resources management. The HRD is composed of two services:

• Training and Follow-up Service This section takes care of new recruits, interns, and apprentices, ensures various training for employees and manages their careers. It establishes training and seminar programs, develops training plans and budgets, and ensures their monitoring and implementation, ensures the establishment of the apprenticeship tax, takes care of the posting and general dissemination of internal and external job advertisements targeted by the job exchange.

**• Career management service**

It follows the career path of employees from their recruitment until their departure (retirement, death, etc.), with the objective of establishing a policy that anticipates their replacement and ensures continuity.

It manages the launch and follow-up of the performance evaluation campaign, in terms of achievements and recommendations (weighting rates).

It may suggest upgrading or improving training to enhance the professional qualification level of employees. It is responsible for processing personnel movement files to be submitted to the Human Resources Committee (HRC), which is composed of managers and worker representatives.

The section maintains career files for all complex employees, containing all information concerning their career paths (promotion, interim, training, seminar).

It handles the recruitment of temporary and permanent staff, programs and ensures the progress of professional tests (selections, invitations, recruitment files, medical examination, induction) until assignment to their work positions. The section maintains an updated database of recruitment requests

#### II.6.2.8 General Administration Department (ADM)

The objective of this department is to establish all the fundamental human and material means to raise the level of qualifications of the workers through generalized and appropriate training, the optimal use of the professional and intellectual capacities of the workers, training and integrating the recruited personnel, guaranteeing promotion to the most deserving employees, and ensuring a healthy work environment by strictly applying the regulatory provisions of labor, hygiene, and safety. On the other hand, the department ensures the well-being of workers on an indicative basis by providing transportation, catering, furniture, and office supplies. This department is composed of three services:

- **Personnel service**

The main management tools are the company collective agreement, the internal regulations, the HR management procedures manuals, the organizational chart, the job classification, and various circulars resulting from amendments to the company collective agreement.

- **General Means service**

This section is responsible for the supply and distribution of office supplies to different departments. This section's mission is also to provide transportation for the complex's personnel, for which it subcontracts transport means from the SOTRAZ Company.

The complex has its own means of transportation for the needs of the staff.

• Payroll department

This department is responsible for salary accounting.

**• Social Benefits section**

This section acts as an intermediary between the staff and various social security organizations (CNASAT, CNR, MIP, etc.), in matters of medical expense reimbursements, sick leave, work accidents, retirement pensions... etc. The section is responsible for:

• Declaration and affiliation of new hires.

• Declaration of work accidents and follow-up of sick leave.

• Family Allowances: the AF listing is transmitted by CNAS, the section

**• External Relations Section**

Its role is to provide transportation for internal and external mission workers, and it takes care of their needs in terms of ticketing, catering, and accommodation

### II.6.2.9 Finance and Legal Department (F)

This department is responsible for monitoring the financial and legal operations of the complex, and includes the following services:

• General Accounting Service

• Management Information Service

• Treasury Service

• Legal Cell

### II.6.2.10 Procurement Cell

This unit is responsible for organizing and setting the practical modalities related to the development and execution of acquisition contracts for supplies, construction, services, studies, and consulting services within the CP2/K complex. This activity is governed by a referenced procedure E-025 of 02/01/2013 that ensures the effectiveness of the procurement process and the control of costs, quality, and deadlines, in compliance with the principles of freedom of access to orders, equal treatment of candidates, and transparency of procedures.

#### II.6.2.11 Security Department

The Security Department plays a very important role in complex-level security where danger can arise at any moment. The activity of a company is accompanied by various risks, and it must strive to prevent them, which means detecting incidents before accidents occur through a systematic organization of property and personal security.

The security department consists of two (02) services:

- **Intervention Service** :

Despite all precautions, the complex cannot escape certain random damages. To combat accidents, which can be very costly for the company, the complex is equipped with the most advanced human and material resources to intervene promptly and prevent the spread of danger.

- **Prevention Service :**

Prevention is a constant necessity due to the multiple risks associated with the work, such as risks of manual handling, mechanical hazards accompanying machine users, and chemical risks from corrosive or toxic substances. Safety inspectors are responsible for ensuring compliance with regulations and procedures regarding the safety of workers. Their actions involve making observations and suggestions during complex visits, signing work permits, and ensuring equipment protection through various means (gas detectors, surveillance stations, etc.).

## II.7 General Description of the Process

The POLYMED plant in Skikda has two production processes in the same facility:

The Phillips Process

The Ziegler Process

However, since its initial startup, it has only been using the Phillips Process because the catalyst used in the Ziegler Process is expensive compared to the one used in the Phillips Process. The Phillips Process, also known as the PF process or particle process, was designed specifically for the POLYMED plant and requires high purity of raw materials and only tolerates small amounts of poisons that can impede the proper functioning of the reactor or alter the quality of the resulting product.

- **The charges uses**
- Ethylene in the gaseous phase: the main charge.
- Isobutane in the liquid phase: the reaction medium.
- Hexene in the liquid phase and hydrogen in the gaseous phase in small quantities.
- **The catalyst**: chromium oxide ($Cr_2 O_3$) supported on silica.
- **The operating conditions of the polymerization reaction:** The two essential conditions in the reactor are:

The temperature: varies between 93 and 110°C, depending on the grade to be produced.

The pressure: is between 42 and 44 bars, depending on the opening or closing of the discharge valves.

It is necessary to subject the raw materials to a conditioning and purification process to obtain the degree of purity required by the polymerization reaction, which essentially consists of producing polyethylene.

### II.7.1 Treatment of raw materials and activation of catalyst

• Ethylene is the main reactant of the process, received at the plant through a pipeline from the adjacent ethylene plant, at 16.9 $kg/cm^2$ g and at room temperature. In general, the ethylene stream first passes through the acetylene removal reactor. From the bottom of this reactor, it flows to the Ethylene compressor suction separator where the pressure increases. The ethylene enters the oxygen removal reactor from the top, and then moves to the Carbon Monoxide Removal Reactor, passing through both reactors in a downward direction. From there, the ethylene passes through the Carbon Dioxide Removal Reactor in an upward direction and then is directed to the ethylene dryer**. [3]**

• Hexene is a comonomer added to the reactor for the production of copolymers. Comonomers in small quantities alter the molecular structure of the polymer and thus change its physical properties. The product density is controlled by adding hexene, and the antistatic agent (a product that prevents fouling of the walls) is found in hexene in the antistatic addition pot.

Hexene is subjected to a process of removal of water and gas absorbed in the stream. For this, it is treated in a degassing column. The column consists of two 0.50 $m^3$ beds filled with stainless steel pall rings, for the removal of water and other light compounds present in the hexene stream. **[3]**

The column has a chimney tray at the top, with a side extraction to collect the water that has condensed in the head condenser in the pot. The column feed enters above the chimney tray and falls with the reflux from the head condenser to the liquid distributor. The degassed hexene falls into the tank at the bottom of the column. At the outlet of the column, the hexene is dried in the water removal treater, which operates by adsorbing water in molecular sieves.

**• Isobutane**

There are two types of isobutane: fresh isobutane and recycled isobutane.

**Fresh isobutane:** is used in the catalyst addition systems, co-catalyst addition system, scavenger loading deposition, and reactor pump, as a cleaning and washing product to prevent possible polymer plugs from blocking small diameter orifices and lines. It is also used to provide the necessary makeup for the proper functioning of the reaction (**Figure II.4).**

Fresh isobutane is subjected to a process of elimination of water and absorbed gas in a degassing column, at a design pressure of 10.7 kg/cm$^2$ g and a design temperature of 90ºC. It consists of two beds of 0.40 m$^3$ each, filled with stainless steel pall rings with a diameter of 25mm, for the removal of water and other light materials from the isobutane stream. The column has a chimney and a withdrawal plate at the top to collect the water that has condensed in the top condenser. At the exit of the column, the isobutane is dried in the water elimination processor, which operates by adsorption using molecular sieves. **[3]**

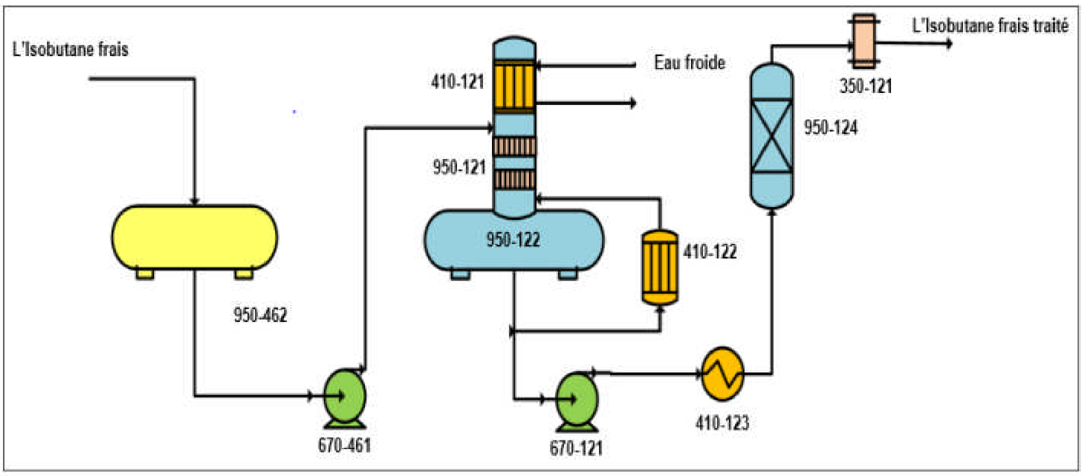


**Figure II.4 :** Fresh Isobutane Degassing System

**- Recycling Isobutane:** this is the main isobutane used in the unit as it is almost completely recovered. It is pumped from the storage tank to the recycling isobutane dryers. It feeds the dryers through the cooler, in which the heat generated during pumping is removed. After the cooler, water is removed from the isobutane stream and retained in a molecular sieve bed. The purified and dried recycling isobutane is used as a solvent (reaction medium) in the reactor (**Figure II.5**). **[3]**

• Hydrogen is received at the Plant at 203 $kg/cm^2g$ and 40ºC. It is added to the reactor to control the polymer fluidity index.

Before being incorporated into the production process, hydrogen must be dried in dryers. At the outlet of the dryers, the hydrogen passes through a filter. **[3]**

• The PF (PHILLIPS) type polymerization reaction catalyst requires a prior oxidation process on a fluidized bed using dry hot air, at temperatures that reach 982ºC. The main objective of catalyst activation is to remove water and volatiles by contact with dry and hot air in a fluidized bed. In addition to removing water from the catalyst, the oxidation state of chromium changes from $Cr^{+3}$ to $Cr^{+6}$. In the reactor, in contact with ethylene, the valence of chromium changes from $Cr^{+6}$ to $Cr^{+2}$. The $Cr^{+2}$ polymerizes ethylene into polyethylene. The PF catalyst is added to the reactor in the form of a fresh isobutane catalyst slurry. The activated chromium catalyst (PF) is added as a dry powder from the catalyst discharge hoppers to the catalyst depots, where it is mixed with fresh isobutane fed from the bottom of the depot. The catalyst feeding to the reactor is carried out by means of the PF catalyst feeders, with a dosing volume of 35 $cm^3$**. [3]**

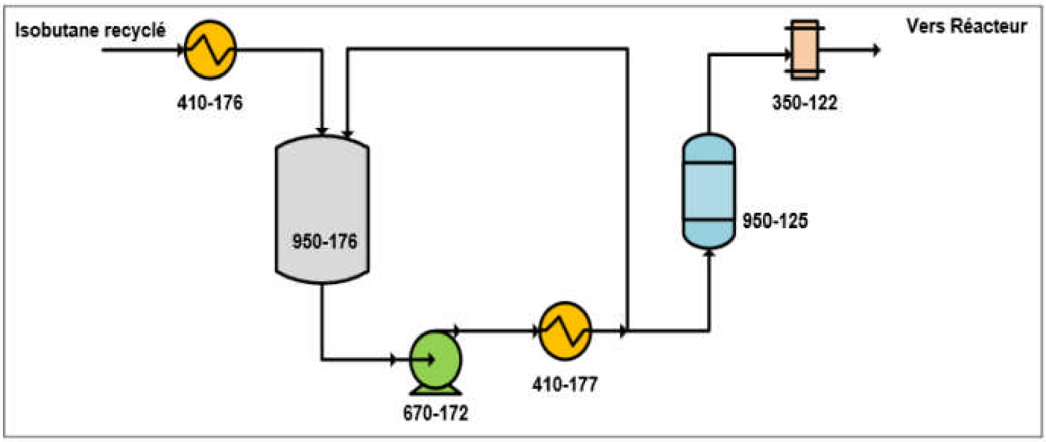


**Figure II.5**. Diagram representing the recycled isobutane treatment system.

### II.7.2 The reactor and the purification and recovery zone

• The reactor is a 560 mm internal diameter loop-shaped pipe consisting of four vertical sections joined by horizontal sections. The polymerization reaction is exothermic, at a rate of 800 kilocalories per kilogram of the polymer formed. This reaction heat is removed by the reactor's cooling system; it is designed for both heating and cooling. The refrigerant circulates in the jackets of the four vertical legs of the reactor. The reactor has six settling legs, 2210 mm long and 27.3 mm in outer diameter. The function of the settling leg is to concentrate the solid polymer contained in the polyethylene-isobutane mixture by settling before the product is discharged into the flash chamber**. [3]**

• The mixture discharged from the reactor through the product discharge valves, PTO, reduces its pressure from 42.2 kg/cm$^2$ g, the normal operating pressure in the reactor, to 0.37 kg/cm$^2$ g, the normal operating pressure in the flash chamber. It is transported from the reactor to the flash chamber through the flash lines. In these lines, the mixture is heated with hot water, promoting the vaporization of the present isobutane, ethylene, hexene, and hexane. The hydrocarbon vapors exit through the head of the flash chamber and are directed to the solvent purification and recovery system for gas recycling. The polymer is discharged by gravity from the bottom of the flash chamber to the Purge Column. **[3]**

The hydrocarbon present in the polymer pores is removed in the purge column. Nitrogen is injected at the base of the column to remove traces of hydrocarbon. The already-dried polymer is discharged from the bottom of the column to the powder silos through pneumatic transport. The purge gas steam, which exits through the head of the column, is sent to the purge gas recovery system through the column's bag filter to separate the isobutane and nitrogen in the stream. **[3]**

• An emergency device is provided for the reactor, the alternative flash chamber. In case of fire, failure of the reactor pump, or obstructions in the lines between the settling legs of the reactor and the flash chamber, the contents of the reactor are sent to the alternative flash chamber. The discharge steam from the discharge tank goes to the cyclone of the fines of the flash chamber through the head of the latter to be incorporated into the solvent purification and recovery system for gas recycling. The polymer is discharged from the discharge tank at the bottom of the latter to the ground or transferred by pneumatic transport to the powder silos. **[3]**

• The flash gas from the head of the flash chamber or the alternative flash chamber will be subjected to a solid elimination and solvent purification and recovery system. To do this, the flash gas, after passing through the flash chamber fines cyclone, is sent to the flash chamber bag filter and the recycling gas guard filter to recover the solids carried by the stream. Once the solids are recovered, the gas is sent to a gas purification system through the recycling gas compressor. After compression, the stream enters the recycling isobutane column to separate the isobutane from components such as ethylene, hexene, hexane, and other heavy materials it contains. The lateral extraction product of the column is recovered by recycling isobutane, which is sent to storage. The stream from the bottom of the recycling isobutane column is sent to the hexane stripper column, where the recovered hexene/hexane from the bottom of the latter is sent to the torch

## II.8 Conclusion

This introductory chapter has focused on a brief presentation of the importance of plastics in everyday life, including the SKIKDA petrochemical complex (HDPE manufacturing process, history, location, structure, material produced, and annual production over the past three years).

# References

**Chapter II Presentation of the CP2k Petrochemical Complex**

**[1]** Jean-Marie RETIF, «Advanced Control Engineering», Butterworth–Heinemann, edition **2001**.

**[2]** Raymond KONN, «Commande analogique et numérique des systèmes : Méthodes fréquentielle et polynomiale, espace d'état», Collection : Technosup, Ellipses édition

**[3]** Manuel d’opération, CP2K, INTEDRA.

# Chapter III Experimental Procedures, Results and Discussion

## III.1. Introduction

The aim of the Philips process (PF) is to produce a desired HDPE with a certain melt index, density, and minimum ash content value. These desired characteristics are obtained through the manipulation of other variables. Many of these variables in the PF process are interdependent. A thorough understanding of these variables and their relationships is required for precise reactor control and ultimately for uniform product quality and trouble-free operation.

## III.2. Certificate of Analysis

The CP2K plant is designed for the production of several grades of HDPE. Each grade corresponds to a technical data sheet that is either given to the customer or requested by them. This sheet includes all information regarding the product. Each batch produced is subjected to a series of analyses, the results of which are reported on a certificate of analysis including the grade, batch number, analysis date, and certification date. This certificate is signed by the responsible analyst and given to production, which can then proceed with lot packaging. The most determining analyses are melt index, density, and ash content (which are basic properties); the batch is within standards if these three parameters fall within the defined intervals for each grade. Other properties such as bulk density, number of grains/g, contamination on pellets, etc., are also documented on the certificate but do not affect the lot classification.

## III.3. Influence of operating parameters on HDPE properties

Density and Melt Flow Index control are experimentally carried out on various grades of HDPE (in this study, all analyses were performed on grade 5502) using measurement methods that will be presented along with their results in the following sections.

### III.3.1. Melt Flow Index

The Melt Index is the amount of polymer extruded in 10 minutes through a 2.09 mm diameter orifice at a fixed temperature of 190°C, under a weight of 2.16 kg. It is an important indication of the polymer's molecular weight, with a high melt index corresponding to good processability, while a low melt index indicates polymers with high mechanical strength.

### III.3.1.1. Apparatus

To carry out this test, we need plaster, and the following parts make up the apparatus.

-Steel cylinder

-Steel piston

-Heating and temperature control elements

-Thermometer

-Tempered steel die

-Removable load

-Tools for cleaning and measurement.

**Figure III.1**: Photo of the elastomer used in the Flow Melt Indexer analysis

### III.3.1.2. Procedure

-Heat the elastomer apparatus to a temperature of 190°C ± 2C° for at least 15 minutes, then clean the cylinder with cotton and install the die.

-Pour 4g of the pre-treated powder with the antioxidant into the cylinder and introduce the piston with a slight pressure (either 30g of powder for 0.06g of antioxidant).

-Preheat the product to be analyzed without weight for 3 minutes, then with weight for 3 minutes, and then cut the extruded part that contains air bubbles.

-Let the product flow for 10 minutes, and cut the extruded part in one go.

-Finally, weigh this mass which corresponds to the MFI of this product in g/10 min.

### III.3.1.3. Parameters influencing the Melt Flow Index are

-Ethylene concentration

-Reactor temperature

-Catalyst productivity

-Hydrogen concentration.

### III.3.1.3.1. Ethylene concentration

To study the influence of Ethylene Concentration on the Melt Flow Index, we analyzed several samples of HDPE taken from different ethylene contents. The results are presented in the following Table and Figure, respectively (**Table III.1, Figure III.**)

**Table III.1:** Presents the variation of MFI as a function of Ethylene Concentration.

| **Ethylene (mol %)** | 2.5 | 2.7 | 3.1 | 3.5 | 3.8 | 4.1 | 4.5 | 5.0 |
|---|---|---|---|---|---|---|---|---|
| **MFI (g/10min)** | 0.79 | 0.77 | 0.74 | 0.70 | 0.68 | 0.66 | 0.64 | 0.62 |

| **Ethylene (mol %)** | 5.3 | 5.8 | 6.5 | 6.9 | 7.1 | 7.6 | 8.0 | 8.2 |
|---|---|---|---|---|---|---|---|---|
| **MFI (g/10min)** | 0.61 | 0.59 | 0.55 | 0.49 | 0.52 | 0.50 | 0.48 | 0.45 |

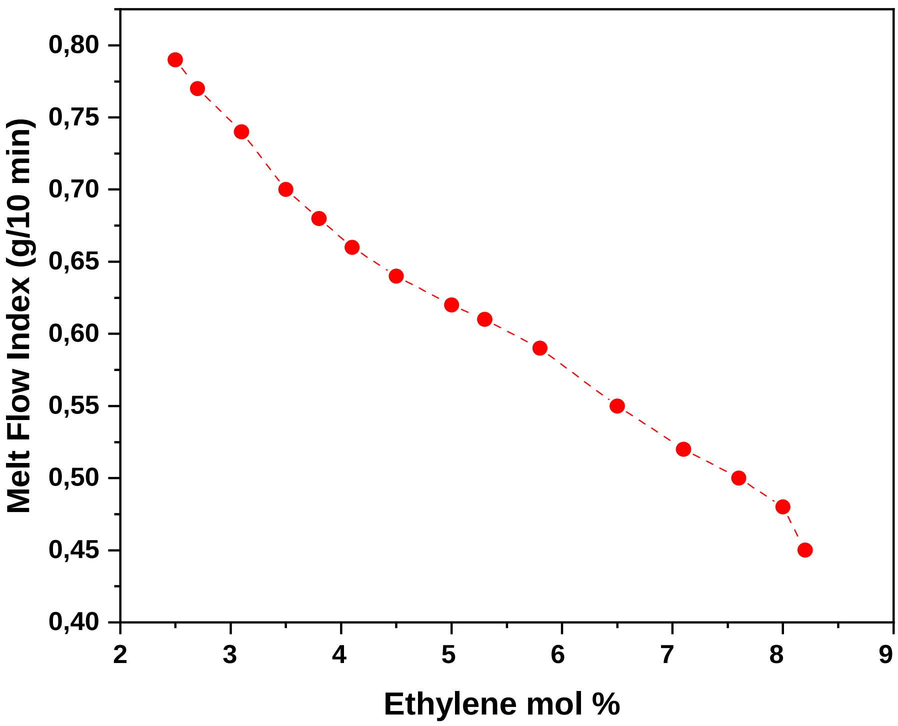


**Figure III.2:** Variation of MFI as a function of Ethylene Concentration.

**Figure III.2** Shows the variation of the Melt Flow Index as a function of Ethylene Concentration. It can be clearly seen that the Ethylene Concentration affect much in MFI, in other words, when ethylene content increased in the reactor, the melt flow index decreased significantly. This could be attributed to the increase of the molecular weight of macromolecular chains, which leads to increase of the viscosity.

By the way, it can be noted that the Ethylene concentration is the most parameter and the important variable that provides the quickest response to changes in the physical parameters.

To obtain an HDPE within the standard value, with a MFI between **"0.55-0.70",** it is necessary to work with Ethylene Concentrations between **"3.5 mol percent (%) - 6.5 mol %".**

#### III.3.1.3.2. Reactor Temperature

To study the influence of reactor temperature on Melt Flow Index, we analyzed several samples taken at different temperatures.

The results obtained are shown in the following Table (**Table III.2**):

**Table III.2:** Variation of MFI as a function of Reactor Temperature

| **Temperature (°C)** | 101.7 | 101.9 | 102.3 | 102.6 | 103.0 | 103.5 | 103.8 | 104.0 | 104.2 | 104.8 |
|---|---|---|---|---|---|---|---|---|---|---|
| **MFI (g/10min)** | 0.55 | 0.57 | 0.61 | 0.64 | 0.67 | 0.70 | 0.75 | 0.82 | 0.86 | 0.90 |

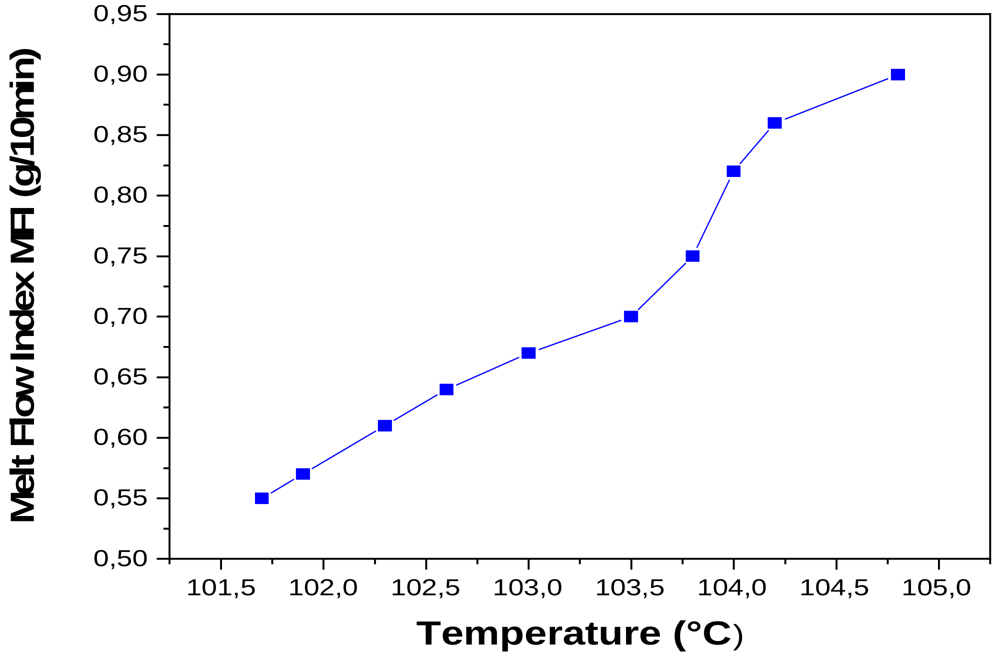


**Figure III.3**: Variation of MFI as a function of Reactor Temperature.

**Figure III.3** shows the variation of the Melt Flow Index as a function of Reactor Temperature. It can be clearly seen that the Melt Flow Index increases as the reactor temperature increased. This effect could be attributed to destruction of the macromolecular chains of polyethylene molecules (Physical interaction between PE chains) which leads to decrease of the molecular weight and the viscosity system. It concluded that this parameter affect much on the Melt Flow Index.

The obtained product is within standards, meaning its Melt Flow Index is in the range of **"0.55-0.70"** when reactor temperatures operated between **"101.7°C-103.5°C".**

### III.3.1.3.3. Catalyst productivity

Catalyst productivity is defined as the ratio of production flow rate / catalyst flow rate. The Melt Flow Index of the powder is greatly influenced by the Catalyst Productivity as shown in the following Table (**Table III.3)**.

**Table III.3:** Variation of MFI as a function of Catalyst Productivity.

| **Productivity** | 2 | 2.1 | 2.3 | 2.4 | 2.5 | 2.7 | 2.9 | 3.0 | 3.1 | 3.2 | 3.3 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **MFI (g/10min)** | 0.75 | 0.72 | 0.71 | 0.69 | 0.67 | 0.65 | 0.63 | 0.61 | 0.59 | 0.57 | 0.55 |

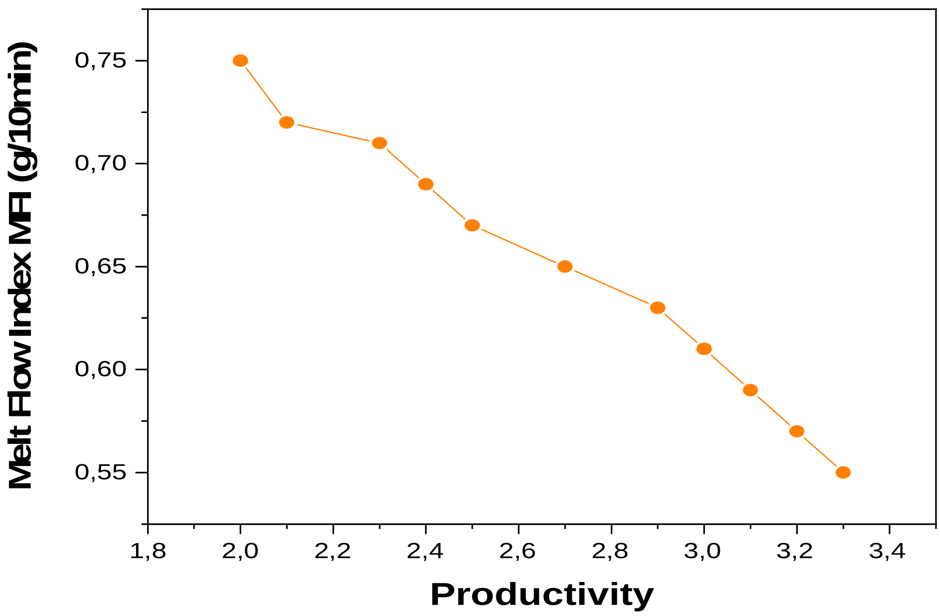


**Figure III.4:** Variation of MFI as a function of Catalyst Productivity.

**Figure III.4** represents the variation of the Melt Flow Index as a function of Catalyst Productivity. It can be clearly seen that the Melt Flow Index decreases as the Catalyst Productivity increases. As we know, in the case of Polymerization process; the Catalyst Productivity depends on: The residence time in the reactor; The Concentration of Ethylene in the reactor; The concentration of solids in the reactor; The concentration of poisons in the various feeds; The type of catalyst; The activation temperature of the catalyst; The temperature in the reactor; The type of polymer to be produced. This effect can be attributed to the increase of molecular weight of macromolecular chains which leads to the increase of the viscosity system in the reactor, and consequently, decreased the Melt Flow index (i.e: There is an inversely proportional relationship between the productivity of catalyst, and Melt flow: When the productivity increased, Melt Flow system decreased).

### III.3.1.3.4. Hydrogen concentration

To study the variation of the Melt Flow Index as a function of Hydrogen Concentration, we analyzed several samples taken at different hydrogen concentrations under stable operating conditions. The results are illustrates in the following table (**Table III.4**):

**Table III.4:** Variation of MFI as a function of Hydrogen Concentration.

| **Hydrogen Concentration (mol %)** | 0.05 | 0.075 | 0.088 | 0.096 | 0.12 | 0.15 |
|---|---|---|---|---|---|---|
| **MFI (g/10min)** | 0.55 | 0.60 | 0.63 | 0.65 | 0.68 | 0.71 |

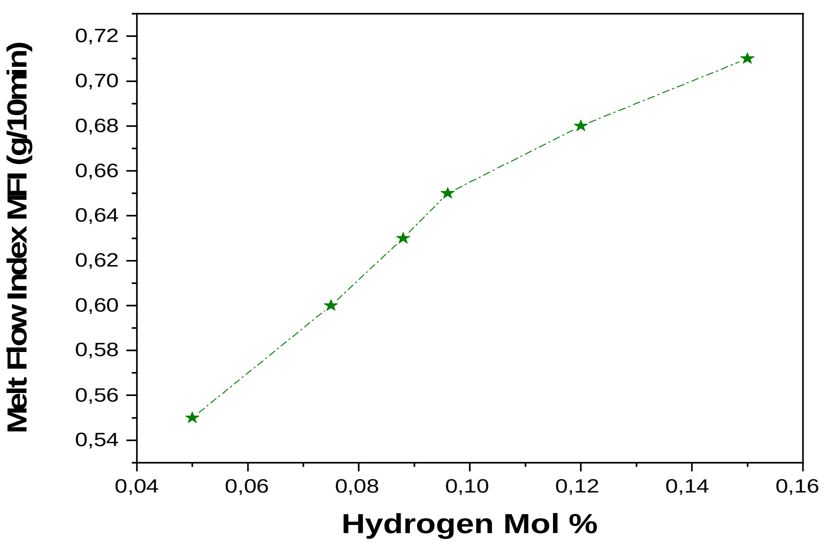


**Figure III.5**: Variation of MFI as a function of Hydrogen flow rate.

From **Figure III.5**, it can be observed and noted that as the Hydrogen Contents increases in the reactor system, the Melt Flow Index increased. This effect could be attributed to the decrease of molecular weight of the macromolecular chains, which leads to the decreased of the viscosity system and increased the flow rate. Hydrogen concentration is a variable that has a slow response to changes in Melt Flow Index. It is used as a last resort to increase the Melt Flow Index, because it generates too many fines and reduces the efficiency of settling legs.

In our case, and to obtain polyethylene within the standard range, it is recommended to work with hydrogen concentrations between **"0.05 mol% - 0.15 mol%".** The addition of hydrogen to the reactor terminates the molecular chain of polyethylene. A short chain has a high melt index, so hydrogen is a reliable parameter for controlling the melt index.

### III.3.2. Density of PEHD

Density is determined by locating and comparing the level of the stabilized sample to the levels of standards with known density, which are constantly present in the density gradient column.

#### III.3.2.1.Procedure

A small sample is immersed in the density gradient column, and after equilibrium is reached (≈ 15 min), the heights of the specimen and the beads above and below it are recorded. The calculation of the density is done using the equation:

Density ($g/cm^3$) = (y/z) x (b-a) + a

Where:

y = Distance between the specimen and the low-density standard.

z = Distance between the two standard beads

a = Density of the bead below the specimen (high density)

b = Density of the bead above the specimen (low density)

The sample preparation is done in a hydraulic press, by melting and compressing the powder at 177°C and 100 bars.

The liquid forming the density gradient column is obtained through a procedure of mixing water and isopropanol in a glass column to form a density gradient.

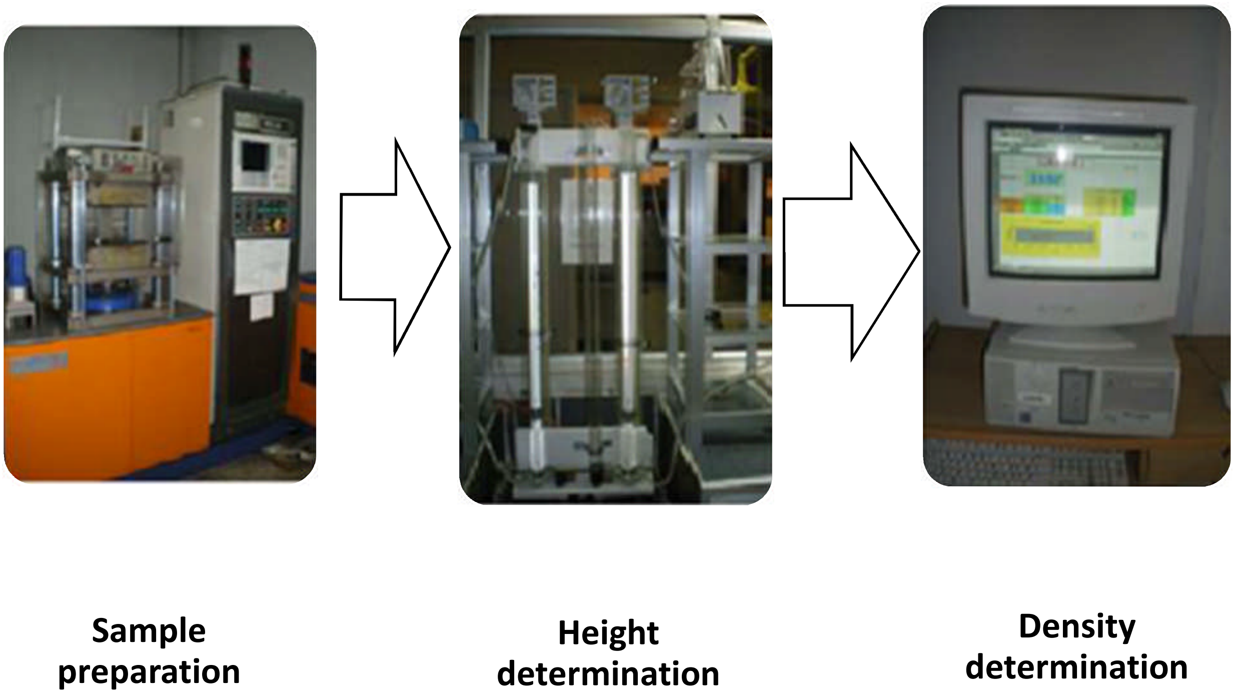


**Figure III.6**: Series of photos of the device used in density analysis.

### III.3.2.2. Parameters influencing the density of HDPE

The density of the polymer is controlled by adjusting the concentration of hexene in the reactor. The hexene/ethylene ratio in the reactor feed has an influence on the amount of hexene that is incorporated into the polymer. Generally, the incorporation of hexene into the polymer is proportional to the hexene/ethylene ratio in the reactor feed.

In order to study how the Hexene/Ethylene ratio affects the Density of HDPE, we analyzed powder samples taken at different Hexene/Ethylene ratios in the reactor while keeping the other parameters within operating limits.

The results are shown in the following table (**Table III.5)**

**Table III.5:** Variation of Density as a function of Hexene/Ethylene ratio.

| **Hexene/Ethylene** | 2.7 | 2.8 | 2.9 | 3.0 | 3.1 | 3.2 | 3.3 | 3.4 |
|---|---|---|---|---|---|---|---|---|
| **Density** | 0,9590 | 0,9583 | 0,9579 | 0,9776 | 0,9570 | 0,9565 | 0,9563 | 0,9559 |

| Hexene/ethylene | 3.6 | 3.7 | 3.8 | 3.9 | 4.0 |
|---|---|---|---|---|---|
| Density | 0.9551 | 0.9548 | 0.9547 | 0.9538 | 0.9525 |

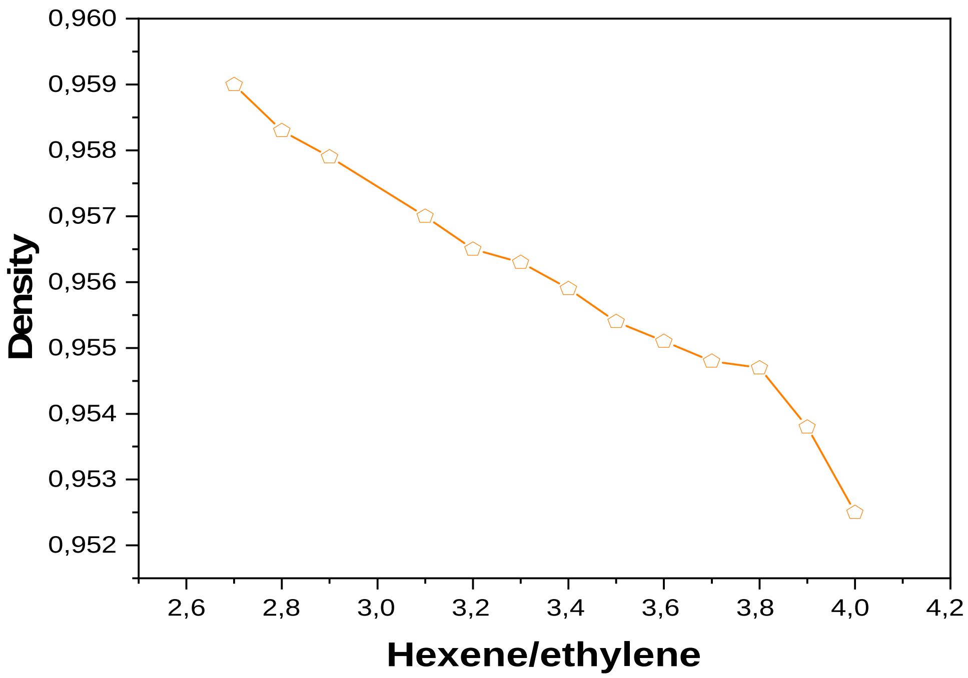


**Figure III.7**: Variation of Density as a function of Hexene/Ethylene ratio.

From **Figure III.7**, it can be observed that as the hexene/ethylene ratio increases, the density of the polymer decreases and vice versa, (since hexene reduces the branching in the polymer's molecular chain).

To obtain a polymer within the standards whose Density is between **(0.9530-0.9580),** we need to work with a Hexene/Ethylene ratio between **"2.9-3.9"** Kg of Hexene/ 1T of Ethylene.

The weight ratio of Hexene/Ethylene in the reactor must remain constant to maintain a uniform density in the polymer.

## III.4 Conclusion

Despite the emergence of the production of new plastic materials, HDPE occupies a significant share of global polymer production, as it is a basic material for the polymer and plastic processing industry. It has been able to replace a large number of materials for various uses during the past century and continues to do so today.

The demand for polyethylene is only growing worldwide and Algeria is no exception to this trend, which is why it has acquired the "POLYMED" unit located in the CP2K complex, which aims to produce various grades of high-density polyethylene. Some grades of HDPE are produced more than others, and this is because CP2K is required to follow the market trend by trying to meet the demand expressed by its customers. All of CP2K's production is subject to compliance testing that guarantees good quality necessary for the manufacture of finished products.

The process used by CP2K is the particle process. It is divided into a series of steps, which are the treatment of raw materials, the activation and addition of the catalyst, the polymerization in a loop reactor, and the recovery and purification of the solvent. The process ends with the polymer finishing and bagging system.

All of CP2K's production is subject to compliance testing that guarantees good quality necessary for the manufacture of finished products. The main parameters that need to be controlled in product quality are density; melt index (MI), and ash content. The product is considered acceptable when the values of these parameters are within the intervals defined on the "manufacturing control sheets (MCS)" for each grade.

The desired parameters of HDPE are obtained by manipulating other variables such as ethylene concentration, reactor temperature, catalyst productivity, hydrogen concentration, and hexene concentration. By effectively controlling these variables, not only do we obtain high-quality HDPE, but we also avoid problems of reactor clogging and fouling.

Although the internship period was not sufficient, it allowed us to notice two things: the importance of the theoretical part, in which we must understand the scientific explanation of the problem, and the importance of the practical part, in which we must manage the problems from their experimental side.

# *Conclusion*

## Conclusion

In conclusion, it is clear that various factors, such as monomer concentration, reactor temperature, and catalyst productivity, have an effect on the physical properties of polyethylene during the polymerization process.

Firstly, monomer concentration plays a crucial role in polyethylene polymerization. Higher concentration can lead to increased polymer density as it promotes the formation of tighter intermolecular bonds. Conversely, lower concentration can result in reduced density.

Therefore, careful control of the monomer concentration is necessary to achieve the desired physical properties.

Secondly, reactor temperature is another essential factor. Increasing the temperature can accelerate the polymerization reaction, which may lead to increased polymer fluidity, as measured by the melt flow index. However, excessively high temperature can also cause polymer degradation. Hence, a balance must be struck to maintain optimal physical properties.

Finally, catalyst productivity significantly impacts the physical properties of polyethylene.

Higher productivity can result in increased molecular weight, leading to greater density and higher viscosity. Lower productivity can yield a polymer with lower molecular weight, resulting in reduced density and viscosity. Therefore, careful selection and optimization of the catalyst are crucial to achieving the desired physical characteristics.

In conclusion, factors such as monomer concentration, reactor temperature, and catalyst productivity all play critical roles in determining the physical properties of polyethylene during the polymerization process. A comprehensive understanding of these factors is necessary to control and adjust the characteristics of the polymer material to meet specific end-application requirements.

## Abstract

In this Master-Thesis, we have studied the influence of the operating parameters on the physical properties of the Polyethylene produced in the complex CP2K, SKIKDA, ALGERIA, using PHILIPS process, which contains many sections: Raw materials treatment section, Catalyst activation, injection section, and Reactor section.

The PE is considered as a specific raw material if it has a certain melt flow index, and density. The control of these properties is done experimentally on the various grades of PE by methods of measurements.

These characteristics are obtained by the manipulation interdependent variables such as ethylene concentration, temperature of the reactor, the productivity of catalyst, hydrogen and hexene/ethylene ratio.

## Keywords

Ethylene, Polymerization Process, Polyethylene, Temperature of the reactor, Productivity of catalyst, Hydrogen and hexene/ethylene ratio.

## Résumé

Dans cette Mémoire de Master, nous avons étudié l'influence des paramètres de fonctionnement sur les propriétés physiques du polyéthylène produit dans le complexe CP2K, SKIKDA, ALGÉRIE, en utilisant le procédé PHILIPS, qui comprend plusieurs sections : section de traitement des matières premières, activation du catalyseur, section d'injection et section de réacteur.

Le PE est considéré comme une matière première spécifique s'il possède un indice de fluidité à l'état fondu et une densité particulière. Le contrôle de ces propriétés est réalisé expérimentalement sur les différentes qualités de PE grâce à des méthodes de mesure.

Ces caractéristiques sont obtenues par la manipulation de variables interdépendantes telles que la concentration d'éthylène, la température du réacteur, la productivité du catalyseur et le rapport hydrogène/hexène-éthylène.

## Mots clés:

Éthylène, Processus de polymérisation, Polyéthylène, Température du réacteur, Productivité du catalyseur, Rapport hydrogène/hexène-éthylène.

## ملخص

في رسالة الماستر هذه ، درسنا تأثير معلمات التشغيل على الخواص الفيزيائية للبولي إيثيلين المنتج في مجمع CP2K ، SKIKDA، الجزائر ، باستخدام عملية PHILIPS ، والتي تحتوي على العديد من الأقسام: قسم معالجة المواد الخام ، تنشيط المحفز ، الحقن وقسم المفاعل. تعتبر PE مادة خام محددة لديها مؤشر تدفق ذوبان معين وكثافة معينة. يتم التحكم في هذه الخصائص بشكل تجريبي على درجات مختلفة من PE بواسطة طرق القياس. يتم الحصول على هذه الخصائص من خلال المتغيرات المتداخلة مثل تركيز الإيثيلين ، ودرجة حرارة المفاعل ، وإنتاجية المحفز ، ونسبة الهيدروجين والهكسين / الإيثيلين.

## الكلمات المفتاحية

الإيثيلين ، عملية البلمرة ، البولي إيثيلين ، درجة حرارة المفاعل ، إنتاجية المحفز ، نسبة الهيدروجين والهكسين / الإيثيلين.