

# A Study of the Gas Phase Polymerization of Propylene: The impact of catalyst treatment, inject conditions and the presence of alkanes on polymerization and polymer properties.

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**ABSTRACT:** The effect of changing reaction conditions on propylene polymerization using a Ziegler-Natta catalyst is studied. It is observed that the instantaneous rate of polymerization increases performing a prepolymerization. This is 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 affects the instantaneous rate of polymerization, once it reactivates dormant sites of the catalyst. A lower rate is observed in the absence of hydrogen, since there are less active sites where polymerization reaction can occur.

**INTRODUCTION:** Polypropylene is one of the most important polyolefins along with polyethylene and is one of the most versatile thermoplastic polymers available. It is widely used thanks to its properties, which include low density, high stiffness, heat resistance, recyclability, easy to weld, etc, making it one of the most produced polymers in the world, with a production exceeding 50 Mton per year.

Despite the already massive market for polyolefins (estimated to be 125 million tons in 2011), its global consumption is expected to grow over the next years, continuing holding a major portion of the market share of the commodity plastics 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, what makes heat removal one of the main limitations to achieve higher production rates. Gas phase processes are even more affected by this, given the known limitations of heat transfer in gas state. In the current paper, will be studied the impact of changing some reaction conditions that

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

The presence of an alkane increases 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.

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

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can have an effect on the heat removal and the deactivation of the catalyst.

It has already been studied that performing a prepolymerization step before the main polymerization reaction can significantly help controlling the growth of the polymer particle and avoiding the overheating of the particles during the initial reaction times, when catalyst is highly activated.<sup>[1],[2]</sup> 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.

The injection of an alkane, to the best of our knowledge, it has not ever been made during propylene polymerization. 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 and Namkajorn observed that the instantaneous rate of ethylene polymerization is promoted when a higher amount of ICA is introduced [3].

In other hand, 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 diffusivity of ethylene, boosting its concentration inside the active sites of the catalyst, increasing the reaction rate. It is also true that more the alkane is soluble in the polymer, greater is the observed effect.

In propylene polymerization, 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.

Another important aspect in olefin polymerization is the presence of hydrogen in the reaction medium because it plays a decisive role in the way the reaction proceeds. Mori et al.<sup>[4]</sup> studied the effect of hydrogen in slurry polymerization and concluded that it acts as a chain transfer agent and increases activity, since it has the capacity of reactivating dormant sites.

As it is known Ziegler-Natta catalysts produce polymers with high regioregularity<sup>[5]</sup>, favoring 1-2 insertions and head-to-tail enchainment. If the insertion of the polymer is from 2-1 or with other enchainment, it will affect the melting point and the crystallinity of the polymer, as well as the activity, since these can also block active sites. Having this type of regioregularity problem, the active site of the catalyst will stay dormant, which can be reactivated by the hydrogen.

Several patents show that adding a small amount of hydrocarbon to the catalyst prior to its injection in the reactor can help polymer production. As a way of testing the influence of catalyst injection, two systems were studied: solid-solid with salt and solid-liquid with mineral oil. In both cases, the suspension media can absorb some of the reaction heat, improving heat transfer between catalyst particles and surrounding environment. In the case of wet injection, the oil can also 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.

In the current paper, kinetic profiles and powder characterization obtained from gas phase semibatch polymerization reactions have been compared using different reaction conditions such as prepolymerization step, hydrogen concentration, catalyst injection and condensed mode cooling using a commercial Ziegler-Natta catalyst.

## Experimental Section

### Chemicals

The precatalyst was a commercial  $MgCl_2$  supported  $TiCl_4$  fourth generation Ziegler Natta, with titanium content 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  $\mu m$ .

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 190 Al/Ti and the external Lewis base used in a 10 Si/Ti ratio.

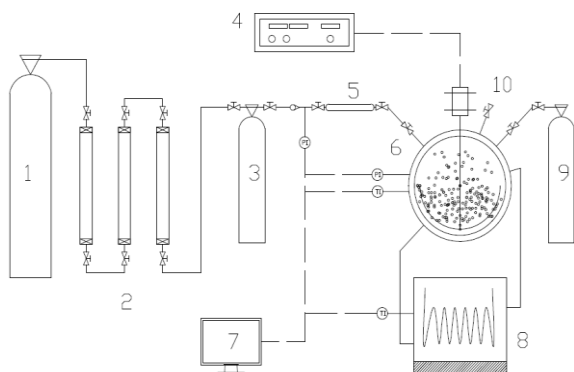
The salt was previously vacuum-dried during five hours at 200°C and kept under argon atmosphere at room temperature. The oil was degassed frozen under vacuum and then kept under argon. The experiments performed with dry injection were made with 30 mg of ZN catalyst, injected along with 10 g of salt. The wet injection was made injecting 250  $\mu L$  of oil, which cores 15 mg of ZN catalyst.

The propylene used was obtained from Scott Specialty Gases with a purity of 99,95% and passed through a three stage system of columns 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 Selextorb 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.

The alkane used in this work was iso-hexane from Sigma-Aldrich with a minimum purity 99%, previously degassed frozen under vacuum and then kept under argon.

## Polymerization Methods

Gas phase homopolymerizations were done in a 2,5L semibatch reactor with injection valves for the catalyst and monomer feeds. The system was kept under isothermal conditions and constant agitation of 300 rpm. Reactor system is schematically shown in **Figure 1**.



**Figure 1 – Polymerization setup represented schematically.**

(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)

## Reaction Preparation

### Precatalyst Preparation

Regardless of the method of injection, the precatalyst was prepared in a glovebox (Jacomex, France) under argon atmosphere. 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. For the solid suspension system precatalyst was diluted with coarse salt in a 100 cm<sup>3</sup> cartridge injector. The precatalyst was not pre-activated before injection to the turbosphere reactor.

### Reactor Preparation

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

### Polymerization Procedure

After the system had reached the desired initial temperature, the TEA/heptane mixture was injected

to the reactor and agitation (300 rpm) was started. Subsequently, about 5 minutes after the first injection the donor/heptane mixture and the catalyst suspension were injected under an argon stream. Finally the reactor is pressurized with a mixture of monomer-hydrogen in the desired ratio.

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.

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 °C to remove the remaining traces of solvent.

### Prepolymerization Procedure

Gas phase prepolymerization was performed at 3,5 bar of propylene pressure, without hydrogen, at 40 °C during 10 min. Then temperature and pressure were gradually increased at full reaction conditions over the course of approximately 20 min. Thus, an isothermal/non-isothermal prepolymerization method is applied (INM) <sup>[1]</sup>. The prepolymerization rate profiles are not shown, but the yields were always approximately 200 g g<sup>-1</sup>.

## Powder Characterization

### Bulk Density

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

### Differential Scanning Calorimetry

The crystallinity and melting point was analyzed in a Differential Scanning Calorimeter from Mettler Toledo. During this analysis, each polymer sample is individually cooled until it reaches -80°C, then it is heated to 200°C, followed by a decrease until -80°C and a second heat step to 200°C.

### Size Exclusion Chromatography

The molecular weight distribution was analyzed in high temperature size exclusion chromatography equipment. The samples were dissolved in trichlorobenzene and left heating and agitating for one hour and a half. After this time, each sample was passed by the three columns inside the equipment.

## Results and Discussion

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 1.

**Table 1 - Reaction conditions used in each run.**

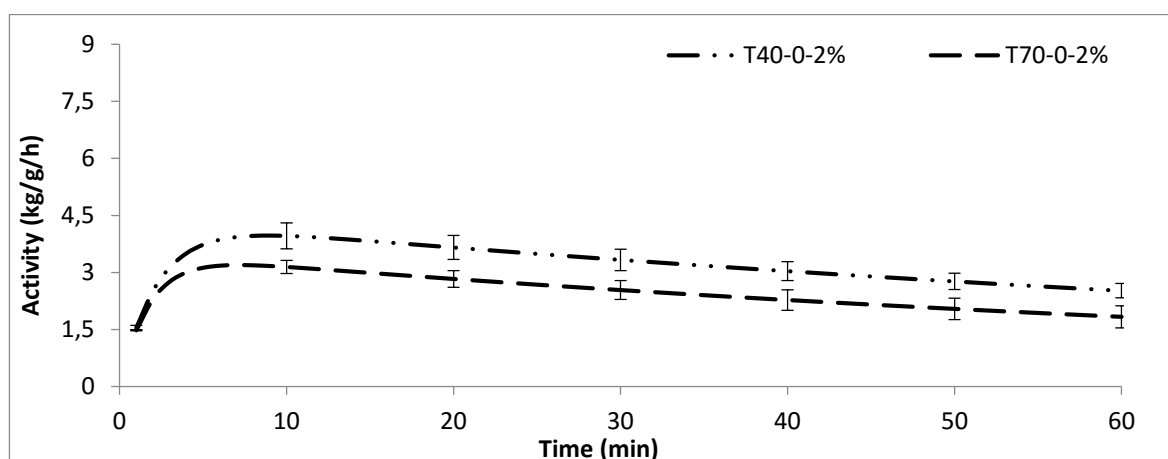
Run	Prep.	Alkane (bar)	Cat. Inj.	H <sub>2</sub> (%)
T40-0-2%	YES	0	WET	2
T40-25-2%	YES	0,33	WET	2
T40-50-2%	YES	0,67	WET	2
T40-75-2%	YES	1,00	WET	2
T40-100-2%	YES	1,33	WET	2
T70-0-2%	NO	0	WET	2
T70-25-2%	NO	0,33	WET	2
T70-50-2%	NO	0,67	WET	2
T70-75-2%	NO	1,00	WET	2
T70-100-2%	NO	1,33	WET	2
T40-0-0%	YES	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

The name of the experiments is generally given by TXX-Y-Z% where XX is 40 in case of prepolymerization is performed and 70 if not (except in the case of dry injection); 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.

### Influence of prepolymerization

The effect of a prepolymerization step is shown in Figure 2 where it can be seen that over the course of one hour the activity is higher the one obtained by direct polymerization. As we can see below there is a boost in the rate of reaction when prepolymerization is performed which is due to a higher catalyst 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 it occurs in a lower reaction rate, there is less heat of reaction generated resulting in less deactivation of the catalyst particles.

At the beginning of the polymerization reaction, a high catalytic activity can lead to a rapid temperature increase of the catalyst particle. Owing to the small surface area and to difficulties on heat transfer between particle and reaction environment, there is an uncontrolled fragmentation of the catalyst particle, destroying it [2] and leading to a polymer with lots of fines. When using a prepolymerization technique before the polymerization itself, the catalyst surface area is gradually increased at a low reaction rate [1], which improves the heat transfer and leads to a better polymer particle formation and catalyst replication.



**Figure 2 - Kinetic profiles of reactions with and without performance of prepolymerization step.**

### 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 3**, the activity decreases to the lowest values when catalyst injection is made in dry.

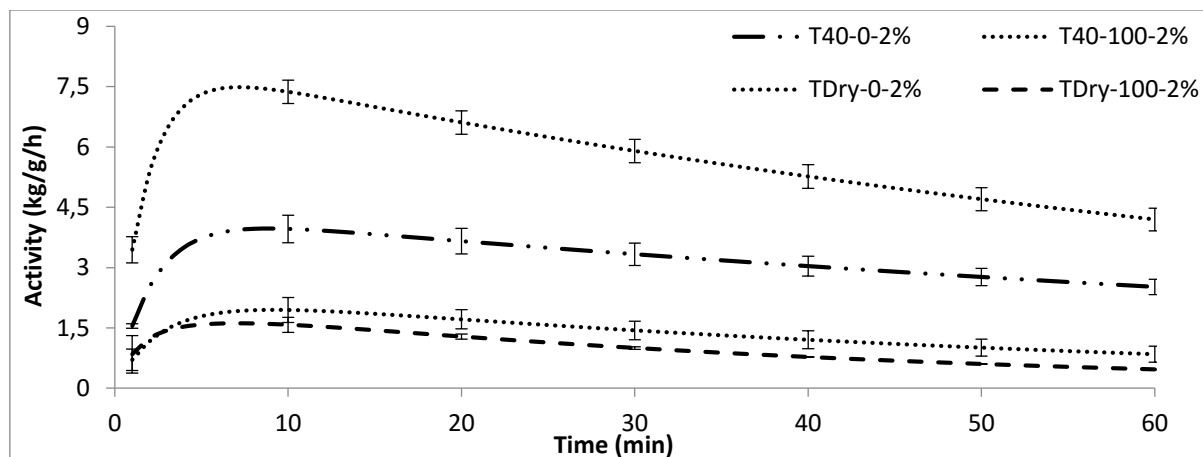


Figure 3 - Kinetic profiles using different type of catalyst injection.

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.

### Hydrogen Concentration

**Figure 4 and 5** shows the difference of introducing in the reactor different amounts of hydrogen and also how the injection of alkane effects it.

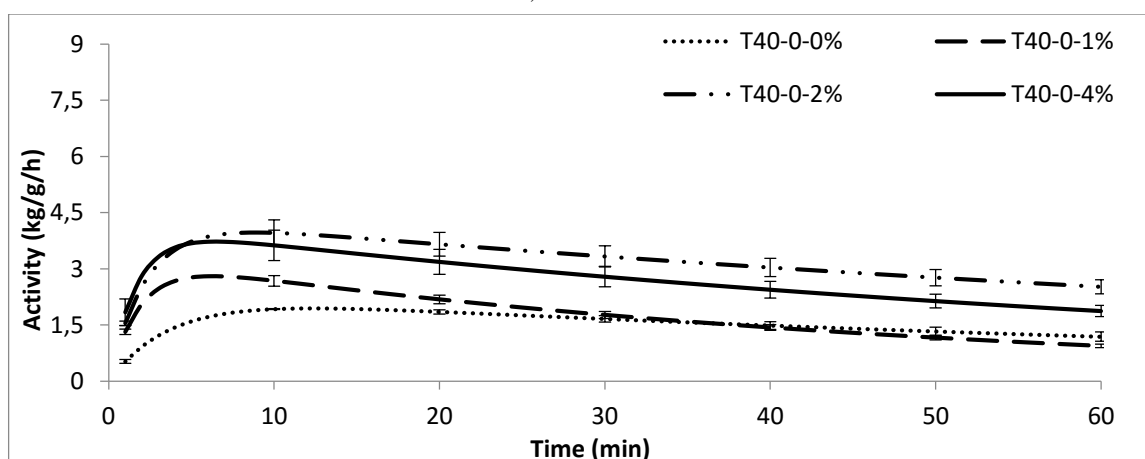


Figure 4 - Kinetic profile using different amounts of H<sub>2</sub>: 0, 1, 2 and 4% in the absence of alkane.

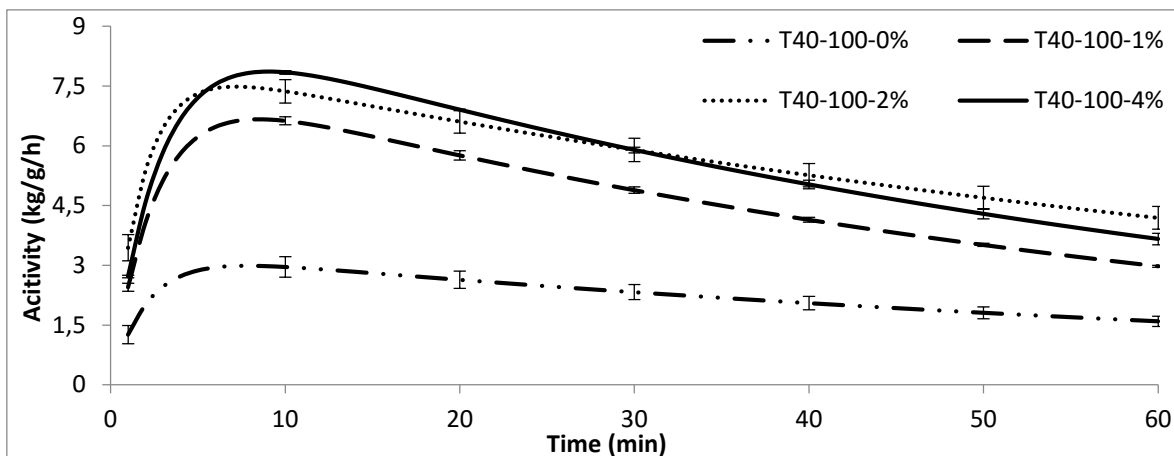


Figure 5 - Kinetic profile using different amounts of H<sub>2</sub>: 0, 1, 2 and 4% in the presence of alkane.

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<sub>2</sub>. The injection of alkane amplifies even more this difference, since it does not just enhance the local concentration of propylene inside the active sites but also the use 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<sub>2</sub> resulting in no activity.

### 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 6** it is possible to analyze the influence of feeding different amounts of alkane to the reactor, when there is no performance of a prepolymerization step. **Figure 7** represents the influence of the amount of alkane fed to the reactor in rate of activity, when a prepolymerization step is performed.

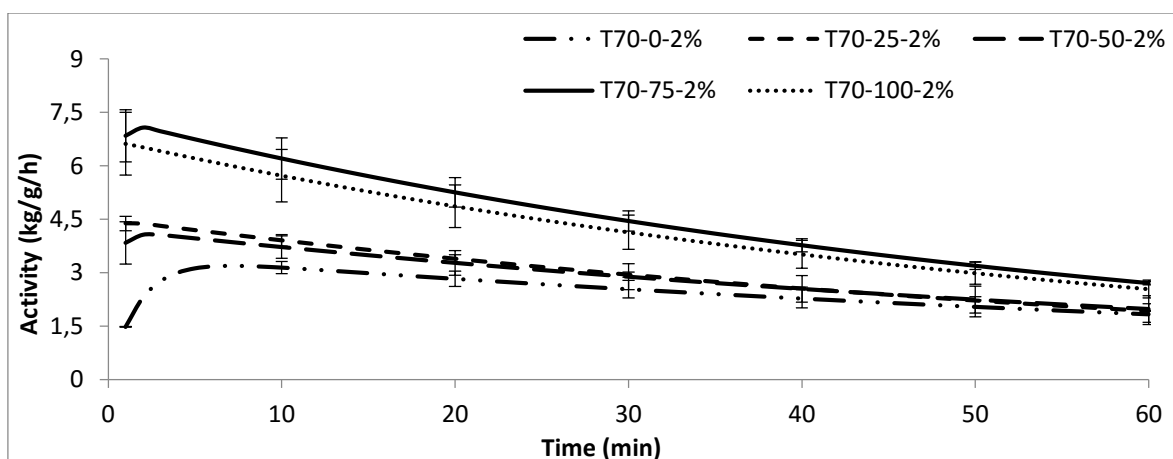


Figure 6 - Kinetic profile using different amounts of alkane without prepolymerization step.

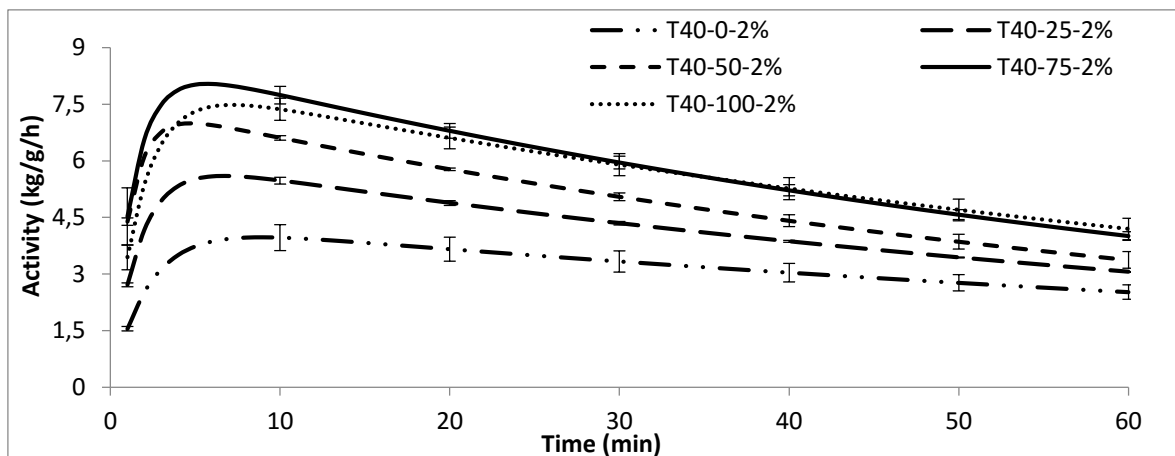


Figure 7 - Kinetic profile using different amounts of alkane with prepolymerization step.

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.

### Molecular Weight Distribution

Table 2 shows the variation of  $M_w$  and  $M_n$  with the different reaction conditions studies.

Table 2 - 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 <sup>1</sup>	580 <sup>1</sup>
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

<sup>1</sup> - Only one sample analyzed.

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.

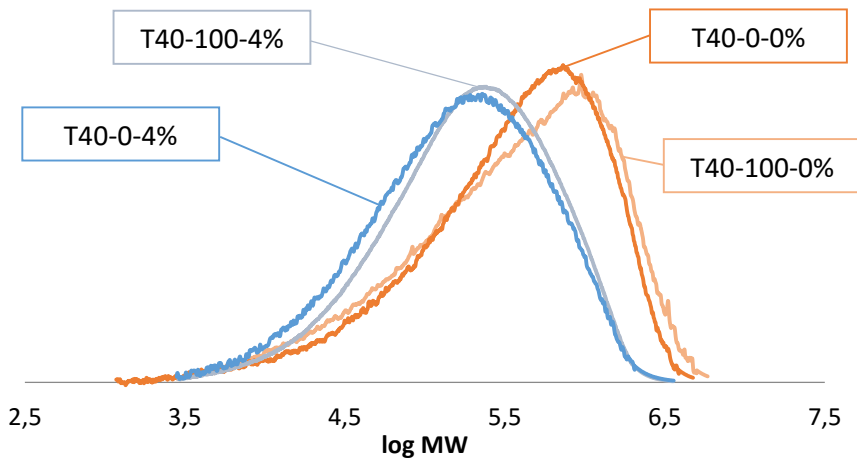


Figure 8 – MWD for the polymers produced in experiments with different amounts of hydrogen.

When there is not hydrogen injected in the reactor, there is no chain transfer agent, increasing the chain length and so the molecular weight of the produced polymer.

### Bulk Density

The bulk density of the produced polymer in each run can be analyzed in the next figures. **Figure 9** shows the difference of bulk density with the type of injection.

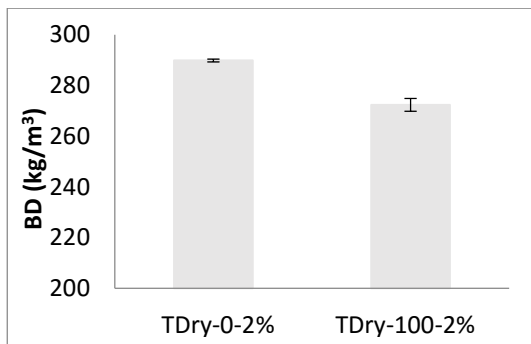


Figure 9 - Variation of bulk density with the type of catalyst injection.

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 hollow and flaky.

In other hand, when the polymerization is performed with the injection of alkane, the bulk density of the polymer obtained is a slightly higher, once there is an enhancement of the local concentration of propylene inside the particle.

**Figures 10 and 11** show the variation of bulk density with different amounts of alkane introduced in the reactor, with and without prepolymerization, respectively.

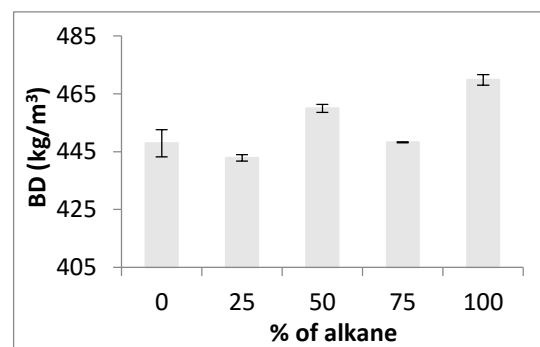


Figure 10 - Variation of bulk density with the quantity of alkane injected when a prepolymerization step is performed.

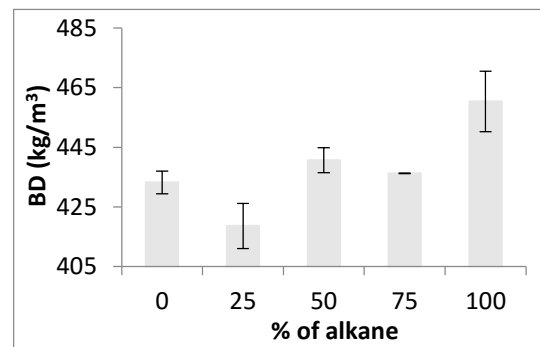


Figure 11 - Variation of bulk density with the quantity of alkane injected without prepolymerization.

Analyzing the bulk density of the polymers, we can conclude that there is slightly 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 12 and 13** show the difference between each concentration of hydrogen and how does it change with the presence of alkane.



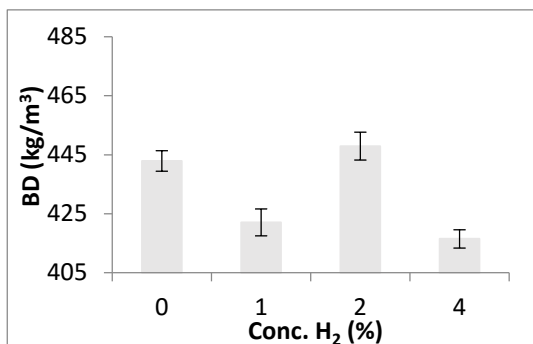


Figure 12 - Variation of bulk density with the concentration of hydrogen without alkane.

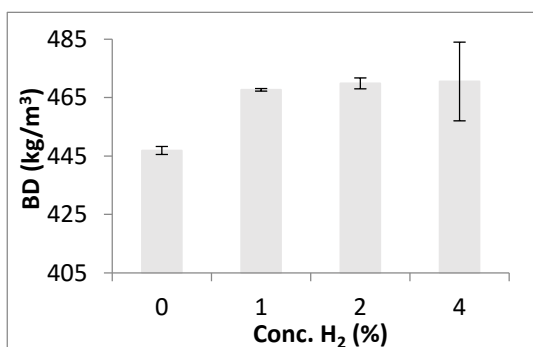


Figure 13 - Variation of bulk density with the concentration of hydrogen in the presence of alkane.

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.

### Differential Scanning Calorimetry

The crystallinity of the produced polymers in each run can be analyzed in the next figures. **Figure 14** shows the effect of alkane presence on the polymers produced when catalyst injection is made in dry mode, **Figure 15 and 16** represent the crystallinity of samples produced with and without prepolymerization with different amounts of isohexane introduced. **Figure 17 and 18** represent how crystallinity is affected by the concentration of hydrogen and its relation with amount of alkane. The black bar represents the first heating curve and the white one the second heating curve.

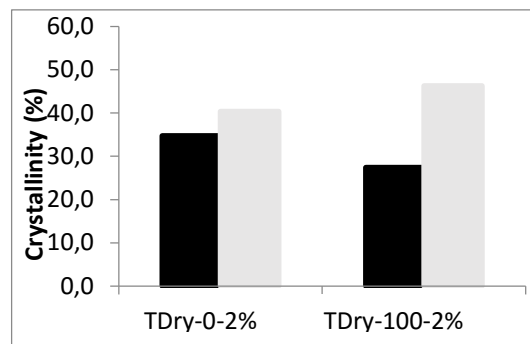


Figure 14 - Variation of crystallinity with the type of catalyst injection.

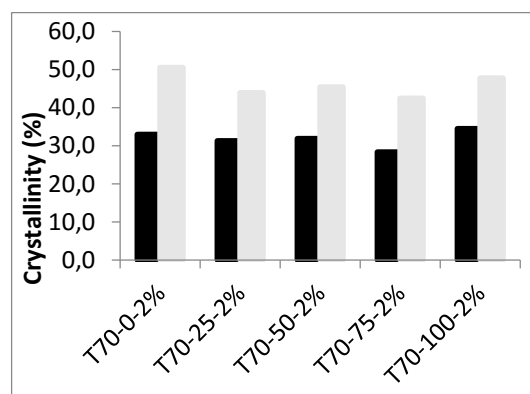


Figure 15 - Variation of crystallinity with the quantity of alkane injected without prepolymerization.

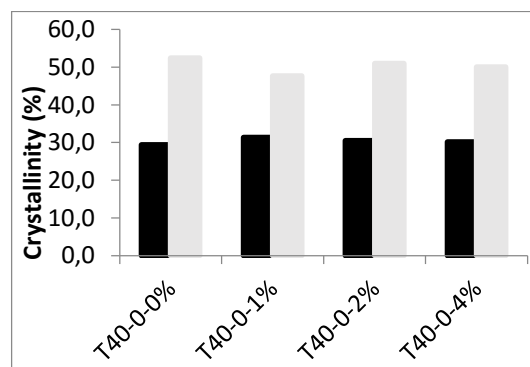


Figure 16 - Variation of crystallinity with the quantity of alkane injected when a prepolymerization step is performed.

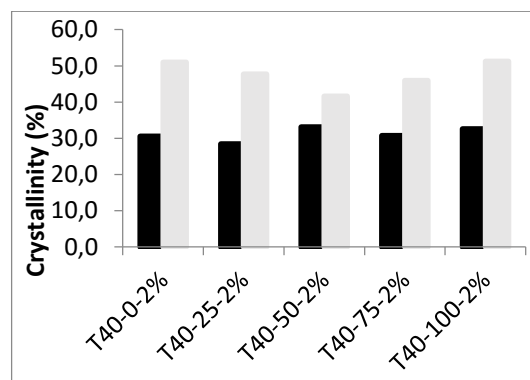
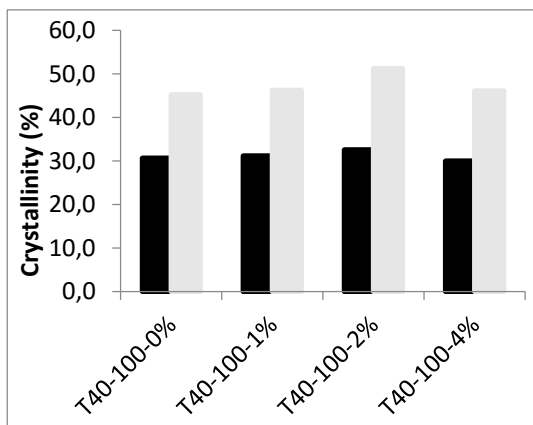


Figure 17 - Variation of crystallinity with the concentration of hydrogen without alkane.



**Figure 18 - Variation of crystallinity with the concentration of hydrogen with alkane.**

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

### Acknowledgements

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### Conclusions

The instantaneous rate of polymerization increases with the performance of a prepolymerization step, thanks to a decrease of the local particle overheating in the initial instants of reaction. The bulk density is higher when a prepolymerization

step is performed, but not the molecular weight. By the absorption of the reaction heat and also by enhancement of the local concentration of propylene inside the active sites of the catalyst, the presence of an alkane leads to a higher activity profiles. The presence of an alkane also affects the bulk density in both cases (with and without prepolymerization) but not the molecular weight distribution.

Hydrogen concentration affects the instantaneous rate of polymerization, the bulk density and the molecular weight. A lower polymerization rate, higher molecular weight and lower bulk density are observed in the absence of hydrogen. It is observed also that the rate of polymerization is higher when the catalyst is injected with mineral oil, having the produced polymer higher bulk densities.

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