



MINISTRY OF HIGHER EDUCATION AND SCIENTIFIC RESEARCH



UNIVERSITY OF 20 AUGUST 1955 SKIKDA

FACULTY OF TECHNOLOGY

DEPARTMENT OF PROCESS ENGINEERING/ PETROCHEMICAL ENGINEERING

Memory

In preparation for the diploma of

Master

Stream: Process Engineering

Specialty: Polymer Engineering

Synthesis Methods, Processing, Properties and Industrial Applications of High-Density Polyethylene (HDPE) “The study of the state in Sonatrach Skikda CP2K- Complex

Supported on 03/07/2023

Directed by:

1- SALAH AIECH Hana

Framed by:

Dr. BELHAOUES Abderrahmane

Dr.SAADI Chahrazed

The Academic year 2022- 2023

Dedication

Dedications

I would like to dedicate our Master-thesis:

- To my family especially my parents whose unbelievable endurance, unconditional love, and untouchable devotion have been monumental;

-To all my brothers;

-To those who will be happy with this new goal in my study career;

-To all my best friends;

- To anyone who has ever taught me anything.

There are many friends and other family members who need to be listed for their part in this Master-thesis.

Finally, this Master-thesis is dedicated to all those who believe in the richness of learning, and I would like also to dedicate this modest review to all those who have devoted their lives to bringing the faded light of ambiguity to the complete shininess of clarity.

Salah Aiech Hana

Acknowledgements

Acknowledgements

In the name of Allah, The Most Beneficent and the Most Merciful.

All praises to Allah the Almighty for giving me the strengths, guidance, and patience in completing this Master-thesis. With His blessing, this Master-thesis is finally accomplished.

First of all, there are a lot of people that helped me significantly throughout these years to reach the end of this beautiful journey. All those people were very influential and supportive, and I would like to thank them and show our appreciation for what they did.

I would like to take this opportunity, first and foremost, to express my heartiest thanks and deep gratitude to our supervisor, *Dr. Belhaoues Abderrahmane* for his helpful guidance, valuable discussions, and support throughout this research.

I wish to express my gratitude to *Dr. Krid Ferial* the Head of the Process Engineering Department, Faculty of Technology, Skikda University, for all kinds of official help, and for offering facilities and support to carry out this work.

I would like also to place on record my great appreciation to all my teachers at Skikda-University, where I have studied a Polymer Engineering specialty.

These acknowledgments would not be complete without thought to my family. I want to especially express my deep gratitude to my dearest parents for their endless support. They have always been there for me during all these years of study and encouraged me to finish my Master's studies.

Last but not the least; I would like to thank each and every member of my family, who spurred my efforts with their love and affection, inspiration, and care.

To this end, I fully take all responsibility for any mistakes that may have occurred in this work.

*Table
of
contents*

Table of Contents

| | |
|----------------------------------|----------|
| Dedications..... | I |
| Acknowledgements..... | II |
| Contents..... | III |
| List of Figures..... | VI |
| List of Tables..... | VII |
| List of Abbreviations..... | VIII |
| General Introduction..... | 1 |

Chapter I

Synthesis Methods of Polyethylene, Properties and Applications

| | |
|---|-----------|
| I. Introduction..... | 2 |
| I.1 Description of polyethylene..... | 2 |
| I.2 Polyethylene synthesis method..... | 2 |
| I.3 Transition Metal Catalysts for Ethylene Polymerization | 3 |
| I.4 Free radical polymerization of ethylene..... | 4 |
| I.5 Polymerization processes and catalysts..... | 4 |
| I.5.1 PHILIPS process..... | 6 |
| I.5.2 Ziegler-Natta process..... | 7 |
| I.6 High-density polyethylene (HDPE)..... | 7 |
| I.6.1 High-density polyethylene synthesis methods..... | 8 |
| I.6.2 Polymerization of high-density polyethylene by metal oxide..... | 8 |
| I.6.3 Polymerization of high-density polyethylene by Ziegler-Natta catalyst..... | 9 |
| References..... | 10 |

Table of Contents

Chapter II

Presentation of the CP2k Petrochemical Complex

| | |
|---|-----------|
| II. Introduction..... | 11 |
| II.1 Historical..... | 11 |
| II.2 Location..... | 11 |
| II.3 Description of the factory..... | 12 |
| II.3.1 Division of the complex..... | 12 |
| II.3.2 CP2k organization..... | 13 |
| II.3.2.1 Department of Production..... | 14 |
| II.3.2.2 Technical Department..... | 14 |
| II.3.2.3 Maintenance Department..... | 15 |
| II.3.2.4 Safety Department..... | 16 |
| II.4 Operation of the PHILIPS process..... | 16 |
| II.4.1 The fillers used..... | 16 |
| II.4.2 Operating conditions of the polymerization reaction | 16 |
| II.4.3 Steps of the PF process..... | 16 |
| II.5.High-Density Polyethylene (HDPE)..... | 25 |
| II.5.1 Use of HDPE..... | 26 |
| II.5.2 Grades of HDPE produced at CP2K..... | 26 |
| References..... | 27 |

Chapter III

Experimental Procedures, Results and Discussion

| | |
|---|-----------|
| III.1. Introduction..... | 34 |
| III.2. Certificate of Analysis..... | 34 |
| III.3. Influence of operating parameters on HDPE properties..... | 34 |
| III.3.1. Melt Flow Index..... | 34 |
| III.3.1.1. Apparatus | 34 |
| III.3.1.2. Procedure..... | 35 |
| III.3.1.3. Parameters influencing the Melt Flow Index..... | 35 |
| III.3.1.3.1. Ethylene concentration..... | 36 |
| III.3.1.3.2. Reactor Temperature | 37 |
| III.3.1.3.3. Catalyst productivity..... | 38 |
| III.3.1.3.4. Hydrogen concentration | 39 |
| III.3.2. Density of PEHD..... | 40 |
| III.3.2.1. Procedure..... | 40 |
| III.3.2.2. Parameters influencing the density of HDPE..... | 41 |
| III.4 Conclusion..... | 42 |
| Conclusion..... | 44 |

Abstract

List
of
Figures

List of Figures

| | | |
|---------------------|--|-----------|
| Figure I.1 | Chemical structure of ethylene monomer..... | 2 |
| Figure I.2 | Rates of polymerization with transition metal catalysts | 3 |
| Figure I.3 | Mechanism of polymerization of Ethylene..... | 6 |
| Figure II.1 | Satellite view of the SKIKDA industrial zone..... | 12 |
| Figure II.2 | Ethylene treatment..... | 17 |
| Figure II.3 | O ₂ removal reactor..... | 18 |
| Figure II.4 | CO Removal Reactor..... | 19 |
| Figure II.5 | CO ₂ removal reactor..... | 19 |
| Figure II.6 | H ₂ O Removal Reactor..... | 20 |
| Figure II.7 | Hexene processing..... | 21 |
| Figure II.8 | Representative Schematic of Isobutane Degassing System..... | 21 |
| Figure II.9 | Representative diagram of the recycled isobutane treatment system..... | 22 |
| Figure II.10 | Catalyst activation step..... | 23 |
| Figure II.11 | Schematic diagram of the process..... | 25 |
| Figure II.12 | Different uses of Polyethylene grade 5502..... | 27 |
| Figure II.13 | Small bottles made from Polyethylene grade 6006 L..... | 28 |
| Figure II.14 | Agricultural film and bags made from polyethylene grade TR140..... | 29 |
| Figure II.15 | Different uses of Polyethylene grade TR-144..... | 30 |
| Figure II.16 | Different uses of Polyethylene grade TR-402..... | 31 |
| Figure II.17 | Different uses of Polyethylene grade TR-418..... | 32 |
| Figure III.1 | The Flow Melt Indexer analysis..... | 35 |
| Figure III.2 | Variation of MFI as a function of Ethylene Concentration..... | 36 |
| Figure III.3 | Variation of MFI as a function of Reactor Temperature..... | 37 |
| Figure III.4 | Variation of MFI as a function of Catalyst Productivity..... | 38 |
| Figure III.5 | Variation of MFI as a function of Hydrogen flow rate..... | 39 |
| Figure III.6 | Series of photos of the device used in density analysis..... | 41 |
| Figure III.7 | Variation of Density as a function of Hexene/Ethylene ratio..... | 42 |

List
of
Table

List of Tables

| | | |
|--------------------|--|-----------|
| Table I.1 | Polyethylene (PE) manufacturing processes and product range..... | 5 |
| Table II.1: | Characteristics of HDPE grade 5502..... | 26 |
| Table II.2: | Characteristics of HDPE grade 6006-L | 27 |
| Table II.3: | Characteristics of HDPE grade 4903 | 28 |
| Table II.4: | Characteristics of HDPE grade TR-140 | 29 |
| Table II.5: | Characteristics of HDPE grade TR-144 | 30 |
| Table II.6: | Characteristics of HDPE grade TR-402 | 31 |
| Table II.6: | Characteristics of HDPE grade TR- 418..... | 31 |
| Table III.1 | Variation of MFI as a function of Ethylene Concentration..... | 36 |
| Table III.2 | Variation of MFI as a function of Reactor Temperature..... | 37 |
| Table III.3 | Variation of MFI as a function of Catalyst Productivity..... | 38 |
| Table III.4 | Variation of MFI as a function of Hydrogen Concentration..... | 39 |
| Table III.5 | Variation of Density as a function of Hexene/Ethylene ratio..... | 41 |

List
of
Abbreviations

List of Abbreviations

| Abbreviations | Description |
|----------------------|--|
| ADM | General Administration Department |
| AF | Family Allowances |
| AIBN | Azobisisobutyronitrile |
| 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 |
| 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 |
| ITD | IT Department |
| LDPE | Low-Density Polyethylene |
| LLDPE | Linear Low Density Polyethylene |

List of Abbreviations

| | |
|---------------|--|
| MAO | Methylalumoxane |
| MCS | Manufacturing control sheets |
| MFI | Melt Flow Index |
| MI | Melt Index |
| MIP | Mutuelle de l'Industrie du Pétrole |
| MW | Molecular weight |
| PE | Polyethylene |
| PF | Phillips Process |
| UHMWPE | Ultra High Molecular Weight PolyEthylene |
| SSC | Single-Site Catalysts |
| UV | Ultraviolet |

Introduction

General Introduction

Polymers are a class of materials that have revolutionized modern society. They are composed of large molecules made up of repeating units called monomers, which are chemically bonded together to form long chains. This repeating structure gives polymers unique physical and chemical properties that make them incredibly versatile and useful in many different applications. The importance of polymers cannot be overstated. They have transformed many industries, such as packaging, transportation, construction, and healthcare. Polymers are used in a variety of everyday products, from plastic bags and water bottles to medical implants and drug delivery systems.

During the second half of the 20th century, polymers garnered increasing interest from industrial sectors. The objective was to develop and introduce materials that could replace metals and other substances while possessing favorable mechanical properties. The significance of polymer materials has become so profound that it is difficult to imagine our environment without them. The production and consumption of polymers have become indicators of development, triggering a continuous race to discover new processes that give rise to new grades and materials.

Global polymer production has steadily risen from the 1970s onwards and this growth became more noticeable and continues to escalate even today. Polyethylene alone accounted for a quarter of this production due to its low manufacturing cost and excellent physical and mechanical properties. Furthermore, this polymer allows for easy shaping through processes like extrusion or injection. It also possesses outstanding electrical insulation properties, and impact resistance, and exhibits significant chemical and biological inertness, making it suitable for food contact applications. The demand for polyethylene continues to surge worldwide, and Algeria is no exception. To meet the domestic market needs and reduce importation, Algeria acquired the POLYMED unit located at CP2K, aiming to potentially export any production surplus.

This manuscript is divided into three chapters. The first chapter provides an overview of polyethylene, while the second chapter focuses on the presentation of the CP2K complex and the description of the high-density polyethylene (HDPE) production process. The third chapter provides a detailed account of the experimental study conducted at CP2K, along with the experimental results and their interpretations. The work concludes with a general conclusion.

Chapter I
Synthesis
Methods of
Polyethylene,
Properties and
Applications

I. Introduction

Polymers are large molecules composed of repeating subunits called monomers. These monomers are covalently bonded in long chains, giving polymers unique physical and chemical properties.

Polymers can be classified based on their structure, composition, and properties. The three main categories of polymers are thermoplastics, thermosets, and elastomers.

The classification of polymers is essential for identifying the best-suited polymer for specific applications based on its properties and performance requirements[1].

I.1 Description of polyethylene

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 first produced, it is still a very promising material.

This widely used plastic is a polymer of ethylene, $\text{CH}_2=\text{CH}_2$ (**Figure I.1**), having the formula $(-\text{CH}_2-\text{CH}_2)_n$. 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 of 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 [2].

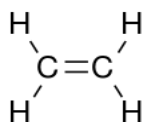


Figure I.1: Chemical structure of ethylene monomer.

I.2 Polyethylene synthesis method

The German chemist Hans von Pechmann discovered polyethylene by accident in 1898. The substance was then named polymethylene when further analyzed by colleagues Eugen Bamberger and Friedrich Tschirner. The first practical synthesis of polyethylene was discovered in 1933 by Eric Fawcett and Reginald Gibson. Michael Perrin developed the accidental discovery into a reproducible high-pressure synthesis for polyethylene, which was

used for industrial low-density polyethylene production starting in 1939. During World War II, polyethylene was used to produce insulation for UHF and SHF coaxial cables of radar sets. The commercial production of polyethylene improved with the development of catalysts for polymerization at mild temperatures and pressures. The Phillips catalyst based on chromium trioxide was discovered in 1951, and in 1953, Karl Ziegler developed a catalytic system based on titanium halides and organo-aluminium compounds. The Ziegler and metallocene-based catalysts families have proven to be very flexible at copolymerizing ethylene with other olefins and have become the basis for the wide range of polyethylene resins available today [2].

I.3 Transition Metal Catalysts for Ethylene Polymerization

Transition metal catalysts are commonly used in the industrial production of polyethylene through a process called coordination polymerization. In this process, the transition metal catalyst facilitates the formation of the polymer chain by coordinating with the ethylene monomers. The most commonly used transition metal catalysts for ethylene polymerization are based on group 4 metals such as titanium, zirconium, and hafnium. These metals are typically used in the form of organometallic compounds, such as metallocene or non-metallocene catalysts. Metallocene catalysts consist of a transition metal center sandwiched between two cyclopentadienyl ligands. These catalysts are highly active and selective, producing polyethylene with well-defined molecular weights and narrow molecular weight distributions. Non-metallocene catalysts, on the other hand, have a more varied structure and are often based on ligands such as pyridine or imidazolines. (Figure I.2)

The use of transition metal catalysts allows for greater control over the polymerization process, resulting in more precise molecular weight distribution, improved product quality, and higher yields. Additionally, the use of these catalysts allows for the production of a wide range of polyethylene products with different properties, such as high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE), which have important applications in a variety of industries, including packaging, construction, and automotive.

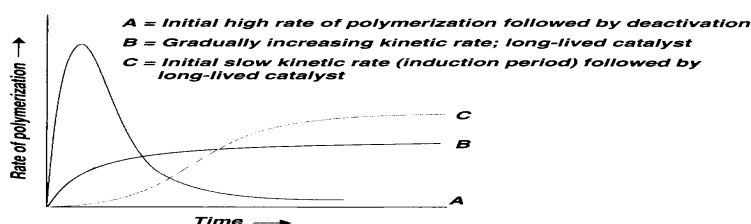


Figure I.2: Rates of polymerization with transition metal catalysts

I.4 Free radical polymerization of ethylene

Free radical polymerization of ethylene is a process by which many individual ethylene monomers are chemically bonded together to form a long-chain polymer. This process involves the use of free radicals, which are highly reactive species with unpaired electrons.

The process begins by adding a small amount of a radical initiator, such as a peroxide or azo compound, to a reaction vessel containing ethylene gas under pressure. The initiator decomposes under heat or light, generating free radicals that attack the ethylene monomers, initiating a chain reaction. The growing polymer chain can also react with additional ethylene monomers, leading to further chain growth.

The reaction is typically carried out at high pressures and temperatures to promote ethylene monomer conversion and polymerization. As the reaction progresses, the resulting polymer chains become increasingly entangled, leading to a high molecular weight polymer.

The properties of the resulting polymer can be tuned by adjusting the reaction conditions, such as the type and amount of initiator, temperature, pressure, and the presence of other monomers or additives. The resulting polymer can have a wide range of applications, including as packaging materials, electrical insulation, and coatings[2].

I.5 Polymerization processes and catalysts

Polyethylene (PE) is a complex field with a wide range of types and manufacturing processes that offer versatile tailor-made products. The processes are classified based on the physical state of the medium and reactor type.

The processes include suspension, solution, gaseous phase, and bulk, occurring at low or high pressure by a coordination mechanism or in the presence of free radicals (**Table I.1**). Advances in catalyst technology and reactor design have allowed producers to improve the performance of end-use products.

New concepts for PE manufacture and the use of combined processes, such as Borstar of Borealis, have been introduced, but each process presents its advantages and disadvantages. (Pascu, 2005)

Chapter I Synthesis Methods of Polyethylene, Properties and Applications

| Product | Process | | | | |
|---|--------------------------|------------------------|--------------------------|----------------------------|---------------------|
| | Autoclave, high pressure | Tubular, high pressure | Gas phase, fluidised bed | Autoclave/loop, suspension | Autoclave, solution |
| Low-density PE (LDPE) | + | + | – | – | – |
| Linear low-density PE (LLDPE) | + | 0 | + | 0 | + |
| Very-low-density PE (VLDPE) | + | 0 | + | – | + |
| High-density PE (HDPE) | 0 | – | + | + | + |
| High-molecular-weight HDPE (HMWHDPE) | – | – | + | + | – |
| Ultra-high-molecular-weight PE (UHMWPE) | – | – | 0 | + | – |
| Ethylene–vinyl acetate (EVA) copolymer | + | + | – | – | – |
| Acrylic copolymer | + | + | – | – | – |

+: *adequate*
 0: *technically possible with limitations*
 –: *inadequate or impossible*

Ethylene polymerization is the process by which ethylene monomers are chemically bonded together to form a polyethylene polymer. Ethylene is a simple hydrocarbon molecule that consists of two carbon atoms and four hydrogen atoms. When ethylene monomers are subjected to heat and pressure in the presence of a catalyst, they undergo a polymerization reaction that results in the formation of a long chain of ethylene units. There are two primary methods for ethylene polymerization: high-pressure polymerization and low-pressure polymerization. (**Figure I.3**)

High-pressure polymerization involves subjecting ethylene monomers to very high pressures (usually around 2000-3000 atmospheres) in the presence of a free-radical initiator. This process typically results in the production of high-density polyethylene (HDPE), which is a dense, strong, and relatively stiff material.

Low-pressure polymerization, on the other hand, uses a catalyst (usually a Ziegler-Natta catalyst) to facilitate the polymerization reaction at lower pressures and temperatures. This process typically results in the production of linear low-density polyethylene (LLDPE) or

Chapter I Synthesis Methods of Polyethylene, Properties and Applications

low-density polyethylene (LDPE), which are more flexible and have better resistance to stress cracking than HDPE [2].

Ethylene polymerization is a widely used industrial process for the production of polyethylene, which is used in a variety of applications, including packaging, pipes, films, and coatings.

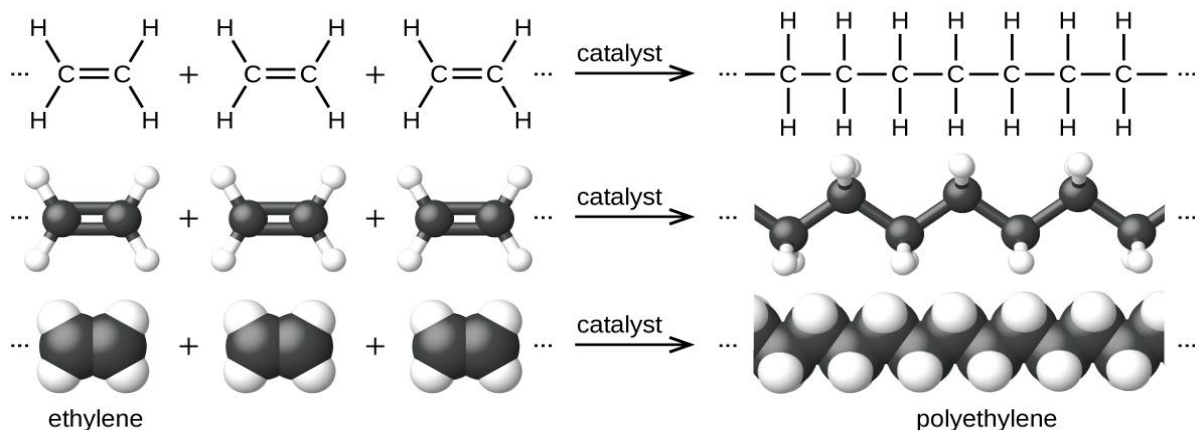


Figure I.3: Mechanism of polymerization of Ethylene.

I. 5. 1 PHILIPS process

The Phillips process is a well-known method of polyethylene polymerization that was developed by scientists at Phillips Petroleum Company in the 1950s. It is a type of high-pressure polymerization that involves the use of a catalyst system based on chromium oxide.

In the Phillips process, ethylene is polymerized under high pressure and high temperature in the presence of a catalyst system consisting of chromium oxide and a co-catalyst, typically a metal alkyl compound such as triethyl aluminum. The chromium oxide serves as the active catalyst species, while the co-catalyst helps to activate the catalyst and increase its reactivity towards the ethylene monomer.

The polymerization process takes place in a tubular reactor that is maintained at a pressure of around 1000-3000 bar and a temperature of around 180-300 °C. The high-pressure environment allows for the production of high-density polyethylene (HDPE) with a high molecular weight and a narrow molecular weight distribution.

The Phillips process is characterized by its high conversion rates, high reactor productivity, and the ability to produce a wide range of polyethylene grades with varying properties. The process can be adjusted to produce polyethylene with different melt indices, densities, and molecular weights, depending on the application requirements[3].

Chapter I Synthesis Methods of Polyethylene, Properties and Applications

One of the main advantages of the Phillips process is its scalability, as it can be easily adapted for use in large-scale industrial production. The process is widely used in the production of HDPE for various applications, including pipe, film, and blow molding.

I. 5. 2 Ziegler-Natta process

The Ziegler-Natta process is a commonly used method of polyethylene polymerization that was developed in the 1950s by Karl Ziegler and Giulio Natta. It involves the use of a catalyst system consisting of a transition metal compound and an organoaluminium compound. In the Ziegler-Natta process, ethylene is polymerized at low pressure and low temperature in the presence of a catalyst system. The transition metal compound acts as the active catalyst species, while the organo-aluminium compound serves as a co-catalyst and helps to activate the catalyst. The polymerization process takes place in a reactor vessel that is maintained at a pressure of around 10-50 bar and a temperature of around 50-100 °C. The low-pressure environment allows for the production of low-density polyethylene (LDPE) with low molecular weight and a broad molecular weight distribution.

The Ziegler-Natta process is characterized by its ability to produce polyethylene with a high degree of stereo-regularity, resulting in improved mechanical and processing properties. The process can be adjusted to produce polyethylene with different melt indices, densities, and molecular weights, depending on the application requirements.

One of the main advantages of the Ziegler-Natta process is its versatility, as it can be used to produce a wide range of polyethylene grades with varying properties. The process is widely used in the production of LDPE for various applications, including packaging materials, films, and coatings. In summary, the Ziegler-Natta process is a widely used method of polyethylene polymerization that is characterized by its ability to produce polyethylene with a high degree of stereo-regularity and its versatility in producing a wide range of polyethylene grades [3].

I.6 High-density polyethylene (HDPE)

HDPE stands for High-Density Polyethylene, which is a type of thermoplastic polymer. It is commonly used in the manufacturing of various products, including plastic bottles, pipes, and packaging materials[3].

HDPE was developed in the 1930s by Paul Hogan and his team at IG Farben. It became popular in the 1950s due to the development of efficient catalysts. It was used in packaging

materials, pipes, and electrical insulation. Advancements in technology in the 1970s and 1980s improved its properties, including the development of metallocene catalysts. HDPE is now widely used in various industries due to its strength, durability, and recyclability.

I. 6. 1 High-density polyethylene synthesis methods

There are several methods for synthesizing high-density polyethylene (HDPE), which is a thermoplastic polymer with a high molecular weight and a high density. Some of the most common methods for HDPE synthesis include:

- **High-pressure polymerization:** In this method, ethylene monomers are subjected to high pressures (around 2000-3000 atmospheres) in the presence of a free-radical initiator, such as oxygen or peroxide. This process typically results in the production of HDPE with a narrow molecular weight distribution.
- **Ziegler-Natta catalysis:** This method involves the use of a Ziegler-Natta catalyst, which is a type of transition metal complex that can facilitate the polymerization of ethylene monomers. This process is typically carried out under low pressures and temperatures, and it can result in the production of HDPE with broader molecular weight distribution.
- **Metallocene catalysis:** This method involves the use of a metallocene catalyst, which is a type of single-site catalyst that can provide better control over the polymerization process. This method can result in the production of HDPE with very narrow molecular weight distribution and improved properties [4].
- **Solution polymerization:** In this method, ethylene monomers are dissolved in a solvent, such as hexane or heptane, and then subjected to polymerization in the presence of a catalyst. This process can result in the production of HDPE with a high degree of control over the molecular weight distribution and the properties of the final product.

Overall, the choice of HDPE synthesis method depends on the desired properties of the final product, as well as the cost and availability of the necessary equipment and materials.

I. 6. 2 Polymerization of high-density polyethylene by metal oxide

High-density polyethylene (HDPE) can be polymerized using metal oxide catalysts, such as molybdenum or chromium oxide. These catalysts are typically used in a high-pressure process, where ethylene gas is pressurized and heated to initiate the polymerization reaction. The metal oxide catalysts help to control the molecular weight and branching of the polymer, resulting in a more uniform and predictable product. This process has been used in the

industrial production of HDPE since the 1950s and continues to be a widely used method for the production of this versatile polymer.

I. 6. 3 Polymerization of high-density polyethylene by Ziegler-Natta catalyst

Polymerization of HDPE by Ziegler-Natta catalyst involves the use of a catalyst composed of a transition metal compound (usually titanium or vanadium) and an organoaluminium compound. The catalyst is activated by adding an alkyl aluminum compound, which leads to the formation of active sites for the polymerization reaction. In the polymerization process, ethylene gas is pressurized and fed into a reactor containing the catalyst system. The reaction takes place at high pressure and temperature, causing the ethylene monomers to react and form long chains of HDPE. The resulting polymer is then cooled and removed from the reactor.

The Ziegler-Natta catalyst system provides several advantages over other catalysts, including high activity, good control over molecular weight distribution, and the ability to produce polymers with high crystallinity and melting points. These properties make HDPE produced by Ziegler-Natta catalysts suitable for a wide range of applications including packaging, pipes, and automotive component [5-14].

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

2

Presentation of the CP2k Petrochemical Complex

II. Introduction

This chapter aims to present the CP2K complex by reviewing its geographical location, and the key dates related to the construction and start-up of the HDPE unit. The organization and structure of the complex, as well as the tasks assigned to each department, will also be presented. A description of the PHILIPS HDPE production process will be provided, followed by an overview of the range of HDPE grades produced by CP2K[1].

II.1 Historical

The CP2K complex was established in the industrial zone of Skikda in January 2004, after the project to build a high-density polyethylene unit was signed in April 1991 between ENIP (National Petrochemical Industries Company) 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%. Later on, ENIP decided to buy out the shares of REPSOL and BAD after they decided to withdraw. Today, Sonatrach has taken over the unit, which is now called CP2K [2].

II.2 Location

The CP2K petrochemical complex is located within the Skikda industrial zone, covering an area of 166,800 square meters (16.68 hectares), of which 10% is built-up.

Figure II.1

It is located on the coast, 6 km east of the capital of Skikda province, at an average height of about 6 meters above sea level. The geographical position is limited as follows:

- **To the north:** The Mediterranean Sea
- **To the south:** The main road of the industrial zone.
- **To the east:** The intervention and reserve force.
- **To the west:** CP1K (plastic material complex).



Figure II.1: Satellite view of the SKIKDA industrial zone.

II.3 Description of the factory

II.3.1 Division of the complex

The complex is composed of 4 important zones which are:

Zone off-site

- Utilities (boilers, nitrogen, and instrument air, desalinated water, fire water, potable water, and natural gas treatment).
- Torch
- Isobutane and hexene storage tanks.
- Wastewater treatment plant.
- Catalyst activation unit.

Wet Zone:

- Treaters.
- Reactors.
- Compressors.
- Capacities.

Dry area:

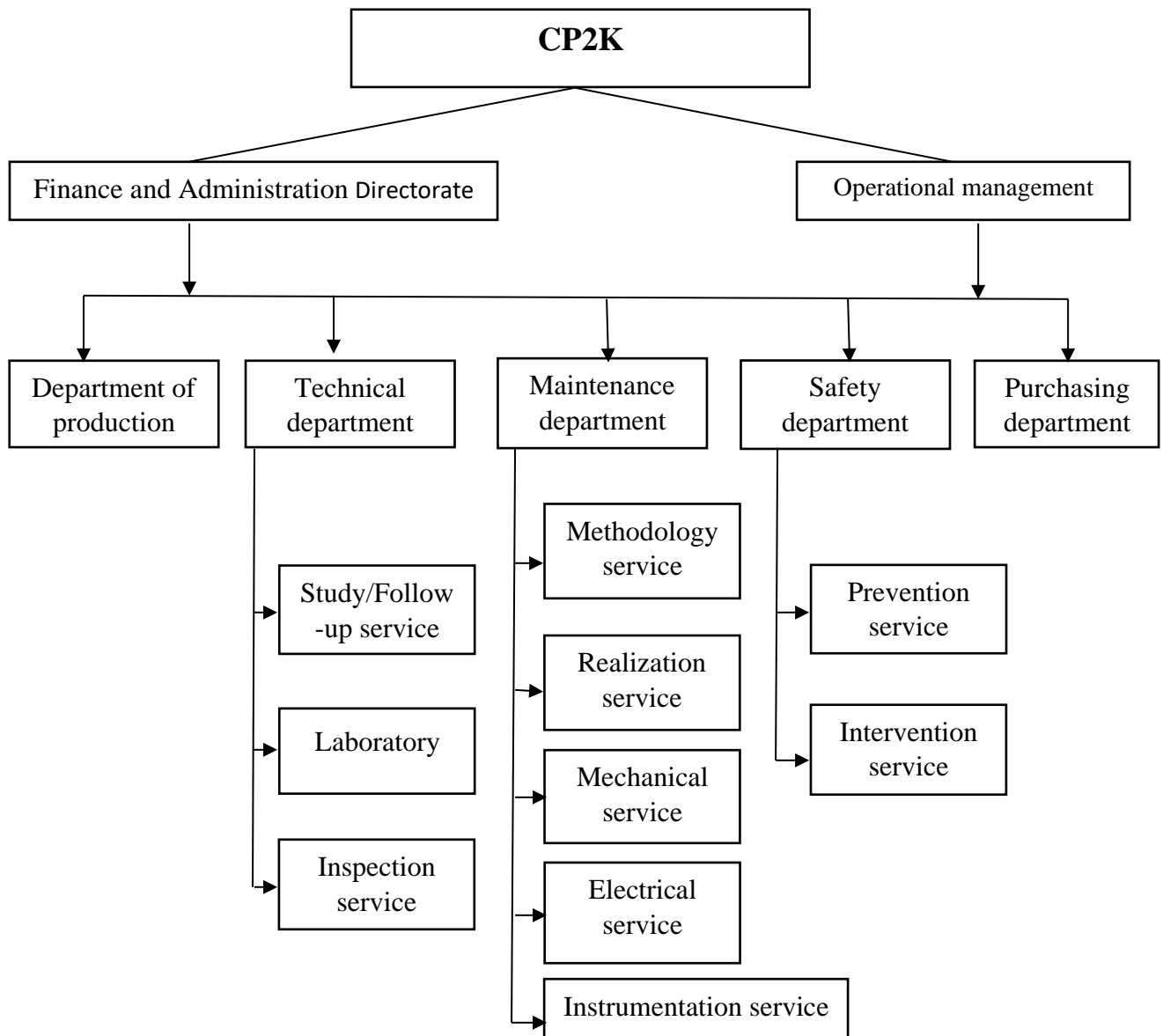
- Extruder.
- Blowers.
- Finished product storage silos (powder and granules).
- Bagging.

Building area:

- ADM and Finance block
- Canteen and locker rooms
- Security and infirmary block
- Spare parts store, workshops, and technical block
- High and low voltage substations
- Process control room and laboratory.

II.3.2 CP2k organization

A chart summarizing the organization of CP2K is presented below:



The complex is made up of two departments:

- ✓ Finance and Administration department
- ✓ Operations department, which is divided into 5 departments.

II.3.2.1 Department of Production

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

- **Main installations of the factory:**
 - Raw material preparation and processing unit.
 - Reactor where polymerization and obtaining of HDPE in powder form take place.
 - Extruder that transforms the powder into pellets.
 - Intermediate storage (Capacity 3500 tones).
 - Packaging unit.
- **Auxiliary installations**
 - Steam, electricity, air production, etc.
 - Effluent treatment.
 - Storage of raw materials, utilities and additives (Water, Hydrogen, Hexene, Isobutane).
 - Storage warehouse for finished products with an area of 18,000 m², providing a capacity of 12,000 tons.

II.3.2.2 Technical Department

This is a very important department that works in parallel with other departments and is composed of three services:

- Study/Follow-up Service: whose work is focused on studying problems that may be encountered in different departments and making necessary modifications. The study of new projects is also done at the level of this service.

- Inspection Service: whose role is to validate equipment and installations through programmed systems.
- Laboratory Service: whose task is to continuously analyze raw materials, catalysts, and finished products.

The different tests and analyses carried out in the laboratory are:

- Analysis of the purity of the raw material
- Catalyst activation at the laboratory scale
- Production of pellets and films using a blow extruder at the laboratory scale, and plates using a press.
- Mechanical and physical tests such as stress cracking resistance, torsion resistance, rupture resistance, tear resistance of films, opacity, softening point, time required for degradation (service life), density, and melt flow index (MFI) [3].

II.3.2.3 Maintenance Department

This department is responsible for the maintenance and upkeep of equipment and is composed of five services:

- Methods Service: divided into two sections, the planning section and the preparation section.
- Execution Service
- Mechanical Service
- Electrical Service
- Instrumentation Service

The work of this department is divided into two parts: scheduled periodic work for each equipment, and work carried out in response to requests from the production department in the event 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.3.2.4 Safety Department

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

- Prevention Service
- Intervention Service

II.4 Operation of the PHILIPS process

The CP2K plant has two production processes in one facility:

- Phillips process.
- Ziegler method.

But since its first start, it only uses the Phillips process, because the catalyst used in the Ziegler process is expensive compared to that used in the Phillips process.

The Phillips process, known as the "PF process" or particle process, which was designed for the POLYMED plant, requires high purity of the raw material and only tolerates minute quantities of poisons whose presence can prevent the proper functioning of the reactor or alter the quality of the product obtained.

This process makes it possible to obtain polymers in a range of melt index from 0.10 to 36 and a density between 0.935 and 0.965.

II.4.1 The fillers used

- **Ethylene:** the main charge in the gas phase;
- **Isobutane:** the reaction medium in the liquid phase;
- **Hexene:** in the liquid phase;
- **Hydrogen:** in the gas phase with small quantities;
- **The catalyst:** Chromium trioxide (Cr₂O₃) on a silica support.

II.4.2 Operating conditions of the polymerization reaction

The two essential conditions in the reactor are:

- **Temperature:** from 93 to 110°C, depending on the grade to be produced.
- **Pressure:** from 42 to 44 bars, depending on the closing or opening of the discharge valves.

II.4.3 Steps of the PF process

The "PF" particle process is divided into a series of steps or systems:

- Processing of raw materials ;
- Activation and addition of the catalyst;
- Polymerization in a reactor in the form of a loop;
- Flash system and polymer drying;
- Purification and recovery of recycled gas;
- Finishing system ;
- Bagging.

II.4.3.1 Raw Material Processing

The raw material undergoes a series of treatments before being injected into the reactor, which differs between ethylene and the other reagents; the latter has multiple caterers each according to its role of elimination of a specific poison which is in the following order: acetylene, oxygen, mono then carbon dioxide finally humidity; on the other hand, the other reagents such as isobutane (fresh and recycled), hexene and hydrogen have only one caterer for each.

II. 4. 3. 1. 1 Ethylene

The raw material of the process is received at the Plant through piping from the ethylene plant adjacent to it, at 16.9 kg/cm²g and at room temperature. For the elimination of the impurities found in ethylene which result from its cracking or its storage and transport, they go through the stages presented in the diagram below:

Figure II.2

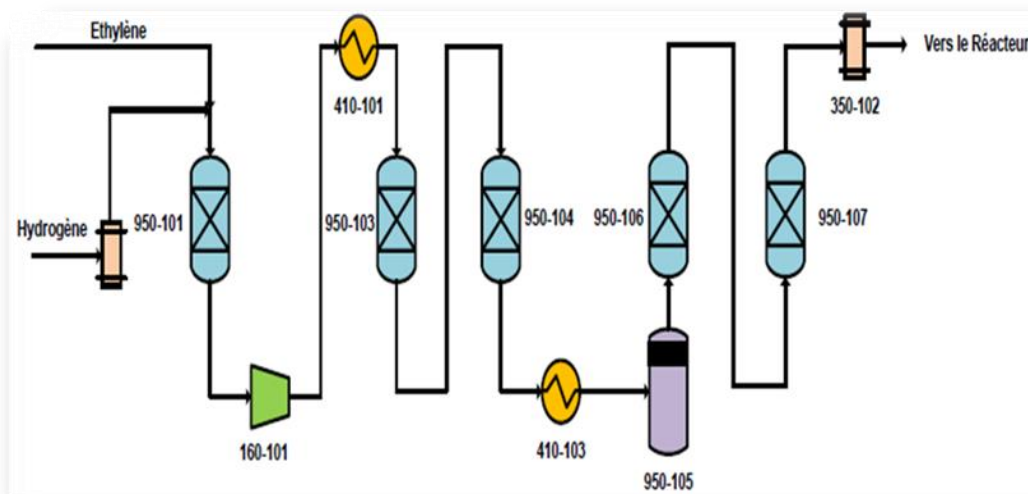
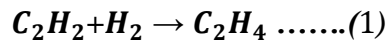


Figure II.2: Ethylene treatment

○ **Elimination of acetylene**

The hydrogen passes through the 350-133 filter, where the solid particles are eliminated, then it mixes with the ethylene and they pass to the acetylene converter 950-101. It contains 2453 kg of BASF RO-20/13 catalyst, for the elimination of acetylene by the addition of hydrogen and conversion to ethylene according to the reaction.



○ **Oxygen elimination**

The oxygen removal reactor contains 12350 kg of BASF R3-15 catalyst, as shown in **Figure II.3**.

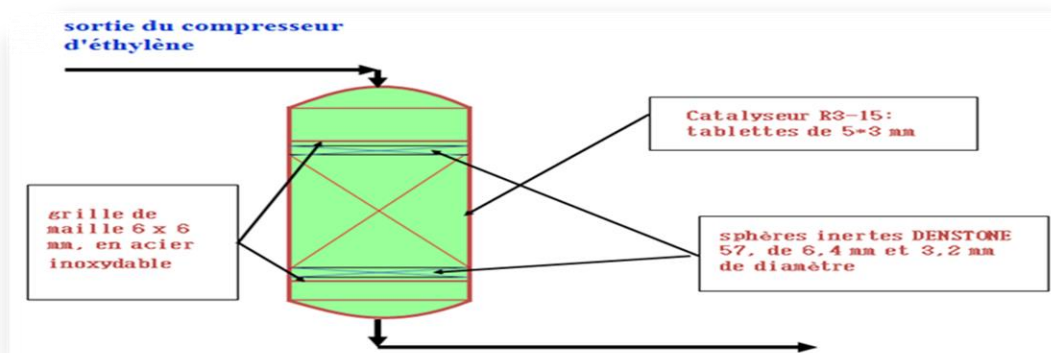
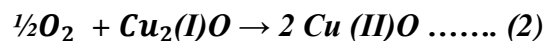
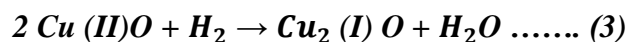


Figure II.3: O₂ removal reactor

In normal operation, the flow of ethylene through the reactor is in a downward direction. The reaction between O₂ and the solid support is mentioned below:



Only one reactor will be in service, but the second will be in regeneration, which takes place according to the following chemical reaction:



○ **Elimination of carbon monoxide (CO)**

The ethylene stream continues its course passing through the carbon monoxide removal reactors 950-104 A/B which contain 12350 kg of a BASF R3-15 catalyst based on CuO as shown in **Figure II.4**, the elimination takes place according to the reaction:



The catalyst used in this treatment undergoes saturation so it is necessary to make regeneration according to this reaction:

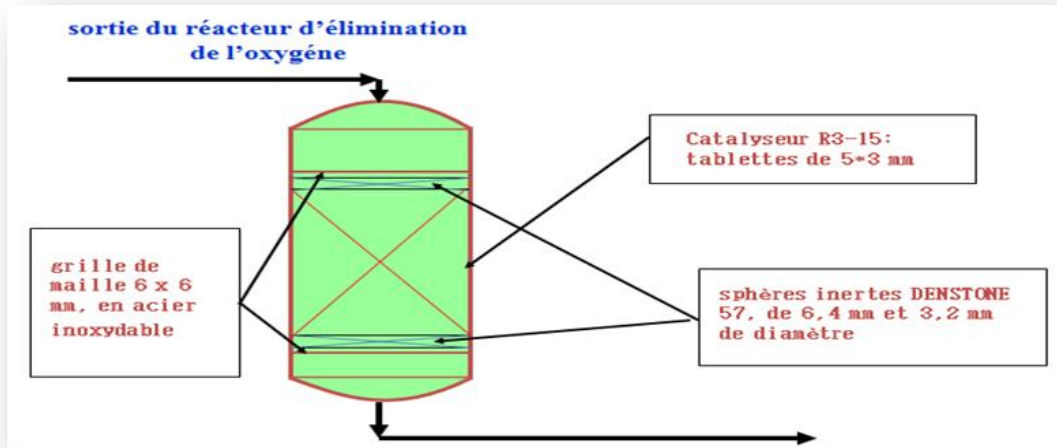
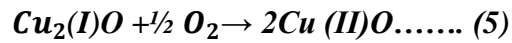


Figure II.4: CO Removal Reactor

○ Removal of carbon dioxide (CO₂)

The carbon dioxide present in the ethylene stream must be removed, as it is a strong poison for the XPF catalyst used in the polymerization reaction **Figure II.5**. The 950-106 A/B reactors contain 2 types of alumina Selexsorb CD and Selexsorb COS.

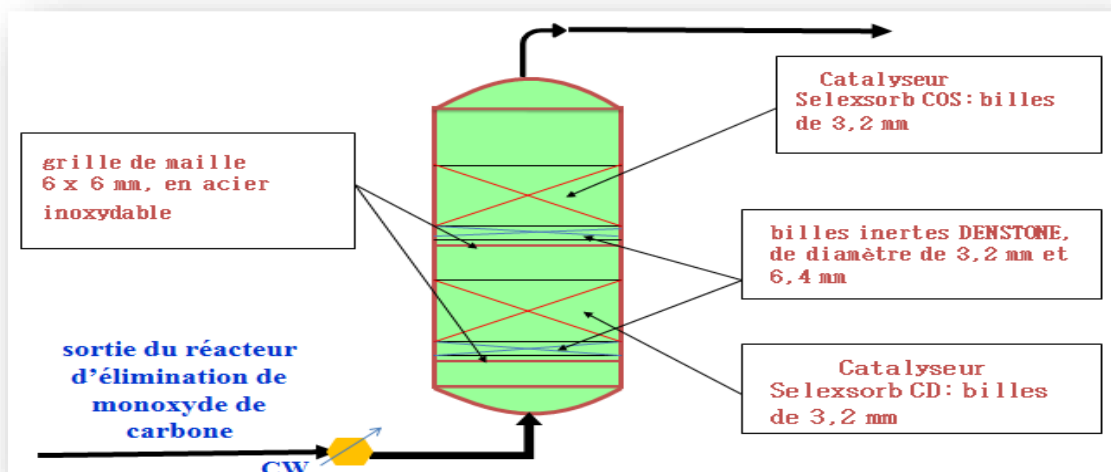
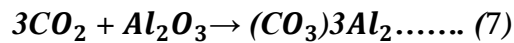
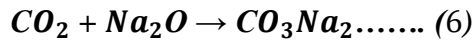
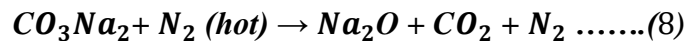


Figure II.5: CO₂ removal reactor

The catalyst used in this operation is based on Al_2O_3 , Na_2O_3 from which carbon dioxide forms a complex compound with sodium oxide inside the molecular structure of alumina according to the following chemical reactions:



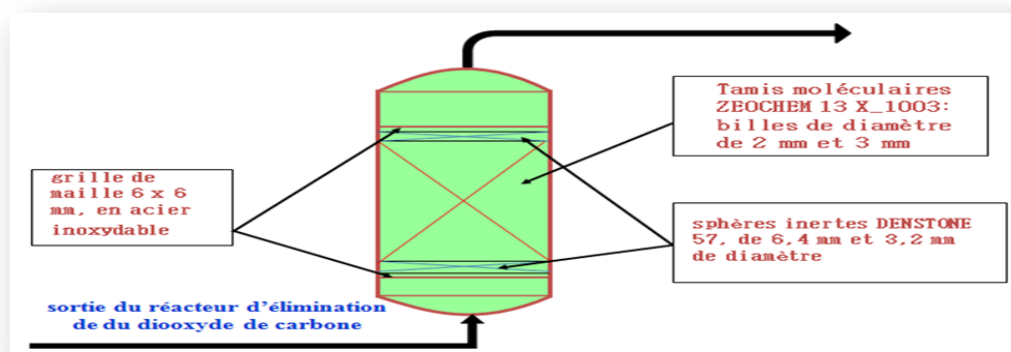
The CO_2 will be retained by the alumina until the hot regeneration gases break the bonds and the carbon dioxide is driven out of the bed. As explained by the following reaction:



○ H₂O removal

The ethylene is dried in the 950-107 A/B dryers. The flow of ethylene through the bed is in the upward direction. The water and methanol which are removed from the ethylene stream are retained in a molecular sieve bed, ZEOCHEM 13X.

The dryer works according to a principle of physical adsorption which is a fixation of H_2O molecules on the adsorbent's porous surface until the latter's



saturation. Which will be regenerated every 14 days with a stream of hot nitrogen.

Figure II.6: H₂O Removal Reactor

II. 4. 3. 1. 2 Hexene

Hexene is the compound added in small quantities to the reactor to produce copolymers, it alters the molecular structure of the polymer and therefore changes the physical properties of the latter. **Figure II.7**

Before it enters the reactor, it goes through treatment stages. It goes through the degassing column 950-111 to eliminate the gas absorbed in the stream then it will be dried in the water elimination treater 950-114, which works by adsorption on a molecular sieve ZEOCHEM 13X, type 1003.

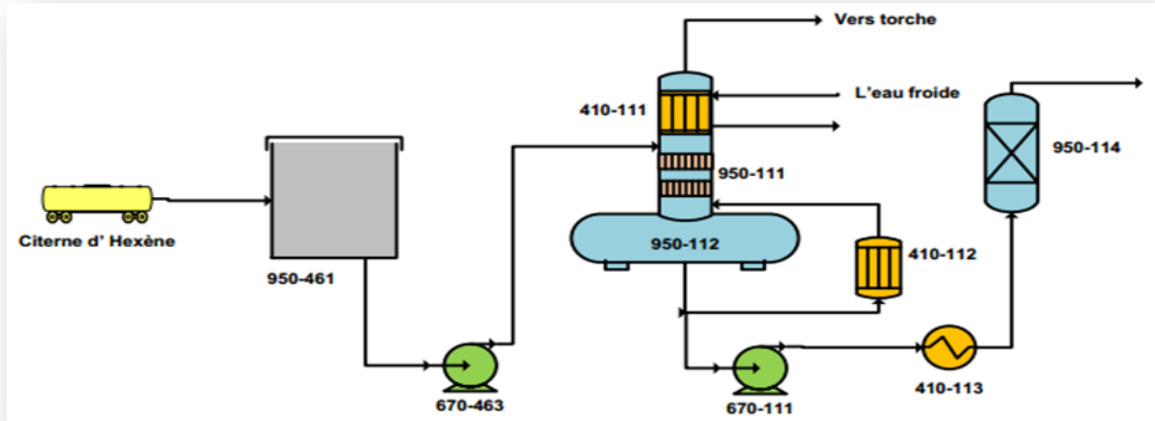


Figure II.7: Hexene processing

II. 4. 3. 1. 3 Isobutane

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

○ Treatment of fresh isobutane

Fresh isobutane, before being incorporated into production, goes through treatment stages. It passes through the 950-121 degassing column to eliminate the gases absorbed in the stream and then it will be dried in the 950-124 A/B water elimination treater, which works by adsorption on a ZEOCHEM molecular sieve. 13X, type 1003, these dryers require regeneration every 30 days. **Figure II.8**

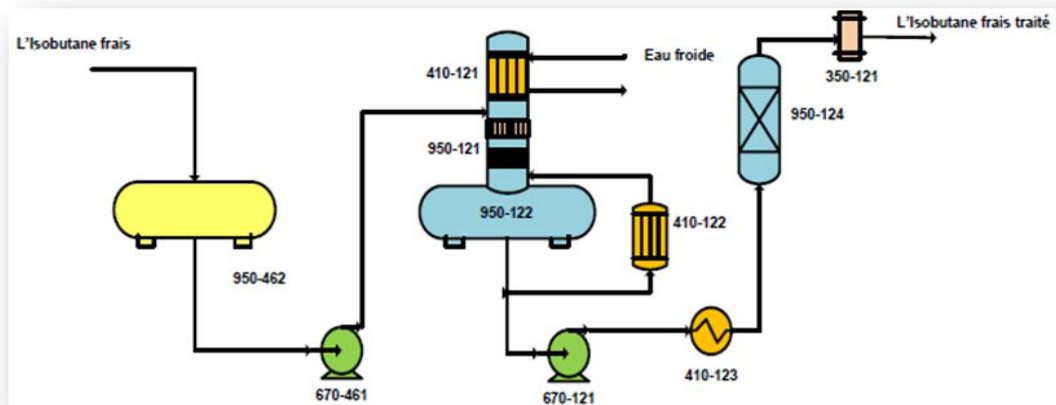


Figure II.8: Representative Schematic of Isobutane Degassing System

○ Treatment of recycled isobutane

Is the bulk of the isobutane used in the unit because it is almost completely recovered? It is pumped from storage tank 950-176 to recycle isobutane dryers 950-125 A/B, these dryers require regeneration every 30 days. **Figure II.9**

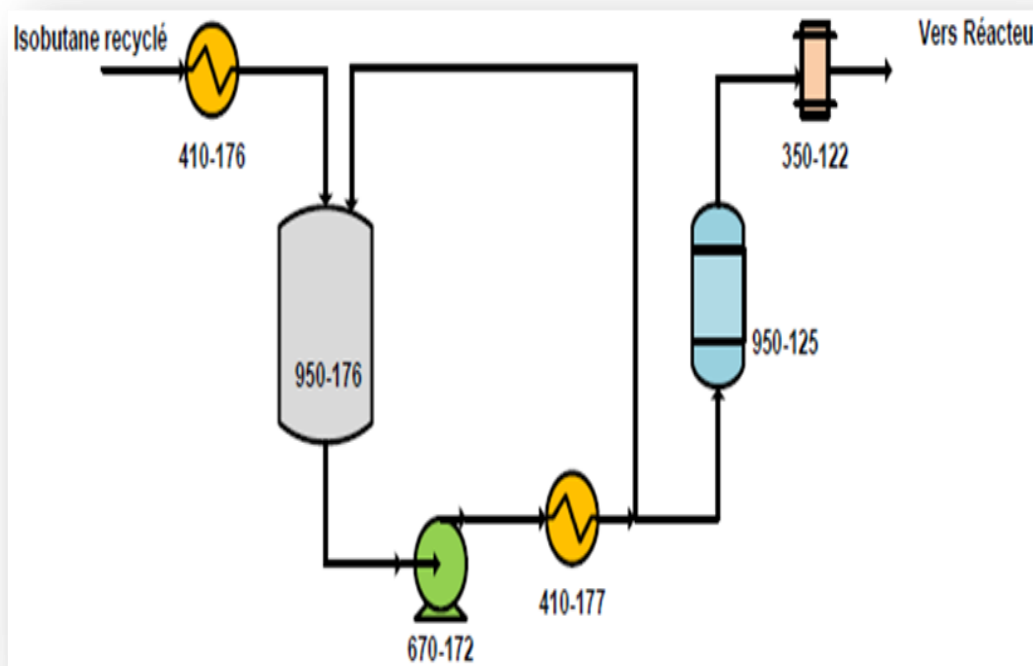


Figure II.9: Representative diagram of the recycled isobutane treatment system.

II. 4. 3. 1. 4 Hydrogen

Hydrogen is added to the reactor to control the melt index while modifying the length of the polymer chain. Before being incorporated, it must be subjected to the drying process in the 950-132 A/B dryers where the water present in the hydrogen stream is retained on two superimposed beds of the ZEOCHEM 13X molecular sieve.

II.4.3.2 Activation and addition of the catalyst

Catalyst type PF (PHILLIPS) before being incorporated into the reactor the polymerization must be activated; the objective of this activation is the change the oxidation state of chromium from Cr+3 to Cr+6 according to reaction (1.10) to eliminate water and volatiles by contact with dry and hot air in a fluidized bed.

The catalyst is added to the reactor in the form of a fresh isobutane catalyst solution (catalyst sludge). In the reactor in contact with ethylene, it changes valence from Cr+6 to Cr+2. **Figure II.10**



Figure II.10: Catalyst activation step.

II.4.3.3 Polymerization of ethylene

The polymerization reaction takes place in the 950-155 reactor in the form of a closed loop, which is a carbon steel pipe with an internal diameter of 560 mm, made up of four vertical sections, joined by horizontal sections. These, 760 mm outside diameter, have operating conditions for pressure and temperature of 42.2 kg/cm² and 85 to 110°C respectively.

The polymerization reaction is exothermic, at a rate of 800 kilocalories per kilogram of polymer formed. This heat of reaction is eliminated by means of the coolant which circulates in the jackets of the four vertical sections of the reactor. The latter has six legs for decanting the solid polymer contained in the polyethylene-isobutane mixture, then the product is unloaded and transferred to the flash chamber 950-161.

II.4.3.4 Flash system and polymer drying

The mixture discharged from the reactor via the "PTO" discharge valves with a pressure of 42.2 kg/cm² is transported by means of the flash lines from the reactor to the flash chamber 950-161 where the normal operating pressure is 0.37 kg/cm². In these, the mixture is heated by hot water which promotes the vaporization of isobutane, ethylene, hexene and hexane. The latter in the form of vapors leave through the head of the flash chamber and go to the purification system and recovery of the

recycle gas and the traces that are present in the pores of the polymer, are separated and eliminated in the presence of nitrogen. in the purge column.

The polymer is discharged by gravity from the bottom of the flash chamber to the purge column or it will be dried and discharged from the bottom of the latter to the powder silos by means of pneumatic transport.

In the event of a fire, reactor pump failure, or obstructions in the lines between the reactor settling legs and the flash chamber, the contents of the reactor are sent to the alternate flash chamber 950-164 which is an emergency device for the reactor.

II.4.3.5 Purification and recovery of recycled gas

The flash gas from the flash chamber head or alternate flash chamber will be subjected to a system for solids removal and solvent purification and recovery. For this, the flash gas, after passing through the cyclone, is sent to the bag filter and then to the Guard filter, once the solids have been recovered, the gas is sent to a gas purification system through the gas compressor of recycling.

After compression, the stream enters the recycling isobutane column to separate the isobutane from the components such as ethylene, hexene, hexane, and other heavy materials that it contains.

The side stripper from the purification column is recovered recycled isobutane is sent to storage. The current from the bottom of the recycling isobutane column is sent to the dehexanizer column from where the hexene/hexane recovered from the bottom of the latter is sent to the torch.

II.4.3.6 Finishing System

The produced polyethylene is transported in powder form from the purge column discharge to the storage silos or the extruder feed tank. This is done by means of a closed-circuit pneumatic nitrogen transport system. Polyethylene in powder form, after the addition of specific additives for each grade, is subjected in the extruder to a finishing process which essentially consists of giving it the final shape for the sale of the product. In this extrusion installation, polymer melting and granulation take place. The melting temperature of the product is around 250-275°C.

The granulation is carried out in a closed circuit of pressurized water. The polyethylene produced is pneumatically transported to the mixing silos for homogenization. From there it can be transferred to the loading silos by bulk trucks or to storage silos or to feed silos to bagging and palletizing lines.

II.4.3.7 Bagging

Is a complete line of automatic HDPE granule packing systems. This line is equipped with equipped bagger net weight mass feeder and a bag sealer, a conveyor with a printer and a metal detector, a palletizer with a speed controller, and a packaging machine with a holder and an oven, in order to obtain a pallet with 11 layers, each one contains 5 bags of 25 kg. **Figure II.11**

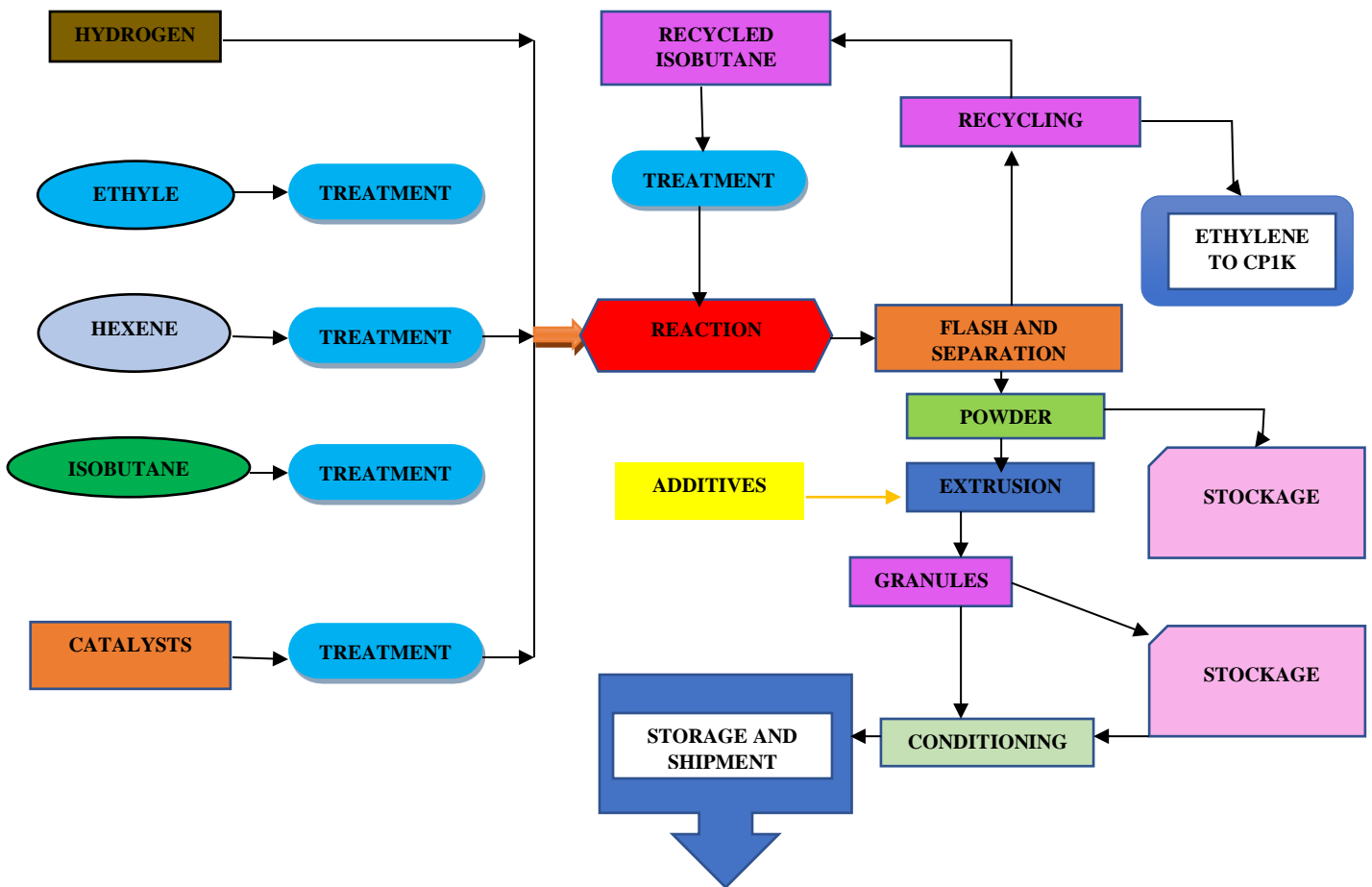


Figure II.11: Schematic diagram of the process

II.5. High-Density Polyethylene (HDPE)

High-density polyethylene, often abbreviated to HDPE, is a polymer whose monomer is ethylene. It is a thermoplastic with a very high strength-to-density ratio. HDPE is a very versatile plastic that has a wide range of applications – from pipes to storage bottles. When compared to other plastics, the melting point of high-density polyethylene is relatively high. (BYJU'S, s.d.)

II.5.1 Use of HDPE

HDPE is a highly versatile polymer that offers numerous advantages, making it an ideal choice for the production of various materials. Below are some of the uses of HDPE:

- Bottle caps and bottles are commonly made of this polymer.
- HDPE is used in 3D printing filaments.
- It is widely used in the fuel tanks of different types of automobiles.
- The piping system responsible for the distribution of natural gas is typically made of HDPE due to its corrosion resistance and other beneficial attributes.
- HDPE is used in the production of plastic lumber and wood plastic composites.
- HDPE is also used in skeletal and facial reconstruction surgeries, which are part of plastic surgery. (BYJU'S, s.d.)

II.5.2 Grades of HDPE produced at CP2K

Given that HDPE has a wide range of applications, such as the production of pipes, plastic films for various uses, bottles, etc., different grades must be produced. Therefore, the CP2K complex offers a whole range of HDPE, comprising eleven different grades. These grades are characterized by their melt flow index and density.

HDPE GRADE : 5502

Special characteristics

- ✓ Exceptional resistance to cracking (ESCR)
- ✓ Excellent rigidity and impact resistance
- ✓ Good machinability

Table II.1 : Characteristics of HDPE grade 5502.

| PROPERTIES | METHODS | UNITY | VALUE |
|----------------------------------|------------|----------|-------|
| ➤ Melt flow index (2.16 g/190°C) | ASTM D1238 | Gr/10min | 0,35 |
| ➤ Density (23°C) | ASTM D1505 | Gr/cm3 | 0,955 |
| ➤ Hardness, Shore D | ASTM D2240 | | 67 |

Chapter II Presentation of the CP2k Petrochemical Complex

| | | | |
|--|------------|-----|-------|
| ➤ Tensile strength at break (50mm/min) | ASTM D638 | MPa | 28 |
| ➤ Elongation at break (50mm/min) | ASTM D638 | % | > 600 |
| ➤ Flexural modulus | ASTM D790 | MPa | 1200 |
| ➤ Stress crack resistance (ESCR), F50 | ASTM D1693 | H | 20 |
| ➤ Brittleness temperature | ASTM D 746 | °C | > -76 |

Applications

Polyethylene 5502 is used for the production of small and medium capacity bottles for: Mineral water, Cosmetics, Pharmaceuticals, Bleach, etc.

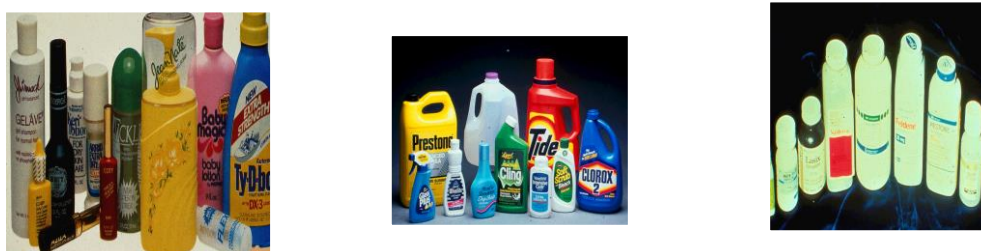


Figure II.12: Different uses of Polyethylene grade 5502.

HDPE GRADE: 6006-L

Special Characteristics

- ✓ Excellent implementation,
- ✓ Excellent mechanical properties

Table II.2: Characteristics of HDPE grade 6006-L

| PROPERTIES | METHODS | UNITY | |
|---|------------|----------|-------------|
| ➤ Melt index (2,16 Kg/ 190 °C) | ASTM D1238 | Gr/10min | 0,5-0.7 |
| ➤ Density (23°C) | ASTM D1505 | Gr/cm3 | 0.955-0.958 |
| ➤ Hardness, Shore D | ASTM D2240 | | 68 |
| ➤ Tensile strength at break (50 mm/min) | ASTM D638 | MPa | 30 |
| ➤ Elongation at break (50mm/min) | ASTM D638 | % | > 600 |
| ➤ Flexural modulus | ASTM D790 | MPa | 1350 |
| ➤ Stress Crack Resistance (ESCR), F50 | ASTM D1693 | H | 15 |
| ➤ British temperature | ASTM D746 | °C | <-76 |

Applications

Polyethylene 6006 L is used for the production of small bottles for:

- ✓ Sterilized milk
- ✓ Fruit juice and soft drinks
- ✓ Mild solvents such as distilled water, alcohol, acetone



Figure II.13: Small bottles made from Polyethylene grade 6006 L

HDPE GRADE: 4903

Special characteristics

- ✓ Excellent resistance to stress cracking
- ✓ Excellent surface appearance
- ✓ Easy implementation

Table II.3 : Characteristics of HDPE grade 4903.

| PROPERTIES | METHODS | UNITY | VALUE |
|----------------------------------|------------|----------|------------|
| ➤ Melt flow index (2.16 g/190°C) | ASTM D1238 | Gr/10min | 0,18-0,4 |
| ➤ Density (23 °C) | ASTM D1505 | Gr/cm3 | 0,947-0,95 |
| ➤ Bulk density | ASTM D1895 | Gr/cm3 | 0,5-0,6 |
| ➤ Number of grains per gram | MA-55-3011 | Nbr/g | 30-40 |
| ➤ Average particle size | MA-55-3011 | % | 25.0 |

Applications

Polyethylene 4903 is used for the production of:

- ✓ Large and medium-sized bottles

- ✓ Industrial containers
- ✓ Tanks
- ✓ Automotive accessories

HDPE GRADE : TR-140

Special characteristics:

- ✓ Exceptional implementation and Good resistance to impact and tearing,
- ✓ Excellent solderability and printing

Table II.4 : Characteristics of HDPE grade TR-140.

| PROPERTIES | METHODS | UNITY | VALUE |
|----------------------------------|------------|----------|-------|
| ➤ Melt flow index (2.16 g/190°C) | ASTM D1238 | Gr/10min | 0.3 |
| ➤ Density (23 °C) | ASTM D1505 | Gr/cm3 | 0.947 |
| ➤ Hardness | ASTM D2240 | ShoreD | 64 |
| ➤ Flexural modulus | D790 | MPa | 1100 |
| ➤ Dart drop, 26" (66 cm) | D1709 | g | 100 |
| ➤ Elongation : MD | D882 | % | 500 |
| TD | | | 600 |
| ➤ Tensile strength at break: | D882 | Mpa | |
| MD | | | 45 |
| TD | | | 30 |
| ➤ Elmendorf tear: | D1922 | G | |
| MD | | | 30 |
| TD | | | 300 |

Applications

Polyethylene TR 140 is used for the production of: Agricultural film and bags



Figure II.14: Agricultural film and bags made from polyethylene grade TR140

HDPE GRADE: TR-144**Special characteristics:**

- ✓ Good implementation, impact and tear resistance
- ✓ Excellent solderability and printing

Table II.5: Characteristics of HDPE grade TR-144.

| PROPERTIES | METHODS | UNITY | VALUE |
|----------------------------------|------------|----------|-------------|
| ➤ Melt flow index (2.16 g/190°C) | ASTM D1238 | Gr/10min | 0,16-0,22 |
| ➤ Density (23°C) | ASTM D1505 | Gr/cm3 | 0,943-0,947 |
| ➤ Hardness | ASTM D2240 | ShoreD | 64 |
| ➤ Flexural modulus | D790 | MPa | 1100 |
| ➤ Dart drop, 26" (66 cm) | D1709 | g | 120 |
| ➤ Elongation:MD | D882 | % | 500 |
| TD | | | 600 |
| ➤ Tensile strength at break: | D882 | Mpa | |
| MD | | | 45 |
| TD | | G | 30 |
| ➤ Elmendorf tear: | D1922 | | |
| MD | | | 25 |
| TD | | | 300 |

Applications

Polyethylene TR 144 is used for the production of: Film for bags, Garbage bags, General-purpose sachets.

**Figure II.15:** Different uses of Polyethylene grade TR-144**HDPE GRADE: TR-402****Special Characteristics**

- ✓ Excellent tensile strength
- ✓ Good processability

- ✓ Good impact and crack resistance
- ✓ Excellent weldability and printability
- ✓ Excellent resistance to ESCR (Environmental Stress Crack Resistance)

Table II.6 : Characteristics of HDPE grade TR-402.

| PROPERTIES | METHODS | UNITY | VALUE |
|---|------------|----------|-------------|
| ➤ Indice de fluidité (2,16 g/190°C) | ASTM D1238 | Gr/10min | 0,08-0,14 |
| ➤ Densité (23 °C) | ASTM D1505 | Gr/cm3 | 0,941-0,946 |
| ➤ Dureté | ASTM D2240 | Shore D | 65 |
| ➤ Résistance à la traction | D638 | Mpa | 23 |
| ➤ Résistance à l’allongement à la rupture | D638 | % | >600 |
| ➤ Module de flexion | D790 | Mpa | 800 |
| ➤ Impact IZOD (23°C) | D256 | J/m | NB |
| ➤ OIT (Indice Temps d’Oxydation) | D3895 | Mn | >20 |
| ➤ ESCR (condition B F50) | D1693 | h | >2000 |

Applications

Polyethylene TR 402 is used for the production of pipes for networks of drinking water distribution, combustible gases, irrigation, and industrial and non-potable water applications.



Figure II.16: Different uses of Polyethylene grade TR-402

HDPE GRADE: TR- 418

Special characteristics

- ✓ Good resistance to impact and cracking
- ✓ Excellent tensile strength
- ✓ Good implementation

- ✓ Excellent resistance to ESCR
- ✓ Excellent solderability and printing

Applications

Polyethylene TR 418 is used for the production of pipes for networks of drinking water distribution, combustible gases, irrigation, and industrial and non-potable water applications.

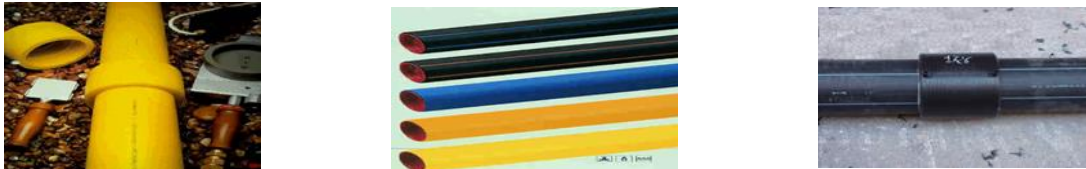


Figure II.17: Different uses of Polyethylene grade TR-418.

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: The Flow Melt Indexer analysis.

III.3.1.2. Procedure

- Heat the elastomer apparatus to a temperature of $190^{\circ}\text{C} \pm 2^{\circ}\text{C}$ 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: Variation of MFI as a function of Ethylene Concentration.

| | | | | | | | | | | | | |
|----------------------|------|------|------|------|------|------|------|------|------|------|------|------|
| Ethylene (%) | 2.63 | 2.91 | 3.30 | 3.64 | 3.92 | 4.31 | 4.75 | 5.15 | 5.55 | 6.15 | 6.70 | 7.00 |
| MFI (g/10min) | 0.78 | 0.76 | 0.72 | 0.69 | 0.67 | 0.65 | 0.63 | 0.61 | 0.60 | 0.57 | 0.52 | 0.50 |

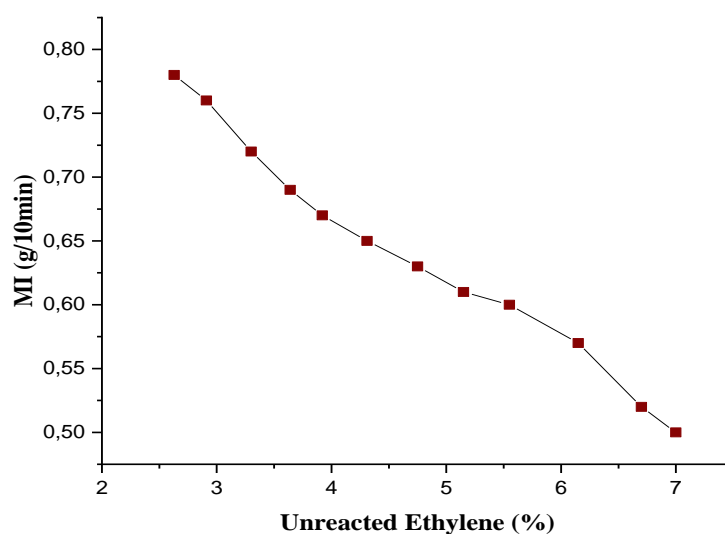


Figure III.2: Variation of MFI as a function of Ethylene Concentration.

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 affects 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 in the molecular weight of macromolecular chains, which leads to an increase in 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 an MFI between "0.55-0.70", it is necessary to work with Ethylene Concentrations between "3.64 mol percent (%) - 6.15 mol %".

III.3.1.3.2. Reactor Temperature

To study the influence of reactor temperature on the 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

| | | | | | | | | | | |
|--------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| T (°C) | 101.90 | 102.31 | 102.90 | 103.07 | 103.30 | 103.60 | 103.77 | 103.89 | 104.06 | 104.39 |
| MI(g/10min) | 0.55 | 0.57 | 0.59 | 0.62 | 0.65 | 0.68 | 0.69 | 0.75 | 0.82 | 0.84 |

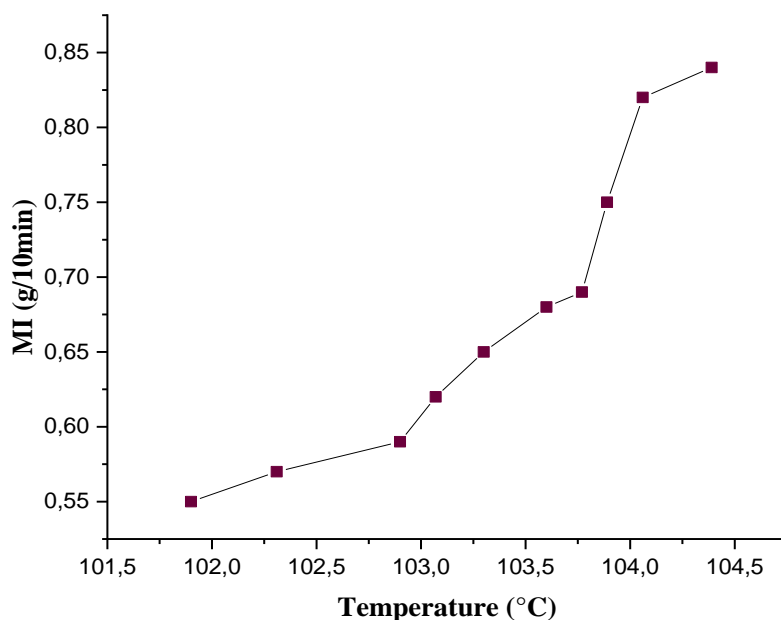


Figure III.3: Variation of MFI as a function of Reactor Temperature.

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 the destruction of the macromolecular chains of polyethylene molecules (Physical interaction between PE chains)

which leads to a decrease in the molecular weight and the viscosity system. It concluded that this parameter affects 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 "101.9°C-103.77°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 |

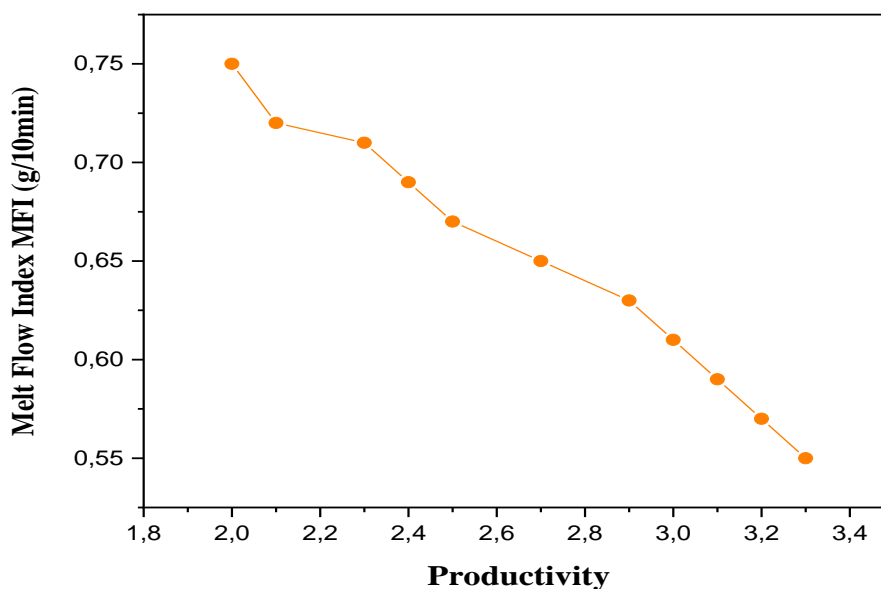


Figure III.4: Variation of MFI as a function of Catalyst Productivity.

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 |

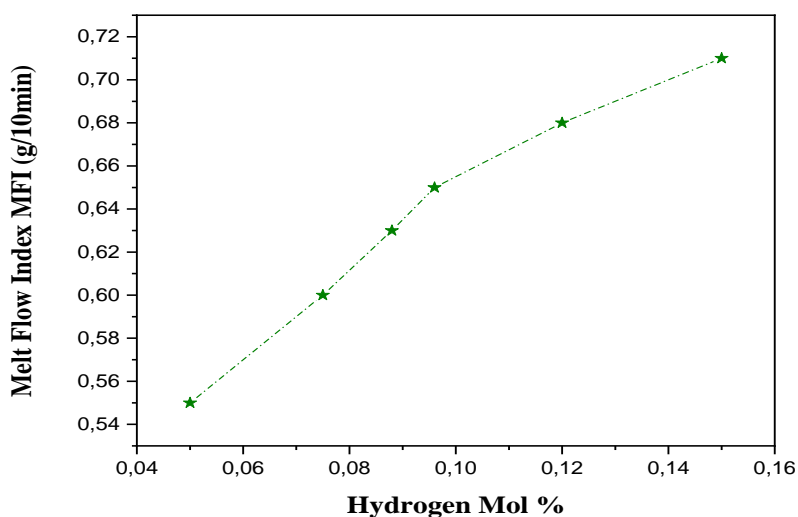


Figure III.5: Variation of MFI as a function of Hydrogen flow rate.

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:

$$\text{Density (g/cm}^3\text{)} = (y/z) \times (b-a) + a$$

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.

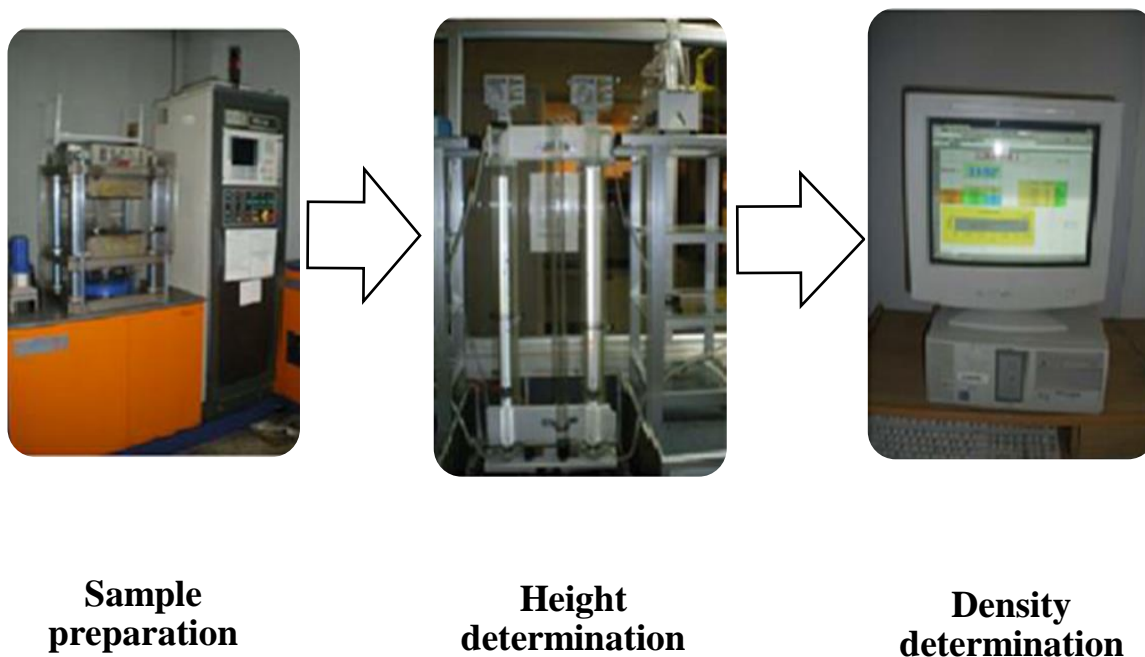


Figure III.6: Series of photos of the device used in density analysis.

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 |

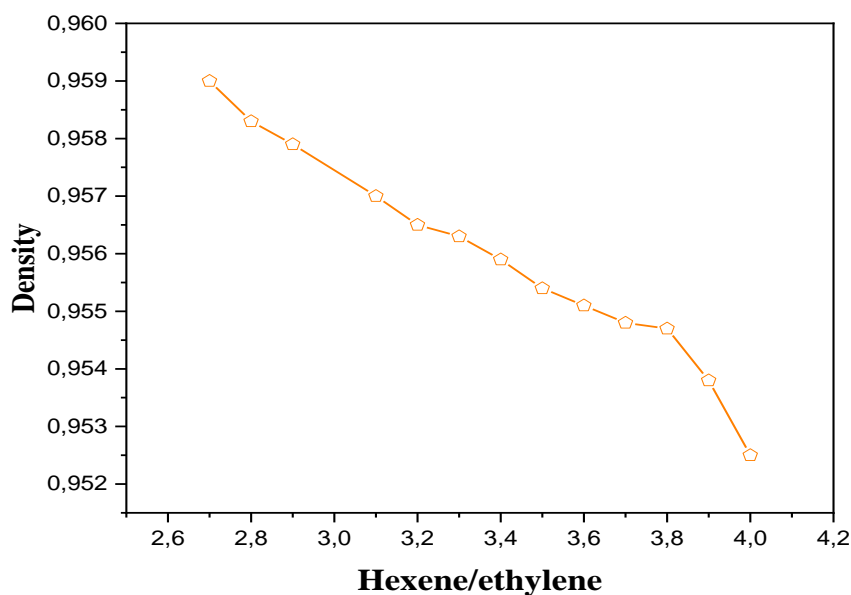


Figure III.7: Variation of Density as a function of Hexene/Ethylene ratio.

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 الماجستير 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.