Proceedings of the 5th International Conference on Materials Chemistry and Environmental Engineering
DOI: 10.54254/2755-2721/122/2025.19911

An Review of the Production of Polyolefins

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Abstract: Polyolefins, including polyethylene (PE) and polypropylene (PP), are important high molecular weight plastics derived from olefins. They are used in various industrial and everyday uses due to their sustainability, low density and resistance to degradation. This paper reviews the development and current situation of polyolefin production methods emphasising the progress of the catalyst and polymerization process. The key process of synthesis of olefin, Fischer-Tropsch synthesis, is summarized, and its variation, low temperature method (LTFT) and high temperature method (HTFT), as well as the role of catalyst accelerator in improving the reaction efficiency and selectivity are discussed. Various polymerization techniques, including high pressure, low pressure and gas phase polymerization, have also been studied, each of which has unique advantages for the molecular weight and crystallinity of polyolefin. Notable advances include the development of Ziegler-Natta and supported metallocene catalysts, which have significantly improved polymer quality and production efficiency. Recent work has focused on improving sustainability through recycling, renewable raw materials, and creating biodegradable and functionalized polyolefins. Future directions emphasize the need for more efficient catalysts, reduced carbon emissions, and optimized processes to improve environmental and economic benefits. This comprehensive review highlights the progress and challenges facing the polyolefin production industry, highlighting its importance and the potential for future innovation.

Keywords: Polyolefin, Chemical industry, Catalysts, Industrial process.

1. Introduction

Polyolefins, especially polyethylene (PE) and polypropylene (PP), are a widely used olefin-derived plastic [1]. These polymers are praised for their sustainability, low density, and resistance to degradation, making them an integral part of a variety of industrial and everyday applications [2]. This paper discusses the development of polyolefin production, with emphasis on the development of catalyst technology and polymerization process. This paper will explore key methods such as Fischer-Tropsch synthesis and its low and high temperature variations, emphasizing the role of catalyst promoters in improving reaction efficiency. In addition, the important polymerization techniques-high pressure, low pressure and gas phase, and their effects on molecular weight and crystallinity of polyolefin are reviewed. Recent innovations include the development of Ziegler-Natta and supported metallocene catalysts, which have significantly improved polymer quality and production efficiency. Emphasis is also placed on sustainable development efforts,

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including recycling, renewable raw materials, and the creation of biodegradable and functionalized polyolefins. This paper aims to provide a comprehensive overview of the current situation and future direction of polyolefin production, highlighting its importance and the potential for further innovation.

2. The production of polyolefins

2.1. Fischer-Tropsch Synthesis of hydrocarbons

Fischer-Tropsch Synthesis of hydrocarbons is a process of producing olefins or other organic by-products. It was first developed in 1925 by German chemists Franz Fischer and Hans Tropsch. It has been developed for a long time and has a complete system to produce olefins and methods of increasing yields of target products.

Fischer-Tropsch synthesis is a crucial chemical process for converting synthesis gas, a mixture of carbon monoxide and hydrogen, into a diverse array of hydrocarbons.[3] It is related to the production of polyolefins of the selection from hydrocarbons. The separation between various by-products and olefins or polyolefins, which are target products is the main purpose.

Fischer-Tropsch synthesis has two parts: LTFT refers to low temperature Fischer-Tropsch and HTFT refers to high temperature Fischer-Tropsch. According to LTFT, the low temperature Fischer-Tropsch synthesis, it has a reaction condition of lower than 260 degrees centigrade. It mainly produces wax, diesel and naphtha by using an ebullated bed reactor. [3]According to HTFT, the high temperature Fischer-Tropsch synthesis, it has a reaction condition of over 300 degrees centigrade and produces high amounts of olefins by using circulating fluidized bed (CFB).[3] Both of these parts of Fischer-Tropsch synthesis use iron-based catalysts which could increase the rate of the reaction, enhance the selectivity towards olefins which leading to a higher yield. However, LTFT can also use iron-based catalysts supported by cobalt catalysts. According to the experiment, it has a high activity of 60.4 per cent and a low carbon monoxide selectivity of 4.5 per cent [3].

Catalysts promoters are introduced in the process of Fischer-Tropsch Synthesis to improve the efficiency of catalysts and the selectivity of catalysts towards olefins instead of other by-products such as methane, ethanol, methanol or carbon monoxide from carbon deposition [3]. Three kinds of catalysts promoters have been used. Firstly, there are some alkali metal promoters, such as sodium and potassium, which donate electrons and create an alkaline surface environment of the catalysts to facilitate the adsorption of carbon dioxide. Also, it raises the carbon/hydrogen ratio and inhibit the adsorption of olefins. Under the condition of using iron-based catalysts, using alkali promoters can also strengthen the interaction between iron and carbon. Moreover, sodium and potassium can also cause the isomerization and hydrogenation of alpha-olefins, which leads to more branched-chain alkanes.

Secondly, transition metals can also act as promoters for catalysts of Fischer-Tropsch Synthesis. Copper, Zinc, Manganese and Cobalt used as promoters can enhance the olefin's hydrogenation capability to reach high yields of olefins. Those transition metals and their oxides have a strong interaction with iron, which refers to iron-based catalysts. They will improve the performance of the catalysts by preventing hydrogen poisoning and increasing the stability of iron catalysts [3].

Thirdly, nitrogen and sulfur doping is a common method that enables nitrogen-doped carbon materials to serve as catalyst supports. Nitrogen doping could enhance the surface basicity of carbon materials, which would improve carbon dioxide adsorption and suppress the absorption and dissociation of hydrogen, thereby inhibiting the secondary hydrogenation of light olefins [3].

DOI: 10.54254/2755-2721/122/2025.19911

2.2. Polymerization of olefins

To get the polyolefins that are useful in the chemical industry, people polymerize olefins to make them long chained and have higher molecular weight. There are several steps that polymerization takes place.

2.2.1. Feedstock preparation

Olefins are usually obtained through petrochemical processes, such as the cracking of hydrocarbons in refineries [4]. Ethylene and propylene are commonly produced by steam cracking hydrocarbons or through other chemical methods.

2.2.2. Polymerization

Polymerization of olefins is a chemical process in which these molecules undergo a reaction to form long chains or networks of repeating units, resulting in polymers. [5]Those polymers that are formed have specific chemical and physical properties such as low density, high flexibility, and high strength [5]. It is normally used in human daily supplies and industrial products.

There are three methods of polymerization that differ from the target products. Different target products are in different physical forms. Also, with the different lengths of the chain of the molecules, the forces needed to break and form the bonds are different, which refers to different reaction conditions.

(1) High-pressure polymerization

High-temperature polymerization of polyolefin involves high-temperature polymerization using olefin monomers such as ethylene or propylene. This process is usually carried out in the presence of catalysts such as Ziegler-Natta or metallocene, which can form polymers with specific properties, such as polyethylene and polypropylene. The ultimate goal is to achieve the desired polymer properties, such as strength and durability.

There are three advantages of high-pressure polymerization. Firstly, by using this type of polymerization, can control molecular weight by using high temperatures and catalysts to control the polymer structure. [6]Secondly, the resulting polymers typically exhibit high crystallinity, which gives the material high tensile strength and rigidity [6]. Thirdly, high-temperature polymerization processes can be very efficient and can handle many monomers.

(2) Low-pressure polymerization

Low-temperature polymerization of polyolefin involves polymerization of olefin monomers at temperatures significantly lower than those used in high-temperature processes. This method contrasts with the more common high-temperature method, which can yield different polymer properties and processing advantages.

The polyolefins produced from this type of polymerization have three properties. Firstly, low temperature polymerization can produce polymers with different molecular weight distributions than the high temperature process. This affects the mechanical properties of the material, such as toughness and flexibility. Secondly, polymers produced at lower temperatures may exhibit different crystallinity, which may result in the material having different hardness and clarity [7]. Thirdly, compared to high-temperature methods, low-temperature processes may be more energy efficient, although this depends on the specific process and the catalyst used.

(3) Gas phase polymerization

Gas phase polymerization of polyolefin is a process of polymerization of olefin monomers in a gas phase reactor. Ziegler-Natta or metallocene catalysts suitable for gas-phase environments are usually used. [8]The catalyst promotes the polymerization of gases such as ethylene or propylene into solid polymers.

DOI: 10.54254/2755-2721/122/2025.19911

It has three advantages that are different from other types of polymerization. Firstly, it has a higher productivity, which allows for continuous production with high efficiency and lower operational costs. Secondly, it offers precise control over polymer properties, such as molecular weight and density. Thirdly, it reduces solvent use and minimal waste compared to solution or slurry processes [8].

2.2.3. Compounding and processing

The raw polymer is often compounded with additives to improve its properties or processability. This can include stabilizers, colorants, or fillers. The compounded polymer is then processed into the final product form using various techniques, such as extrusion (for making sheets, pipes, or films) or molding (for making parts).

2.2.4. Quality Control

The final product undergoes quality control to ensure it meets the specifications and standards for its intended application. This step is important since there are a great possibility of certain amounts of by-products such as alkanes, carbon monoxide and methanol, ethanol [3]. With the control of the quality, those polyolefins produced can be purer. In this case, the polyolefins produced have better quality and meet the demand of industry or chemical

3. The achievements people have in the production of polyolefins

Polyolefins have been important industrial raw materials, and the methods of production of polyolefins have been developing for a certain amount of time. Chemists have certainly achieved several achievements of the processes of producing polyolefins in several aspects including improving the yield of the certain amounts of polyolefins, enhance the selectivity of target products during manufacturing, putting different types of polyolefins in use and many other aspects.

3.1. The developments of catalysts

To increase the yield of the products and the selectivity towards polyolefins, chemists have successfully found two types of catalysts, Ziegler-Natta catalysts and metalloncene catalysts. By inventing different catalysts, during production, people can choose certain types of polyolefins by adding different kinds since the catalysts can improve the selectivity of certain types of polyolefins.

3.1.1. The developments of Ziegler-Natta catalysts

Zieglar-Natta catalysts are named after two chemists: Karl Zieglar and Giulio Natta. Zieglar-Natta catalysts are powerful tools to help polymerize α-olefins. It can help produce polyethylene during the process of polymerization with high linearity and stereoselectivity. Zieglar-Natta catalysts make it possible to polymerize ethylene into linear, high molecular weight polyethylene, a type of longer chained, more linear polyolefins.

A complete typical Zieglar-Natta catalysts system has two parts: a transition metal compound and an organoalumnuim compound.

The Ziegler-Natta catalyst mechanism involves three main stages. It starts with initiation, where active sites like free radicals, cations, or anions are generated to begin polymerization. In the propagation phase, these active sites react with olefin double bonds, extending the polymer chains. The process ends with termination, when active sites are deactivated or the growing chains combine or react in other ways.

DOI: 10.54254/2755-2721/122/2025.19911

Differences with the traditional catalysts used in radical polymerization lead to a problem that radicals formed during the processes of polymerization will lead to branched polymers with large weight distribution but shorter chained molecules [9]. The invention of Zieglar-Natta catalysts can give a linear α-olefins polymers and controllable molecular weights and make the fabrication of polymers with specific tacticity possible as well. By controlling the stereochemistry of products, either syndiotactic or isotactic polymers can be achieved.

ZN catalysts have provided a worldwide profitable industry with production of more than 160 billion pounds and creation of numerous positions. Polyethylene and polypropylene are reported to be the top two widely used synthetic plastics in the world.

3.1.2. The developments of supported metalloncene catalysts

Supported metallocene catalysts are used in polymerization processes, especially for producing high-performance polymers such as polyethylene and polypropylene.

These organometallic compounds have metal centers (usually zirconium or titanium) sandwiched between two cyclopentadiene (Cp) rings. They catalyze the polymerization of olefin by providing a highly controlled polymerization environment and specific polymer properties. The support enhances the stability and reactivity of the metallocene catalyst, improves the dispersion of the catalyst, and can better control the polymerization process [10].

It is widely used in the production of high density polyethylene (HDPE), linear low density polyethylene (LLDPE) and polypropylene with custom properties.

In essence, supported metallocene catalysts combine the high activity and selectivity of metallocene with the stability and practicality provided by solid support, making them essential in modern polymerization processes.

3.2. The increased sustainability of polyolefins produced

Advances in recycling technologies to recover and reuse polyolefins, contributing to sustainability efforts and reducing environmental impact [11].

Renewable Feedstocks: Exploration of bio-based feedstocks to produce polyolefins, reducing dependency on fossil fuels and lowering carbon footprint.

3.3. Biodegradable and functionalized polyolefins

Biodegradable Polyolefins are those types of polyolefins that degrade under specific conditions and are very useful. Research has been taken into modifying polyolefins with degradable additives. Functionalized Polyolefins are those introducing functional groups or additives to enhance properties such as adhesion, UV resistance, flame retardancy, or antimicrobial properties [12]. Chemists have successfully developed functionalized polyolefins that are used in human daily lives, such as medical treatments and chemical recycling.

4. The outlook of the production of polyolefin

The production of polyolefins has been developing for decades. People are still searching for a more efficient, portable way to produce such widely used chemical materials. There are three aspects that people can keep focusing on with further innovations, improvements and developments.

4.1. Developing more efficient catalysts

Chemists can still keep inventing more efficient types of catalysts instead of Zieglar-Natta and metalloncene catalysts used in industry now. Improved catalysts will probably be more efficient, and its selectivity towards certain types of olefins or polyolefins that are supposed to be the target products.

4.2. Using renewable feedstocks and minimizing carbon emissions

Nowadays, environmental problems have been a major problem blocking the development of human society. The process of polymerization of olefins creates large amounts of carbon emissions. Although polyolefins and their related sources have provided enough benefits for humans, such as job opportunities, good properties of sustainability, high resistance and so on, it is important to look out for the damage caused by the production of polyolefins. Under this situation, innovations and improvements in the processes of polymerization are necessary.

What's more, as resources are scarce on the earth, it is important to find some renewable feedstocks to take place those nonrenewable feedstocks that are being used nowadays.

4.3. Innovations in process optimization

This is a common problem that industry factories are aiming at earning profits. With the innovations in process optimization, the methods of producing polyolefins would probably be much more simplified with less steps. Under these conditions, the costs of producing will be lower, which will lead to more profits. Also, with the innovations in process optimization, the target products may be more easily produced, which means it can save more feedstocks.

5. Conclusion

In summary, driven by innovations in polymerization methods and catalysts, the production of polyolefin (primarily polyethylene (PE) and polypropylene (PP)) has witnessed remarkable progress over the past several decades. The main production techniques of polyolefin are reviewed, encompassing Fischer-Tropsch synthesis, high-pressure polymerization, low-pressure polymerization, and gas-phase polymerization, each of which makes a distinctive contribution to the efficiency and properties of polyolefin.

The advancement of catalysts, particularly Ziegler-Natta and supported metallocene catalysts, has been pivotal. The Ziegler-Natta catalyst enables precise regulation of the structure and molecular weight of the polymer, leading to the manufacture of high-quality linear polymers. Supported metallocene catalysts further enhance polymer performance by offering superior control and stability, which is crucial for the production of high-performance polymers.

Recent accomplishments have also emphasized the increasing focus on sustainability. Advances in recycling technology and the utilization of renewable raw materials have made the production of polyolefin more eco-friendly. Additionally, the development of biodegradable and functionalized polyolefins is a significant step in fulfilling the requirements of changing environments and specific applications.

Looking ahead, the field will persist in exploring opportunities for enhancement. Discovering more efficient catalysts, reducing carbon emissions, and optimizing production processes remain at the core of driving the polyolefin industry. Innovations in these domains are anticipated to improve the environmental and economic aspects of polyolefin production, guaranteeing its continuous relevance and contribution in industry and daily life.

References

[1] *Gaines, L. L., & Shen, S. Y. (1980). Energy and materials flows in the production of olefins and their derivatives (No. ANL/CNSV-9). Argonne National Lab.(ANL), Argonne, IL (United States).*

DOI: 10.54254/2755-2721/122/2025.19911

[2] Lohse, D. J. (2005). The influence of chemical structure on polyolefin melt rheology and miscibility. Journal of Macromolecular Science, Part C: Polymer Reviews, 45(4), 289-308.
[3] Jia, J. Y., Shan, Y. L., Tuo, Y. X., Yan, H., Feng, X., & Chen, D. (2024). Review of Iron-Based Catalysts for Carbon Dioxide Fischer–Tropsch Synthesis. Transactions of Tianjin University, 1-20.
[4] Fakhroleslam, M., & Sadrameli, S. M. (2019). Thermal/catalytic cracking of hydrocarbons for the production of olefins; a state-of-the-art review III: Process modeling and simulation. Fuel, 252, 553-566.
[5] Masuelli, M. A. (2013). Introduction of fibre-reinforced polymers− polymers and composites: concepts, properties and processes. In Fiber reinforced polymers-the technology applied for concrete repair. IntechOpen.
[6] Starkweather, H. W. (1934). Polymerization under high pressure. Journal of the American Chemical Society, 56(9), 1870-1874.
[7] Wertheimer, M. R., Fozza, A. C., & Holländer, A. (1999). Industrial processing of polymers by low-pressure plasmas: the role of VUV radiation. Nuclear instruments and methods in physics research section B: Beam interactions with materials and atoms, 151(1-4), 65-75.
[8] Xie, T., McAuley, K. B., Hsu, J. C., & Bacon, D. W. (1994). Gas phase ethylene polymerization: Production processes, polymer properties, and reactor modeling. Industrial & Engineering Chemistry Research, 33(3), 449-479.
[9] Sinn, H., & Kaminsky, W. (1980). Ziegler-Natta catalysis. In Advances in organometallic chemistry (Vol. 18, pp. 99-149). Academic Press.
[10] Ciardelli, F., Altomare, A., & Michelotti, M. (1998). From homogeneous to supported metallocene catalysts. Catalysis Today, 41(1-3), 149-157.
[11] Wang, X. Y., Gao, Y., & Tang, Y. (2023). Sustainable developments in polyolefin chemistry: Progress, challenges, and outlook. Progress in Polymer Science, 101713.
[12] Manjula, B., Reddy, A. B., Sadiku, E. R., Sivanjineyulu, V., Molelekwa, G. F., Jayaramudu, J., & Kumar, K. R. (2017). Use of polyolefins in hygienic applications. In Polyolefin Fibres (pp. 539-560). Woodhead Publishing.