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THE EFFECT OF A ZIEGLER-NATTA CATALYST AND THE POLYMERIZATION PARAMETERS ON THE BASIC PROPERTIES OF POLYETHYLENE

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In our article, some of the basic correlations concerning the polymerization behaviour of a Ziegler-Natta catalyst are presented. We have examined a general, commercial $MgCl_2$ supported catalyst, the effect of the main polymerization parameters, such as hydrogen concentration, Al/Ti mol ratio, monomer (ethylene) concentration and residence time on the productivity of the catalyst and the properties of the final polyethylene product.

Keywords: olefin polymerization, Ziegler-Natta catalyst, polymer properties, polyethylene

Introduction

One of the biggest achievements in the history of polyolefin production is connected with the names of Ziegler and Natta. In 1953 it was discovered in the laboratory of Ziegler, that with the mixture of metal-alkyl and transition metal salts, it is possible to produce high density polyethylene (HDPE) at low pressure. As an addition, Natta and his coworkers justified that the same catalyst system is capable for the production of isotactic polymers, based on different α-olefins. The two scientists were awarded by Noble-price for their discovery in 1963. Heterogeneous Ziegler-Natta catalysts usually consists of Ti- or V-trichloride and some kind of Al-organic compound, and are used already more than half century for the polymerization of α-olefins and dienes.

In the past decades the development of these catalysts is continuous. Nowadays, the most "state of the art" types are referred as 5th generation catalysts, and although they also inherit the basics of their ancestors, also contain a lot of improvements. These improvements (for example: new methods in catalyst production, application of carriers, electron donors – that are essential in case of monomers with atactic carbon – and of course new technological solutions ensure still the importance of this catalyst family.

Table 1: Generations of Ziegler-Natta catalysts

Generation	Catalyts	Productivity g/g	Isotact. Index %
I.	δ-$TiCl_3$. 0,33$AlCl_3$ + DEAC	1500	90-94
II.	γ-$TiCl_3$ + DEAC	4000	94-97
III.	$TiCl_4$/mono-ester(ID)/$MgCl_2$+TEAL/ester(ED)	<20000	90-95
IV.	$TiCl_4$/di-ester(ID)/$MgCl_2$+TEAL/silane(ED)	>25000	95-99
V.	$TiCl_4$/di-ether, succiante(ID)/$MgCl_2$ + TEAL (silane(ED)-not essential)	>50000	95-99

DEAC: diethyl-aluminum-chloride; TEAL: triethyl-aluminum; ID: internal (electron) donor; ED: external (electron) donor

The variety of Ziegler-Natta catalyst systems is very wide. They can differ in transition metal, metal-alkyl (so called cocatalyst), structural properties (particle size, morphology, porosity, stiffness, etc.), composition (Ti content, ID content) [1-6], but the commercial catalysts usually are based on $TiCl_4$ on $MgCl_2$ carrier with TEAL cocatalyst. The mechanism of the polymerization is still not absolutely clear, although in the literature we can find several theories in this topic. The most common ones are the bimetallic model by Natta, Patat and Sinn [7-10], the monometallic model by Arlman and Cossee [11-12] and the trigger mechanism by Ystenes [3, 13]. Although the importance of electron donors is also very considerable, within the polymerization of ethylene they do not have a big concern [1-6].

In industrial sizes the most paramount parameters that have to be taken into consideration to make different, tailor-made polyolefin products with special

properties, are for example reaction temperature, concentration of monomer, comonomer, cocatalyst, hydrogen, and residence time in the reactor, etc. The effects of the parameters we have investigated in our project are as follows [1, 3, 4, 15-16]:

1. Hydrogen concentration: hydrogen is used as molecular weight (Mw) controller substance via chain transfer. With increasing hydrogen concentration the weight of chain transfer reactions increase and the molecular weight of the macromolecule decrease. Because all base properties are in connection with Mw, the structure of the chain, this also affects actually every properties of the final product (mechanical, optical, thermal). Notable fact is that the concentration of hydrogen also affects the productivity of the catalyst, but differently with different monomers. For example with increasing hydrogen concentration the productivity increases in case of propylene, and decreases in case of ethylene monomer.
2. Al/Ti mol ratio: this ratio comes from the ratio of cocatalyst (triethyl-aluminum) and the catalyst (Ti content). The cocatalyst has a double effect. First it eliminates impurities from the different reaction components, and second, it activates the catalyst (reduces Ti^{4+} to the active Ti^{3+}) form. Based on these effects the concentration of the cocatalyst has a very sensitive role. With increasing amounts, as more impurities can be eliminated, and more active sites can be formed, the productivity of the catalyst increases. After an optimal value, the productivity decreases due to over reduction of Ti^{3+} to the inactive Ti^{2+} form.
3. Monomer concentration: with increasing monomer concentration, as the ratio of monomer/active sites is increasing, the productivity of the catalyst increases, and also the Mw.
4. Residence time: the produced amount of polyethylene increases with increasing residence time. This connection is not similar for all catalysts, as it is based on kinetic behaviour. Some types are starting with high initial rates that decrease in time, some others are able to maintain an almost constant value.

Experimental

Within our experiments we have investigated a $MgCl_2$ supported $TiCl_4$ based Ziegler-Natta catalyst, with 4.5% titanium content. As cocatalyst, we have used TEAL. The polymerization tests were carried on in a 20 litre volume batch-scale laboratory reactor in isobutane media. Along the project we have measured the effect of the above mentioned parameters on the productivity of the catalyst, and the properties of the final product. The following measurements were carried out:

1. MFR (melt flow rate): with different weights based on ISO 1133,
2. Density based on ISO 1183,
3. Molecular weight (Mn, Mw) with GPC (PL-GPC 210),
4. Thermal measurements (melting and crystallization temperatures, enthalpies) were made on a Netzch DSC 2004 Phoenix scanning micro calorimeter,
5. Micro-structure characteristics (number of methyl, vinyl, vinylidene, vinylene groups) were carried out on a Mattson Galaxy 3020 FTIR spectroscope,
6. Particle size distribution based on ASTM D 1921.

Results and evaluation

Effects of different hydrogen concentrations

To be able to see only the effect of hydrogen in our experiments, all the other parameters were constant, even monomer concentration in the liquid phase (this means, that experiments with different hydrogen concentrations were carried out on different polymerization pressure with the same ethylene concentration). The needed component amounts were calculated by a software developed by Department of Process Engineering at University of Pannonia. Referring to our literature summary, it is clear, that at HDPE production with increasing hydrogen concentration the activity of the catalyst is decreasing. The cause of this is the slow addition of a new monomer to the Ti-H bond, formed at the previous chain transfer reaction. The amount of hydrogen was changed between 0 and 200 Nl (normal litre).

The tests were carried out at standard Al/Ti mol ratio (100), temperature (80 °C) and stirring (500 1/min) for 2 hours. On the next figures we present the correlation between hydrogen amount and catalyst productivity, and the kinetic flow of the reaction (ethylene feed to maintain standard pressure in the reactor).

As it can be seen, that at lower rates the productivity of the catalyst is increasing, and after a certain amount it decreases as it is awaited based on the literature. The cause of the difference from the logical tendency at the point without any hydrogen is linked also to the effect of hydrogen. Because there is no hydrogen, the productivity of the catalyst is very high at the beginning of the reaction.

This increased productivity is so high, that the heat and stress that appears at the catalyst particle, destroys partially the structure of the catalyst itself, so after a short period the productivity decreases more dramatically then in the case of some hydrogen. Because of this, the overall, average productivity will be lower, than “expected”. In all other cases when there is hydrogen in the system, it controls the catalyst, and this damage doesn’t occur.

Concerning to the base properties of the polymer the effect of hydrogen as chain transfer agent can be seen at all of our data. With increasing hydrogen amount, the average molecular weight of the chains is decreasing (that causes higher melt flow rates) that also affects the density (shorter chains increase the density via overall crystallinity).

The effect of hydrogen can be seen on the results of our other analytical measurements (FTIR, GPC, DSC), that are not detailed here.

Table 2: Test parameters with different hydrogen amounts

Reactor pressure (barg)	Hydrogen amount (Nl)	Hydrogen concentration in liquid phase (mol%)	Ethylene amount (for filling up to pol. pressure) (g)	Ethylene concentration in liquid phase (mol%)
17	0	0	152	4,5
18,4	14,7	0,3	152	4,5
21,8	50	1,0	153	4,5
26,7	100	2,0	155	4,5
31,7	150	3,0	157	4,6
36,8	200	4,0	159	4,6

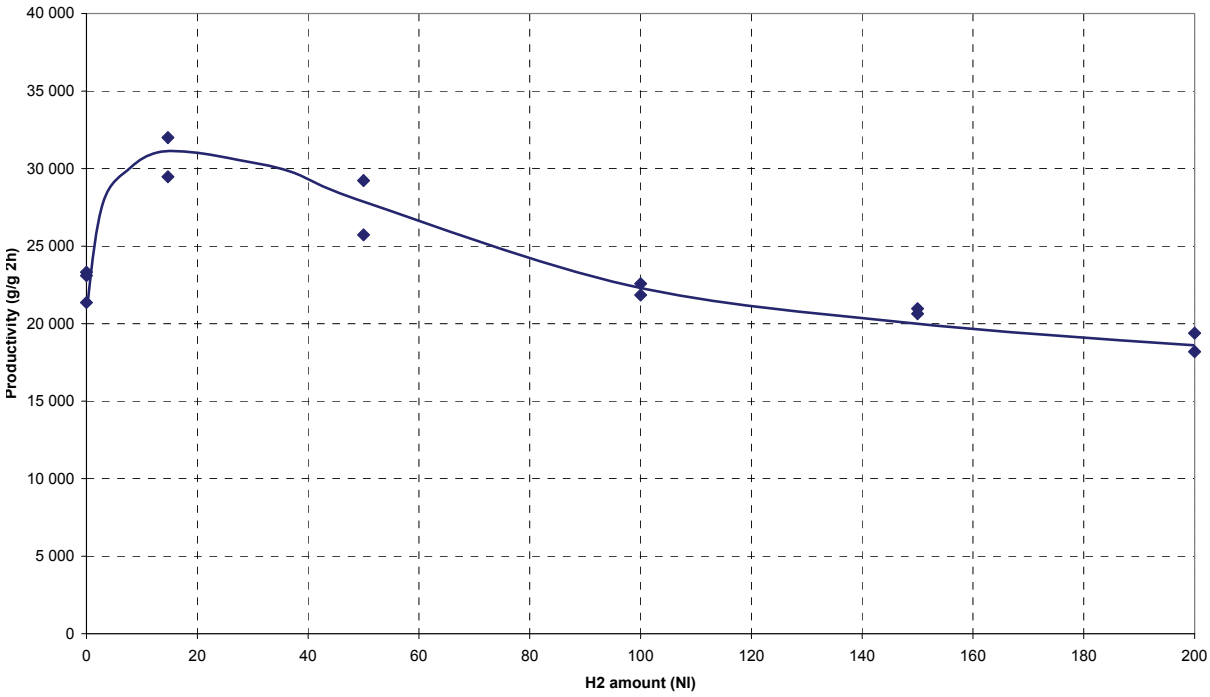

Figure 1: Productivity vs. hydrogen amount

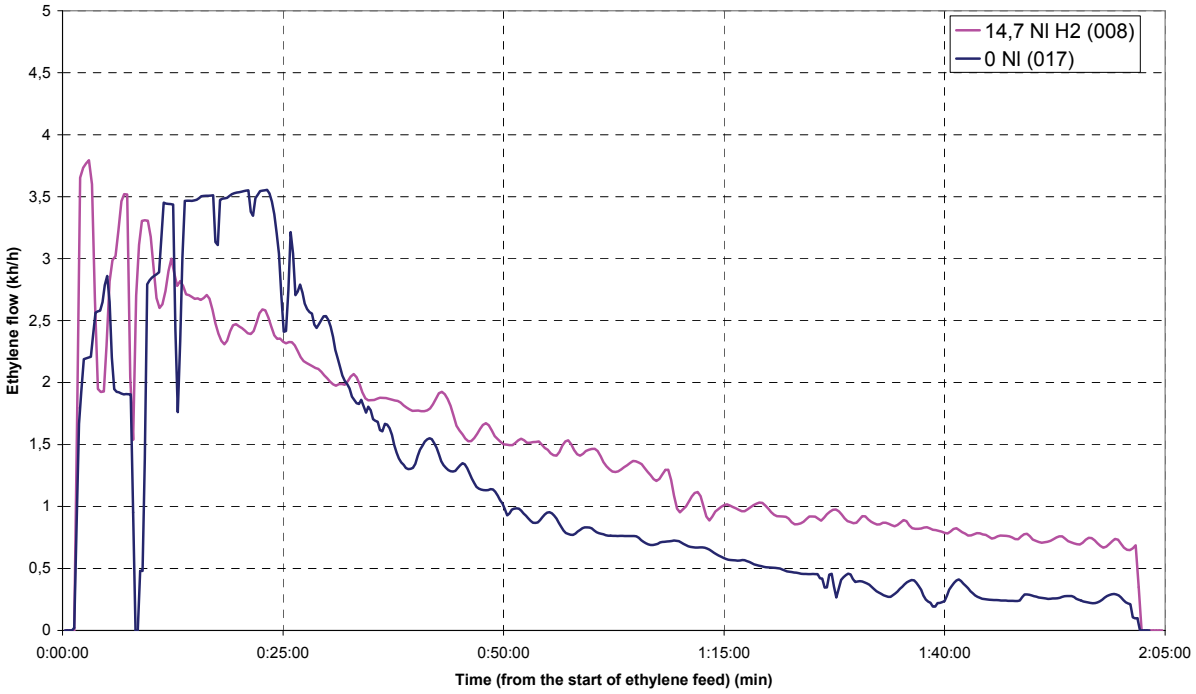

Figure 2: Ethylene flows at different hydrogen amounts

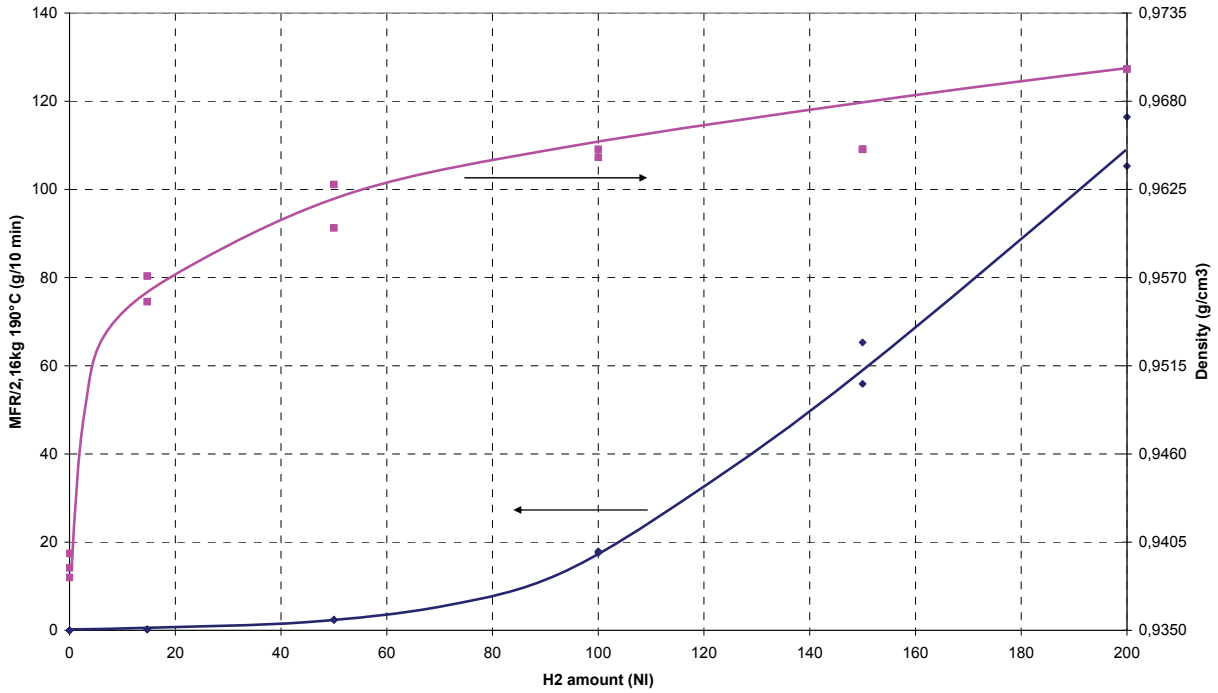

Figure 3: Effect of hydrogen amount on the MFR and density of the HDPE product

The effects of different Al/Ti ratios

As we explained before, the optimal Al/Ti mol ratio is very important in the polymerization reactions, due to its double function (elimination of impurities, reduction of Ti4+). In our experiments we have changed the ratio between 0 and 400, while the other parameters were constant (hydrogen: 50 Nl, temperature: 80 °C, pressure: 21,8 barg, stirrer: 500 1/min, residence time: 2 hours).

As it can be seen on the figure below, the optimal Al/Ti mol ratio was 25, this value resulted the highest productivity. The Al/Ti mol ratio has of course other effects also on the properties of the polymer, but they are not very important. With high redundancy it decreases molecular weight, as it has also minor chain transfer function.

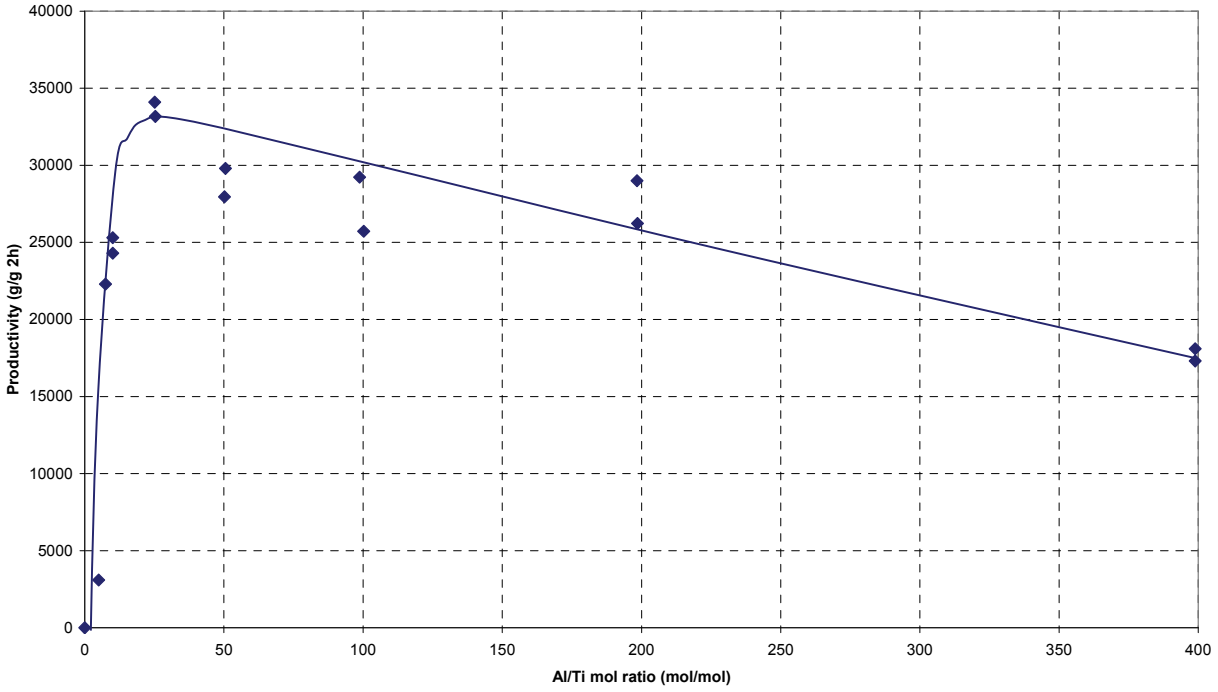

Figure 4: Effect of Al/Ti mol ratio on the productivity of the catalyst

Effects of monomer (ethylene) concentration

To be able to examine a wider concentration interval, we had to do some changes at our tests. The cause of this is, that at higher concentrations with the standard amount of catalyst and residence time, the amount of the polymer powder was too much for the reactor to handle, and the efficiency of the temperature control decreased heavily. So beside of the untouched standard parameters (hydrogen amount: 50 Nl, temperature: 80 °C, Al/Ti mol ratio: 100, stirrer: 500 1/min) we decreased residence time to 1 hour, and at the tests with the highest ethylene concentrations, we also decreased the amount of the catalyst.

Our changes in ethylene concentration and catalyst amount increased the C2/Ti ratio that is the monomer/active site ratio. The main affect of this can be seen in catalyst productivity and molecular weight increase (decreased MFR values).

Table 3: Test parameters with different ethylene amounts

Pressure (barg)	20,1	21,8	25,2	25,2	25,2
Ethylene amount (for filling up to pol. pressure) (g)	75,1	153	313,5	313,5	313,5
Ethylene concentration in liquid phase (mol%)	2,27	4,52	8,96	8,96	8,96
Catalyst amount (g)	0,1	0,1	0,1	0,05	0,025
C_2/Ti ratio in liquid phase (mol/mmol)	22,5	46,0	95,9	191,9	383,8

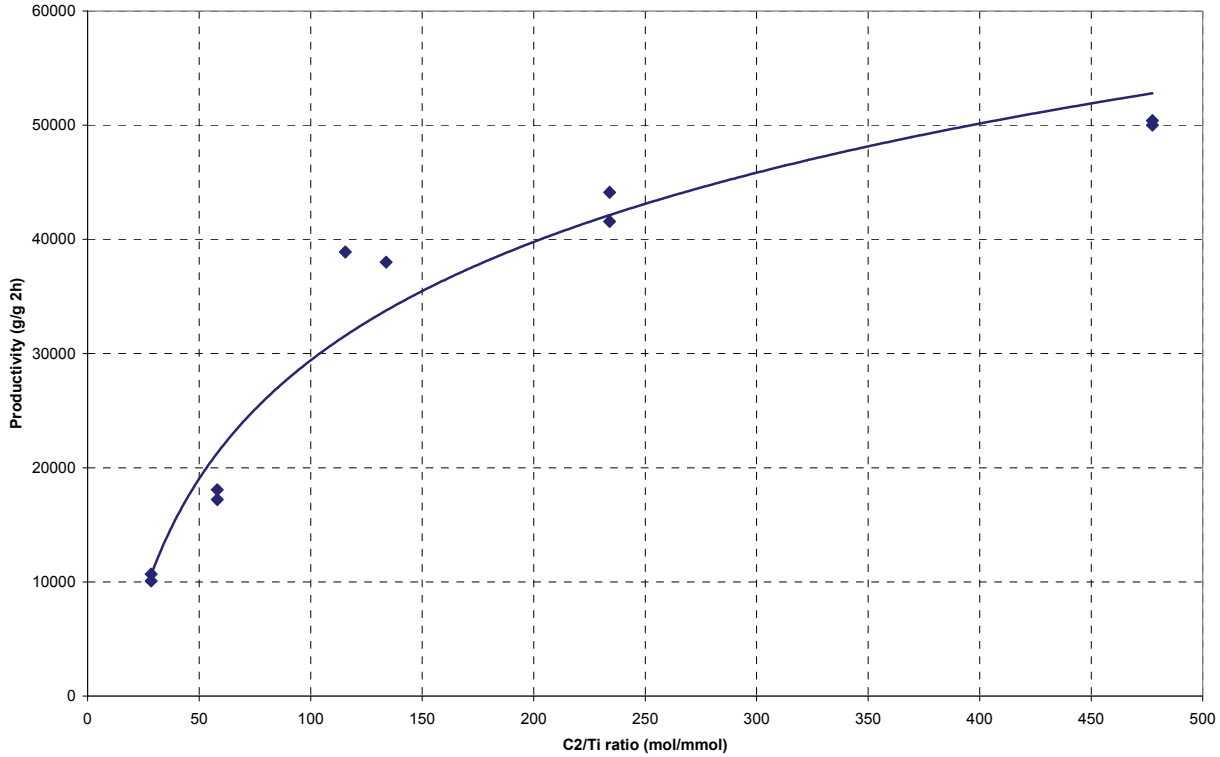

Figure 5: Effect of monomer concentration on the productivity of the catalyst

The reason of productivity increase is, that the speed of the chain growing reaction changes linear with monomer concentration (the difference here can be the result of the maximal surface cover), whereas the increase of molecular weight is the result of the previous cause, and that the speed of chain transfer reactions to monomer are neglectable. The decrease of density (crystallinity) is the outcome of the increase of molecular weight.

Effects of polymerization time

With the increase of polymerization (residence) time, the amount of the produced polymer is increasing obviously, but among the kinetic behaviour of different catalysts, there can be essential variations. This is very important in industrial processes, where the residence time can be quite long, and the catalyst along its production time, progresses through more reactors (e. g. Spheripol PP technology, or Mitsui CX PE process). Generally we can say that the productivity of the catalyst along the polymerization process is decreasing. On the figure below, we can see the kinetic profiles (ethylene flow to maintain constant pressure) and productivities of reactions with different polymerization times (from 30 to 180 min). As usual, the other parameters were constant (hydrogen amount: 50 Nl, temperature: 80 °C, pressure: 21,8 barg, stirrer: 500 1/min, Al/Ti ratio: 100).

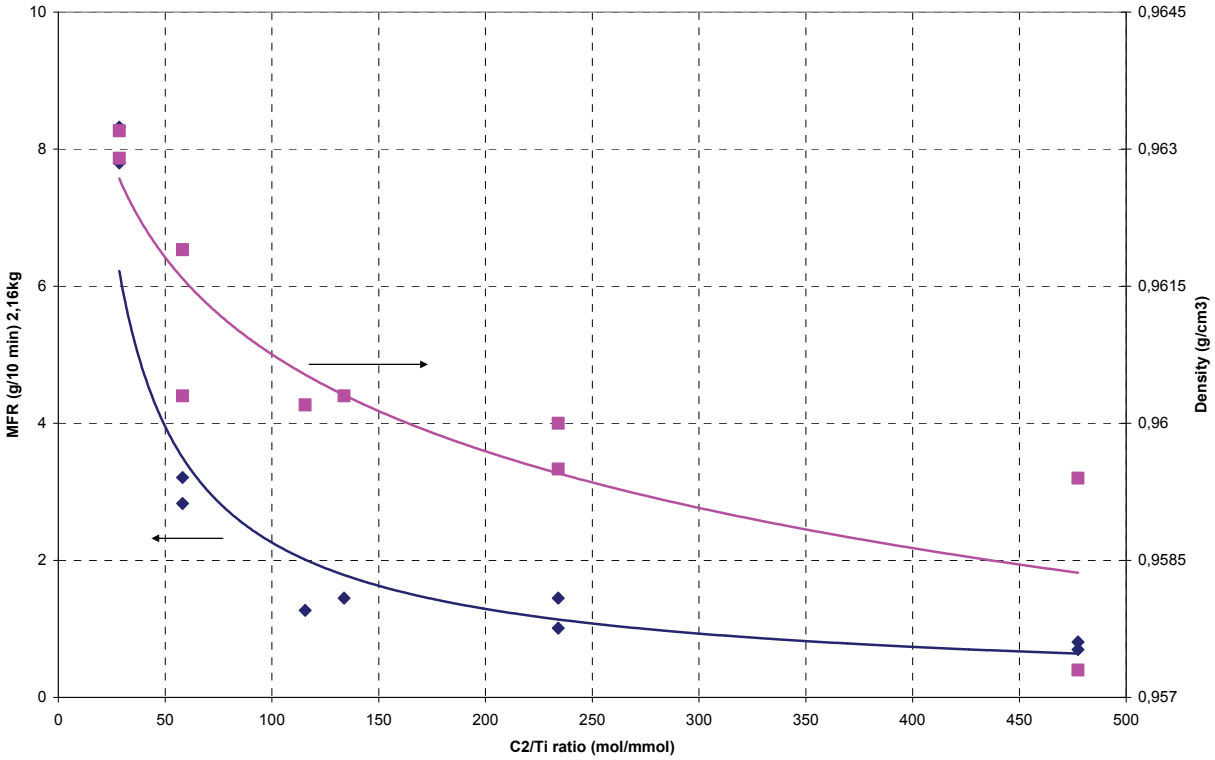

Figure 6: Effect of monomer concentration on the product MFR and density

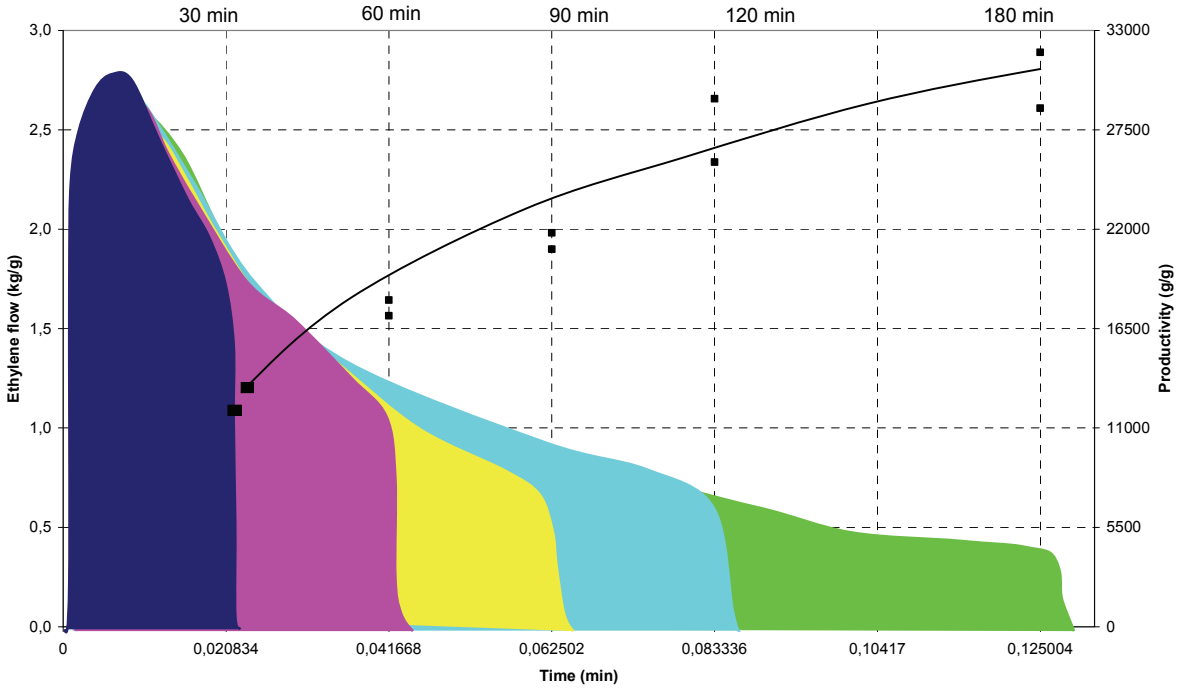

Figure 7: Kinetics of tests with different polymerization time

The possible cause of the productivity decrease within time could be the spontaneous deactivation of the active sites on one hand, and the higher diffusion resistance for ethylene in the bigger polymer particle. The scale of the decrease depends on the catalyst type also (structure). In our case we couldn't observe any effect of the residence time on the properties of the final product.

Summary

The aim of our paper was to introduce the basic properties, behaviour of Ziegler-Natta catalysts, and highlight the most paramount parameters that can play a major role in forming the productivity of the catalyst, and/or the properties of the final product. We have shown these effects through the experiments with a traditional Ziegler-Natta catalyst for HDPE production.

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