

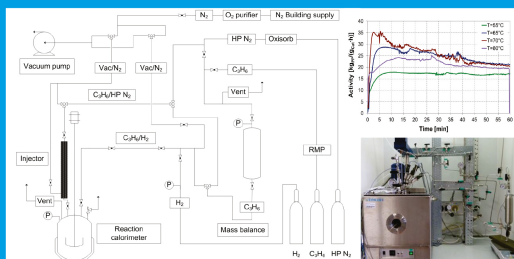


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Kinetic investigation of different supported catalysts for the polymerization of propylene under industrially relevant conditions

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1 Introduction

1.1 Polypropylene – markets and applications

Polypropylene (PP) belongs to the group of polyolefins and is next to polyethylene (PE) the second most important polymer for daily life applications. In Europe, the total polymer demand in 2014 reached 47.8 million tons, wherein polypropylene had the largest marked share of 19.2 % (9.18 million tons) compared to PE-LD and PE-LLD with 17.2 % and PE-HD with 12.1 %, see Figure 1 [1]. The global demand of polypropylene in 2013 was 55.1 million tons [2]. More than the half of the polypropylene is used as packaging material such as flexible packaging made from polypropylene films or rigid packaging e.g. containers or caps. Further applications are polypropylene fibers and consumer goods, which reached a marked share of 12 % in each case. Other applications are in the automobile industry, in the building and construction sector as well as in the electro and electronic sector. Also the application of special materials like fiber-reinforced or foamed polypropylene and copolymers (e.g. with ethylene) as technical thermoplastics is increasing [2],[3]. The market research institute Ceresana expected until 2021 an annually revenue growth for polypropylene of 5.8 %. Especially due to the opening of new application areas, the substitution of other materials and the development of bio-based polypropylene materials will lead to the high growth potential for the polypropylene market [2].

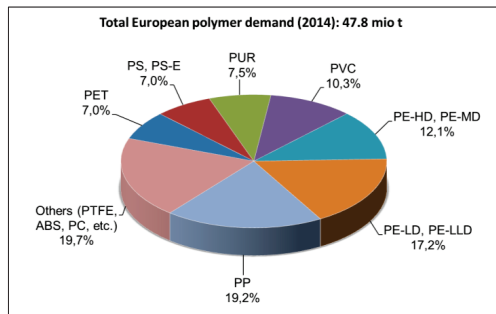


Figure 1: European polymer demand by type 2014 [1]

In 2012, 65 million tons of polypropylene were produced worldwide. Half of the production capabilities are located in Asia, 17 % in Europe, 14 % in North America and 12 % in Middle East [4]. The major polypropylene producers are LyondellBasell, Sinopec, PetroChina, Braskem, Borealis, Sabic, Exxon Mobil, Reliance Industries, Total Petrochemicals and Formosa Plastics Corporation [5].

1.2 A brief description of polypropylene microstructure and properties

The basic repeating unit propylene consists of three carbon atoms, where the methyl group is chiral leading to different stereochemical configurations of the methyl group in the polymer chain. The three main configurations of polypropylene are ^[6]:

a) *Isotactic polypropylene:*

The methyl groups are oriented on the same side of the backbone of the polymer chain.

b) *Syndiotactic polypropylene:*

The methyl groups alternate regularly from side to side in the polymer chain.

c) *Atactic polypropylene:*

The methyl groups are randomly oriented in the polymer chain.

The different stereoisomers of PP are shown schematically in Figure 2. The most common form in industry is isotactic polypropylene, which is easily produced with state-of-the-art heterogeneous Ziegler-Natta and metallocene catalysts ^{[5],[6],[7]}. It is characterized by a high crystallinity (60-70%) and a high melting temperature in the range of 160-165°C. Syndiotactic polypropylene is also semi-crystalline but is less stiff than isotactic PP and has a lower melting temperature of 130 °C. Atactic PP is amorphous and a rubbery material. Generally, it is an undesired product but some applications can be found in the electro industry as casting compound or as insulating or sealing material ^{[3],[8]}.

Modern coordination catalysts used in industry are able to produce very high isotactic PP with only minor atactic fractions (the catalysts are described in more detail in chapter 2.1). The polymer chains have a high regioregularity, wherein a 1,2 insertion of the monomer and head-to-tail enchainment is favored. Regioerrors caused by 2,1 insertion of propylene create irregularities along the polymer chain leading to a decrease in crystallinity and a lower melting temperature ^{[6],[7],[9]}.

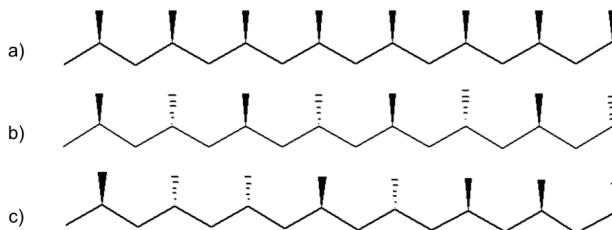


Figure 2: Main polypropylene types: a) isotactic, b) syndiotactic, c) atactic [7]

The properties of PP are also dependent on the molecular weight and the molecular weight distribution (MWD). They are influenced by the process conditions (e.g. production of unimodal

or bimodal MWD), the used catalyst type and additives such as hydrogen which acts as chain transfer agent ^{[5]-[7],[10]}. Bimodal polymers can be produced in different ways ^[11]: In multi-stage processes using same or different reactor types with different hydrogen concentrations in each stage (e.g. Borstar PP process), in multi-zone reactors (e.g. Spherizone PP process, both see chapter 1.3) or with multisite catalysts ^[12]. The control of the MWD allows the production of polymers with defined properties as well as new property combinations (Figure 3). With Ziegler-Natta catalysts produced polymers have a relatively broad MWD with a polydispersity index (PDI) in the range from 4 to 20 ^{[5],[13]}, whereas polymers produced with metallocene catalysts have a narrow MWD with a PDI of approx. 2 ^{[7],[14]} (see chapter 2.1).

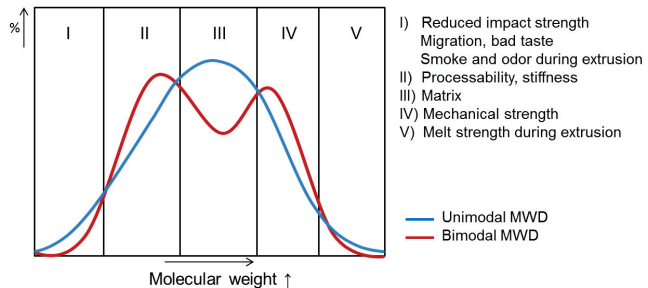


Figure 3: Molecular weight distributions of unimodal and bimodal polymers (PE and PP) and its impact on polymer properties [7], [11]

Commercial PP grades are grouped in three different grade classes:

- Homopolymer
- Random copolymer
- Heterophasic or impact copolymer

Polypropylene homopolymers are characterized by a good tensile strength and stiffness but a poor (low-temperature) impact resistance and film clarity ^{[3],[5],[6]}.

Random copolymers are copolymers of propylene and ethylene (E/P-RACO). The ethylene content is in the range of 1 to 8 wt%. The ethylene molecules are randomly distributed in the polypropylene backbone. Ethylene is the most commonly used comonomer to modify the properties of propylene but also 1-butene or terpolymers of ethylene and 1-butene are used. In E/P-RACO, optical properties (good film clarity), impact resistance and flexibility are improved. In contrast, with increasing comonomer content, crystallinity, stiffness and melting temperature decrease ^{[3],[6],[11]}.

Heterophasic copolymers (PP-HECO) consist of a continuous phase (matrix) of homopolypropylene or random copolymer and an elastomeric phase of amorphous, rubber-like propylene/ethylene copolymer. The ethylene content in the elastomer is typically in the range of 20 to 60 wt%. The heterophasic copolymer consists of 10 to 20 wt% of elastomer which is not



miscible with the matrix phase ^[11]. Main advantages of the heterophasic copolymer are the improved low-temperature impact strength, a high thermal stability and an improved blush resistance ^[6]. Beside these three basic types, additional modification of the polypropylene properties can be achieved by mixing with other polymers, with filling or reinforcing materials, pigments or by the chemical reaction with the final product ^[3].

Polypropylene is characterized by good electrical insulation properties and is highly resistant to a wide range of chemicals, except of strong acids and oxidants. The density of PP is with approx. 0.85 g/cm³ (atactic PP) to 0.94 g/cm³ (isotactic PP) low, which makes it to an important material for packaging applications or materials where low weights are desired. As polypropylene is a thermoplastic, it can be melted and shaped into a desired form and subsequently remelted and reshaped into other forms. In terms of sustainability it is therefore a good recycling material. Due to its good mechanical and thermal properties, it can be processed in a variety of ways, mainly by injection molding, fiber extrusion and film extrusion ^{[3],[8]}.

1.3 Processes for the industrial production of polypropylene

Industrial polymerization processes for the production of polypropylene can be categorized into following main groups:

- Gas-phase polymerization
- Bulk polymerization in liquid monomer
- Slurry polymerization in inert diluent

PP is produced either in one phase or in combination of different phases (hybrid or mixed-phase processes). The development of PP polymerization processes is strongly related to advances in catalyst development (see chapter 2.1) and the demand of improved product performance. In early polymerization processes, additional process steps for the removal of catalyst residuals and atactic PP were necessary ^[6]. The development of more active and highly stereoselective catalysts led to the design of more efficient processes where such treatment steps are not required anymore ^{[7],[9],[15]}. Modern polyolefin processes are very efficient and produce large quantities of polymer. Starting with 5 kt/y in 1963, world scale plants have grown from 80 kt/y in 1980 to more than 750 kt/y for the newest plants ^[7].

Liquid phase processes use autoclaves or (more common today) loop reactors. Gas-phase polymerizations are carried out in fluidized bed reactors (FBR) or in stirred bed reactors. In FBR, a gaseous stream of monomer and nitrogen is used to fluidize the polymer particles in the reactor, whereas in stirred gas-phase reactors mechanical stirring is used to suspend the polymer particles. The stirred gas-phase reactors can further divided into horizontal and vertical reactor configurations. The polymerization can be carried out in one reactor, but typically two or more reactors of same or different configuration are connected in series in order to produce



polymer products with a more complex structure. Propylene homopolymer and random copolymers are produced in various configurations of gas-phase and bulk reactor systems. Heterophasic copolymers are only produced in an additional gas-phase reactor (often FBR) because of the stickiness of the polymer and the solubility of the propylene/ethylene rubber phase in the monomer and diluent [7].

A detailed description of the several reactor configurations as well as polyolefin processes can be found in [6], [7] and [15]. Table 1 shows an overview of the current commercial PP polymerization processes with the reactor configurations. The named technology suppliers are the current technology licensors. In the following, an overview of the main polymerization processes for the production of PP will be given.

Table 1: Industrial polypropylene processes, based on [15]

Process	Technology supplier	Reactor type		Mode of operation
		Homopolymer	Impact copolymer	
Unipol PP	Grace	Fluidized bed reactor (FBR)	FBR, gas	Condensed gas phase/gas
Novolen	Novolen Technology Holdings	Vertical stirred bed gas-phase reactor	Vertical stirred bed gas-phase reactor	Gas/gas (non-condensed)
Innovene PP	Ineos	Horizontal stirred gas-phase reactor	Horizontal stirred gas-phase reactor	Gas/gas
Horizone	JPP (Japan Polypropylene Corp.)	Horizontal stirred gas-phase reactor	Horizontal stirred gas-phase reactor	Gas/gas
Spherizone	LyondellBasell	Multizone circulating reactor	FBR, gas	Gas/gas
Spheripol	LyondellBasell	Loop reactor	FBR, gas	Bulk/gas
Borstar PP	Borealis	Loop reactor and FBR	FBR, gas	Bulk+gas/gas
Hypol I	Mitsui	Stirred autoclave reactors	FBR, gas	Bulk/gas
Hypol II		Loop reactors	FBR, gas	Bulk/gas
Exxon Mobile	Exxon Mobile	Loop		Bulk
Slurry	Several	Series of autoclaves	Series of autoclaves	Slurry

Slurry (inert diluent) processes

The first commercial processes for the production of PP were slurry processes, where the polymerization took place in an aliphatic hydrocarbon such as hexane as inert diluent. Many different slurry processes were developed in the early 1970's. The Ziegler-Natta catalysts available at this time (1st and 2nd generation ZN catalysts, see section 2.1.1) had low activity and produced polymer with large amounts of atactic polymer. Therefore, processes include a series of CSTR's of up to 5 to 7 reactors in order to achieve good monomer conversion. Additional post-reactor treatment was necessary to remove catalyst residuals (deashing) and atactic polymer. Diluents used in the different variations of slurry processes ranges from C6 to C12 hydrocarbons [6],[7],[15]. An overview of early PP manufacturing processes is given by Moore [6].



Diluent slurry processes are very cost intensive because of the high number of equipment (workup section for diluent) and the costly operation of the plant. Over the past few decades, slurry processes have been replaced by more efficient bulk and gas-phase processes. However, there are still remaining diluent slurry plants in operation producing specialty polymers, e.g. high-crystallinity polypropylene (HCPP) ^[15].

Bulk (liquid propylene) processes

Polymerization processes carried out in liquid propylene are known as “bulk” or “liquid pool” processes. Advantages to the diluent slurry process are that the usage of liquid monomer as reaction medium increases the polymerization rate due to the higher monomer concentration. Propylene can easily separate from the polymer by flushing and no extensive diluent recovery system is needed. Polymerization processes are performed in continuous stirred tank reactors or loop reactors. They are used to produce homopolymer and random copolymers (<8 wt% ethylene). The first bulk process was developed by Dart Industries in the 1960's, also called Rexene, Rexall or El Paso bulk process. Other bulk processes are Exxon Sumitomo and early process from Mitsui. All of them uses CSTR's or stirred autoclaves ^[6]. Chevron Phillips Chemical developed the “loop slurry” process for the production of HD-PE, where polymerization is carried out in a series of pipe reactors (up to 8 legs) ^{[5],[6]}. The loop design provides a maximum surface area improving the heat removal from the polymerization reaction leading to an increase of the reactor throughput. They were also adapted very quickly to PP processes. Nowadays, loop reactors are used to produce about 50% of all commercial polyolefins ^[9]. Therein, single bulk configurations are often combined with further gas-phase reactors in order to provide a full range of polymer grades (see section hybrid processes).

Gas-phase processes

Gas-phase processes are in comparison to slurry processes (diluent or bulk) economically and energy efficient. The polymer can easily separate from the monomer since monomer is in gas-phase. There are no diluents which have to be separated and treated or to flash off large amounts of monomer like in bulk phase. This leads to a simple plant configuration with lower investment and operational costs. One drawback of gas-phase processes is the limited heat transfer capacity in comparison to slurry processes. In order to remove the heat from the system, gas is removed from the reactor, condensed in an external heat exchanger and recycled into the reactor (condensation cooling). When liquid monomer is injected into the reactor, it immediately evaporates leading to a further cooling effect. Polypropylene is produced in gas-phase processes either in fluidized bed reactors or in continuous stirred bed reactors of different configurations ^{[6],[7],[15]}.

The Unipol polypropylene process, originally developed for the gas-phase polymerization of ethylene by Union Carbide (later part of Dow Chemical, now licensed by Grace), utilizes

fluidized bed reactors for the production of polypropylene. Currently 48 operating lines and 15 reactor lines are using the Unipol process technology accounting for 17 % of the global propylene output ^[16]. A scheme of the process is shown in Figure 4. A single large fluidized bed reactor is used for the production of homopolymer and random copolymer. A second smaller FBR can be connected in series for the production of heterophasic (impact) copolymer.

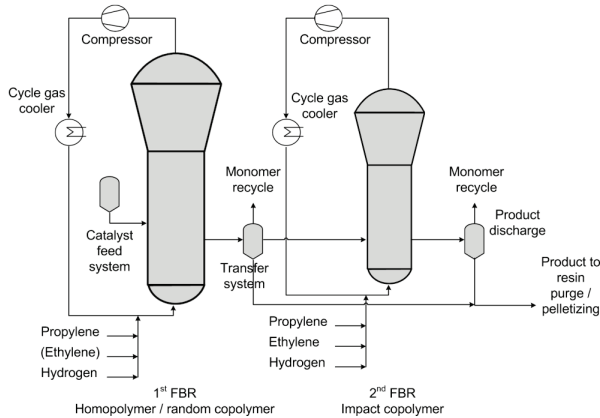


Figure 4: Scheme Unipol PP process [17]

Fresh, purified monomer as well as recycled monomer are fed to the reactor bottom. Therein, the monomer is fed in condensed mode, where 10 to 12 % of propylene is liquid propylene. Catalyst, cocatalyst and donor are fed via a feeding system into the reactor. The polymerization takes place in the reaction zone, where the gas stream is circulated through the bed. The upper section of the reactor is wider in order to reduce the gas velocity and particle entrainment. The gas stream is removed at the top of the reactor, goes through a compressor and is then cooled down in an external heat exchanger to remove the reaction heat. The first reactor operates at 60°C to 70°C and in a pressure range of 25 to 30 bar. The residence time is typically one hour. Monomer is periodically removed from the reactor and separated in a series of high-pressure gas/solid separators. The separated gas is recycled back and the polymer goes through further processing or is transferred to the second FBR. The second reactor is smaller because only 20 % of the reaction takes place. Also copolymerization is carried out at lower temperatures and pressures. The reactor as well as the recycle cooler system is operated only in gas-phase ^{[7],[9]}.

The Novolen process uses one or two identical vertical stirred bed gas-phase reactors. The process was originally developed by BASF in 1967 and is now licensed by Lummus Novolen Technology holding CB&I ^[18]. The reactors can be operated very flexible in parallel or cascade mode. The production of homopolymer and random copolymer can either be carried out in a single reactor, parallel in two reactors or in two reactors in cascade mode depending on required

capacity and product range. For the production of heterophasic copolymer, the two reactors are operated in the cascade mode, wherein the homopolymer (or random copolymer) matrix is produced in the first reactor and in the ethylene-propylene rubber phase is produced in the second reactor. Reactor cooling is achieved by flash evaporation of liquefied reactor gas (condensed in an external heat exchanger) which is mixed with fresh feed and injected into the reactor. The polymer/gas mixture is discharged from the reactor through dip tubes and transferred to the other reactor or to the powder and gas separation system. Unreacted monomer is compressed and recycled into the reactors. The PP powder is transferred via gravity flow to the purge silo, where residual propylene is removed by flushing with nitrogen. Finally, the polymer powder is fed into the extruder, where it is converted together with additives into pellets ^{[18],[19]}. A scheme of the Novolen process is shown in Figure 5.

The Innovene PP process (Ineos) and the Horizone process (Japan Polypropylene Corporation) are based on horizontal stirred bed reactors. The technology was developed by Amoco/Chiso in the 1970's. In the Horizone process two reactors are arranged one above the other, wherein the polymer powder flows under the influence of gravity into the second reactor. In the Innovene process, the two reactors are on the same level requiring a powder transfer system. Both processes can be run in cascade or parallel modes. The cascade mode is used to produce impact copolymer. Heat removal is accomplished by evaporating of liquid propylene injected over the powder bed. The advantage of the reactor configuration is its plug-flow characteristic with a narrow powder residence time distribution ^[7].

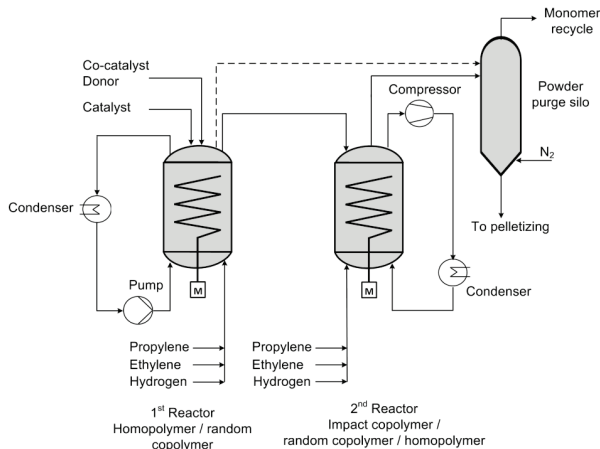


Figure 5: Scheme Novolen® gas-phase process [19]

Hybrid processes

Hybrid or mixed-phase processes combine bulk and gas-phase processes for the production of the full range of polypropylene products (HP, RACO and HECO). The process is divided into one block making homopolymer and random copolymer and a second block producing sticky heterophasic copolymers. While the first block often uses loop reactors or combination of loop reactors and FBR, the second block only consists of a FBR for the reasons described above. The two blocks are separated by a kind of gas lock/ flash system in order to achieve a better control over the polymer properties of the different phases. Advantage of the hybrid processes is the production of a wide range of polymer grades but high capital investment is required [7],[9].

The dominant process is the Spheripol process by LyondellBasell [20], where roughly one third of the world's PP production is based on [9]. Figure 6 shows a scheme of the process. It consists of one to two loop reactors filled with liquid propylene for the production of homopolymer and random copolymer. A small loop reactor is used to prepolymerize the catalyst before it enters into the main loop reactor. Typically, two loop reactors are used in order to narrow the residence time distribution making more uniform polymer product. For the production of impact copolymers a fluidized bed reactor is connected in series. Between the liquid and gas-phase section, a high temperature flush separation is installed in order to depressurize and flush the propylene/PP slurry and to remove H₂ for a better control of the molecular weight distribution in the copolymer reactor. Unreacted monomer is recovered from the system and is completely recycled back into the reactors [7].

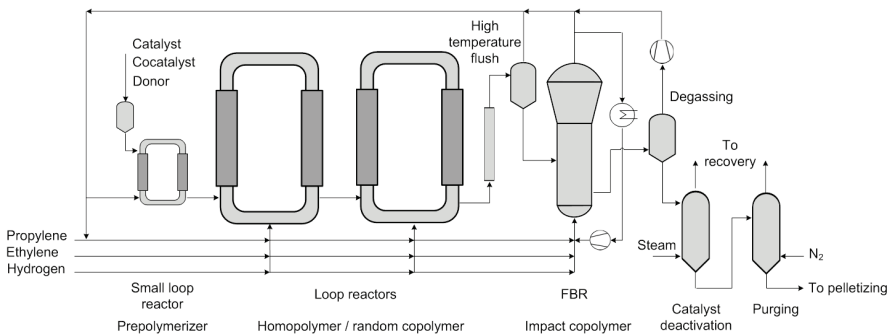


Figure 6: Scheme Spheripol process [7] and [9]

In the Spherizone process, launched by LyondellBasell in 2004, a unique multizone circulating reactor is used instead of the loop reactors which operates in gas-phase [21]. The reactor consists of two interconnected reaction zones separated by a cyclone at the top of the reactor. The riser (first reaction zone) is operated with high gas velocity and acts like a fast fluidized bed. In the cyclone, the polymer particles are separated from the gas and enter the second reaction

zone (downer) which can be characterized as a moving packed bed. The two zones can be operated at different conditions (H_2 and co-monomer concentrations) where polymer with bimodal properties can be achieved [7],[9],[21].

The Mitsui Hypol process consists of two stirred autoclave reactors working under liquid pool conditions followed by two fluidized bed gas-phase reactors. The gas-phase reactors are stirred fluidized bed reactors with wall scrapers in order to eliminate fouling and sheeting problems. They claimed to achieve higher rubber contents in the production of impact copolymers compared to conventional FBR. The two gas-phase reactors can also be used for the production of homopolymers with a wider range of polymer properties. In the Hypol II process, the stirred autoclaves are replaced by loop reactors enabling a higher throughput and a reduction of capital costs [7],[22].

A third major player for slurry/gas-phase processes is Borealis. They provide the Borstar process technology for PE and PP [23]. The basic design of the Borstar PP process is shown in Figure 7. The catalyst is firstly prepolymerized in a small prepolymerization loop reactor. Homopolymer and random copolymer are produced in a loop reactor followed by a fluidized bed reactor. With this configuration a bimodal polymer matrix can be achieved due to the different reaction conditions. For high impact copolymers one (or two) additional FBR can be connected in series. This FBR are smaller compared to the FBR in the first stage because of the higher reaction rates and typically shorter residence times [9],[23].

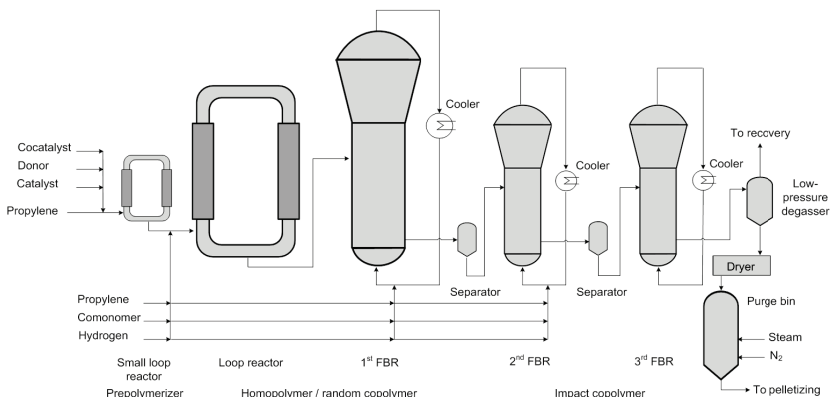


Figure 7: Scheme Borstar PP process (four-reactor setup) [9]