Impact of reaction conditions on propylene gas phase polymerizations

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“Nothing worth having was ever achieved without effort.”

Theodore Roosevelt

Abstract

The effect of changing reaction conditions on propylene polymerization using a Ziegler-Natta catalyst was studied. It was observed that the instantaneous rate of polymerization increased with the performance of a prepolymerization step. This was attributed to the effect of prepolymerization step in decreasing local particle overheating in the initial instants of reaction, due to a lower catalyst activity.

Hydrogen concentration effected the instantaneous rate of polymerization, once it reactivates dormant sites of the catalyst. A lower rate was observed in the absence of hydrogen, since there were less active sites where polymerization reaction can occur.

It was also observed that polymerization rate was higher when the catalyst was pre-contacted with a liquid hydrocarbon instead of injecting it dry.

The presence of an alkane increased the rate of polymerization by the absorption of the reaction heat by its latent heat of vaporization but also by enhancing the local concentration of propylene inside the active sites.

Regarding to polymer analysis, it was observed that when hydrogen was not present in the reaction media, it leaded to a higher molecular weight. The particle size distribution was mostly affected by the type of pre-catalyst injection, which is also the only condition which has an effect in the morphology of the powders produced. Also the crystallinity and melting point of the produced polymers were not significantly affected.

Keywords: propylene, prepolymerization, dry injection, wet injection, hydrogen concentration, alkane, turbosphere reactor

Resumo

O efeito de alterar condições reaccionais na polimerização de propileno foi estudado utilizando um catalisador Ziegler-Natta. Observou-se que a velocidade instantânea de polimerização aumentou com a realização de um passo de prepolimerização. Isto deve-se ao efeito da prepolimerização em reduzir o sobreaquecimento local das partículas de catalisador e de prepolímero nos instantes iniciais da reacção, devido a uma baixa actividade catalítica.

A concentração de hidrogénio afecta também a velocidade instantânea de polimerização, uma vez que este é responsável pela reactivação de centros activos dormentes. Quando realizada a reacção na ausência de hidrogénio, verificou-se uma actividade catalítica bastante inferior, devido ao reduzido número de centros activos onde a reacção de polimerização possa ocorrer.

Quando o pré-catalisador é inserido no reactor, tendo estado previamente em contacto com óleo, a actividade catalítica é superior ao caso em que o catalisador é inserido de forma seca, com sal.

A presença de um alcano aumenta a velocidade de polimerização, pois tem a capacidade não só de remover algum do calor libertado pela reacção de polimerização, como também aumenta a concentração local de propileno no interior dos centros activos do catalisador.

Tendo em conta a análise dos polímeros produzidos, observou-se que a ausência de hidrogénio influencia severamente a massa molar do polímero. A distribuição de tamanho das partículas é maioritariamente afectada pelo tipo de injecção do catalisador, tal como a superfície externa do polímero. Quanto à cristalinidade e ao ponto de fusão dos polímeros produzidos, estes não são particularmente afectados por nenhuma das condições estudadas.

Palavras-Chave: propileno, prepolimerização, injecção seca, injecção em óleo, concentração de hidrogénio, alcano, reactor de fase gasosa

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Nomenclature

Acronyms

BD	Bulk Density
DCPDMS	Dicyclopentyldimethoxysilane
DSC	Differential Scanning Calorimetry
EPR	Ethylene-Propylene Rubber
FBR	Fluidized Bed Reactor
HDPE	High Density Polyethylene
hiPP	High Impact Polypropylene
HSBR	Horizontal Stirred Bed Reactor
HT-SEC	High Temperature - Size Exclusion Chromatography
ICA	Induced Condensing Agent
ICP	Impact Co-polymer
IPP	Isothermal Prepolymerization
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
MAO	Methylaluminoxane
MWD	Molecular Weight Distribution
NIPP	Non-Isothermal Prepolymerization
PE	Polyethylene
PP	Polypropylene
a-PP	Atactic Polypropylene
i-PP	Isotactic Polypropylene
s-PP	Syndiotactic Polypropylene
PSD	Particle Size Distribution
RCP	Random Co-polymer
SEC	Size Exclusion Chromatography
SEM	Scanning Electron Microscopy
TEA	Tryethylaluminum
VSBR	Vertical Stirred Bed Reactor
ZN catalyst	Ziegler-Natta catalyst

Symbols

$[Al]$	Concentration of Cocatalyst (TEA)
$[c]$	Concentration of Catalyst
F	Monomer Feed Flow Rate to the Reactor

$[k_a]$	Activation Constant
$[K_a]$	Product of $[k_a]$ and $[Al]$ – Constant
$[k_d]$	Deactivation Constant
$[k_p]$	Propagation Constant
kton	Kilo tonnes
m	Mass
$[M]$	Monomer Concentration at Active Sites
P	Pressure
P_C	Critical Pressure
R	Ideal Gas Constant
R_P	Polymerization Rate
T	Temperature
T_C	Critical Temperature
V_m	Molar Volume
V_R	Reactor Volume
Y_0	Total Molar Concentration of Living Chains in the Reactor

Chapter 1 - Introduction

1.1 - Motivation

Despite the already massive market for polyolefins (estimated to be 125 million tons in 2011 [1]), their global consumption is expected to grow over the few next years, continuing holding a major portion of the market share of the commodity plastic globally. Due to the expected growth of consumption, there is a need to increase the productivity and space-time yield in existing processes, making them able to have a bigger production to satisfy its consumption.

As it is known, olefin polymerization reactions are highly exothermic, heat removal being one of the main limitations to achieve higher production rates. Gas phase polymerization is even more affected by this, since heat transfer is more difficult in a gas phase due to low heat capacity of gases. Reaction heat can cause an overheating of catalyst particles, which can lead to their quick deactivation [2].

1.2 - Objectives

The main objective of this thesis is to study the impact of changing some reaction conditions that can have an effect on the heat removal and the deactivation of the catalyst. Despite the increase of productivity wanted, it is not possible disregard the morphology and properties of the produced polymer.

Thus, in this thesis, will not only compare instantaneous rate of polymerization changing each parameter at a time, leaving the remaining constant, but also how does it affect the molecular weight distribution, crystallinity, melting point, polymer surface and bulk density.

1.3 - Thesis Outline

For a better understanding of the work done, this thesis is organized in six sections.

A first chapter is a bibliographic review that covers what is polypropylene, for what is it used and how is it made industrially.

A second chapter explaining the experimental procedures done, including all equipment and techniques used.

A third chapter divided in two parts: kinetic results obtained in each run and the analysis of the produced powders. In the first part, a general comparison in terms of activity is made for all the runs performed. In the second part, the results of the analysis performed for each powder and correlation between polymerization conditions and properties is made.

A fourth chapter presenting the conclusions withdrawn from the work done and some perspectives for future work in this field.

And finally, a fifth and sixth chapter presenting references and appendices, respectively, in order to obtain a fully comprehension of this work.

Chapter 2 - State of the Art

2.1 - Polymer Materials

2.1.1) Polyolefins

Polyolefins are one of the most important commodity plastics nowadays, thanks to their low production costs, low environmental impact and a wide range of properties that make them suitable for several applications [3].

They can be produced in practically all types of reactors, such as autoclaves, tubular reactors, loop reactors, fluidized-bed reactors, and either in gas or liquid phase processes.

Among polyolefins, polyethylene (PE) is the most produced polymer and is generally classified in three different types: high density polyethylene (HDPE), firstly produced with Ziegler-Natta catalysts, linear low density polyethylene (LLDPE), a copolymer of ethylene and α-olefins, and low density polyethylene (LDPE), obtained by free-radical polymerization.

Polypropylene is the second most important polyolefin, with 40% of the 113 million tons of polyolefins consumed in 2009 [4], as shown in Figure 1.

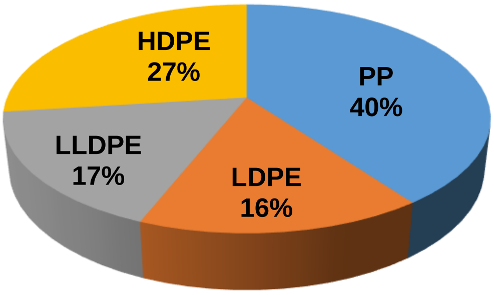

Figure 1 – Distribution of global polyolefin consumption in 2009.[4]

2.1.2) Polypropylene (PP)

Polypropylene is a thermoplastic material formed by the polymerization of propylene, resulting in a polymer that typically contains from one to ten thousand monomer units. It is a colourless, translucent to transparent solid, with an extreme resistance to chemicals (except for some chloride compounds or some hydrocarbons). It also has a higher scratch resistance than other polyolefins and a good processability via injection molding and extrusion [5].

Unlike ethylene, a symmetrical molecule, the way the molecules of propylene link between them leads to different stereochemical configurations (figure 2). These characteristics can be summarized in the following way:

- Isotactic Polypropylene (i-PP): All the methyl groups are located on the same side of molecular backbone. PP produced by ZN catalysts in an isotactic polymer. Since it is difficult to completely control the polymerization reaction, isotactic PP frequently presents atactic content. The lower atactic content, the higher the stiffness which provides a wider spectrum of applications;
- Syndiotactic Polypropylene (s-PP): The methyl groups have an alternate position along the chain. It can be produced only with some metallocene catalysts;
- Atactic Polypropylene (a-PP): The methyl groups are attached in a random manner on the polymer backbone chain. This results in a waxy and tacky solid at room temperature.

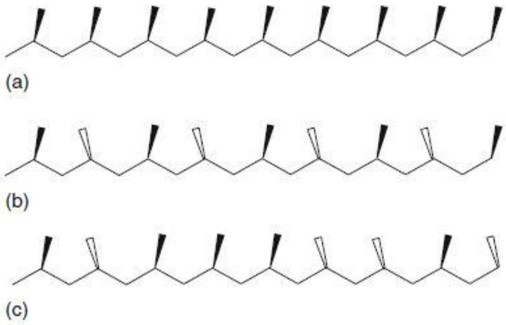

Figure 2 - Main propylene structures: (a) isotactic, (b) syndiotactic and (c) atactic.

Isotactic polypropylene dominates the market because it is easily produced with heterogeneous ZN and metallocene catalysts. In addition, it shows easier processing behavior and better mechanical properties. Syndiotactic polypropylene shows a slower crystallization rate and due to a small range of catalysts that can produce it, it is commercially almost nonexistent [6].

The discovery of how to make polypropylene homopolymer was attributed to the work of Karl Ziegler and Giulio Natta, in 1954. The organometallic catalytic system used was then named after these two scientists as Ziegler-Natta catalysts. Ziegler prepared the $TiCl_3$ catalyst which was capable of producing PE, but also atactic PP. Natta was able to modify Ziegler's catalyst to produce isotactic polypropylene and attributed the variation of melting point of the polymer produced with the distribution of the methyl groups along the carbon chain.

Ziegler-Natta catalysts produce polymers with high region-regularity, favoring 1-2 insertions and head-to-tail enchainment. The presence of 2 - 1 regio-insertion errors will affect the melting point and the crystallinity of the polymer, as shown in figure 3, as well as the activity since these can also block active sites. With metallocene catalysts, it is possible to produce polypropylene with high isotacticity but lower regioregularity, responsible for their lower melting point compared to PP made with a ZN catalyst [7].

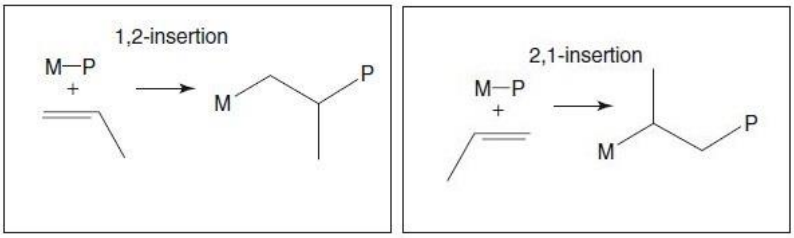

Figure 3 – Regioregularity in polypropylene polymerization.

Polypropylene can be produced in two different types, taking into account its composition, being 60% of its production as a homopolymer and the remaining as a co-polymer.

Within co-polymers, the most produced are impact co-polymers (ICP) and random co-polymers (RCP). It can be produced as a high impact polymer, being high impact polypropylene one of the most important, where the polypropylene acts like the matrix phase and the ethylene-propylene rubber is the dispersed phase. This rubber can absorb a lot more impact, making the polypropylene highly resistant to impact. It can also be produced as a random copolymer by polymerizing certain levels of ethylene with propylene and where the ethylene is randomly incorporated in the polymer chain.

Due to its remarkable properties, it is suitable for several applications, such as film for packaging and into fibers for carpets and clothing. It is also used for injection molded articles ranging from car bumpers to washing up bowls, and can be extruded into pipe [8]. The distribution of applications of propylene is shown in Figure 4.

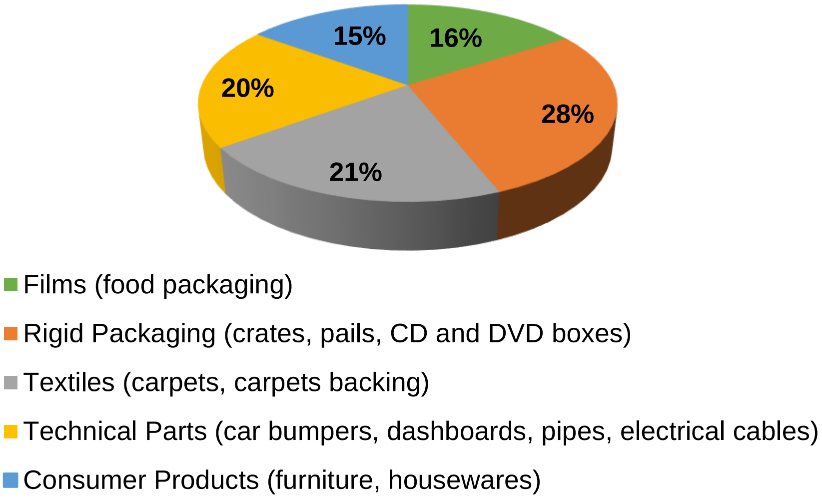

Figure 4 - Distribution of applications of propylene and respective percentages.

2.1.3) High Impact Polypropylene (hiPP)

High impact polypropylene is a homopolymer matrix reinforced by an elastomeric phase, and it is usually produced in at least two reactors in series with heterogeneous ZN catalysts or supported metallocenes. In the first one occurs the homopolymerization of propylene to produce an isotactic matrix that is introduced in the second reactor. A mixture of ethylene and propylene is then injected in this reactor, to produce an ethylene/propylene rubber (EPR) (about 50:50 molar incorporation of ethylene and propylene).

It has two distinguished and immiscible phases: a continuous and rigid homopolymer and a copolymer dispersed phase. The copolymer phase is amorphous or has very low crystallinity and absorbs the energy of the impact and dissipates it. The quantity of rubber introduced in the second step of hiPP production will change the properties of the copolymer produced. A higher amount of rubber, leads to higher impact resistance, but lower the stiffness [9].

Impact resistance is a very important property in several applications and it is important to understand the relation between structure, morphology and deformation phenomena in order to develop polymeric systems with the required mechanical properties [10].

2.2 - Polymerization Catalysts

In polyolefins polymerization, there are four main types of catalysts: Ziegler-Natta, Phillips, Metallocenes and Late Transition Metal. Each catalyst is used depending on the type of polymer that needs to be produced.

2.2.1) Ziegler-Natta Catalysts

Ziegler-Natta catalysts are composed of a transition metal salt of metals from groups IV to VII and a metal alkyl of a base metal from groups I to III. The cocatalysts can be an alkyl aluminum compound such as trimethyl aluminum, triethyl aluminum and diethyl aluminum chloride. There are two broad classes of Ziegler–Natta catalysts: heterogeneous or homogeneous. This catalyst is used to produce polyethylene and polypropylene with high isotactic content.

In figure 4, it is possible to observe that the alkyl aluminum provides one of its alkyl groups, leaving the titanium still with an empty orbital [11].

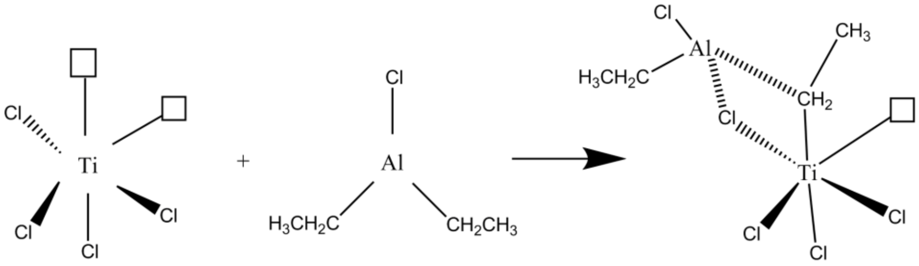

Figure 5 – Activation of catalyst with alkyl aluminum (DEAC).

Secondly, in figure 5 shows the insertion of a propylene molecule into the active site, forming a complex, with an intricate nature.

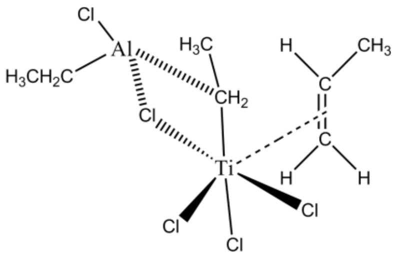

Figure 6 - Insertion of propylene in the active site of the catalyst.

After some electron changing, in figure 7, the active site is capable of having another propylene molecule to continue the chain growth.

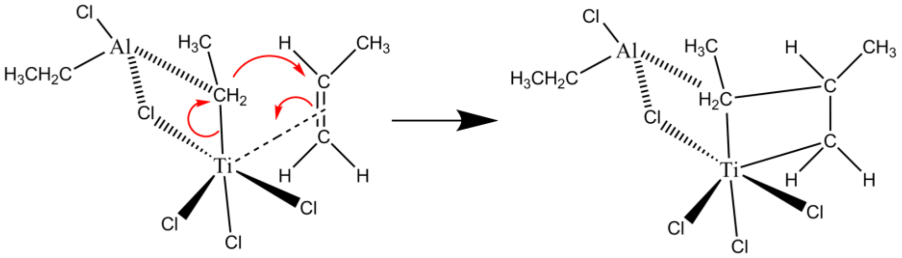

Figure 7 - Electron change to form the first monomer of the polymer chain.

After a process called migration, the aluminum is now complexed with one of the carbon atoms from the propylene monomer and the titanium atom is back where it started, with empty orbital, needing electrons to fill it, which happens when another propylene molecule enters in the active site.

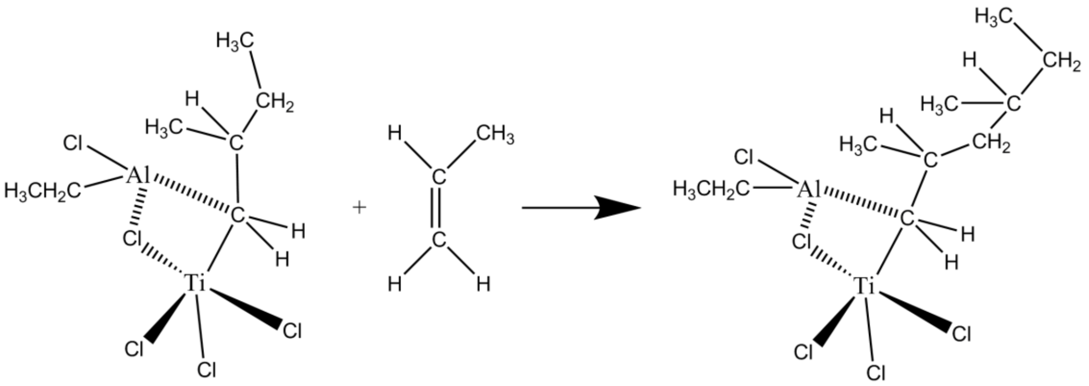

Figure 8 - Insertion of a second molecule of propylene in the catalyst active site.

Ziegler-Natta catalysts have been more and more improved to match the increasing need of higher amount of polymers and also with more challenging properties. It is possible to classify Ziegler-Natta catalysts in four generations:

- 1st generation: $TiCl_3$ activated with DEAC, with yields between 2 to 4 kg of polypropylene per gram of catalyst and an atactic content between 6 and 10%;
- 2nd generation: modification of $TiCl_3$ with donors to increase catalyst stereo-selectivity, increasing yields 5 times and reducing the atactic content to 3 - 6%;

- 3rd generation: development of $MgCl_2$ as a support for $TiCl_4$ and use of internal and external donors to increase stereoselectivity, with yields between 15 to 30 kg of polypropylene per gram of catalyst and an atactic content between 3 to 5%;
- 4th generation: development of catalysts with controlled morphology that in mixed-phase processes reach a yield of 100 kg of polypropylene per gram of catalyst and an atactic content lower than 2%.

2.2.2) Phillips Catalysts

Phillips catalysts, discovered in 1951 by Paul Hogan and Robert Ban, are prepared by adsorption of a chromium compound, mostly chromium trioxide, onto an amorphous silica support and subsequent reduction by exposure to ethylene. This type of catalyst is used to produce high-density polyethylene with particularly high molar mass and do not polymerize propylene [12].

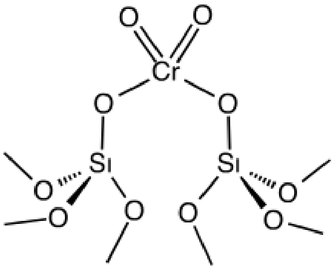

Figure 9 - Structure proposed for the Phillips catalyst.

2.2.3) Metallocene Catalysts

Metallocene catalysts started being used for polyolefin production after Kaminsky and Sinn discover that methylaluminoxane (MAO) could be used to activate and stabilize metallocene catalysts. Until this discovery, metallocenes were activated with a common alkyl aluminum compound, resulting in very small polymerization rates and quick deactivation. They are composed of a transition metal atom between two cyclopentadienyl or a derivate of it rings, that can or cannot be connected through bridges of different types [12].

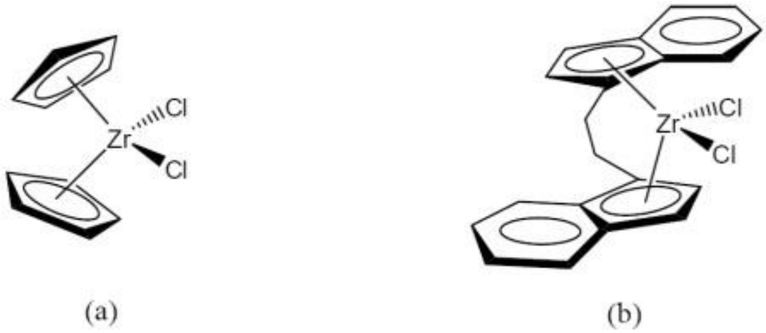

Figure 10 - Example of metallocene catalysts: (a) Cp_2ZrCl_2; (b) rac-$Et(Ind)_2ZrCl_2$.

Polyolefins produced using metallocene catalysts have very good mechanical properties because of their narrow molecular weight distribution, but their narrow MWDs also make them more difficult to process than those produced with Ziegler–Natta and Phillips catalysts with similar melt indices and densities.

Another important characteristic of metallocene is that their stereoselectivity is determined by their ligand configuration, which makes possible to produce atactic, isotactic and syndiotactic polypropylene.

2.2.4) Late Transition Metal Catalysts

Late Transition Metal catalysts were discovered in 1990s and since they are less oxophilic than other polymerization catalysts, they allow the copolymerization of olefins and polar co-monomers. [12]

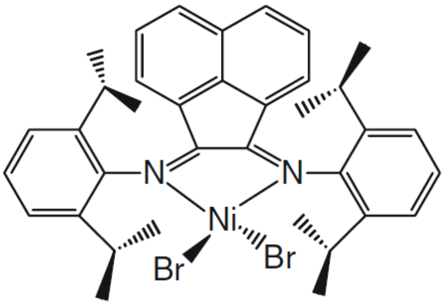

Figure 11 - A Ni-diimine late transition metal catalyst.

2.3 - Production Processes

Processes for polypropylene production need to be able to provide a wide range of products, such as polypropylene with a specific molecular weight distributions, random ethylene/propylene copolymers and heterophasic impact copolymers. Despite propylene homopolymer can be produced in several reactor configurations, the only reactor where is possible to produce impact co-polymer is a gas-phase reactor, due to the solubility of propylene/ethylene rubber phase in the monomer and diluent.

Looking at the existing manufacture processes, it is possible to divide them in three types: slurry (inert diluent), gas-phase processes and mixed-phase [13], being the reaction media the main difference between them. In slurry processes it was normally used a diluent between C_6 to C_{12} hydrocarbons, while in gas-phase it is made in an gas inert atmosphere. In mixed-phase processes, polymerization takes place in liquid propylene, without being necessary the use of an inert diluent.

Since polymerization reaction is extremely exothermic, one of the major problems is heat removal. This makes necessary the use of techniques such as condensed mode, where the vaporization of a liquid or a condensed gas is used to absorb reaction heat, improving heat removal and polymerization itself.

2.3.1) Slurry (Inert Diluent) Processes

Slurry was the first commercial process for polypropylene's production and comprises a series of stirred autoclaves and used a heterogeneous catalyst suspended in an inert diluent. Due to the low catalyst activity, it was necessary a series of reactors to complete the reaction.

Thanks to the number of equipment used in this type of process, it is expensive to build and to operate, therefore it has been replaced by more efficient processes, like gas-phase or mixed-phase. For environmental reasons all processes which run in slurry mode, now use liquid propylene as the continuous phase (mixed-phase processes) [14].

2.3.2) Gas-Phase Processes

Within the gas-phase processes, it is possible to distinguish several different technologies, with different reactor configurations, having each one its own advantages and disadvantages.

The *Unipol* process from *DOW Chemical Company* consists of a large fluidized bed gas-phase reactor, for homopolymer and random copolymer production. In this case it can be used in condensed mode operation, without being necessary an inert diluent because propylene with traces of inert propane is partially fed as a liquid. The second reactor is smaller for two reasons: firstly, not all of the content from the first reactor is used for copolymerization and secondly copolymerization is much faster than homopolymerization. This reactor has a lower pressure rating since copolymerization is carried out at lower pressures and temperatures. Since there is just one homopolymerization reactor, it limits the control that can be exerted over the molecular weight distribution.

Unipol offers several unique advantages being one of the most significant of these the high production capacity from a single line. Thanks to the development of catalysts and advances in process and operating know-how, *Unipol* plants can be designed to produce up to 550 kton per year. [14], [15], [16]

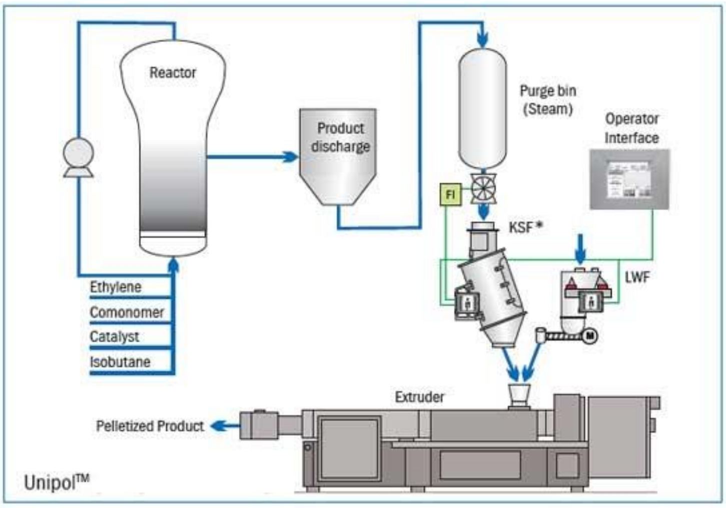

Figure 12 – Scheme of Unipol technology.

To enlarge the control over the MWD, the *Sumitomo* process employs two or three FBRs in series, which make possible the narrowing of residence time distribution of the particles, producing a more uniform product [14], [17].

The *Novolen* process from *Lummus Technology* (originally developed by *BASF*) uses two vertical stirred bed reactors that can be operated in two ways: in cascade, to make impact copolymer or in parallel to produce homopolymers and random copolymers [14], [18].

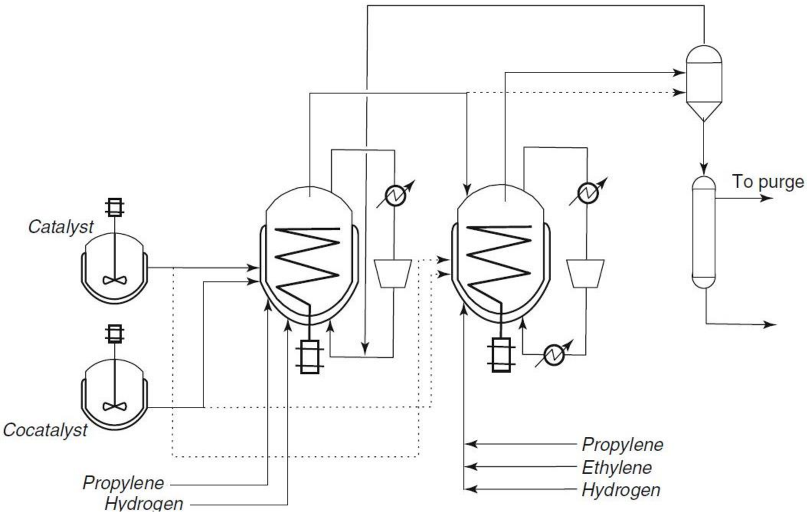

Figure 13 - Process flow diagram of the Novolen process.

The *Horizone* (*Japan Propylene Corporation*) and *Innovene* (*INEOS*) process consist both of horizontal stirred bed reactors (HSBR), with some differences between them. The *Horizone* process has the two reactors arranged one above the other, using gravity to transport polymer particles from the first to the second reactor, while in the *Innovene* process the two reactors are at the same level, being necessary a powder transfer system. Such as in *Novolen* process, both of these processes can be operated in cascade or in parallel depending on the polymer that needs to be produced [14], [19].

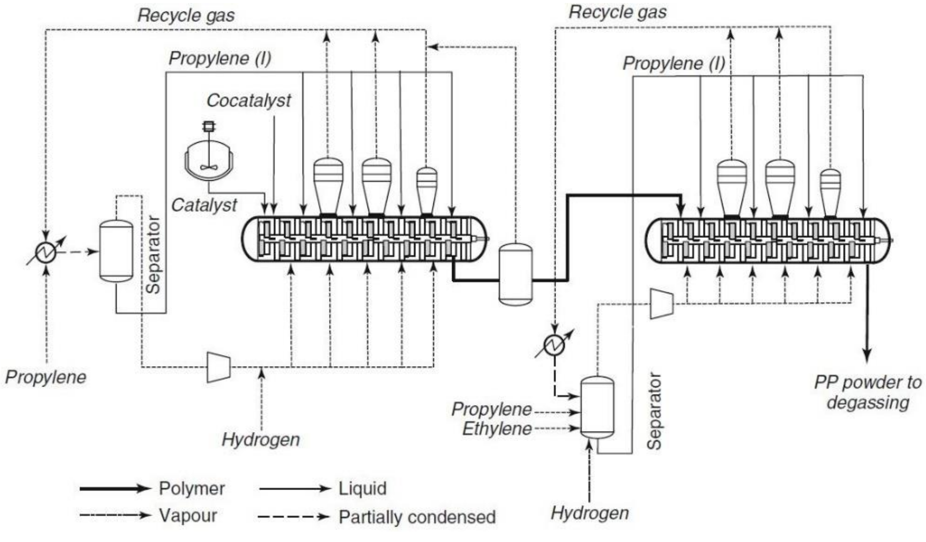

Figure 14 - Process flow diagram of Innovene and Horizone process.

A comparison between gas-phase technologies is shown in Table 1.

Table 1 – Comparison between gas-phase technologies [14].

Technology	***Unipol***	***Sumitomo***	***Novolen***	***Innovene/ Horizone***
Temperature (ºC)	60 - 70	50 - 80	80 - 85	65 - 85
Pressure (bar)	25 - 30	~ 10	30 - 35	25 – 30
Co-polymer production	Yes	Yes	Yes	Yes
Investment to build and to operate	Low	High	High	High
Control over MWD	Low	High	High	High
Uniformity of produced polymer	No	Yes	Yes	Yes
Production capacity	High	Low	High	High

2.3.3) Mixed-Phase Processes

This kind of process is typically to produce high impact polypropylene. In this case, the homopolymerization takes place in liquid propylene, either to the production of homopolymer or of random copolymer, while to produce the EPR phase for hiPP is used a gas-phase reactor. The rate of reaction and productivity is much higher, since the reaction media is liquid monomer, but typically this kind of process uses at least two well back-mixed reactors in series to control the MWD, composition and reaction rate. There are three major mixed-phase technologies: *Spheripol, Mitsui* and *Borstar*.

The *Spheripol* technology by *Basell* can use from one to three loops followed by one to three FBR’s, and also a small loop reactor that is used to prepolymerize the catalyst. Since the solubility of ethylene in liquid propylene is limited, it is necessary a flash operation between liquid and gas section of the reactors in order to remove hydrogen and to make sure that the powder is as dry as possible, for a better impact copolymer production. Almost one-third of propylene production globally uses this technology [20].

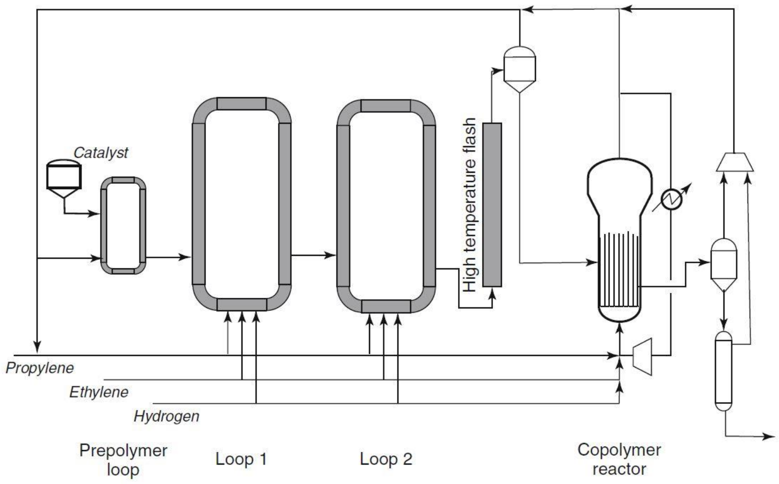

Figure 15 - Process flow diagram of Spheripol process.

The *Mitsui Hypol* process by *Mitsui Chemical Inc*. is based on two stirred autoclave reactors instead of loop reactors as in the previous process, followed by two stirred fluidized bed gas-phase reactors. In *Hypol II* process, stirred autoclaves were replaced by loop reactors, not just reducing capital costs, but also to improve heat transfer and increase production capacity [21].

The third technology is *Borealis* with *Borstar* propylene process where there is a prepolymerizer loop (because of the high catalytic activity) followed by a main polymerization loop and a FBR. The continuous medium in loop reactors is propylene and reaction conditions can be changed so that propylene is either sub or supercritical, avoiding the formation of gas bubbles in the continuous phase [22].

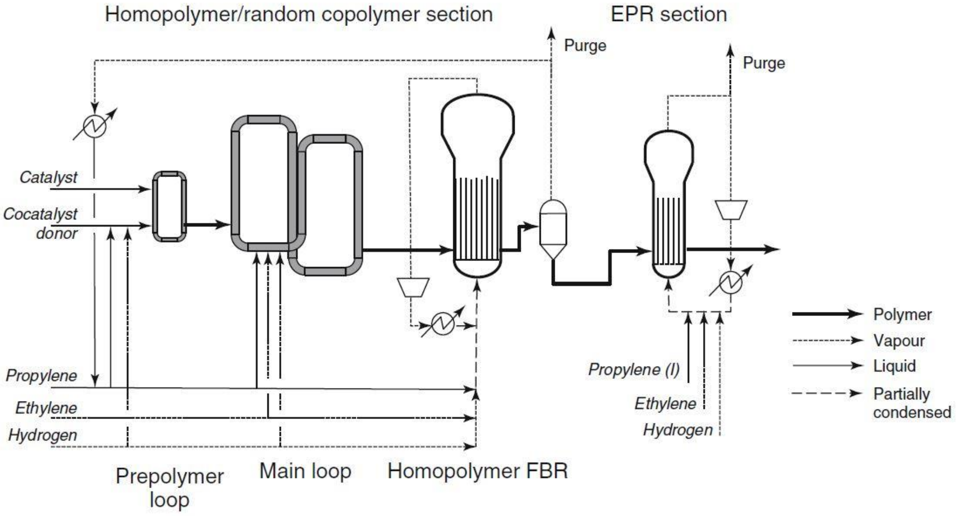

Figure 16 - Process flow diagram of Borstar process.

In mixed-phase processes, stirred autoclaves are being replaced for loop reactors, due to a better heat transfer capacity and thus higher productivity. However, the investment necessary for these plants is high, and grade changes and process stability can be a problem.

In conclusion mixed-phase processes are the dominant kind of process used for polypropylene production, accounting with 58% of the installed capacity, while slurry only have 7% [13].

2.4 - Reaction Conditions

As it is known, polymerization reactions can be performed under a wide range of experimental conditions. In this study, the main objective is to understand the impact of changing some of these conditions in order to maximise the polymerization rate and increase productivity. In the next topics are described the known effect of some of these conditions.

2.4.1) Effect of Prepolymerization

It has already been discussed that performing a prepolymerization step before the main polymerization reaction can significantly help to control the growth of the polymer particle and avoiding the overheating of the particles during the initial reaction times, when catalyst is highly active [23], [24].

At the beginning of the polymerization reaction, high catalytic activity can lead to a rapid temperature increase in the catalyst particle. Because of the low surface area and difficult heat transfer between the particle and the reaction environment, a quick deactivation of the catalyst can occur. Using a prepolymerization step before the polymerization itself, the catalyst surface area gradually increases at a low reaction rate, which improves the heat transfer and leads to a better replication of the catalyst particles.

The prepolymerization must occur at mild conditions, which allows the crystal fragments to be separated and covered by a thin layer of prepolymer. These mild conditions are responsible for the production of the regular fragments’ size and better replication of the catalyst shape.

There are two main methods for the prepolymerization of olefins using ZN catalysts: isothermal prepolymerization (IPP) and non-isothermal prepolymerization (NIPP).[24] The isothermal prepolymerization occurs for a certain time at the same conditions. When the prepolymerization step is finished, temperature of the reactor is set for the polymerization value. The non-isothermal prepolymerization starts at a certain value and then is gradually increased until it reaches the polymerization temperature. In the first there is the advantage of independency between the prepolymerization temperature and some polymer properties. The second one has a disadvantage of shocking the catalyst at high conditions by the rapid rate of changing. There is also a possibility of combine this two techniques, opting by starting the isothermal prepolymerization and after a certain time gradually rise the temperature to the normal polymerization conditions [24].

2.4.2) Injection of Hydrogen

Another important aspect in olefin polymerization is the effect of hydrogen in the reaction medium because it plays a decisive role in the way the reaction proceeds. Mori et al. studied the effect of hydrogen in slurry polymerization and concluded that it acts as a chain transfer agent, regulating the molar mass [25].

As it was said in section 2.1.2, Ziegler-Natta catalysts produce polymers with high regioregularity, favoring 1-2 insertions and head-to-tail enchainment (figure 3). If the insertion of the monomer is from 2-1 or with other enchainment [7], the incorrectly inserted propylene will cause the chain to block the active site, leaving it inactive. By the formation of the metal hydride bond after a secondary insertion of a propylene polymerization into the growing polymer chain, the site will be reactivated, being the hydrogen then expelled by a new propylene molecule to produce another polymer chain.

2.4.3) Type of Injection

This factor is especially crucial in the first moments of the life of a catalyst particle freshly injected into a polymerization reactor, especially in the case of 4th generation Ziegler-Natta catalysts that have a tendency to activate rapidly. The initial instants are extremely important, since what happens during this period will influence the particle morphology, reaction rate and the molecular properties of the final product.

Several patents [26] show that adding a small amount of hydrocarbon to the catalyst prior to its injection in the reactor can help polymer production. The liquid hydrocarbon can fill the catalyst's pores, slowing the diffusion of monomer to the active sites, acting like the prepolymerization step in each pore of the catalyst. After some moments of reaction, this liquid either evaporates or is displaced from the pores, which enables the monomer to enter freely in the active sites.

Wetting the precatalyst prior to its injection, helps reducing local particle overheating significantly, through the resistance offered by the hydrocarbon to the diffusion of the monomer until the active sites.

2.4.4) Presence of an alkane

The use of alkanes during olefins polymerization is becoming more and more used. Since one of the major limitations in olefin polymerization reaction is its high exothermicity, the use of techniques such as condensed mode cooling is becoming more important.

An induced condensing agent (ICA) is a saturated alkane normally between 4 and 6 carbon atoms in its structure, introduced in the beginning of olefin polymerization. Using this type of approach it is possible to increase the rate of heat removal in polyolefin processes. By the vaporization of the liquid alkane, a high amount of heat can be removed thanks to its latent heat of vaporization.

In ethylene polymerization, Alizadeh et al. observed that the instantaneous rate of ethylene polymerization is promoted when a higher amount of ICA is introduced [27]. The presence of a vaporized alkane can modify the way the reaction proceeds. This is caused by the co-solubility effect: the presence of an alkane will provoke an increase of the solubility of ethylene, boosting its concentration inside the active sites of the catalyst, increasing the reaction rate. It is also true that more the ICA is soluble in the polymer, greater is the observed effect.

Being the alkane soluble in the polymer, it will diffuse in its pores and thanks to a bigger molecular chain of the alkane (when compared to propylene), it will provoke a swelling of these amorphous phase. With the swelling of the amorphous phase, the diffusivity of propylene also increases. The co-solubility effect and the increased diffusivity mean that propylene concentration is higher at the active sites.

In propylene polymerization, the propylene is fed partially liquid and by its vaporization it will remove the reaction heat itself, not being necessary a different induced condensing agent to remove heat. On the other hand, the presence of an alkane will affect the activity, increasing it by the enhancement of local concentration of propylene inside the active sites.

2.5) Polymerization Kinetics

Propylene polymerization is a well-known subject that has been being studied for several years, keeping up with the developments in catalysts, co-catalysts and other components that improve productivity and polymer morphology.

Alshaiban studied the effect of changing the external donor and the quantity of hydrogen in the kinetics and microstructure of the produced polymer [28]. In this work, it was used a 4th generation Ziegler-Natta catalyst, in a solution of dry n-hexane, using as co-catalyst tryethyl aluminum and DCPDMS as external donor. Despite some differences to the current work, like the Al/Ti ratio about 5 times higher and a Si/Ti ratio 7 times lower or a temperature of 60ºC instead of 70, it is possible to make some comparison to the kinetic parameters calculated in chapter 4.

Table 2 shows the experimental conditions used in this work and table 3 the activation energies and pre-exponential constants for site activation, propagation and deactivation, for a group of experiments. Using the activation energies and pre-exponential constants and applying Arrhenius equation, it is possible to obtain the respective kinetic constants.

Table 2 – Experimental conditions used in Alshaiban work.

Pressure (bar)	5 to 6
Temperature (ºC)	60
Al/Ti ratio	900
Si/Ti ratio	0 to 1,4
H_2 pressure (bar)	0 to 1,1 bar
Catalyst injection	With heptane

Table 3 - Activation energies and pre-exponential constants for site activation, propagation and deactivation and calculated kinetic constants.

E_A (kcal mol^{-1})	22,8	22,5	22,2	22,2	21,8
E_P (kcal mol^{-1})	8,1	8,3	8,3	8,4	8,1
E_d (kcal mol^{-1})	31,5	31,4	31,4	31,4	32,5
A_A (s^{-1})	5,00E+12	2,50E+12	2,50E+12	1,67E+12	3,50E+12
A_P (L mol^{-1}s^{-1})	1,17E+07	2,83E+07	1,67E+07	3,00E+07	1,50E+07
A_d (s^{-1})	1,33E+17	1,33E+17	1,33E+17	1,17E+17	1,83E+17
k_A (s^{-1}) at 60ºC	9,2E-03	7,2E-03	1,1E-02	7,5E-03	2,9E-02
k_P (L mol^{-1} s^{-1}) at 60ºC	67,9	122,5	72,0	111,7	87,3
k_d (s^{-1}) at 60ºC	5,8E-04	6,8E-04	6,8E-04	5,9E-04	1,8E-04

Chapter 3 - Experimental Procedure

Since coordination catalysts are quite sensitive to impurities, first it was necessary to get familiar with the experimental setup and all the techniques used, in order to perform them in an inert environment and in a reproducible way.

In the next topics, will be described the reagents, the equipment used and some of their major characteristics and the reaction conditions. Finally, in the last topic, the analytical techniques used for powder characterization of the polymer will be summarily described.

All operations done in this experimental work were done under argon, using standard Schlenk techniques.

3.1 - Chemicals

The precatalyst was a commercial $MgCl_2$ supported $TiCl_4$ fourth generation Ziegler-Natta, with a titanium content of 2.8% and with di-isobutyl phtalate as internal donor. The catalyst had a wide particle size distribution and an average size of about 10,6 µm.

Tryethylaluminum (TEA) used as cocatalyst and scavenger in 1M dilution in heptane was purchased from Witco, Germany. Dicyclopentyl dimethoxy silane (DCPDMS) was used as external electron donor, in 0,42M solution with heptane. The catalyst injection was made in two different ways: Sodium Chloride (Acros Organics France) with purity of 99,5% and mineral oil (OIL PRIMOL 352). TEA (1M, heptane solution) was used in a ratio of Al/Ti equal to 190 and the external electron donor used in a Si/Ti ratio of 10.

The heptane used obtained from Prolabo was firstly purified by a purification system named MB SPS-800 from MBRAUN. The alkane used was iso-hexane from Sigma-Aldrich with a minimum purity 99%, previously degassed frozen under vacuum and then kept under argon.

The salt was previously vacuum-dried during five hours at 200ºC and kept under argon atmosphere at room temperature. The oil was degassed frozen under vacuum and then kept under argon.

The propylene used was obtained from Scott Specialty Gases with a purity of 99,95% and passed through a three stage system of columns (figure 17) before use: a first one filled with BASF R3-16 catalyst (CuO on alumina), a second one filled with molecular sieves (13X, 3 Å, Sigma-Aldrich) and a last one filled with Selexsorb COS (Alcoa). Hydrogen with minimum purity of 99,9% were purchased from Air Liquide (France) and used as received. Argon provided by Air Liquide, France, with minimum purity of 99,5%, was used in order to keep the reaction environment free of oxygen. Heptane, pre-treated on 3 Å molecular sieves, was used for preparation of cocatalyst and external donor solutions.

Figure 17 - Propylene purification columns.

3.2 - Experimental Setup

Gas phase homopolymerizations were done in a 2,5L semi-batch reactor with 7,5 bar of propylene pressure and 2% of H_2, using a Ziegler-Natta catalyst from TOHO company [29]. A scheme of the used reactor can be found in figure 18.

To purify the turbosphere reactor, it was heated up to the desired initial temperature before the reaction started, filled with argon and then kept under vacuum for 30 min. The cycle is repeated three times in order to minimize the quantity of impurities remaining in the reactor.

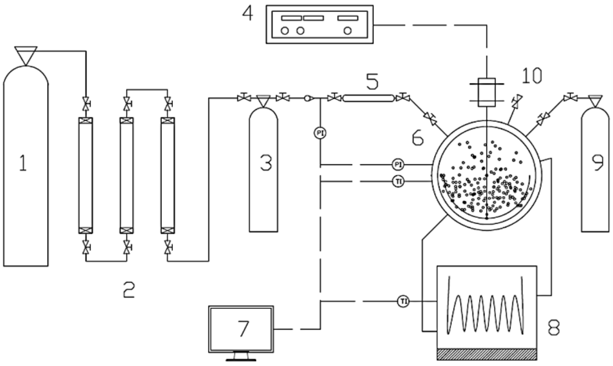

Figure 18 - Scheme of the turbosphere reactor used.

(1: Propylene Reservoir; 2: Propylene Purification Columns; 3: Experimental Propylene Ballast; 4: Reactor Agitation Controller; 5: Catalyst Cartridge Injector; 6: Gas Phase Reactor; 7: Data Processor; 8: Heated Water Bath; 9: Hydrogen Ballast; 10: Liquids Injection Valve)

Figure 19 - Reactor used for propylene polymerization.

Regardless of the method of injection, the precatalyst was prepared in a glovebox (Jacomex, France) under argon atmosphere (figure 20). Oil suspended precatalyst was kept on suspension by permanently agitation, and a micropipette was used to take the required volume and inject it into the turbosphere reactor. For the solid suspension system, precatalyst was diluted with coarse salt in a Schlenk. The precatalyst was not pre-activated before injection in the turbosphere reactor.

Figure 20 – Glovebox used for precatalyst and alkane preparation.

The experiments performed with dry injection were made with 30 mg of ZN catalyst, injected along with 10 g of salt (figure 21). The wet injection was made injecting 250 μL of oil, which cores 15 mg of ZN catalyst (figure 22).

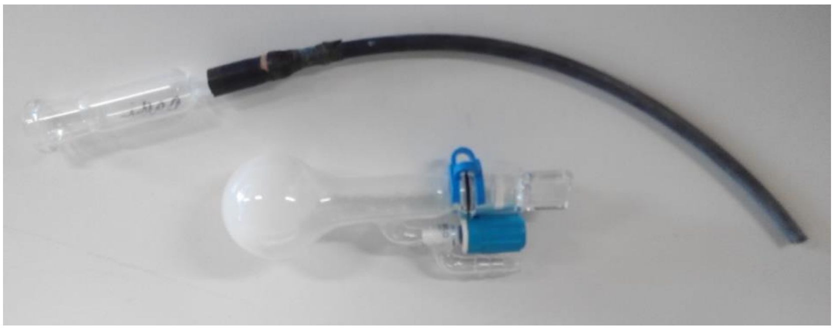

Figure 21 - Schlenk with mixture of catalyst and salt and cup with hose for injection in the reactor.

Figure 22 - Schlenk with mixture of oil and catalyst and micro-pippete for its injection.

3.3 - Polymerization Methods

A prepolymerization is performed as a way to prevent the quick increase of temperature in the catalysts that is believed to cause its deactivation. Before the reaction conditions are established in the reactor, there is a polymerization that occurs at mild conditions, which makes the catalyst surface area gradually increase at a low reaction rate, improving the heat transfer and leading to a controlled growth of prepolymer in the surface of catalyst particles.

To perform this, the temperature of the reactor is set to 40ºC and 3,5 bar of propylene are introduced in it. These conditions were established to make sure that the concentration of propylene was lower in prepolymerization than in the polymerization. The prepolymerization is performed for ten minutes, after this time the temperature is raised to 70ºC gradually. During this non-isothermal prepolymerization the pressure is raised to 6 bar of propylene and the 0,16 bar of hydrogen are introduced in the reactor. When the temperature reaches about 50ºC, the pressure is then raised to 7,5 bar and the homopolymerization begins. The prepolymerization rate profiles are not shown, but the yields were always approximately 200 g of propylene per gram of catalyst.

When there is no need to perform a prepolymerization the reactor is set to the normal polymerization conditions: 7,5 bar, 70ºC.

Once the reaction is finished (normally one hour), the monomer inlet is closed and the reactor is rapidly cooled down and depressurized. Polymer is recovered either directly from the reactor in the mineral oil injection case, either after washing it with demineralized water to dissolve NaCl. In this last case the final powder is then dried for at least one hour at 90 ºC to remove the remaining traces of solvent.

3.4 - Precatalyst Activation

After the system had reached the desired initial temperature, a first injection of TEA/heptane mixture was injected to the reactor and agitation (200 rpm) was started. Subsequently, about 5 minutes after the first injection, a second amount of TEA is introduced, followed by the donor/heptane mixture and the catalyst suspension, injected under an argon stream. Finally the reactor is pressurized with a mixture of monomer-hydrogen in the desired ratio, to start prepolymerization or polymerization depending on the experiment.

Note that propylene polymerizations were performed using 15-30 mg of precatalyst. TEA and DCPDMS amounts were fixed to keep the Al/Ti ratio close to 190 and the Si/Ti ratio close to 10.

3.5 - Injection of alkane

The alkane was injected using a cartridge linked to the reactor (figures 23 and 24) and passing propylene to ensure that all the liquid is inserted in the reactor. The amount of alkane introduced varies from experiment to experiment, as a fraction of the saturation point, calculated as the value of the dew point of the mixture.

Figure 23 - Cartridge used to inject the iso-hexane in the reactor.

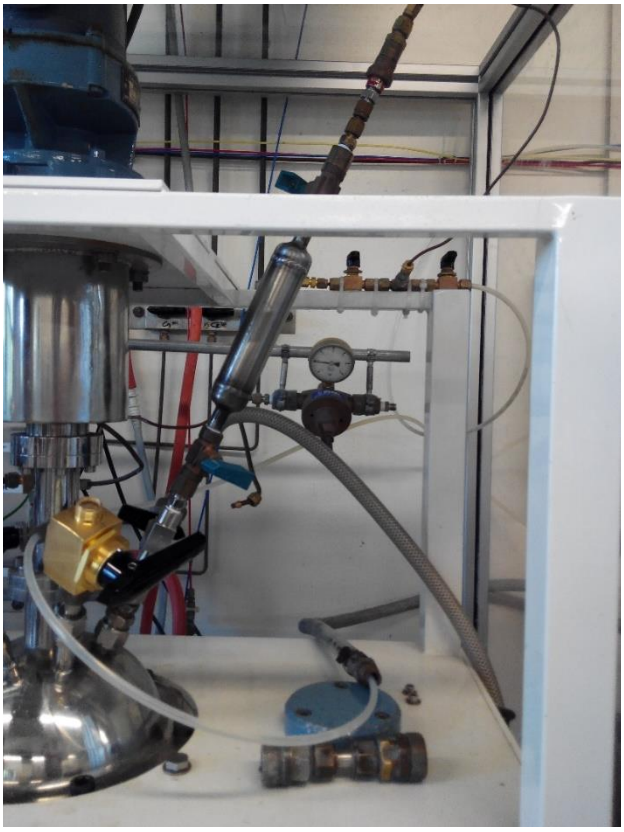

Figure 24 - Cartridge with iso-hexane linked to the reactor.

3.6 - Polymer Analysis

3.6.1) Differential Scanning Calorimetry (DSC)

The crystallinity and melting point was analyzed in a Differential Scanning Calorimeter from Mettler Toledo. During this analysis, each polymer sample is individually cooled from 25 until -80°C (-10°C min^{-1}), it remains at -80°C for 5 minutes, then it is heated to 200°C (10°C min^{-1}) and left at this temperature for 5 minutes, followed by a decrease until -80°C (-10°C min^{-1}) and left for 5 minutes and finally a second heat step to 200°C (10°C min^{-1}).

This temperature sequence allows knowing the crystallinity of the produced powder and the crystallinity after melting it and allowing a slow crystallization process.

To calculate the crystallinity of the analyzed samples, it was used the STARe Software from Malvern. Integrating the area below or above the curves (depending if it is a heating or cooling curve), the value of the fusion enthalpy of the sample is calculated, and also giving the point where the sample melted or crystallized. With the ratio of fusion enthalpy of the sample and the fusion enthalpy for a full crystalline polypropylene (207 J/g), the crystallinity is calculated.

3.6.2) Size Exclusion Chromatography (SEC)

The molecular weight distribution (MWD) is the main polymer property since it has a big influence on its mechanical and rheological properties.

The molecular weight distribution was analyzed in a high temperature size exclusion chromatography equipment, Viscotek system (from Malvern Instruments) equipped with three columns (PPS POLEFIN 1 000 000Å, 100 000Å and 1 000Å). 10 mL of sample solutions with concentrations between of 2-5 $mg.mL^{-1}$ were eluted in 1,2,4-trichlorobenzene using a flow rate of 0,8 $mL.min^{-1}$ at 150°C. The mobile phase was stabilized with butylhydroxyltoluol at 0.2 g/L.

After dissolution, the samples were left heating and agitating for one hour and a half. After this time, each sample was passed by the three columns inside the equipment.

The OmniSEC software was used for data acquisition and data analysis. The molar mass distribution was calculated with a universal calibration curve, due to the high molecular weights of the analyzed samples.

3.6.3) Particle Size Distribution (PSD)

The particle size distribution of the produced polymers was analyzed by laser diffraction using a MasterSizer 3000 from Malvern and using a dry sample dispersion accessory. Each sample was passed in the system at least two times, until reproducible distribution was achieved.

3.6.4) Scanning Electron Microscopy (SEM)

The morphology of the produced polymer particles was observed using a scanning electron microscopy. Particle morphology pictures were recorded using a S800 Hitachi microscope (CTI, UCBL I, France) operating at accelerating voltages of 5 or 10 keV (depending on each case).

3.6.5) Bulk Density

The bulk density was determined using a defined volume of propylene that is weighted. The recipient was firstly filled with water and weighted to know its exact volume. The bulk density is indicated in gram of polymer per liter.

3.7 – Reaction Conditions

The instantaneous rate of propylene polymerization is calculated from the rate of pressure drop in the propylene feed ballast. To ensure that the results were reproducible, all polymerizations were repeated at least twice under a given set of operating conditions. The list of experiments performed in the current study is summarized in Table 4.

The name of the experiments in generally given by TXX-Y-Z% (except in the case of dry injection) where XX is 40 in case of prepolymerization is performed and 70 if not; Y is the quantity of alkane used in terms of the saturation point used (0, 25, 50, 75 and 100%); and finally, Z is the concentration of hydrogen.

Table 4 - Reaction conditions used in each run.

Run	Prepolymerization	Alkane (bar)	Catalyst Injection	H_2 Conc. (%)
T40-0-2%	YES	0	WET	2
T40-25-2%	YES	0,33	WET	2
T40-50-2%	YES	0,67	WET	2
T40-75-2%	YES	1,00	WET	2
T40-100-2%	YES	1,33	WET	2
T70-0-2%	NO	0	WET	2
T70-25-2%	NO	0,33	WET	2
T70-50-2%	NO	0,67	WET	2
T70-75-2%	NO	1,00	WET	2
T70-100-2%	NO	1,33	WET	2
T40-0-0%	YES	0	WET	0
T40-100-0%	YES	1,33	WET	0
T40-0-1%	YES	0	WET	1
T40-100-1%	YES	1,33	WET	1
T40-0-4%	YES	0	WET	4
T40-100-4%	YES	1,33	WET	4
TDry-0-2%	YES	0	DRY	2
TDry-100-2%	YES	1,33	DRY	2

Chapter 4 - Results and Discussion

To start this chapter, first, a small introduction to the calculations made, showing the equations and parameters used. Next, the kinetic profiles obtained are presented and compared between them. And in the end, the results obtained from the analysis done.

4.1 - Calculation Review

4.1.1) Kinetic Equation

In olefin polymerization, for a certain catalyst/cocatalyst system, polymerization kinetics only depends on the concentration of monomers and temperature in the active sites. Although these values may be different from the bulk reactor conditions, in solution processes, it is possible to admit the same values, but not in slurry or gas-phase processes.

The most important reactions are site activation, propagation and catalyst deactivation. Since, according to the fundamental model, chain transfer reactions do not have any effect on the polymerization rate, there is no need to include them in the present treatment [30].

The polymerization rate, R_P (mol·L^{-1}·s^{-1}), is given by equation 1 [30].

$$R_P = -\frac{d[M]}{dt} = k_P[M][Y_0] \tag{1}$$

Where $[M]$ is the monomer concentration inside the active sites, k_P is the propagation constant (L mol^{-1} s^{-1}) and $[Y_0]$ is the total molar concentration of living chains in the reactor.

When performing semi-batch reactions, the polymerization rate can also be described as the ratio between monomer feed flow rate to the reactor, F, and reactor volume, V_R:

$$R_P = \frac{F}{V_R} \tag{2}$$

For practical purposes, $[Y_0]$ is equal to the molar concentration of active sites, since the fraction of polymer outside active sites is negligible. The molar balance for the catalyst precursor added in the beginning of the reaction is given by equation 3 [30].

$$\frac{d[C]}{dt} = -k_a[Al][C] \tag{3}$$

Since the concentration of cocatalyst is present in large excess, it is possible to assume the product between k_a, activation constant (s^{-1}), and $[Al]$, concentration of cocatalyst, to be constant and equal to K_a. With this, it is possible to resolve easily the equation, resulting in equation 4 [30].

$$[C] = [C_0]\exp(-K_a \cdot t) \tag{4}$$

Developing a molar balance for Y_0 and solving it with the initial condition $[Y_0]$(0) =0 it is possible to obtain the next equation [30].

$$\frac{d[Y_0]}{dt} = K_a[C] - k_d[Y_0] = K_a[C_0]e^{-K_a\,t} - k_d[Y_0] \Rightarrow [Y_0] = \frac{1-e^{-K_a\left(1-\frac{k_d}{K_a}\right)}}{\left(1-\frac{k_d}{K_a}\right)}[C_0]e^{-k_d\cdot t} \quad (5)$$

Substituting equation 5 in 1, it is possible to get the expression for olefin polymerization rate that follows first-order deactivation kinetics, where k_d represents the deactivation constant (s^{-1}) [30].

$$R_P = k_P[M]\frac{1-e^{-K_a\left(1-\frac{k_d}{K_a}\right)}}{\left(1-\frac{k_d}{K_a}\right)}[C_0]e^{-k_d\cdot t} \quad (6)$$

The kinetic parameters k_p, K_a and k_d are obtained by fitting experimental monomer consumption curves with the previous equation.

4.1.2) Experimental Data Treatment

During each reaction, is possible to withdraw the evolution of pressure in the monomer ballast with the reaction time. Knowing the pressure value at each time, it is possible to calculate the mass of propylene inside the ballast, using it to calculate the rate of polymerization.

To calculate the mass of propylene inside the ballast was used the Redlich-Kwong [31] equation given by:

$$RT = P(V_m - b) + \frac{a}{V_m(V_m+b)\sqrt{T}}(V_m - b) \quad (7)$$

Where *a* and *b* is respectively given by equations 8 and 9 and depend on the critical pressure, P_c, and critical temperature, T_c.

$$a = 0{,}4275\frac{R^2T_c^{2,5}}{P_c} \quad (8)$$

$$b = 0{,}0867\frac{RT_c}{P_c} \quad (9)$$

In equation 7, T represents the temperature, R is the gas constant in the ideal gas equation, P the pressure inside the ballast at each moment and V_m the molar volume. Knowing that the molar volume, it is easy to calculate the mass of propylene inside the ballast.

With the mass of propylene, it is possible to use equation 10 to calculate the activity.

$$R_P = \frac{m_{n+1}-m_n}{(t_{n+1}-t_n)\cdot m_{catalyst}} \quad (10)$$

Having the activity given by the Redlich-Kwong equation, the kinetic parameters are obtained by fitting it to it.

4.1.2) Data Obtainment

The values of pressure over time can be recorded using *Sirius Stockage* software that collects the data from SPY RF® Wireless System equipment. It results in a profile as can be seen in figure 25, where the grey line represents the pressure inside the ballast and the dark blue the pressure inside the reactor.

It also records temperature values over time, being the light blue line the temperature of the heating water while the red one represents the temperature inside the reactor.

The reaction starts when the temperature inside the reactor is as close as it can be to heating water temperature.

In this experimental work, the values of pressure were recorded manually since the maximum pressure achievable in the ballast was just around 10 bar, which gives a small difference to the working pressure inside the reactor. Since there was a need to often fill the ballast with propylene, the values of pressure over time were recorded manually.

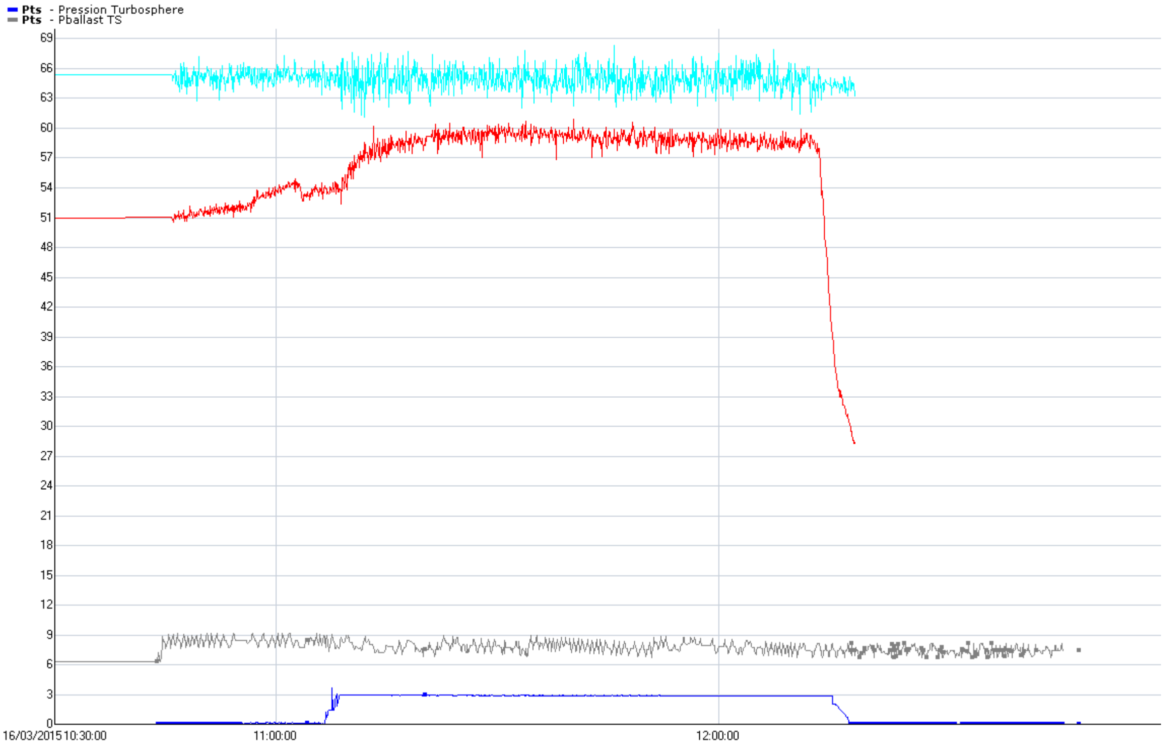

Figure 25 - Temperature and pressure profile obtained using “Sirius, Stockage” software.

4.2 – Treatment and Discussion of the Results

To achieve the results showed in the next topics, it is important to explain that each reaction was at least made twice, in order to ensure that the results obtained were reproducible, as can be seen in figure 26. The fitting of the kinetic profiles, shown next, to the experimental data was confirmed for all reactions and presented in figure 26 to illustrate this. The remaining graphics of the runs performed can be found in appendice B.1.

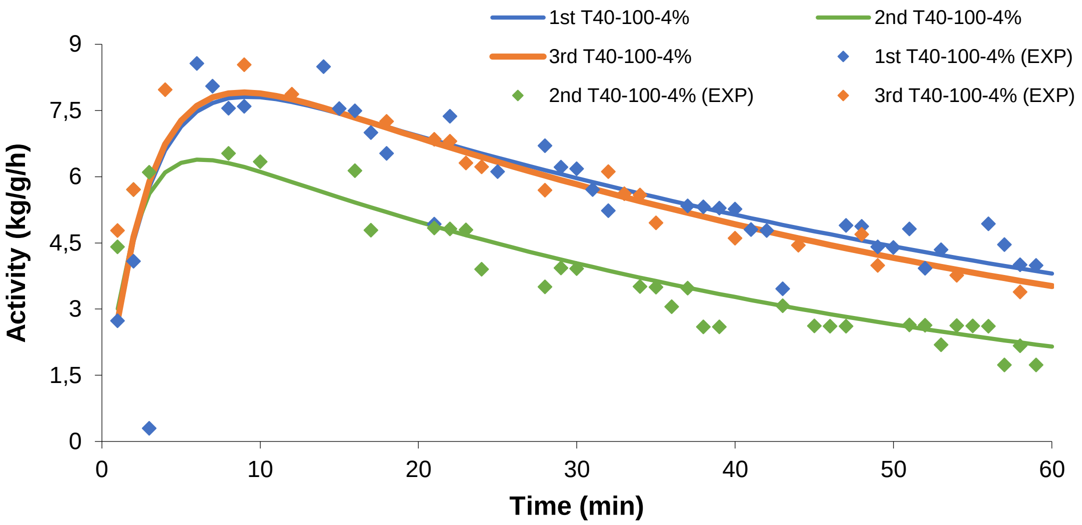

Figure 26 - Experiments representing the achievement of reproducibility.

Since even in reproducible runs exists some deviation between profiles, in the next subchapters, it was chosen to show just one curve, correspondent to the average between the two reproducible runs and the error bars, representing the standard deviation between the two profiles.

<u>4.1.1) Influence of prepolymerization</u>

The effect of a prepolymerization step is shown in figure 27 where it can be seen that over the course of one hour the activity is higher than the one obtained by direct polymerization.

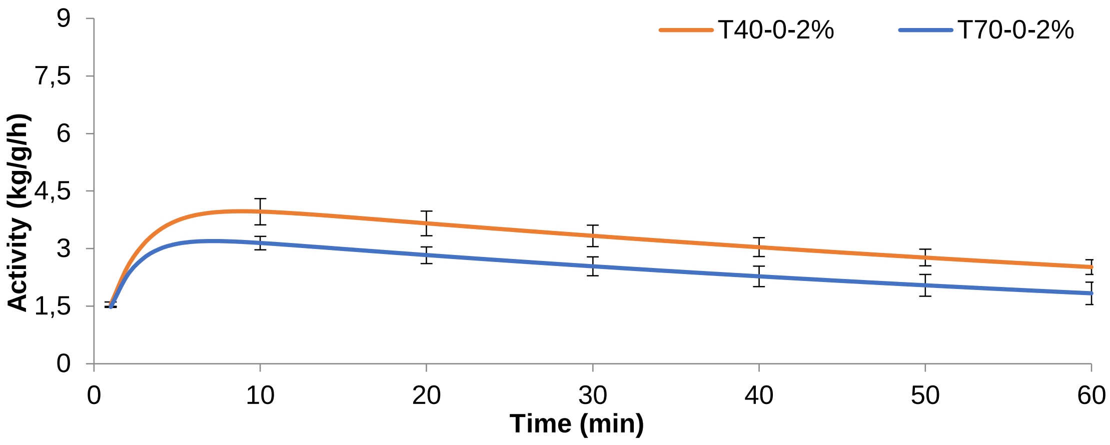

Figure 27 - Kinetic profiles of reactions with and without prepolymerization.

As can be seen above there is a boost in the rate of reaction when prepolymerization is performed which is due to a higher catalytic activity, caused by the gradual increase of the particle surface area at a low reaction rate in the first moments of the polypropylene formation. Since the polymerization rate is slower, the generated heat of reaction is smaller, resulting in less deactivation of the catalyst particles.

4.2.2) Type of catalyst injection

Since the quantity of catalyst injected is in the order of milligrams, its injection has to occur in a suspension media. Two ways of doing it were studied: dry injection and wet injection.

The type of catalyst injection can affect severely the activity of the polymerization reaction and also the morphology of the polymer. As we can see in figure 28, the activity decreases to the lowest values when catalyst injection is made in a dry suspension of salt.

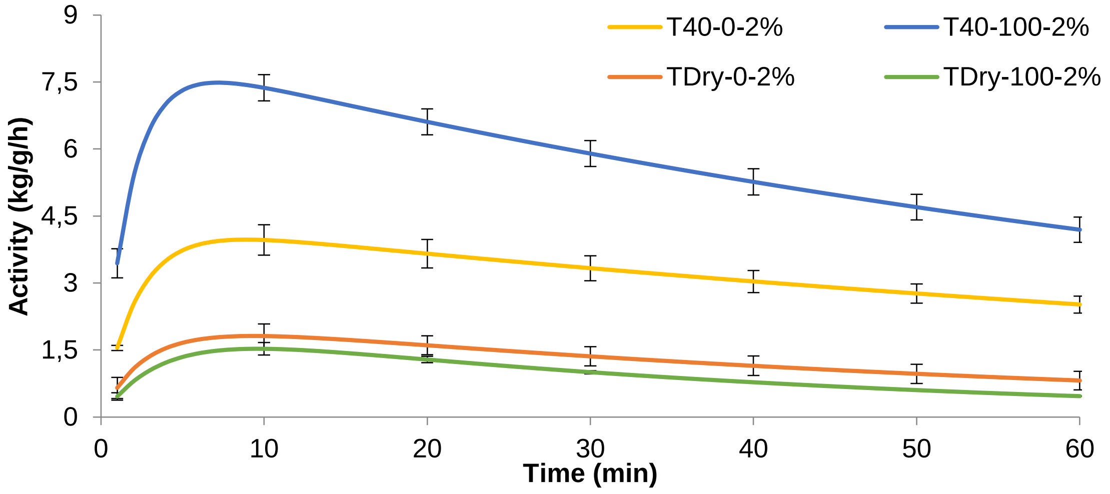

Figure 28 - Kinetic profiles using different types of catalyst injection.

In dry injections there is no resistance to the arrival of monomer to the active sites during the initial instants that follow catalyst injection into the reactor. This most likely provokes a higher initial reaction rate, with its subsequent overheating due to exothermic reaction.

Even when injecting an alkane, the activity does not increase as it was expected. Since the alkane is introduced after the prepolymerization and even with mild conditions during this step, the salt does not have the same capability that oil has to retard the diffusion of monomer into the active sites, resulting in a high amount of heat produced leading consequently to quick catalyst deactivation. There are also some studies which show that adding a small amount of inert liquid hydrocarbon before catalyst injection helps polymer production.

4.2.3) Hydrogen Concentration

Figure 29 and 30 shows the effect of introducing in the reactor different amounts of hydrogen and also how it changes with the introduction of an alkane.

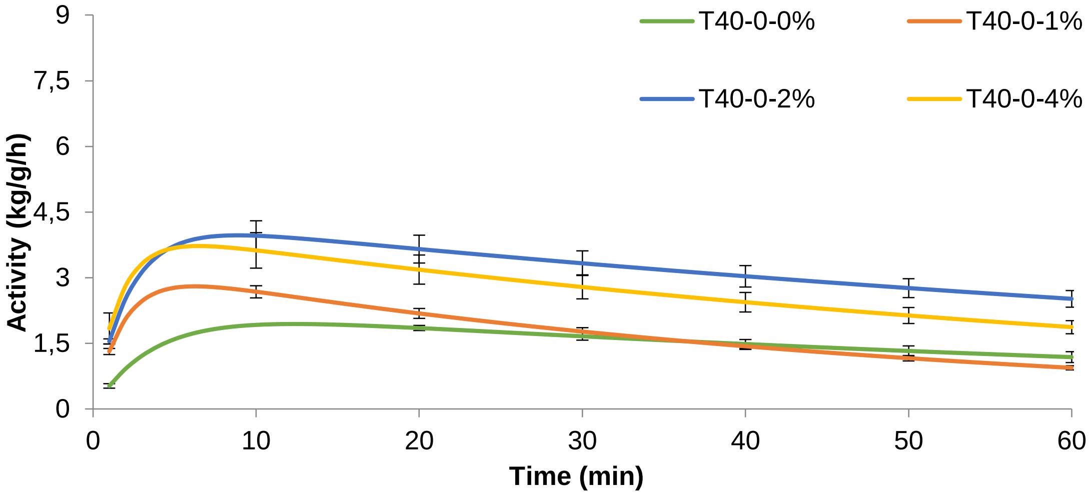

Figure 29 - Kinetic profile using different amounts of H_2 in the absence of alkane.

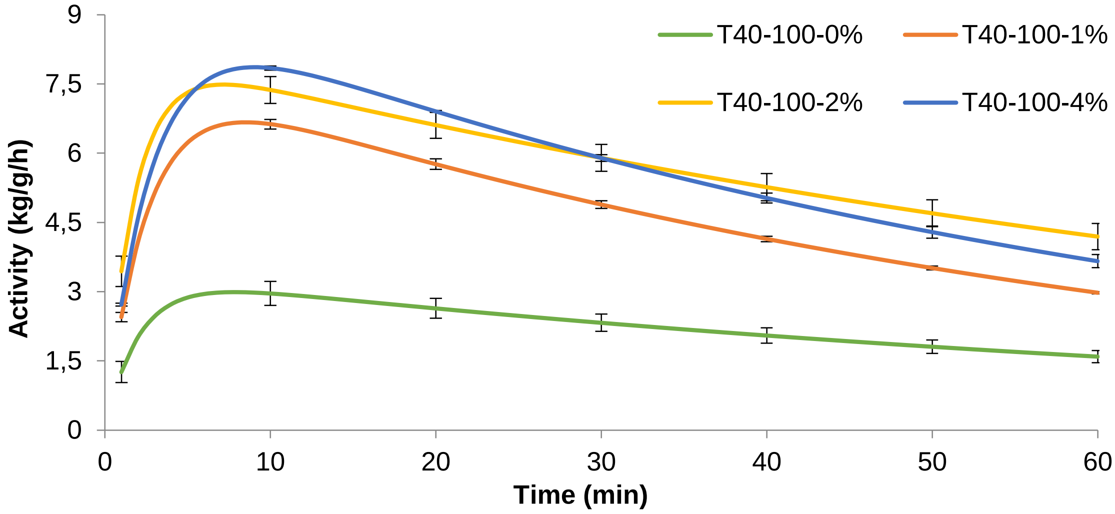

Figure 30 - Kinetic profiles using different amounts of H_2 in the presence of alkane.

Looking at the previous profiles, it is possible to notice the rise of activity with the increasing concentration of hydrogen. As hydrogen has the function of reactivating dormant sites, it is expected that the activity will increase with a higher concentration of H_2. The injection of the alkane amplifies even more this difference, since the alkane does not just enhance the local concentration of propylene inside the active sites but also the concentration of hydrogen, which will boost the activation of dormant sites.

After 2% hydrogen, reaction activity does not change significantly with the increase of hydrogen concentration. This conclusion is supported in both cases, with alkane injection or without. One experiment was also performed with 10% H_2 resulting in no activity.

4.2.4) Presence of alkanes

The quantity of alkane introduced in the reactor was calculated in order to achieve the dew point of the mixture. After knowing that value, experiments were done using fractions of it, like 25, 50, 75 and 100%. In figure 31 and 32 it is possible to analyze the influence of feeding different amounts of alkane to the reactor and the differences with and without the performance of a prepolymerization step.

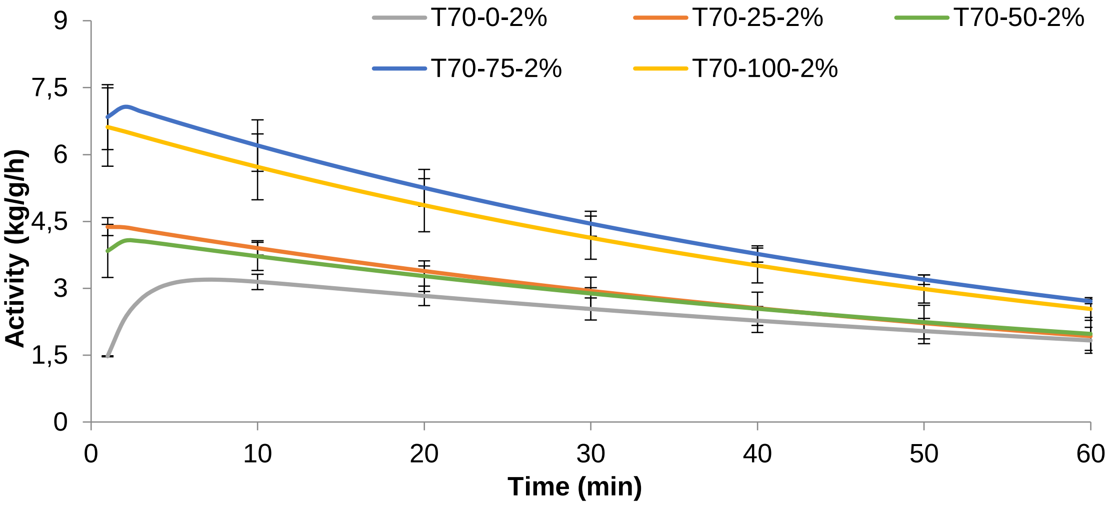

Figure 31 - Kinetic profiles using different amounts of alkane without prepolymerization.

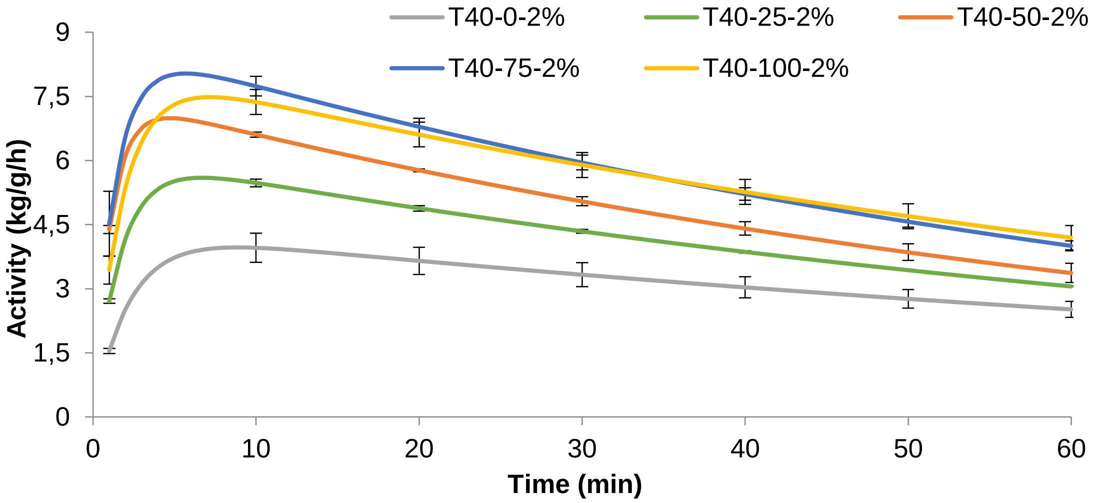

Figure 32 - Kinetic profiles using different amounts of alkane with prepolymerization.

It is possible to conclude from the previous figures that the activity rate increases with the amount of alkane introduced in the reactor. This is due to two main reasons: heat removal and co-solubility effect. The injection of a liquid compound in the reactor can increase the amount of heat removal in polyolefins processes, since it can absorb heat thanks to its latent heat of vaporization. In other hand the co-solubility effect is another reason for the increase of activity. The presence of an alkane increases the solubility of smaller molecules inside the active sites of the catalyst. In other words, the presence of an alkane can enhance the local concentration of propylene inside the active sites of the catalyst, resulting in a higher reaction activity.

Comparing profiles with the different amount of alkane it is possible to conclude that the introduction of 75% of the quantity of the dew point seems to lead to same kinetic profile as the total quantity of the dew point. This happens in both cases, with and without prepolymerization.

The difference between kinetic profiles with distinct amounts of iso-hexane is even more evident when prepolymerization is performed. This happens because prepolymerization helps enlarging the particle surface area, what leads to higher local concentration of propylene enlarged even more due to the co-solubility effect. Combining the presence of an alkane and prepolymerization seems to lead to the highest activity profiles.

Finally, it is possible to conclude that when there is no prepolymerization, the deactivation is much higher than when the first reaction moments happen at mild conditions. This is due to the deactivation of the catalyst caused by the rapid increase of temperature, triggered by the exothermicity of the polymerization reaction.

4.2.5) Kinetic Constants Obtained

The previous shown profiles were obtained by fitting the experimental data to equation 6, the kinetic constants obtained from this fitting are shown on table 5. This way, it is possible to present this constants and do a quantitate comparison between each run, instead of the qualitative evaluation of the previous graphics. In Table 4 are presented the average of kinetic constants values obtained to each experiment.

Table 5 - Kinetic constants obtained.

Run	k_p (L mol^{-1} s^{-1})	k_a (s^{-1})	k_d (s^{-1})
T40-0-2%	277,9	7,50E-03	1,55E-04
T40-25-2%	389,8	1,00E-02	1,95E-04
T40-50-2%	480,0	1,50E-02	2,25E-04
T40-75-2%	559,4	1,25E-02	2,10E-04
T40-100-2%	523,3	9,50E-03	1,90E-04
T70-0-2%	223,8	9,50E-03	1,85E-04
T70-25-2%	288,7	7,50E-02	2,35E-04

T70-50-2%	270,7	6,50E-02	2,15E-04
T70-75-2%	469,2	5,00E-02	2,75E-04
T70-100-2%	425,8	1,00E-01	2,70E-04
T40-0-0%	144,4	4,50E-03	1,90E-04
T40-100-0%	212,9	8,00E-03	2,10E-04
T40-0-1%	205,7	9,00E-03	3,50E-04
T40-100-1%	494,4	6,50E-03	2,75E-04
T40-0-4%	263,4	1,00E-02	2,20E-04
T40-100-4%	584,6	6,00E-03	2,65E-04
TDry-0-2%	138,9	6,00E-03	2,95E-04
TDry-100-2%	126,3	5,00E-03	4,25E-04

As can be seen in the previous table, the propagation constant increases with the amount of alkane introduced in the reactor in both cases, with and without prepolymerization. At 75% of the saturation point, the value obtained is almost the double than when no alkane is introduced. After it, no further increase is observed.

Comparing the kinetic constants with the different amounts of hydrogen, the propagation constant increases with the amount of hydrogen and with the presence of alkane in each case, reaching the highest value between 2 and 4% hydrogen, remaining constant after it.

It is worthwhile to note that deactivation constant values are higher when there is no performance of prepolymerization step. This is caused by the high activity in the initial instants of reaction which seems to cause a quicker catalyst deactivation.

Runs performed with dry injection result in higher deactivation, due to the initial high activity of the catalyst that will cause an overheating of the particles, leading to a muck quicker deactivation. Concerning the propagation constant, in the case of dry injection it reaches the lowest values, decreasing by a factor of 2 when comparing to the same experiments with oil injection and no alkane introduced, and by a factor of 4 in the case when alkane is introduced.

When comparing between these values and the ones found in the bibliography [28], it is possible to verify that both activation and deactivation constants are within the values found in the literature. Regarding the propagation constant, it is where more differences are found. Although they are in the same order of magnitude, all values calculated in the current work are higher than the values found in the bibliography. This may be caused by the catalyst system used, with ratios of Al/Ti and Si/Ti significantly different from the ones used in this work. Also the catalyst treatment, being pre-contacted with a heavy hydrocarbon, wetting the catalyst and reducing local particle overheating significantly, with the resistance offered by the hydrocarbon to the diffusion of the monomer in the active sites, being this effect higher in the case of pre-contact with oil than with heptane.

Also, the presence of an alkane during polymerization increases the propagation constant significantly, resulting in much higher constants than in the values used from literature.

4.3 - Polymer Analysis

4.3.1) Crystallinity and Melting Point

The crystallinity of the produced polymers in each run can be analyzed in the next figures. Figure 33 shows the effect of alkane presence on the polymers produced when catalyst injection is made in dry mode. The blue bar represents the first heating curve and the orange one the second heating curve.

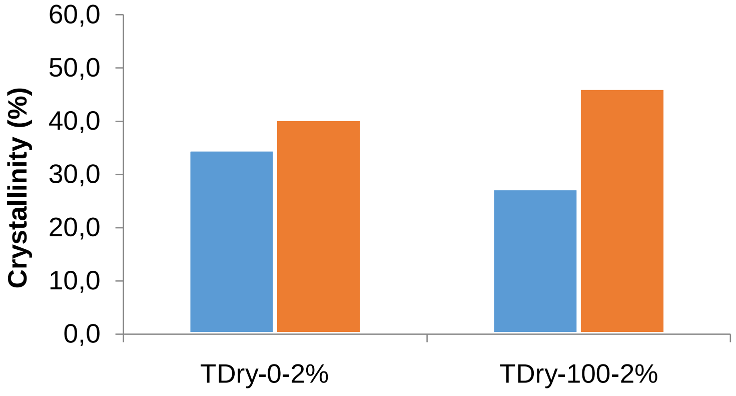

Figure 33 - Crystallinity of polymers produced with dry injection.

Figure 34 and 35 represent the crystallinity of samples produced with and without prepolymerization with different amounts of iso-hexane introduced. Figure 36 and 37 represents how crystallinity is affected by the concentration of hydrogen and its relation with the presence of alkane.

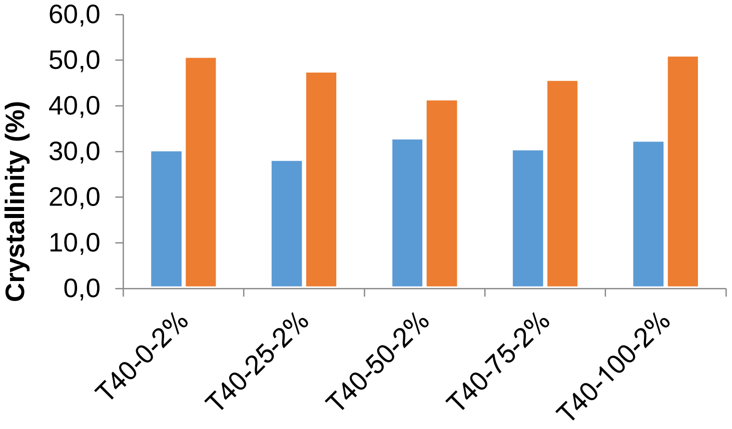

Figure 34 - Crystallinity of polymers produced with different amounts of alkane and with prepolymerization.

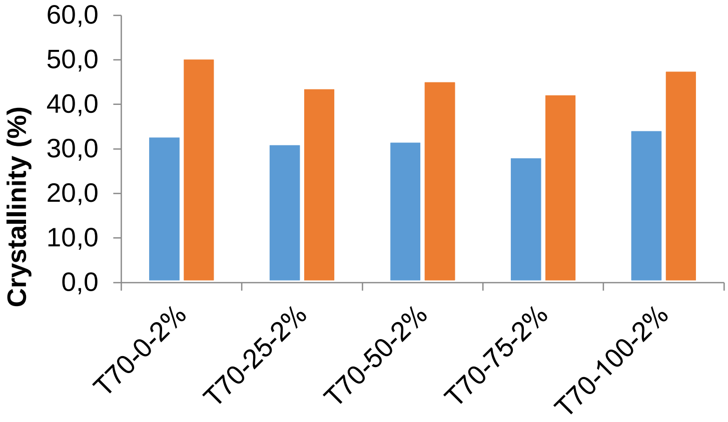

Figure 35 - Crystallinity of polymers produced with different amounts of alkane and without prepolymerization.

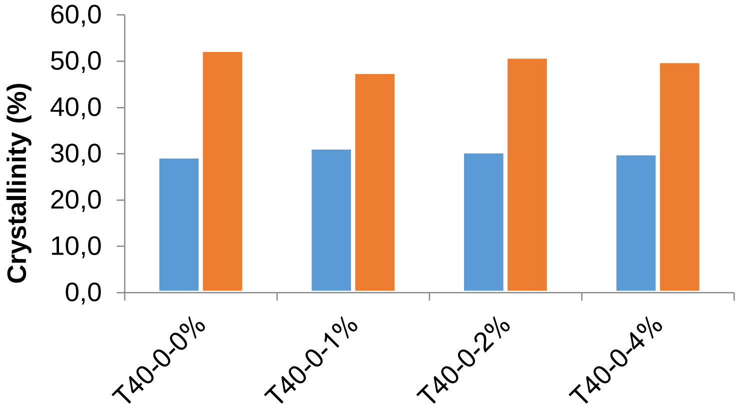

Figure 36 - Crystallinity of polymers produced with different amounts of hydrogen and without alkane.

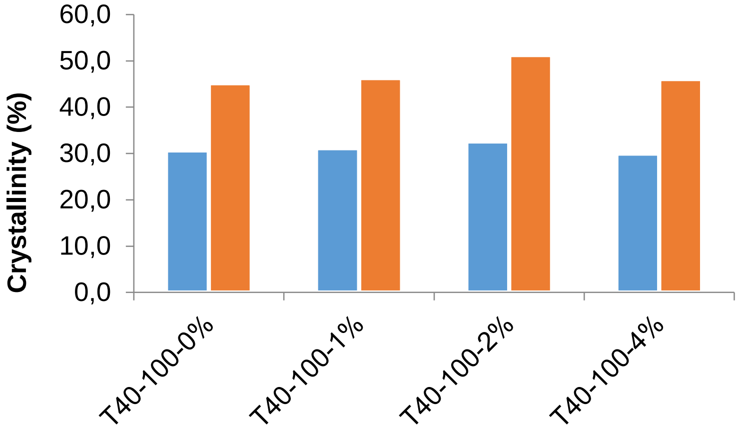

Figure 37 - Crystallinity of polymers produced with different amounts of hydrogen and with alkane.

The crystallinity of the powder produced in all experiments was around 30% and after slow crystallization process it raised up until between 45 and 50%.

The melting point of the produced polymers can be observed in table 6. Regardless the reaction conditions, the melting point of the produced powders is always between 165 and 168°C.

Table 6 - Melting point of produced polymers.

Run	**Melting Point (°C)**
T40-0-2%	167,8
T40-25-2%	167,1
T40-50-2%	165,0
T40-75-2%	167,8
T40-100-2%	168,1
T70-0-2%	167,5
T70-25-2%	168,0
T70-50-2%	167,7
T70-75-2%	167,6
T70-100-2%	168,0
T40-0-0%	167,0
T40-100-0%	167,7
T40-0-1%	167,6
T40-100-1%	167,8
T40-0-4%	168,0
T40-100-4%	167,8
TDry-100-2%	165,3
TDry-0-2%	167,7

4.3.2) Molecular Weight Distribution

Table 7 shows the variation of M_w and M_n with the different reaction conditions studies.

Table 7 - Molecular weight distribution of samples analyzed.

Run	**M_N (kDa)**	**M_W (kDa)**
T40-0-2%	41 / 58	270 / 284
T40-25-2%	33 / 54	301 / 298
T40-50-2%	25 / 80	296 /336
T40-75-2%	77 / 71	287 / 280
T40-100-2%	50 / 51	287 / 280
T70-0-2%	49 / 53	275 / 258

T70-25-2%	30 / 31	289 / 283
T70-50-2%	72 / 70	295 / 313
T70-75-2%	59 / 71	247 / 307
T70-100-2%	60 / 76	301 / 305
T40-0-0%	45 / 93	539 / 541
T40-100-0%	32 / 40	366 / 345
T40-0-1%	27 / 35	227 / 254
T40-100-1%	95[1]	580[1]
T40-0-4%	55 / 53	287 / 313
T40-100-4%	30 / 31	292 / 285
TDry-0-2%	42 / 55	233 / 247
TDry-100-2%	30 / 40	102 / 114

Molecular weight distribution can be represented also with the polydispersity, the ratio between the weight average molecular weight (M_w) and the number average molecular weight (M_n). Ziegler-Natta catalysts produce polymers with high polydispersity, ranging between 4 and 9, taking into account the values showed in table 7.

Concerning the amount of alkane introduced it is possible to conclude that it does not affect MWD, since the values of molecular weight remain similar. The performance of a prepolymerization step does not seem to affect the MWD, unlike the hydrogen concentration which has a strong effect in the molecular weight.

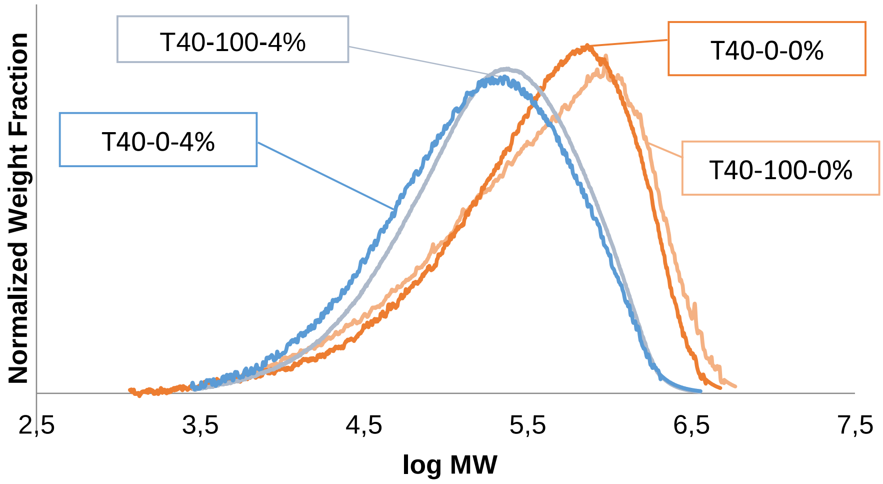

Figure 38 - MWD for the polymers produced in experiments with different amounts of hydrogen.

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[1] Only one sample analyzed.

Looking at the minimum and maximum concentrations of hydrogen, it is possible to see in figure 38 that the peak of molecular weight is much different with 0 or 4% of hydrogen. This can be explained by one of the hydrogen functions in the reactor that acts like a chain transfer agent, reducing the size of the molecular chain, leading to smaller MWD.

4.3.3) Particle Size Distribution

The particle size distribution of the produced polymers was analyzed in order to study if there was a replication of the catalyst shape.

The first step in this analyse was to obtain the PSD of the catalyst, shown in the next figures in grey (for comparison). As can be seen, the catalyst used in this experimental work has a broad distribution which will lead also to a broad polymer distribution.

In figures 39 to 42, it is shown the different DS of polymers produced with different reaction conditions.

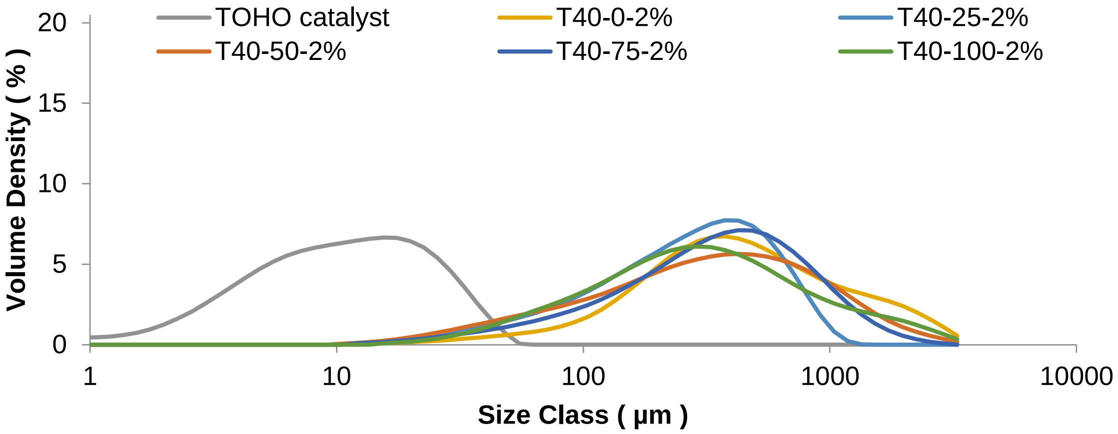

Figure 39 - PSD of polymers produced with prepolymerization.

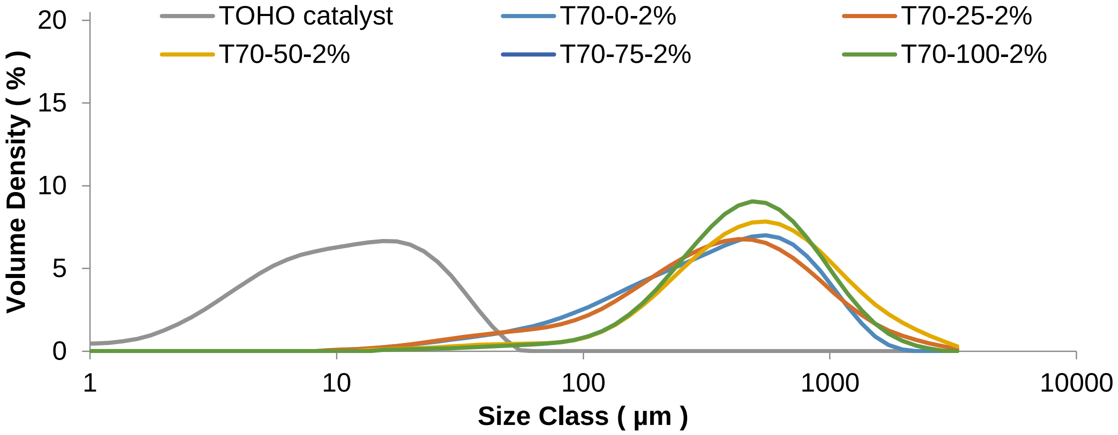

Figure 40 - PSD of polymers produced without prepolymerization.

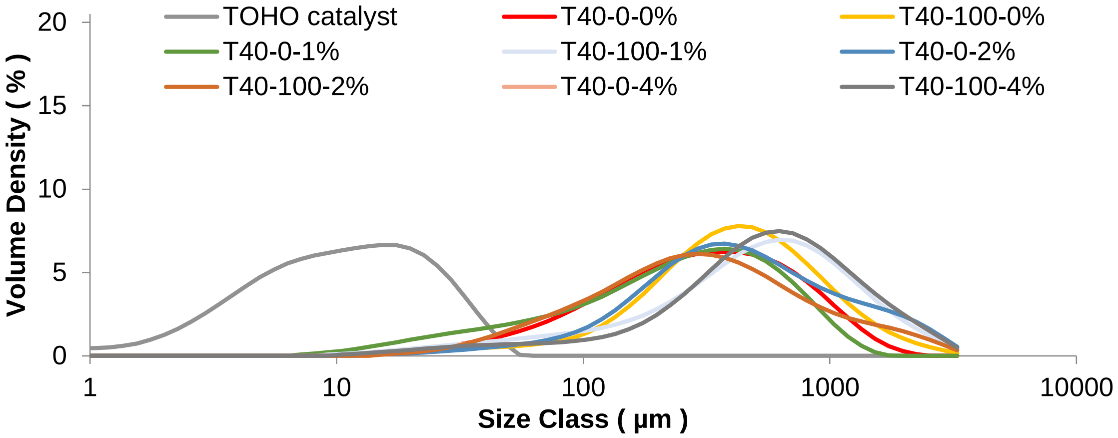

Figure 41 - PSD of polymers produced with different amounts of hydrogen.

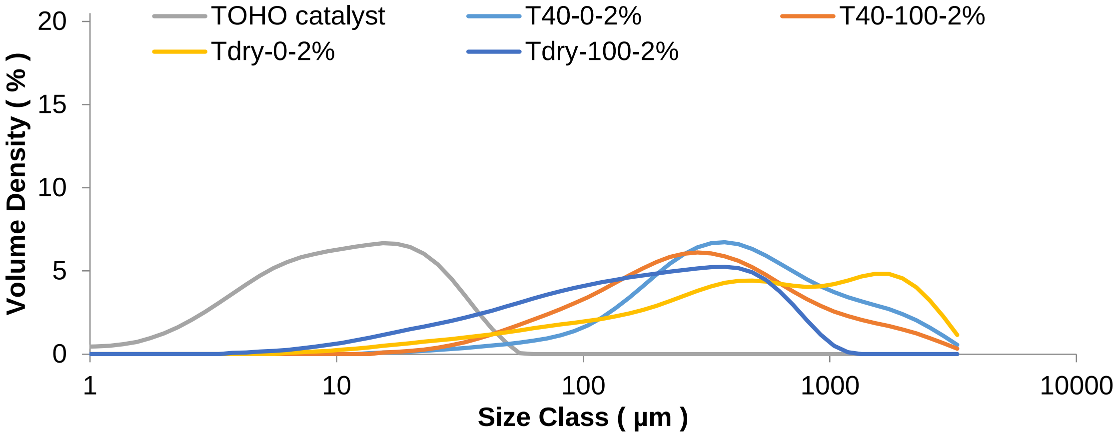

Figure 42 - PSD of polymers produced with different types of catalyst injection.

It is possible to conclude that the PSD of the produced polymers is not significantly influenced by the performance of a prepolymerization step or the injection of an alkane in the reaction media. In other hand, the injection of a catalyst in a dry mode results in a polymers with a different PSD than the catalyst, with a not well defined particle size distribution.

Due to a lower initial reaction rate and more controlled diffusion rate of monomer in the active sites, particles produced with oil injection and prepolymerization are more uniform and smaller.

4.3.4) Polymer Surface Images

SEM pictures were taken in order to evaluate if different reaction conditions made any substantial variation in polymer surface. The first noticeable characteristic of all samples analyzed was the high variety of particle sizes, already confirmed by PSS analysis and that can be noticed in figure 43.

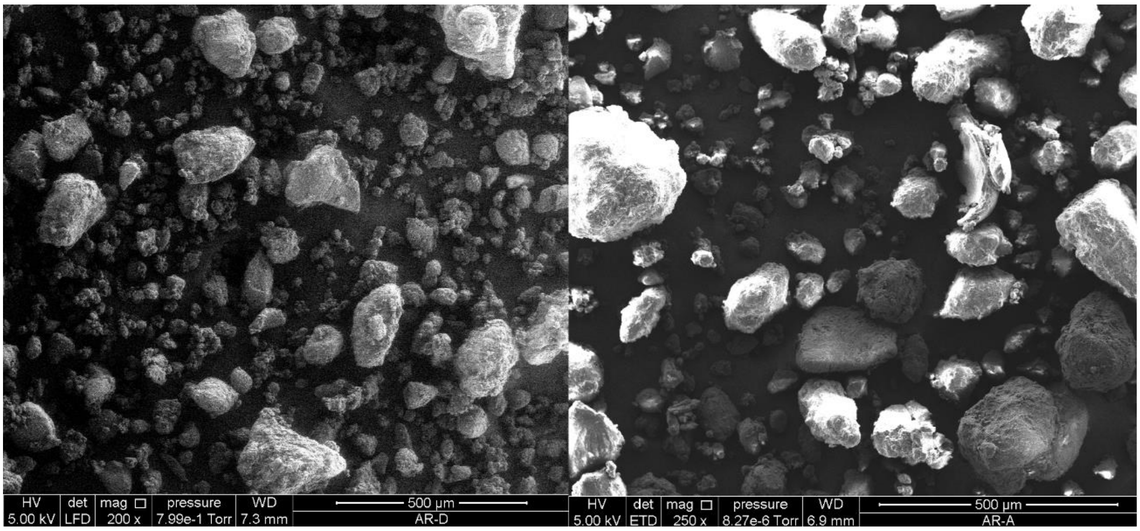

Figure 43 – SEM pictures showing high variety of particle sizes.

The majority of produced polymers were submitted to this analysis, however there was almost no difference between polymers produced with oil injection, even if other reaction conditions were changed. There was no clear evidence of either prepolymerization, quantity of hydrogen or alkane introduced. Figure 44 shows several polymer surfaces from different runs.

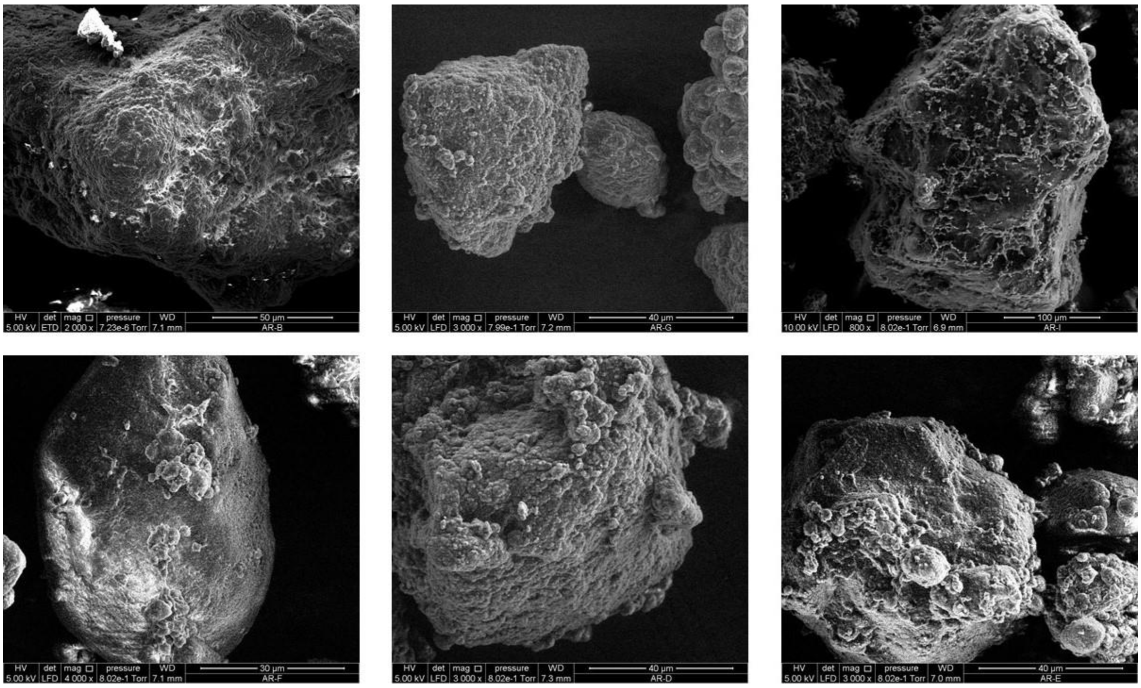

Figure 44 – Polymer surfaces obtained by SEM.

Polymers produced with dry injection were also analyzed with this equipment, and in this case there is a clear difference between polymer morphology, as can be seen in figure 45.

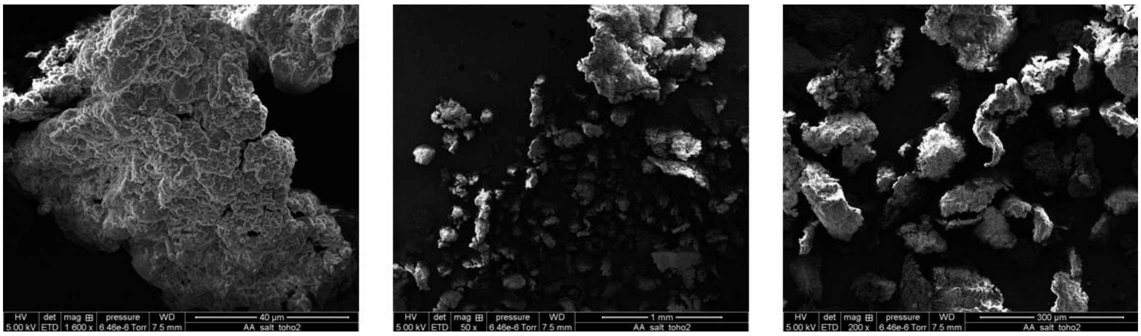

Figure 45 – SEM pictures of polymers produced with dry injection

In dry injection, the produced polymers contain hollow and big flaky particles and a lot of fines that are clearly different from the polymers shown in figure 43, which have a more or less spherical geometry.

4.3.5) Bulk Density

The bulk density of the produced polymer in each run can be analyzed in the next figures. Figure 46 shows the difference of bulk density with the type of injection.

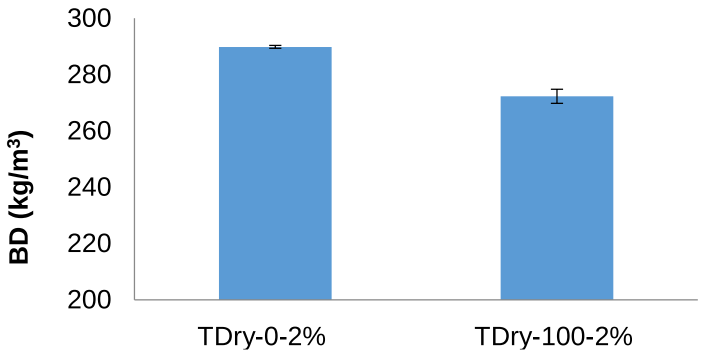

Figure 46 - Variation of bulk density with the type of catalyst injection.

Firstly, it is worthwhile to note the difference of bulk densities of polymers produced with different ways of injecting the catalyst. Polymers produced in a run with dry injection have a much lower density, which is expected since the particles formed are flaky. In other hand, when the polymerization is performed with the injection of alkane, the bulk density of the polymer obtained is slightly higher, once there is an enhancement of the local concentration of propylene inside the particle.

Figures 47 and 48 show the variation of bulk density with different amounts of alkane introduced in the reactor, with and without prepolymerization, respectively.

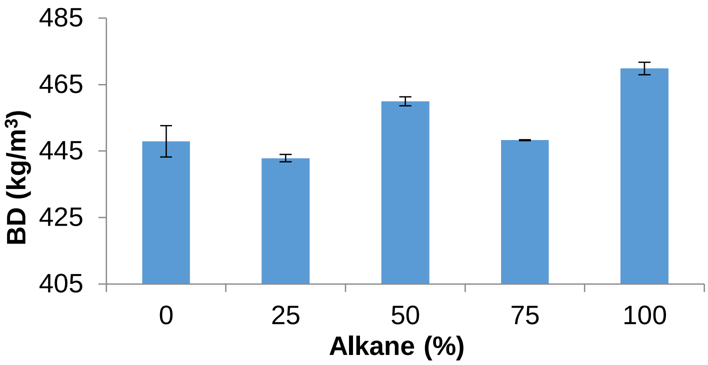

Figure 47 - Variation of bulk density with the quantity of alkane injected with prepolymerization.

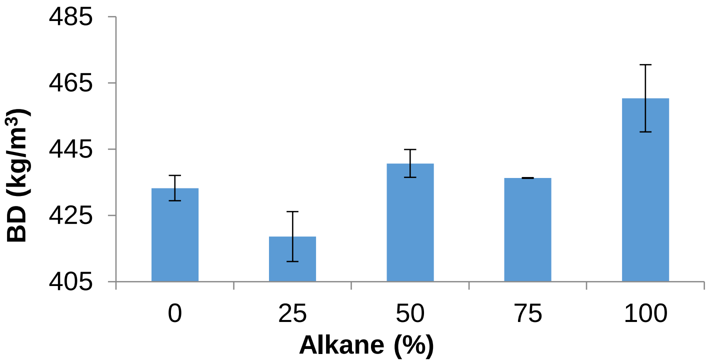

Figure 48 - Variation of bulk density with the quantity of alkane injected without prepolymerization.

Analyzing the bulk density of the polymers, we can conclude that there is a slight increase of bulk density with the increase of amount of alkane introduced in the reactor, which can be attributed to the enhancement of local concentration on propylene inside the polymer. It is also very clear that the prepolymerization leads to higher bulk densities, which is explained by the higher surface area of the polymer, making it better for propylene insertion in the active sites of the catalyst. Figure 49 and 50 show the difference between each concentration of hydrogen and how does it change with the presence of alkane.

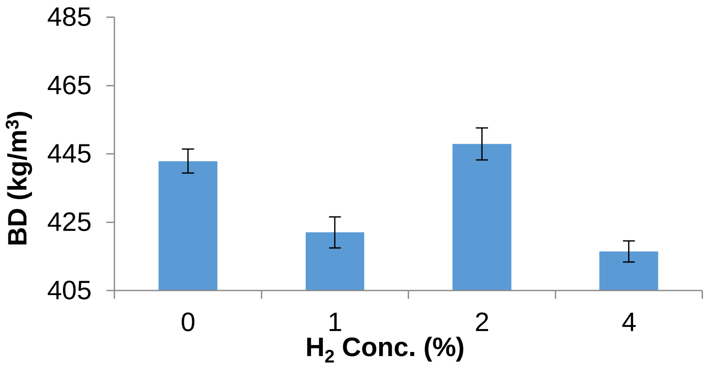

Figure 49 - Variation of bulk density with the concentration of hydrogen without alkane.

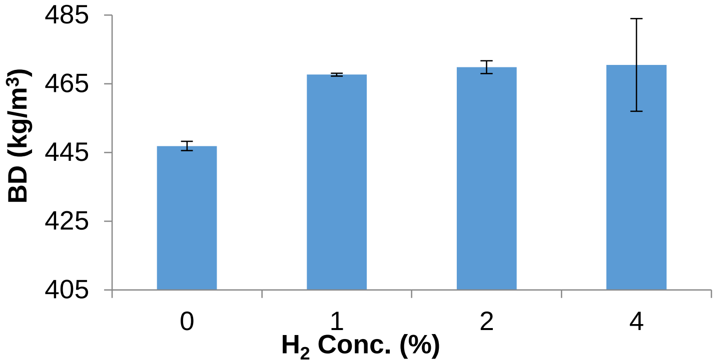

Figure 50 - Variation of bulk density with the concentration of hydrogen with alkane.

Regarding the hydrogen concentration, it is possible to conclude that with alkane there is an increase in density from 0 to 1% hydrogen, remaining constant after 1%. Without alkane it is not possible to find a relation between bulk density and hydrogen concentration.

Chapter 5 - Conclusions

The main objective of this thesis is to understand how reaction conditions affect the way the reaction proceeds and the properties of the produced polymers. Once the experimental procedure was defined, it was studied the effect of performing a prepolymerization step, varying the concentration of hydrogen, introducing several amounts of alkane and different types of injection of catalyst.

It was noticed that the instantaneous rate of polymerization increased when performing a prepolymerization step, thanks to a decrease of the local particle overheating in the initial instants of reaction. When looking the kinetic constants, it is possible to conclude that the prepolymerization step gives a boost, of about 20%, in the propagation constant while leading to a slower deactivation of the catalyst.

Regarding the polymers produced in this case, the bulk density is higher when a prepolymerization step is performed, mainly because the shaping of the powders occurs first at a slow polymerization rate, producing more compact polymers. Concerning the molecular weight, there was no significant difference between polymers produced with or without prepolymerization.

The presence of an alkane during propylene polymerization in gas phase can affect both activity profile and morphology of the produced polymer. By the absorption of some of the reaction heat and essentially by the enhancement of the local concentration of propylene inside the active sites of the catalyst, the presence of an alkane leads to higher activity profiles.

In both cases (with and without prepolymerization), when introducing a higher amount of alkane, related to the saturation point, there was an increase of the instantaneous rate of polymerization, as a result of the higher propagation constants. However, when the amount of alkane introduced exceed 75% of the saturation point no further increase of propagations constant was observed.

The deactivation constant tends to increase with the amount of alkane as well. Due to the activity reached and the high values of exothermicity of the reaction, a stronger catalyst deactivation caused by overheating of the catalyst particles may occur.

The presence of an alkane also affects the bulk density in both cases (with and without prepolymerization). With the increasing amount of alkane, there is an increase of the bulk density of around 10%. Concerning the molecular weight, there was no significant difference of the MWD of the polymers produced with different percentages of alkane saturation.

The concentration of hydrogen has also a severe effect in the instantaneous rate of polymerization. A lower polymerization rate is observed in the absence of hydrogen, as hydrogen, in propylene polymerization has the function of reactivating dormant sites, formed after a wrong propylene insertion.

The molecular weight is one of the properties more affected by the absence or lack of hydrogen, resulting in a higher molecular weight. Since hydrogen acts like a chain transfer agent, its absence or the lack of it results in much higher molecular weights. Regarding the bulk density, it was observed that lower the concentration of hydrogen, lower is the bulk density.

It was observed also that the rate of polymerization is higher when the catalyst is injected with mineral oil than with salt. The injection of the catalyst pre-contacted with a hydrocarbon before being charged to the reactor seems to help productivity. Concerning the bulk density of the polymers produced with dry injection, it is almost half of the polymers produced with oil catalyst injection.

SEM pictures show a broad particle size distribution, with a large variety of particle size which was corroborated by PSD measurements. Polymers morphology does not seem to vary significantly with prepolymerization, injection of alkane or hydrogen concentration. However, a different morphology, visible to the nude eye also, for polymers produced with dry injection. These polymers tend to be a lot more flaky and hollow when compared to polymers produced with oil injection.

No significant difference in particle size distribution was observed for the polymers produced with oil or prepolymerization. More uniform and smaller polymer particles are produced with both procedures. Only polymers produced in runs with dry injection have a more broad and irregular distribution.

Another property analyzed in this thesis, and in which was not found any correlation with the parameters studied, was the crystallinity and melting point of the powders produced. It was not found any relation between any of the variables studied in this work with any of these properties. The crystallinity of the powders is around 30%, a value that rises to 45/50%, after a slow crystallization process, visible in the second heating curve. Both first and second heating curves have the peak in the melting point, around 165 and 168ºC, for all produced polymers.

In this thesis were studied some important features and their influence in terms of kinetic and polymer properties. The application of these features in an industrial way, except the injection of alkane, is already made, in order to produce higher quantities of polymer with a right morphology.

In the future, it would be also important to study the influence of these parameters in co-polymerizations, either to produce random co-polymers or high impact co-polymers.

Chapter 6 – References

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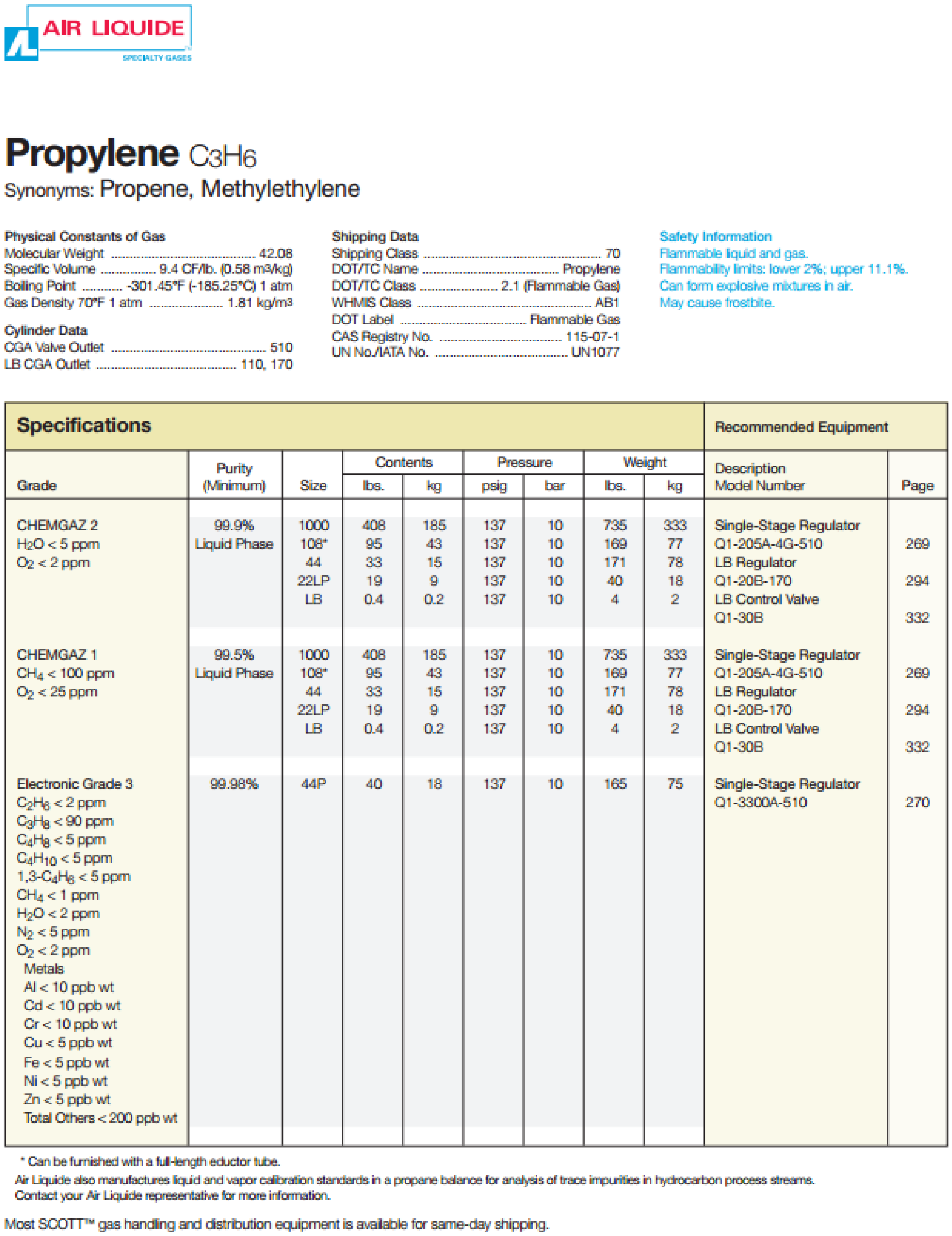
Appendices

A.1 – Ethylene Specification Sheet

[32]



AIR LIQUIDE
SPECIALTY GASES

Propylene C_3H_6

Synonyms: Propene, Methylethylene

Physical Constants of Gas
Molecular Weight 42.08
Specific Volume .... 9.4 CF/lb. (0.58 m3/kg)
Boiling Point .... -301.45°F (-185.25°C) 1 atm
Gas Density 70°F 1 atm 1.81 kg/m3

Cylinder Data
CGA Valve Outlet 510
LB CGA Outlet 110, 170

Shipping Data
Shipping Class 70
DOT/TC Name .... Propylene
DOT/TC Class .... 2.1 (Flammable Gas)
WHMIS Class AB1
DOT Label .... Flammable Gas
CAS Registry No. 115-07-1
UN No./IATA No. UN1077

Safety Information
Flammable liquid and gas.
Flammability limits: lower 2%; upper 11.1%.
Can form explosive mixtures in air.
May cause frostbite.

Specifications | **Recommended Equipment**

Grade	Purity (Minimum)	Size	Contents		Pressure		Weight		Description Model Number	Page
			lbs.	kg	psig	bar	lbs.	kg		
CHEMGAZ 2	99.9%	1000	408	185	137	10	735	333	Single-Stage Regulator	
$H_2O < 5$ ppm	Liquid Phase	108*	95	43	137	10	169	77	Q1-205A-4G-510	269
$O_2 < 2$ ppm		44	33	15	137	10	171	78	LB Regulator	
		22LP	19	9	137	10	40	18	Q1-20B-170	294
		LB	0.4	0.2	137	10	4	2	LB Control Valve	
									Q1-30B	332
CHEMGAZ 1	99.5%	1000	408	185	137	10	735	333	Single-Stage Regulator	
$CH_4 < 100$ ppm	Liquid Phase	108*	95	43	137	10	169	77	Q1-205A-4G-510	269
$O_2 < 25$ ppm		44	33	15	137	10	171	78	LB Regulator	
		22LP	19	9	137	10	40	18	Q1-20B-170	294
		LB	0.4	0.2	137	10	4	2	LB Control Valve	
									Q1-30B	332
Electronic Grade 3	99.98%	44P	40	18	137	10	165	75	Single-Stage Regulator	
$C_2H_6 < 2$ ppm									Q1-3300A-510	270
$C_3H_8 < 90$ ppm										
$C_4H_8 < 5$ ppm										
$C_4H_{10} < 5$ ppm										
1,3-$C_4H_6 < 5$ ppm										
$CH_4 < 1$ ppm										
$H_2O < 2$ ppm										
$N_2 < 5$ ppm										
$O_2 < 2$ ppm										
Metals										
Al < 10 ppb wt										
Cd < 10 ppb wt										
Cr < 10 ppb wt										
Cu < 5 ppb wt										
Fe < 5 ppb wt										
Ni < 5 ppb wt										
Zn < 5 ppb wt										
Total Others < 200 ppb wt										

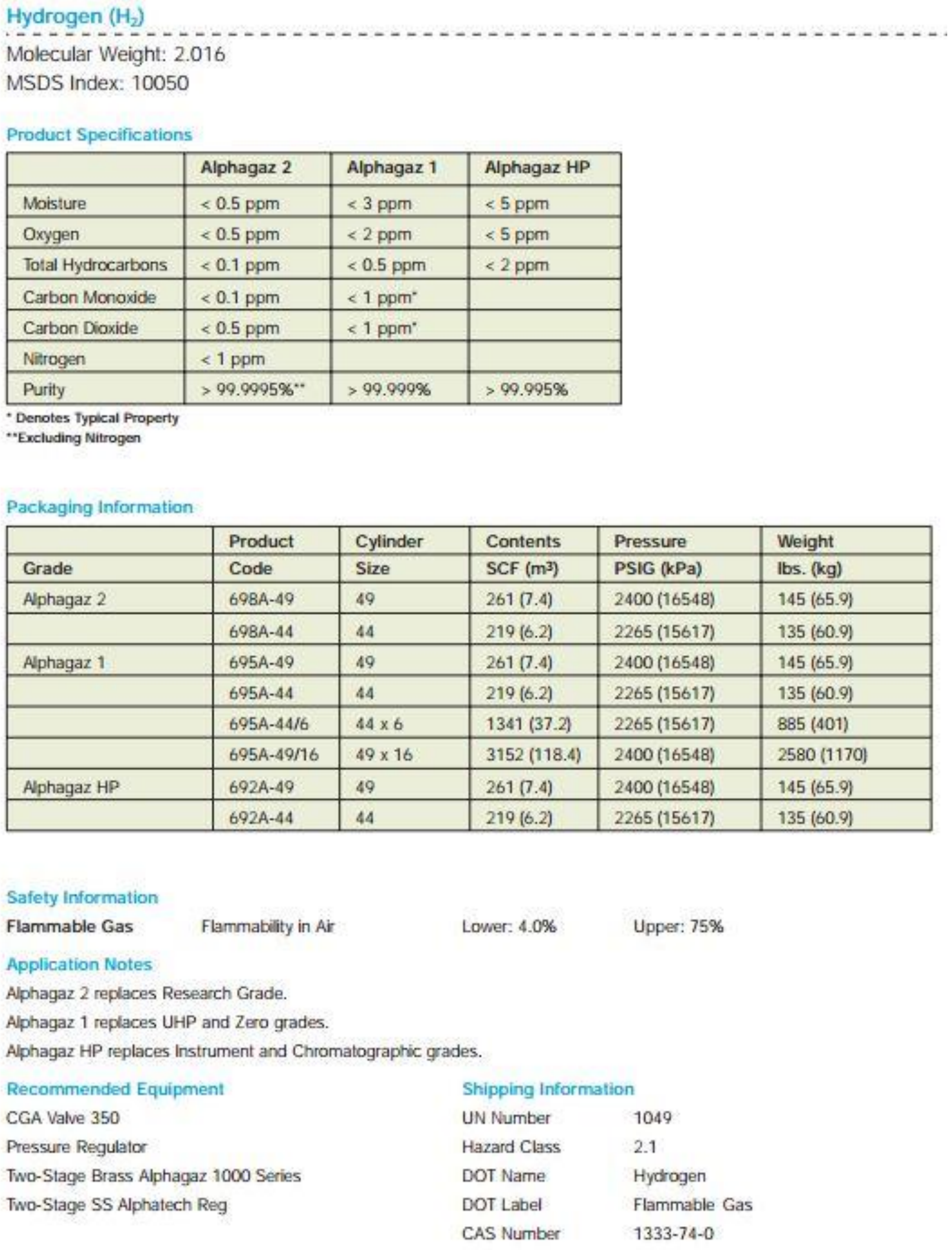
* Can be furnished with a full-length eductor tube.

Air Liquide also manufactures liquid and vapor calibration standards in a propane balance for analysis of trace impurities in hydrocarbon process streams. Contact your Air Liquide representative for more information.

Most SCOTT™ gas handling and distribution equipment is available for same-day shipping.

A.2 – Hydrogen Specification Sheet

[33]



Hydrogen (H_2)

Molecular Weight: 2.016

MSDS Index: 10050

Product Specifications

	Alphagaz 2	Alphagaz 1	Alphagaz HP
Moisture	< 0.5 ppm	< 3 ppm	< 5 ppm
Oxygen	< 0.5 ppm	< 2 ppm	< 5 ppm
Total Hydrocarbons	< 0.1 ppm	< 0.5 ppm	< 2 ppm
Carbon Monoxide	< 0.1 ppm	< 1 ppm*	
Carbon Dioxide	< 0.5 ppm	< 1 ppm*	
Nitrogen	< 1 ppm		
Purity	> 99.9995%**	> 99.999%	> 99.995%

* Denotes Typical Property

**Excluding Nitrogen

Packaging Information

Grade	Product Code	Cylinder Size	Contents SCF (m³)	Pressure PSIG (kPa)	Weight lbs. (kg)
Alphagaz 2	698A-49	49	261 (7.4)	2400 (16548)	145 (65.9)
	698A-44	44	219 (6.2)	2265 (15617)	135 (60.9)
Alphagaz 1	695A-49	49	261 (7.4)	2400 (16548)	145 (65.9)
	695A-44	44	219 (6.2)	2265 (15617)	135 (60.9)
	695A-44/6	44 x 6	1341 (37.2)	2265 (15617)	885 (401)
	695A-49/16	49 x 16	3152 (118.4)	2400 (16548)	2580 (1170)
Alphagaz HP	692A-49	49	261 (7.4)	2400 (16548)	145 (65.9)
	692A-44	44	219 (6.2)	2265 (15617)	135 (60.9)

Safety Information

Flammable Gas	Flammability in Air	Lower: 4.0%	Upper: 75%

Application Notes

Alphagaz 2 replaces Research Grade.

Alphagaz 1 replaces UHP and Zero grades.

Alphagaz HP replaces Instrument and Chromatographic grades.

Recommended Equipment

CGA Valve 350

Pressure Regulator

Two-Stage Brass Alphagaz 1000 Series

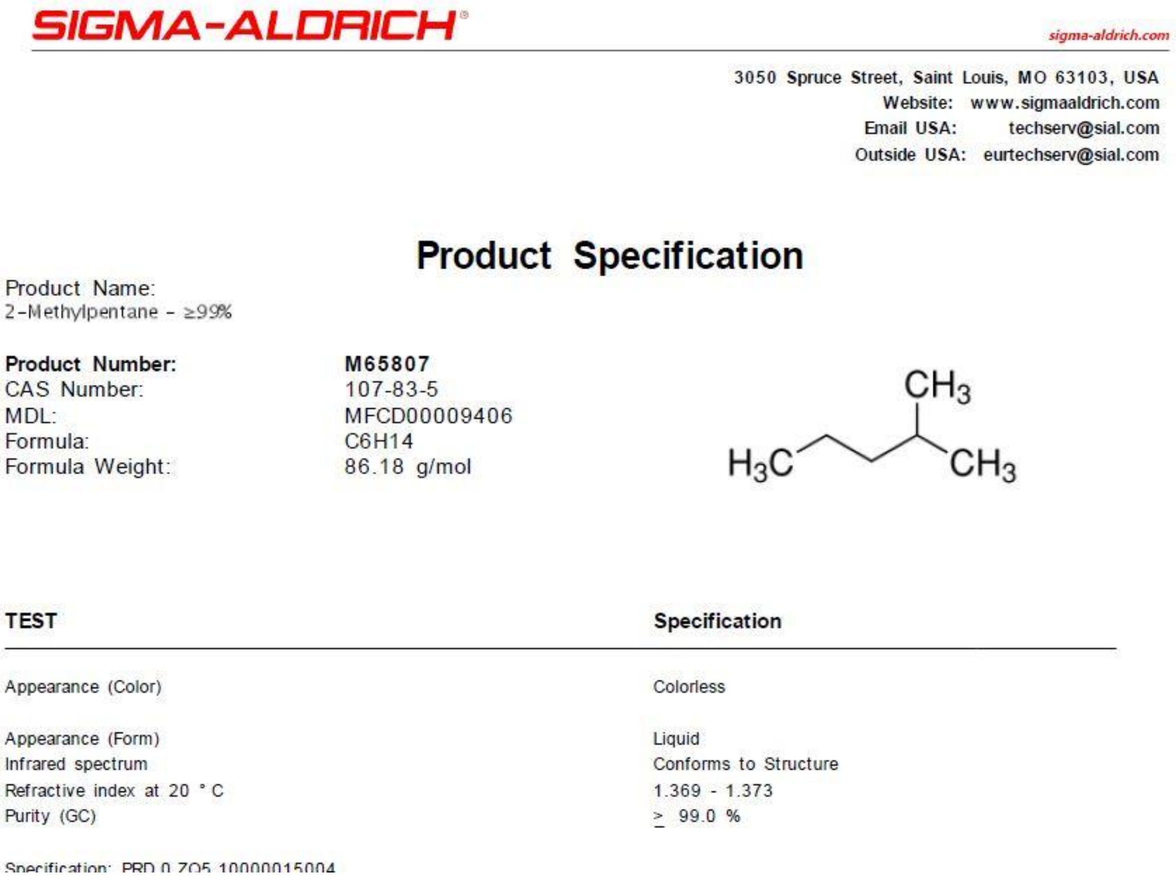
Two-Stage SS Alphatech Reg

Shipping Information

UN Number	1049
Hazard Class	2.1
DOT Name	Hydrogen
DOT Label	Flammable Gas
CAS Number	1333-74-0

A.3 – Iso-Hexane Specification Sheet

[34]



SIGMA-ALDRICH

sigma-aldrich.com

3050 Spruce Street, Saint Louis, MO 63103, USA
Website: www.sigmaaldrich.com
Email USA: techserv@sial.com
Outside USA: eurtechserv@sial.com

Product Specification

Product Name:
2-Methylpentane - ≥99%

Product Number:	**M65807**
CAS Number:	107-83-5
MDL:	MFCD00009406
Formula:	C6H14
Formula Weight:	86.18 g/mol

TEST	**Specification**
Appearance (Color)	Colorless
Appearance (Form)	Liquid
Infrared spectrum	Conforms to Structure
Refractive index at 20 ° C	1.369 - 1.373
Purity (GC)	≥ 99.0 %

Specification: PRD 0 ZO5 10000015004

A.4 – Experimental Procedure

GENERAL PROCEDURE

1. Turn on the vacuum pump and start making vacuum to the reactor that was already set from the previous reaction, for half an hour, by opening the valves to start admitting vacuum inside the reactor. If the experiment there will be performed is one with injection of alkane, first we have to connect the cartridge to the reactor;

2. Start heating the reactor by connecting the heating water and the desired temperature in the heating bath;

3. Make sure that the quantity of oxygen inside is minimum by performing at least three cycles of argon and vacuum;

4. Open the propylene bottle and all the valves that ensure the connection to the ballast. Open the electro-valve, that will regulate the pressure of propylene inside the reactor, and start the data acquisition by turning on the SPY equipment;

5. When the reactor is at the correct temperature, the next step is the injection of the TEA, ELB and the catalyst:

5.1) First, there is a need to ensure that when the valve where all the solution are injection is opened there is no entry of air (oxygen) inside the reactor, for that first we have to fill the reactor with argon;

5.2) Then, there is the injection of the first amount of TEA (0,7 mL), that will not just contribute to the Al/Ti ratio, but it will also act as a scavenger, eliminating any residual oxygen. After this, close the argon feed to the reactor to avoid that the TEA go to the feed system. In this point, start the stirring system at 200 rpm and also open the water to cool the stirrer;

5.3) To inject the second amount of TEA (0,7 mL) and after the ELB (0,2 mL), we need to make sure that there is no air entering the reactor, so we need to always open the feed of argon to the reactor;

5.4) Catalyst injection can be done in two different ways:

5.4.1) To inject the catalyst in oil, the procedure is the same as with the TEA, open the argon feed and open the valve that permits injections in the reactor, inject 250 µL of oil and catalyst mixture and close both valves;

5.4.2) To inject the dry catalyst with salt we need to change the cup of the Schlenk for the one with the hose and do the same thing as in wet injection;

5.5) With all the components needed in the reactor (TEA, ELB and catalyst), quickly start feeding propylene and adjust its pressure When propylene starts entering the reactor the stirring has to be increased to 300 rpm;

6. One experiment with prepolymerization will start at 40 °C and 3,5 bar and will stay in this conditions for 10 minutes. After this time, there is an increase of temperature to 70°C and increase of pressure to 6bar;

7. In order to inject the hydrogen and the alkane (if needed, depending in each individual experiment):

7.1) Having opened previously the hydrogen bottle and the connection to the system, the hydrogen is introduced by filling a certain part of the system with hydrogen which corresponds to 0,08 bar of hydrogen;

7.2) Alkane injection is made with cartridge, previously attached to the reactor in step 1. To injected it is just open the bottom valve of the cartridge, which will permit the liquid alkane to enter in the reactor and then pass some propylene to the cartridge to remove any residual alkane remaining there;

8. When the temperature reaches approximately 50 °C, increase the pressure to 7,5 bar and at this point start taking points (at every minute in the initial instants of the reaction and then more spaced) and whenever it’s necessary fill the ballast again;

9. After one hour is time to stop the reaction:

9.1) Close all the valves;

9.2) Disconnect the heating water and start cooling the reactor;

9.3) When the temperature inside the reactor reaches approximately 30°C,start degassing the reactor, opening slowly the exit valve to the exhaust system;

9.4) After degassing, pass argon to ensure that there is no propylene left inside the reactor;

10. Open the reactor, take out the produced polypropylene, clean the reactor (using first compressed air, then a brush and finally paper and heptane) and close it;

SALT PREPARATION PROCEDURE

1. Enter the glovebox with: two utensils to weight the catalyst and the salt, a balloon, a Schlenk, a tap, a stopcock valve, a little hose and a “cup holder”;

2. Weight in a balloon 30 mg of catalyst, fill up to 10 grams with salt and homogenize the mixture ;

3. Put the mixture inside the Schlenk and then get out of the glovebox with everything;

LIQUID ALKANE PREPARATION

1. Enter the glovebox with: cartridge, connection between cartridge and propylene line, syringe, needle and wrench;

2. Measure the correct amount of alkane and put it inside the cartridge;

3. Connect the cartridge with the connection to the propylene line and get out of the glovebox with everything.

4. Connect the cartridge to the reactor and make vacuum to the junctions in each side.

B.1 – Reproducibility of Experiments

Runs with prepolymerization, 2% H_2 and wet injection

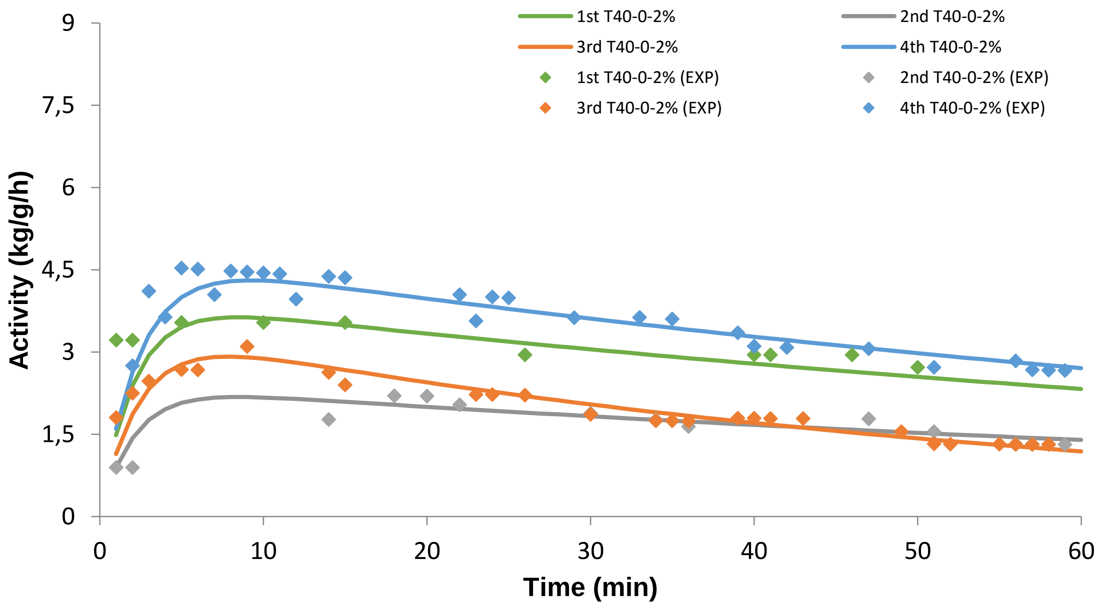


Figure 51 – Reproducibility of T40-0-2%.

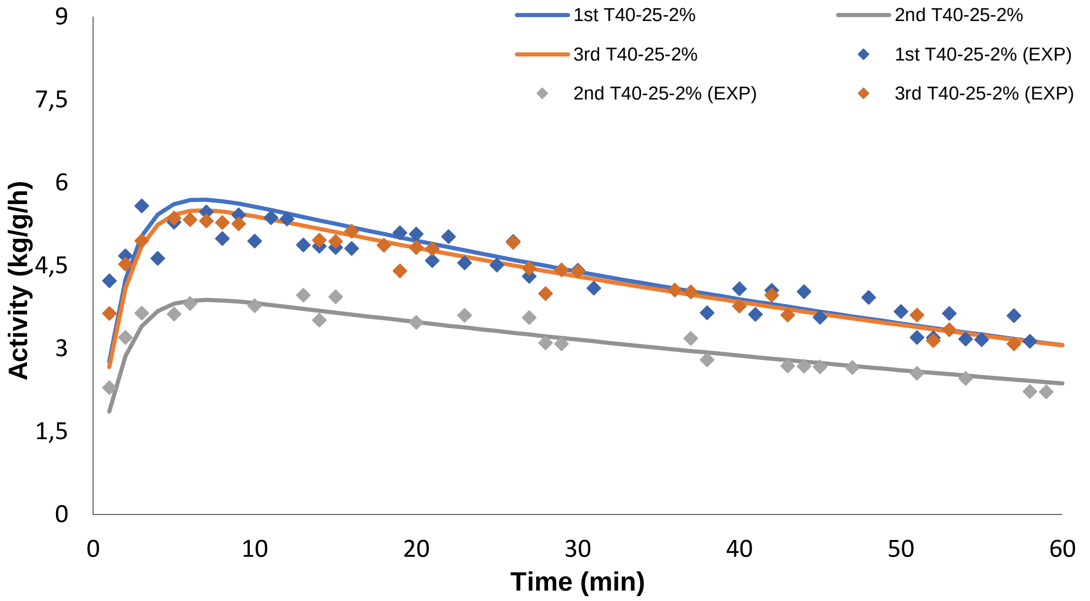


Figure 52 - Reproducibility of T40-25-2%.

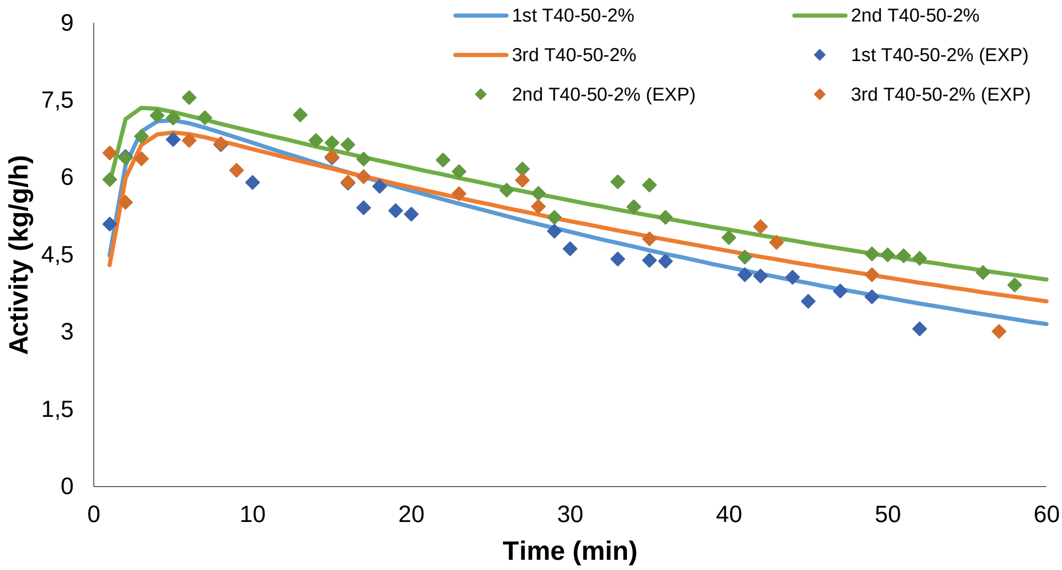


Figure 53 - Reproducibility of T40-50-2%.

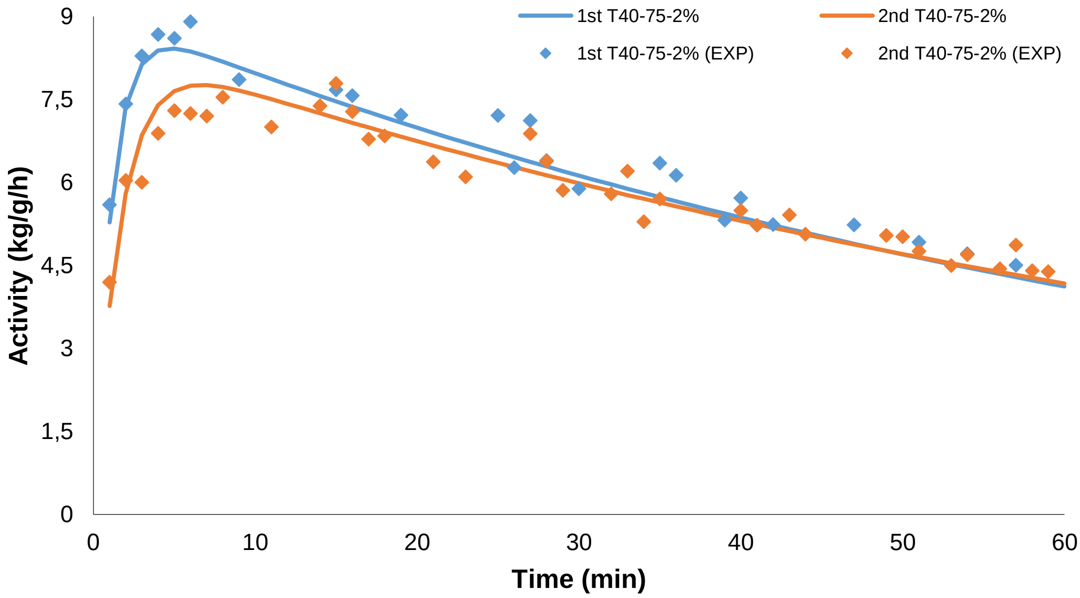


Figure 54 - Reproducibility of T40-75-2%.

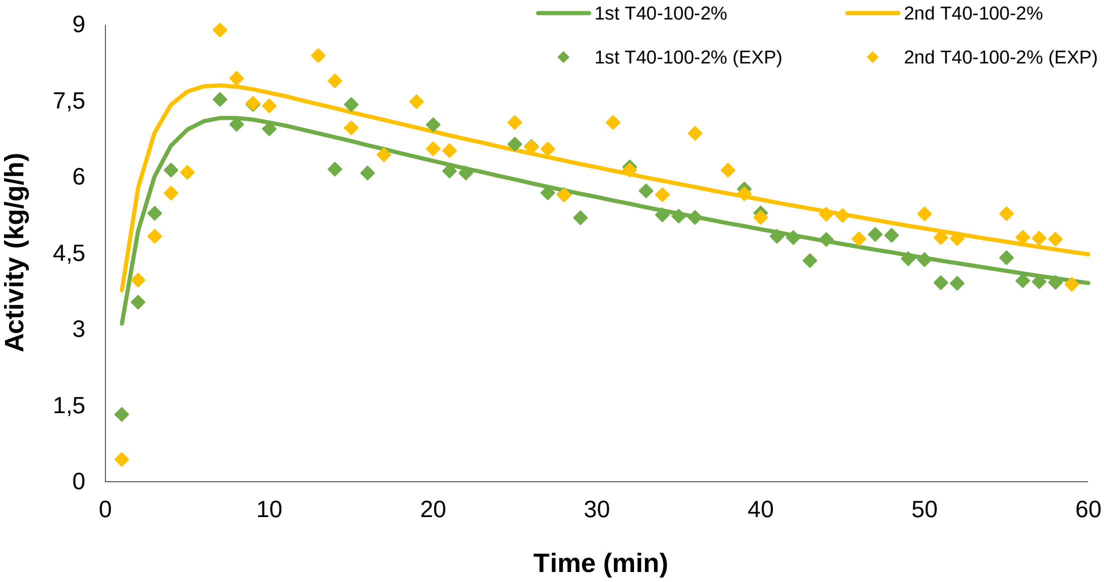


Figure 55 - Reproducibility of T40-100-2%.

Runs without prepolymerization, 2% H_2 and wet injection

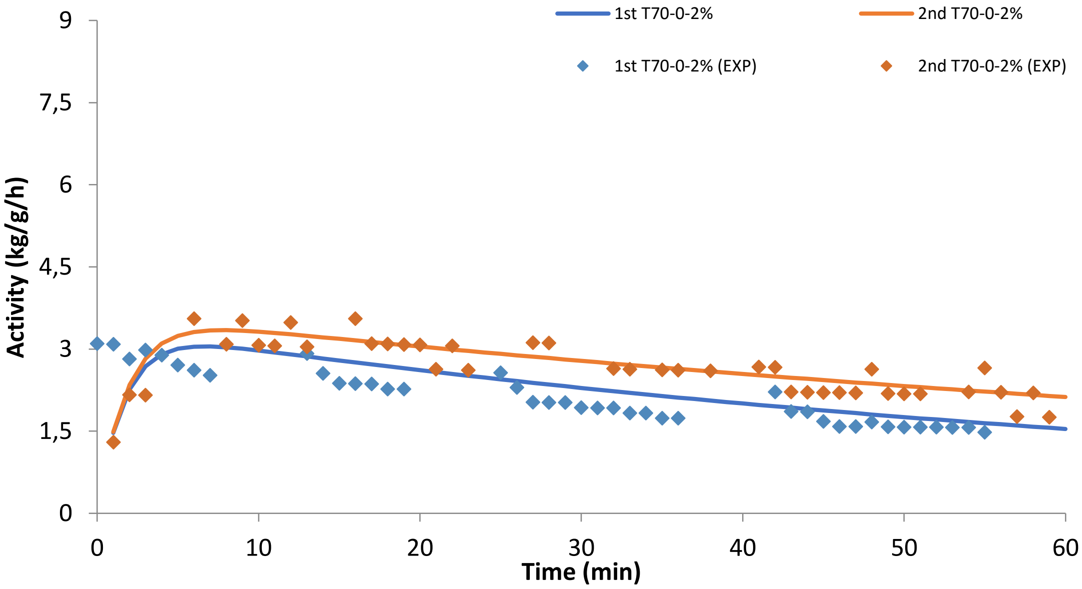


Figure 56 - Reproducibility of T70-0-2%.

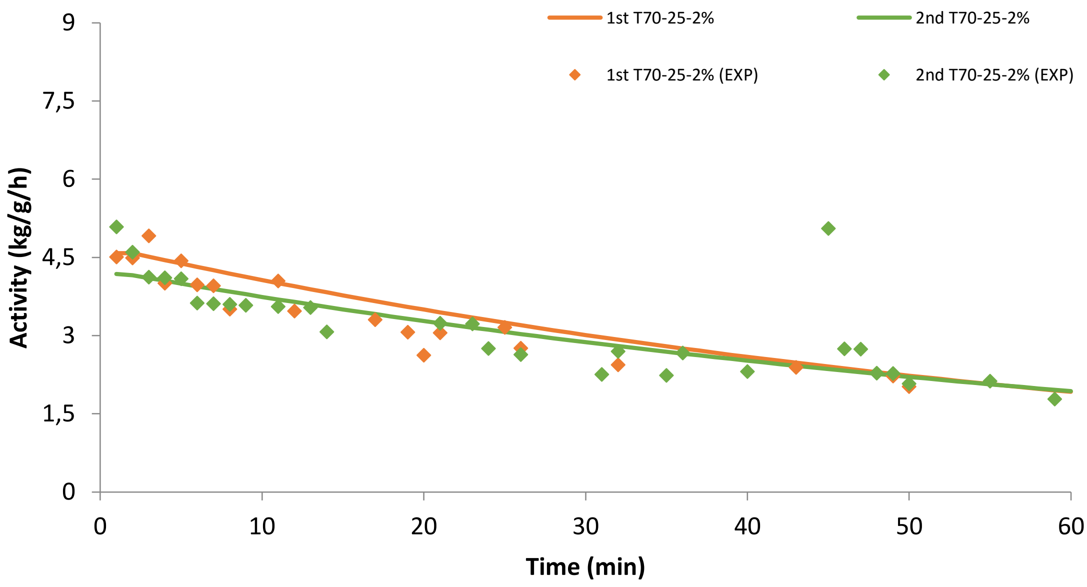


Figure 57 - Reproducibility of T70-25-2%.

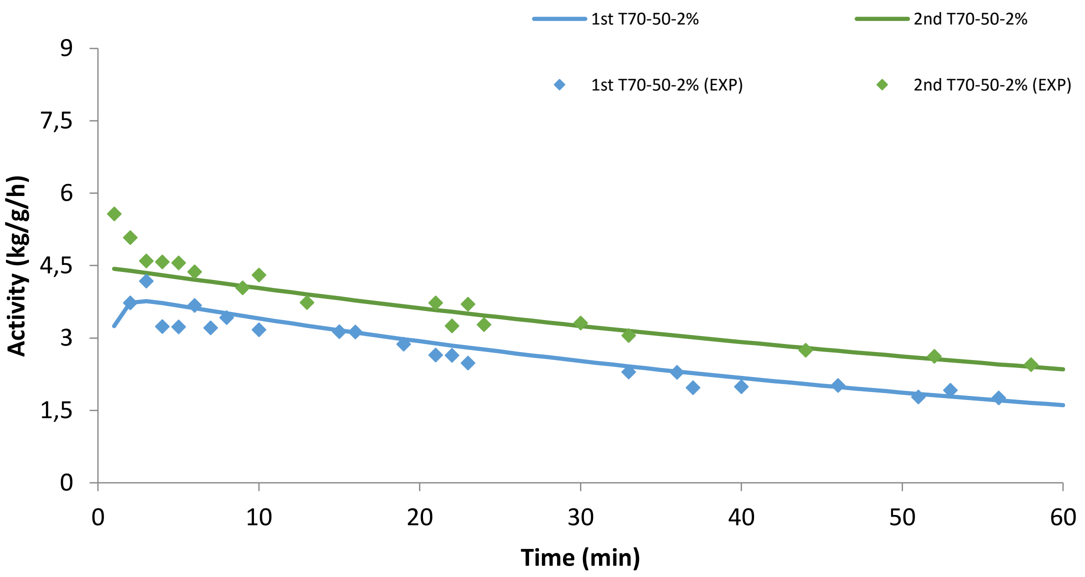


Figure 58 - Reproducibility of T70-50-2%.

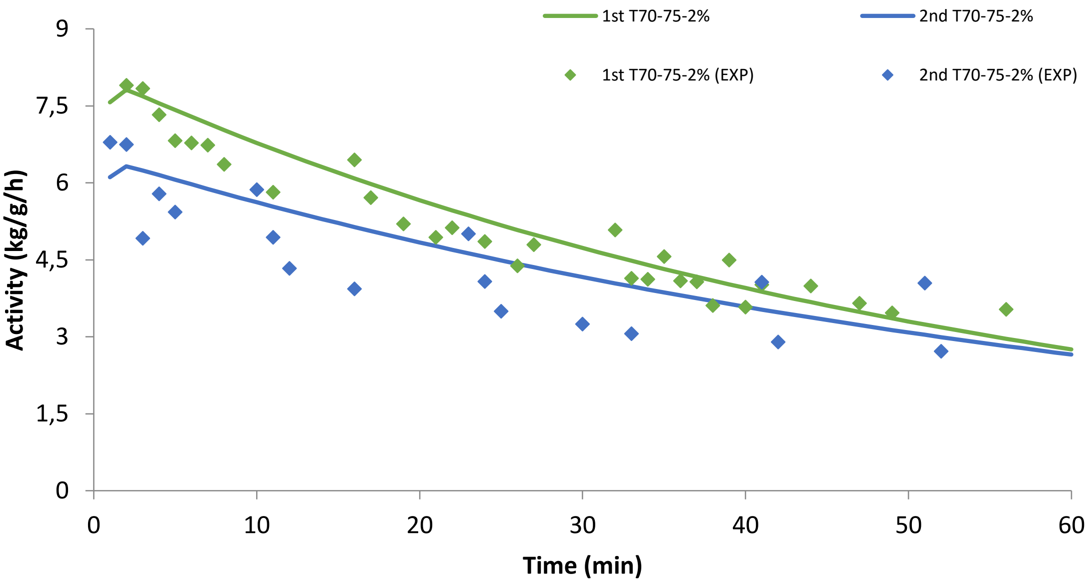


Figure 59 - Reproducibility of T70-75-2%.

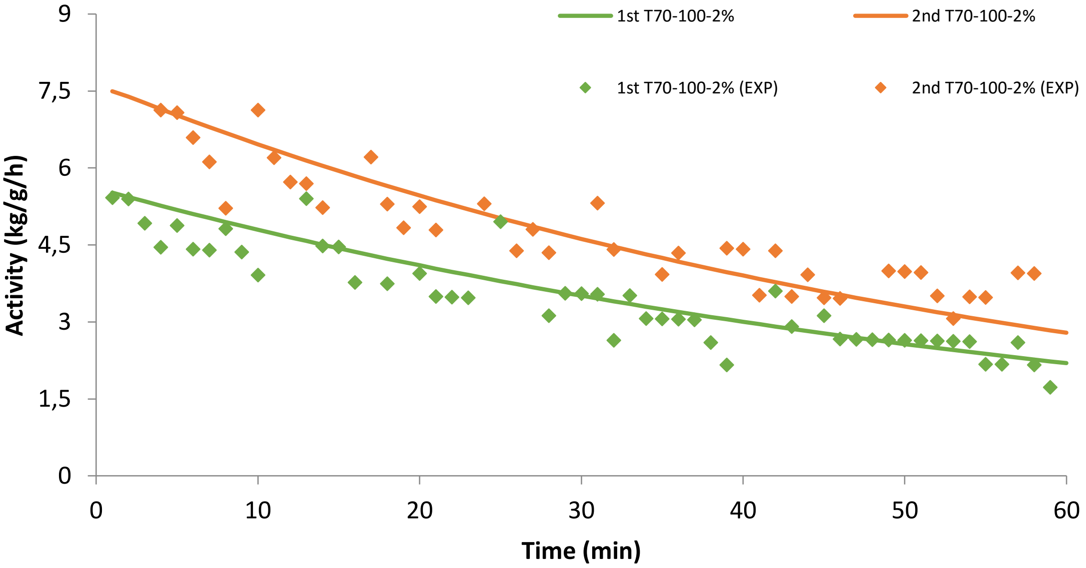


Figure 60 - Reproducibility of T70-100-2%.

Runs with prepolymerization, several amounts of H_2 and wet injection

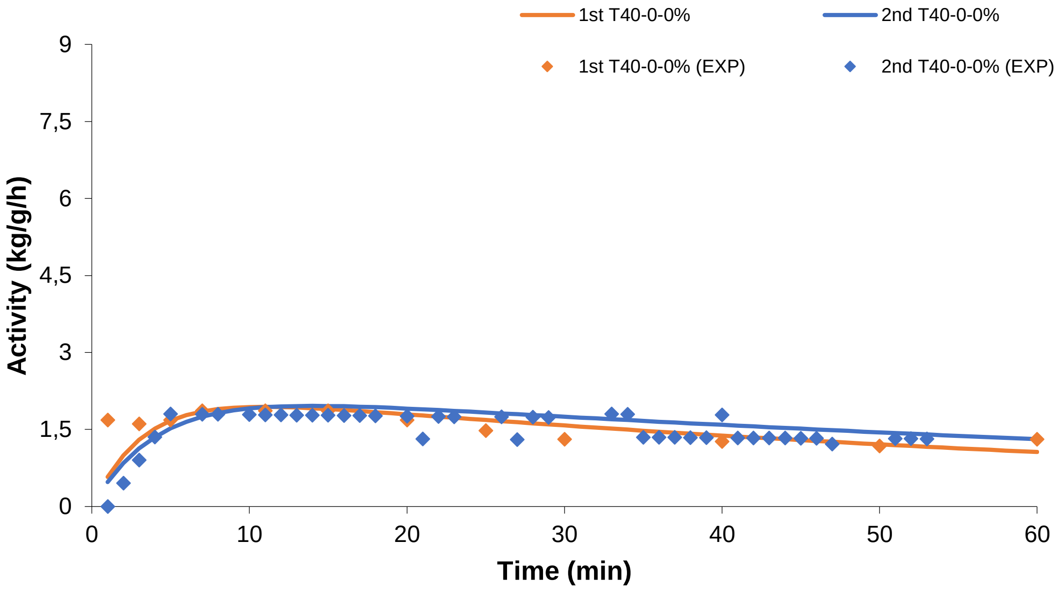


Figure 61 - Reproducibility of T40-0-0%.

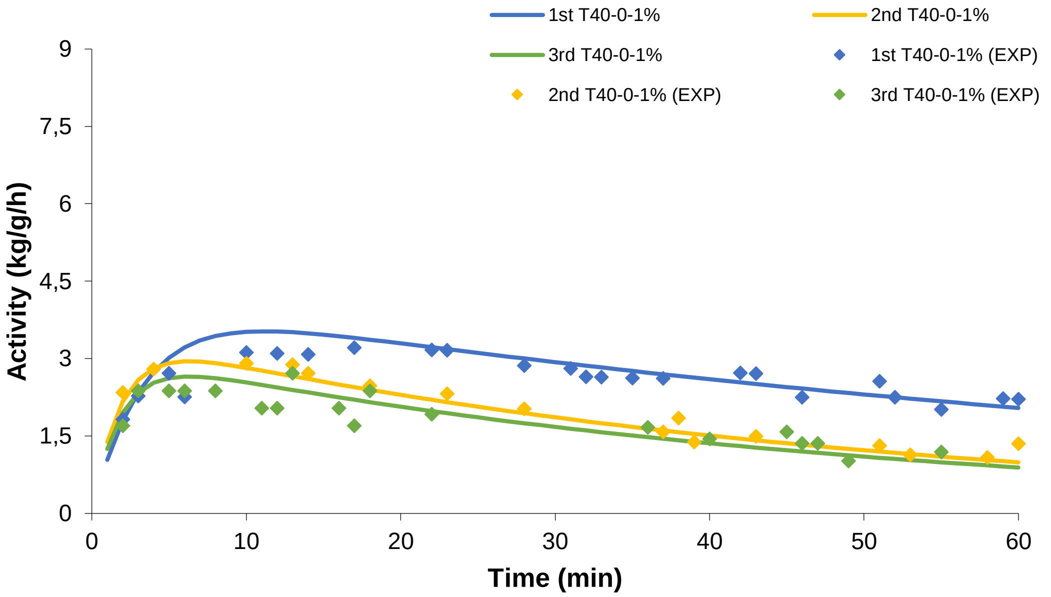


Figure 62 - Reproducibility of T40-0-1%.

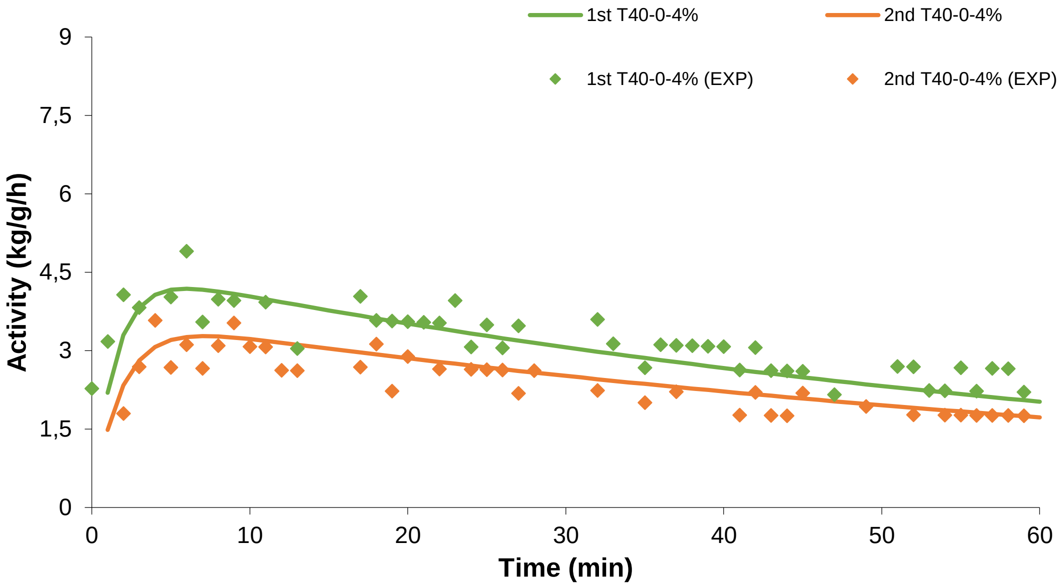


Figure 63 - Reproducibility of T40-0-4%.

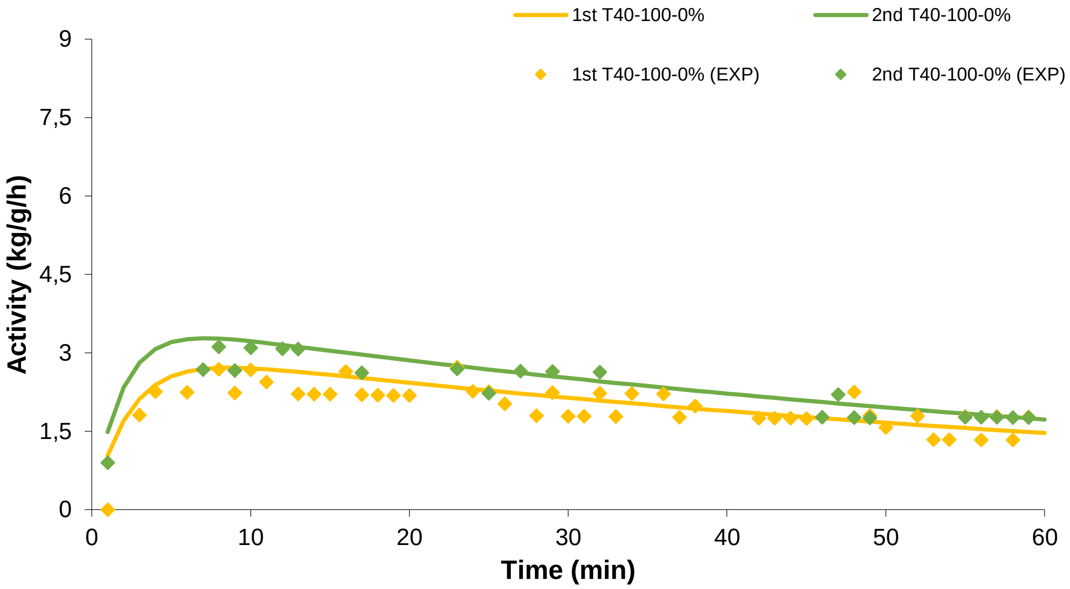


Figure 64 - Reproducibility of T40-100-0%.

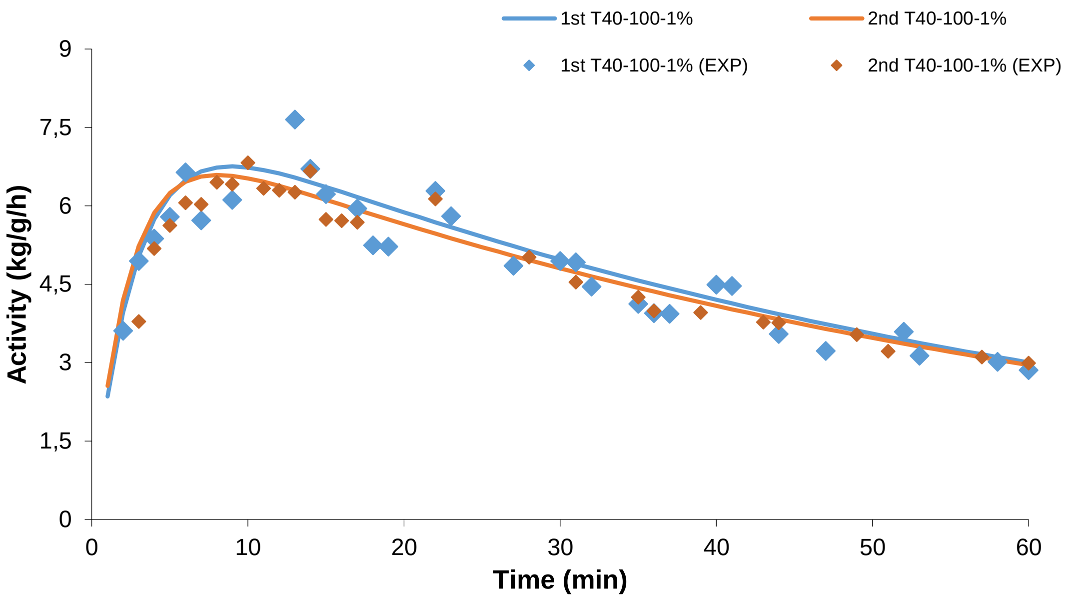


Figure 65 - Reproducibility of T40-100-1%.

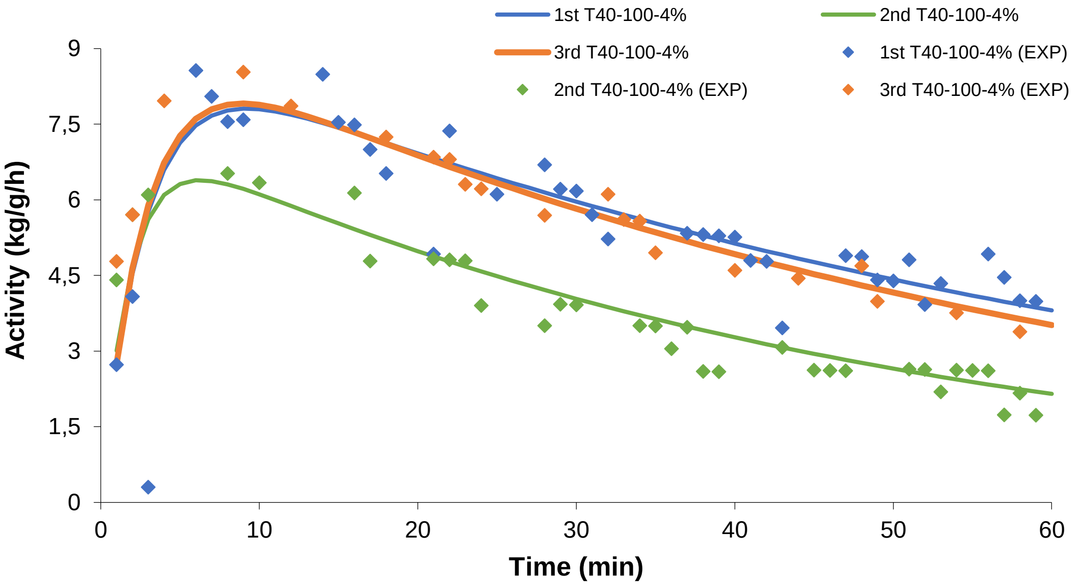


Figure 66 - Reproducibility of T40-100-4%.

Runs with prepolymerization, 2% of H2 and dry injection

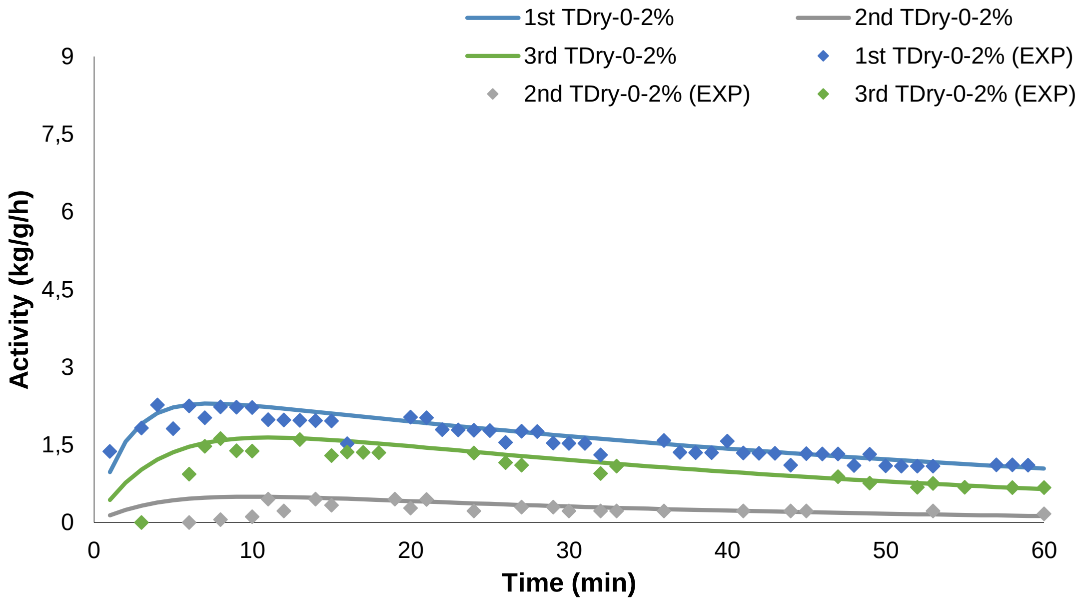


Figure 67 - Reproducibility of TDry-0-2%.

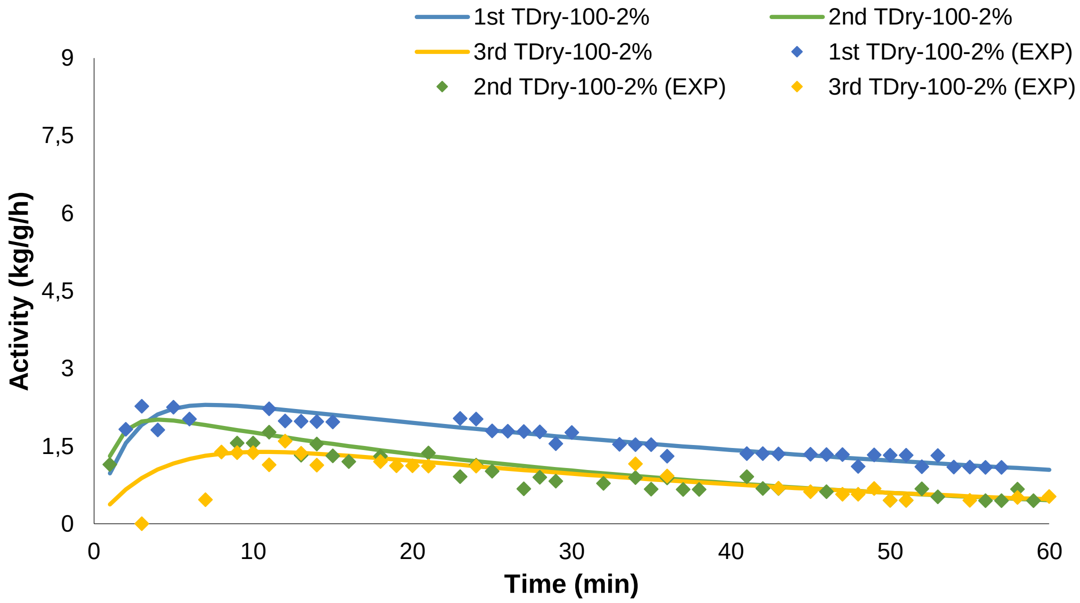


Figure 68 - Reproducibility of TDry-100-2%.

B.2) Kinetic Constants Obtained

Runs with prepolymerization, 2% H_2 and wet injection

Table 8 – Kinetic parameters of runs with prepolymerization, 2% of H_2 and wet injection.

Run	k_p (L mol^{-1} s^{-1})	k_a (s^{-1})	k_d (s^{-1})
1st T40-0-2%	256,2	8,00E-03	1,50E-04
4th T40-0-2%	303,1	7,00E-03	1,60E-04
1st T40-25-2%	397,0	1,00E-02	2,00E-04
3rd T40-25-2%	382,5	1,00E-02	1,90E-04
1st T40-50-2%	490,8	1,50E-02	2,50E-04
3rd T40-50-2%	469,2	1,50E-02	2,00E-04
1st T40-75-2%	577,4	1,50E-02	2,20E-04
2nd T40-75-2%	541,3	1,00E-02	2,00E-04
1st T40-100-2%	505,2	9,00E-03	2,00E-04
2nd T40-100-2%	541,3	1,00E-02	1,80E-04

Runs without prepolymerization, 2% H_2 and wet injection

Table 9 - Kinetic parameters of runs without prepolymerization, 2% of H_2 and wet injection.

Run	k_p (L mol^{-1} s^{-1})	k_a (s^{-1})	k_d (s^{-1})
1st T70-0-2%	216,5	1,00E-02	2,20E-04
2nd T70-0-2%	231,0	9,00E-03	1,50E-04
1st T70-25-2%	303,1	7,00E-02	2,50E-04
2nd T70-25-2%	274,3	8,00E-02	2,20E-04
1st T70-50-2%	252,6	3,00E-02	2,50E-04
2nd T70-50-2%	288,7	1,00E-01	1,80E-04
1st T70-75-2%	519,7	5,00E-02	3,00E-04
2nd T70-75-2%	418,6	5,00E-02	2,50E-04
1st T70-100-2%	360,8	1,00E-01	2,60E-04
2nd T70-100-2%	490,8	1,00E-01	2,80E-04

Runs with prepolymerization, several amounts of H_2 and wet injection

Table 10 - Kinetic parameters of runs with prepolymerization, several amount of H_2 and wet injection.

Run	k_p **(L mol^{-1} s^{-1})**	k_a **(s^{-1})**	k_d **(s^{-1})**
1st T40-0-0%	144,4	5,00E-03	2,20E-04
2nd T40-0-0%	144,4	4,00E-03	1,60E-04
1st T40-100-0%	194,9	7,00E-03	2,10E-04
2nd T40-100-0%	231,0	9,00E-03	2,10E-04
2nd T40-0-1%	216,5	9,00E-03	3,50E-04
3rd T40-0-1%	194,9	9,00E-03	3,50E-04
1st T40-100-1%	505,2	6,00E-03	2,80E-04
2nd T40-100-1%	483,6	7,00E-03	2,70E-04
1st T40-0-4%	295,9	1,10E-02	2,30E-04
2nd T40-0-4%	231,0	9,00E-03	2,10E-04
1st T40-100-4%	577,4	6,00E-03	2,50E-04
3rd T40-100-4%	591,9	6,00E-03	2,80E-04

Runs with prepolymerization, 2% of H_2 and dry injection

Table 11 - Kinetic parameters of runs with prepolymerization, 2% of H_2 and dry injection.

Run	k_p **(L mol^{-1} s^{-1})**	k_a **(s^{-1})**	k_d **(s^{-1})**
1st TDry-0-2%	151,6	8,00E-03	2,40E-04
3rd TDry-0-2%	126,3	4,00E-03	3,50E-04
2nd TDry-100-2%	137,1	5,00E-03	4,50E-04
3rd TDry-100-2%	115,5	4,00E-03	4,00E-04