Kinetics of Slurry and Gas Phase Polymerizations of Ethylene Using a Novel Heterogeneous Ziegler-Natta Catalyst of Specific Morphology

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A B S T R A C T

Ethylene polymerization with $MgCl_2/TiCl_4/TEAl$, as a Ziegler-Natta catalyst, was carried out by slurry and gas phase processes. This catalyst was synthesized with a deliberate morphology by controlling the rate of recrystallization. The particle size distribution of the catalyst was very narrow which provided good stability in the reactor. The effects of temperature, monomer and hydrogen partial pressure on the catalyst activity and its deactivation coefficient were evaluated. The kinetic parameters such as deactivation rate coefficient and activation and deactivation energies were determined for both processes. It was found that deactivation rate coefficient decreased by increased temperature of maximum 70°C, while it decreased beyond this temperature. The initial rate of reaction in slurry and gas phase ethylene polymerizations increased by increasing the reaction temperature to maximum 80°C and in comparison, at longer reaction times (>20 min) it showed a drop with maximum reaction temperature of 70°C. It was also found that the deactivation rate coefficient of gas phase polymerization decreased by increasing the partial pressure (concentration) of hydrogen. The catalyst productivity for slurry phase polymerization of ethylene increased by increasing the Al/Ti molar ratio as high as 90 and beyond this ratio the catalyst productivity dropped for the same polymerization.

INTRODUCTION

Various Ziegler-Natta (Z-N) catalyst systems are used in slurry polymerization of ethylene such as the Mitsui and Hostalen processes. In comparison with the slurry process for ethylene polymerization using conventional Z-N catalyst systems, gas phase polymerization offers versatility and flexibility for polymer properties [1,2]. There have been considerable efforts made to synthesize new catalyst systems for ethylene polymerization and yet few studies are concerned with the kinetics of the Z-N catalyst in gas phase polymerization systems. The kinetic data for gas and liquid phase polymerizations of propylene with metallocene catalyst [3] and also kinetic parameters of olefin polymerization in slurry and gas phase processes [4] have already been reported. A conventional Z-N catalyst with a very high

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activity was used in gas and slurry phase reactions. The kinetic behaviour of the catalyst and physical properties of the produced polymer, such as particle size and its distribution, as important parameters depends on the morphology of the catalyst support. According to the literature, a gas phase process with a conventional Z-N catalyst is associated with lower activity [5] and production of higher molecular weight polymers [6-8]. Lower activity in gas phase polymerization is due to monomer dilution by nitrogen and higher monomer pressure requirement to overcome the monomer diffusion resistance which increases as polymerization proceeds in the vicinity of active sites [5]. Higher molecular weight polymers are produced in gas phase polymerization because of lower hydrogen diffusion towards its active sites compared to the slurry phase polymerization [6], and absence of chain transfer to solvent [7,8].

The reaction rate in gas phase polymerization is lower than in slurry phase, although the reaction mechanism is independent of the reaction phase because polymerization rate depends on the site centre environment, such as temperature, and monomer and hydrogen concentrations [9-11]. The monomer concentration on the surface of polymer can be calculated by thermodynamic relations as reported by Samson et al. [12,13]. The monomer concentration on the surface near the active centres was also determined experimentally [14]. The gas phase polymerization was carried out with Z-N catalyst system composed of $MgCl_2/TiCl_4/TEAl$ [15,16] at high pressure. To improve catalyst performance at medium pressure (about 10-15 bar), a new and highly active catalyst was developed in Bandar Imam Petrochemical Company (BIPC) and used for ethylene polymerization in gas and slurry phase processes in a recently constructed multipurpose pilot plant [17,18]. The most important features of this developed catalyst with higher activity under medium pressure, and better morphology, particularly in gas phase, in comparison with a commercial grade which is used in high density polyethylene (HDPE) plant of BIPC, are given elsewhere [19]. The main purpose of this study was to determine kinetic parameters of this new heterogeneous $MgCl_2$ supported Z-N catalyst.

EXPERIMENTAL

Synthesis and Characterization of the Catalyst

The Zeigler-Natta catalyst with magnesium chloride support was used for the gas and slurry polymerizations. This recently developed catalyst was synthesized in Research and Development Center of Bandar Imam Petrochemical Company with the following procedure. The supported catalyst was prepared by the reaction of $MgCl_2.nC_nH_{2n+1}OH$ with $TiCl_4$ in a glass jacketed reactor. The $MgCl_2$ adduct was prepared in a separate glass reactor by the reaction of $MgCl_2$ with a heavy alcohol $C_8H_{17}OH$ (2-ethyl hexanol) at 130°C under dry nitrogen atmosphere for 2 h and then cooled. A mixture of electron donor consisting of ethyl-benzoate and di-n-butyl phthalate was added to the adduct at temperatures below 60°C and mixed for 2 h [20]. Then, the adduct was added to the solution of $TiCl_4$ and toluene at -20°C and the reaction temperature was increased gradually to 90°C while it was controlled by an internal sensor. The reaction was continued for 2 h at the same temperature. The resulting mixture was kept at 90°C and then filtered out. Finally, the filtrate was cooled down to 60°C followed by the removal of the extra $TiCl_4$ by filtration. The solid phase catalyst was washed out three times with hexane, dried and stored under nitrogen atmosphere. The washed catalyst was cooled to 15°C and a specific amount of heavy alkylaluminium (tri-isopropyl aluminium and mixture of alkyl-aluminium chlorides) was added dropwise under stirring for 30 min. All these operations were carried out under dry nitrogen. The content of titanium in the catalyst was determined by a spectral scan using a Shimadzu (UV-1201) spectrophotometer, Japan. Particle size analysis showed that the $D_{50\%}$ of the catalyst was 15 μm. The total specific surface area of the catalyst was 183 m^2/g and total pore volume was 0.35 mL/g, obtained from nitrogen adsorption measurements (Sorptomatic 1990). This catalyst was used in ethylene polymerization without further treatment by alkylaluminium component.

Slurry Phase Polymerization

Slurry phase polymerization of ethylene was carried out in a 2 L jacketed Butchi reactor with a tube on its top that was isolated by two-ball valves for catalyst

injection. Before the feed inlet to the reactor, there exists a purification system for ethylene, hydrogen, nitrogen and hexane. The reactor was equipped with a helical stirrer and a nozzle on its top for sampling. The reaction rate was determined by a series of mass thermal flow meters. The Butchi reactor was evacuated and purged by dry nitrogen for 2 h while it was warmed up to 80°C. Then the temperature was reduced to ambient temperature. One litre of hexane was charged into the reactor by deep line and under 0.2 bar nitrogen pressure 5 mmol TEAl was charged by a syringe while the stirrer was being started. After a few minutes, the catalyst was also charged and the feeding process began through mass flow controllers. The temperature was controlled at 80°C set point for 2 h and feeding rate was recorded. The solubility of hydrogen and ethylene in hexane was found by Henry's law:

$$C_i^L = K_i P_i \tag{1}$$

where K_i is the Henry's coefficient and P_i is the partial pressure of each component in the gas phase.

Gas Phase Polymerization

The same Butchi reactor setup was also used for gas phase polymerization of ethylene. The catalyst injection system was a stainless steel vessel of known volume. The reactor was equipped by a sampling vessel to sample and measure the composition of the gas phase in the reactor. The temperature of reactor was controlled by a high flow rate circulator. Before starting the polymerization, the reactor temperature was increased to 80°C while the nitrogen was purged through the reactor. Then, the reactor went under vacuum for 2 h and flushed with nitrogen to cool down. A specified amount of screened polyethylene powder with an average particle size less than 100 μm was charged into the reactor and the nitrogen purging was maintained for 2 h from a deep line into the reactor. Every 15 min interval the reactor was put into operation for one additional minute. After 2 h a dew point measuring device was used to determine the amount of water in the reactor. A solution of triethyl-aluminium (TEAl) in hexane was prepared and fed into the reactor under stirring for homogenization of the powders. Then, a mixture of catalyst and dried

polymer was prepared in a glove box and fed into the specified sampling vessel connected to the reactor. The valve below this sampling vessel was opened and the catalyst was injected into the reactor. The feed was charged by mass flow controllers. Temperature and pressure of the reactor were kept constant during the experiment. The temperature was kept constant by a high flow rate circulator. The reaction rate was calculated from the rate of ethylene consumption that is monitored and recorded. To avoid hot zones in the reactor and enforce good mixing, a helical stirrer was employed. After 2 h, the pressure was reduced and the polymer product was washed with water and dried in a vacuum oven at 70°C.

Measurement Equipments

Charged polymer for the gas phase polymerization was obtained from a slurry phase process and screened to separate the fine powders with a particle size less than 100 μm. Pore size distribution and specific surface area of the polymer were determined by a B.E.T instrument (Sorptomatic 1990 Thermo Finnegan) and a mercury porosimeter (Thermo Finnegan Pascal 140/240). The Waters Alliance GPC 2000 was used to determine polymer molecular weight. The measured properties were molecular weight, surface area and pore diameter distribution.

Kinetics of Polymerization

A simple mechanism consisting of catalyst activation, chain propagation, catalyst deactivation and propagated chain deactivation with the equal deactivation rate coefficients for the last two reactions, proposed by Weickert et al. [4], is assumed. The overall reaction rate of ethylene polymerization according to this mechanism can be written as [4]:

$$R_p = \alpha \cdot \left([M]_S - [M] \right) = k_p \cdot C_P^0 \cdot [M]_S \tag{2}$$

where α is the external mass transfer coefficient, $[M]$ is the monomer concentration in the reaction medium, $[M]_S$ is the monomer concentration on the catalyst surface, k_p is the propagation coefficient rate and C_p^0 is the number of active centres per gram of the catalyst.

In slurry polymerization the external mass transfer resistance can be avoided by increasing the stirring rate. Therefore the reaction rate is usually controlled

by diffusion and reaction within the catalyst. Gas phase polymerization was carried out at high stirring rate to overcome the diffusion resistance of external phase.

The Thiele modulus (TM) [21] is usually applied to determine whether reaction rate within catalyst is controlled by internal diffusion resistance or kinetics in slurry and gas phase ethylene polymerizations [22]. The TM is related to catalyst properties by:

$$\eta = \frac{3}{(TM)}[\frac{1}{\tanh(TM)} - \frac{1}{(TM)}];$$

$$TM = r_0 \cdot \left(\frac{k_p \cdot C_0}{D_m} \right)^{1/2} \qquad (3)$$

where k_p, C_0, D_m, r_0 and η are rate coefficients, initial concentration of active centres, monomer diffusion coefficient, initial radius of the catalyst particles and the effectiveness of a catalyst, respectively.

In fact, the extent to which diffusion transport limits the reaction rate can be quantified using the relationship giving the effectiveness of a catalyst as a function of the dimensionless Thiele modulus. When the Thiele modulus is small, the effectiveness factor approaches unity; this means that there is very little variation in reactant concentration and the rate of the reaction is controlled by the intrinsic chemical kinetics. On the other hand, when the Thiele modulus is large, the reactant concentration becomes significantly low and the reaction is said to be diffusion controlled or diffusion limited [23]. Here, the internal diffusion and the kinetics control the polymerization rate for TM >10 and TM <10, respectively. For the catalyst used in this study, Thiele modulus and the effectiveness of catalyst were nearly 2 and 0.8, respectively, indicating that ethylene polymerization was kinetically controlled [15,24].

The reaction rate of polymerization is dependent on several parameters such as monomer concentration, temperature and number of active centres. Also it is dependent on the order of monomer and active sites concentration. The reaction order related to the monomer concentration for ethylene polymerization was reported to be higher than unity even at low monomer concentrations [25]. By considering that there are two or more kinds of active centres in the catalyst, there are also several propagation rate coefficients arising from such environment. Therefore, according to the suggested mechanism, interconversions between different sites lead to an overall order of reaction in the monomer larger than one [25,26]:

$$R_p = k_p \cdot C_m^n \cdot C^0 \quad (1 < n < 2);$$

$$k_p = k_{p_0} \cdot \exp(-E_{ac}/RT) \qquad (4)$$

where k_p is the propagation rate coefficient defined by Arrhenius function, in which E_{ac} is the activation energy for propagation, C^0 is the total number of active centres and C_m is the concentration of monomer absorbed on the polymer produced near the active centres.

At the beginning of polymerization, the maximum rate of polymerization can be achieved because the maximum active centres are accessible for monomer [4,16,27] though after few minutes polymerization rate is gradually decreased. It is believed that the activity decrease is not related to the intra-particle monomer diffusion limitation through the growing polymer layer. The observed decrease of polymerization rate can be mainly related to decreasing number of active centres with time due to the chemical deactivation [15,28]. One can assume that the deactivation of active centres can be described by [15]:

$$\frac{dC^0}{dt} = -k_d \cdot C^0 \qquad (5)$$

$$k_d = k_{d0} \cdot \exp(-E_{dac}/RT) \qquad (6)$$

where k_d and E_{dac} are the deactivation rate coefficient and energy, respectively.

By integration of the above equation, active centre concentration as a function of time can be obtained by:

$$C^0 = C_{max}^0 \cdot e^{-k_d \cdot t} \qquad (7)$$

where, C_{max}^0 is the maximum number of active centres per gram of catalyst at the beginning of

polymerization. Then for low concentrations of monomer, the reaction rate is given by [4,15,29]:

$$R_p = k_p \cdot C_m \cdot C_{max}^0 \cdot e^{-k_d \cdot t} = (R_p)_{max} \cdot e^{-k_d \cdot t} \qquad (8)$$

where $(R_p)_{max}$ is the maximum reaction rate.

RESULTS AND DISCUSSION

Slurry Phase Polymerization
Effect of Temperature
The variation of reaction rate with time at different temperatures is shown in Figure 1. Higher polymerization rates were achieved at 80°C during the first 20 min, and they dropped to lower values in comparison with the rates obtained at 70°C during the remaining reaction time. Therefore, it seems that reaction should be carried out at slightly below 80°C, and yet it was carried out at 80°C to be comparable with gas phase polymerizations. The variation of reaction rate with time is also presented in terms of -ln $(R_p/(R_p)_{max})$ in Figure 2. Polymerization at higher temperatures led to high concentration of polymer after about 20 min and then a very sharp decrease in polymerization rate was observed. The reason for this behaviour is the sudden decrease in heat transfer coefficient and changes in flow behaviour of the reactor contents after 20 min with high concentration of polymer in the reactor [30]. The effect of temperature on the variation of deactivation coefficient of
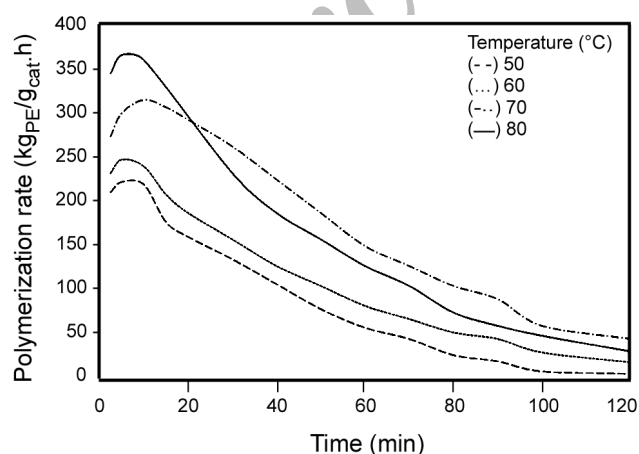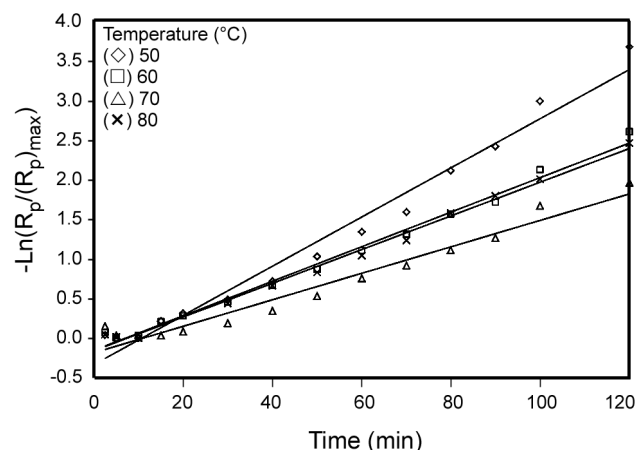

Figure 2. The effect of temperature on -Ln($R_p/(R_p)_{max}$) of ethylene polymerization in slurry phase at 8 atm.

active centres with time, k_d, is shown in Figure 3, which is obtained by fitting eqn (7) to the experimental results presented in Figure 2.

Effect of Al/Ti Molar Ratio
The molar ratio of Al/Ti is a very important parameter in polymerization rate. Before evaluation of temperature effect on polymerization rate, it should be precisely known that under what polymerization condition the maximum active centres may be achieved. Therefore, the ethylene polymerization was carried out with different Al/Ti molar ratios at 80°C and 0.5 bar hydrogen at the top of reactor. The catalyst showed maximum productivity at an Al/Ti
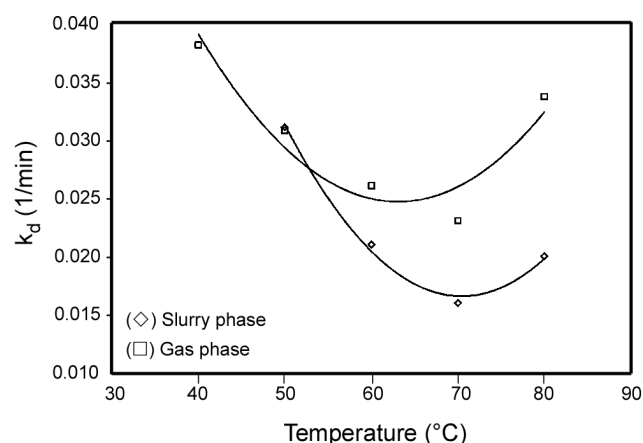

Figure 1. The effect of temperature on the rate of ethylene polymerization in slurry phase at 8 atm.

Figure 3. The effect of temperature on the deactivation rate coefficient of active centres, k_d, in slurry phase polymerization of ethylene at 8 atm and in gas phase at 15 atm.
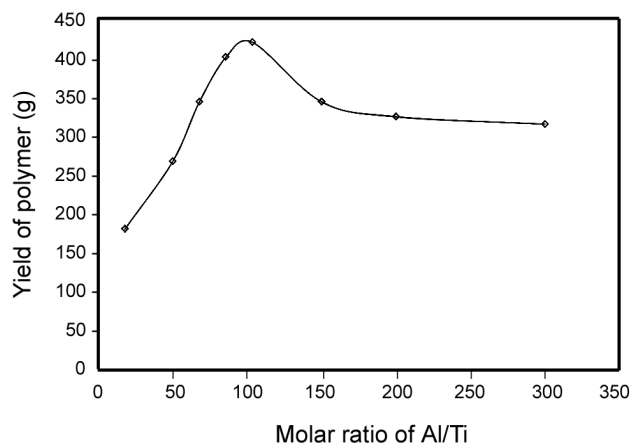
Figure 4. The effect of Al/Ti molar ratio on the polymer yield of ethylene polymerization in slurry phase at 8 atm.

molar ratio of 90. Therefore, all experiments were carried out at this Al/Ti molar ratio. The polymerization rate was measured by the rate of ethylene consumption in terms of $kg_{PE}/g_{cat}.h$. The real fluctuating reaction rates were low and only minor differences were observed in each run if Al/Ti molar ratio was kept above 90.

There is a possible explanation for the increased catalyst activity by increasing Al/Ti molar ratio. By increasing Al/Ti molar ratio, the number of active sites increases to a maximum value and by further addition of Al in the reaction medium, the number of active sites does not change anymore. Excess Al has competition role against monomer consumption on active sites [4,20] and as a result the polymerization
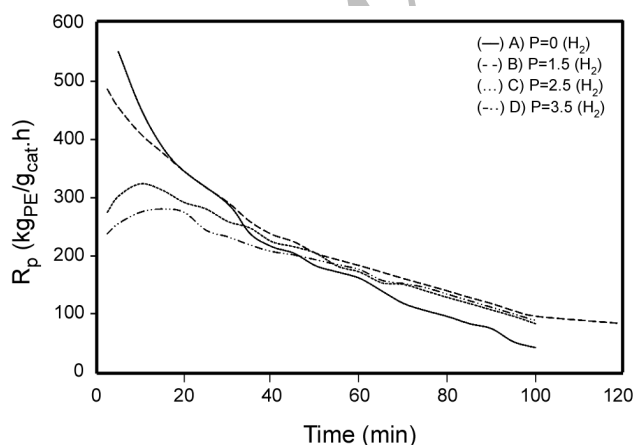

Figure 5. The effect of hydrogen partial pressure on the polymerization rate of ethylene in slurry phase at 8 atm.
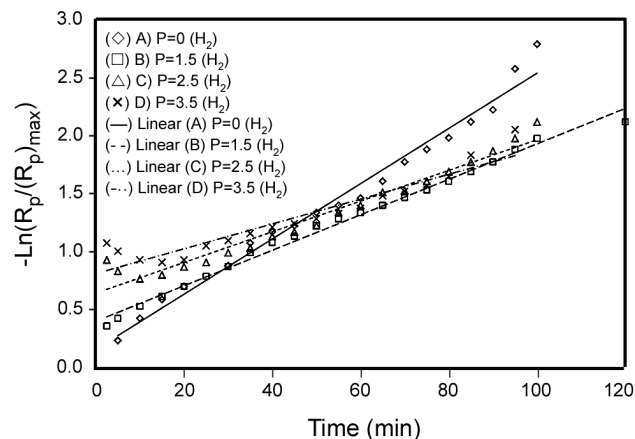

Figure 6. The effect of hydrogen partial pressure on $-Ln(R_p/(R_p)_{max})$ of ethylene polymerization in slurry phase at 8 atm.

rate decreases gradually and polymer yield decreases accordingly, as shown in Figure 4.

Effect of Hydrogen
The effect of hydrogen concentration on the rate and kinetics of polymerization was evaluated at 70°C in the slurry phase reactor. The hydrogen concentration in the reactor top, in terms of partial pressure, varied from 0 to 4 bar. The rates of polymerization versus time at different hydrogen concentrations are shown in Figure 5. These data are also presented in terms of $-\ln(R_p/(R_p)_{max})$ with time in Figure 6. By fitting these data to eqn (8), the deactivation rate coefficient,
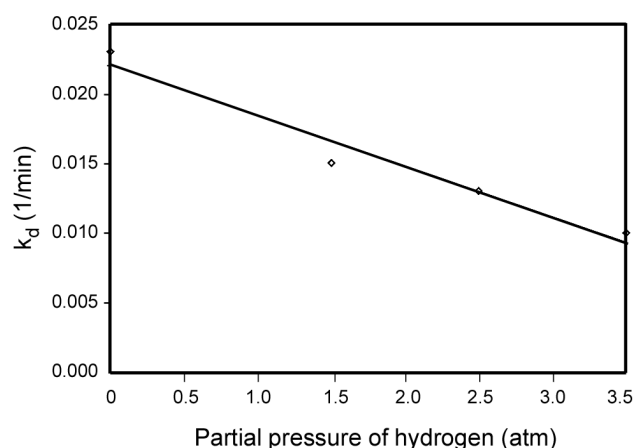

Figure 7. The effect of hydrogen partial pressure on the deactivation rate coefficient, k_d, in slurry phase ethylene polymerization at 8 atm.

k_d, was determined and plotted vs. hydrogen partial pressure in Figure 7. As shown in these figures, the polymerization rate and deactivation rate coefficient are both functions of the hydrogen concentration. The deactivation rate coefficient decreased with the hydrogen concentration. Samson et al. [3] also found the same behaviour for reaction rates, with its subsequent decrease in catalyst centre deactivation.

A possible explanation for the increased catalyst activity in the presence of hydrogen is the short cutting of slow propagation steps. Those catalyst sites which were not able to initiate the activation reactions become fresh again with subsequent increase of propagation rate. These kinds of sites, which do not have enough potential for propagation reactions, always exist after the catalyst activation reactions and impurities which make some of them permanently inactive, but some others can be activated again in the presence of specific concentrations of hydrogen and temperature with a synergistic effect [4,31,32]. On the other hand, as mentioned earlier, the process is kinetically controlled because of the Thiele modulus number. Therefore, in the absence of diffusion controlled ethylene polymerization, chain transfer to hydrogen which may control polymer molecular weight induces sites of slow propagation to acquire enough potential for activation.

Gas Phase Polymerization
Effect of Temperature
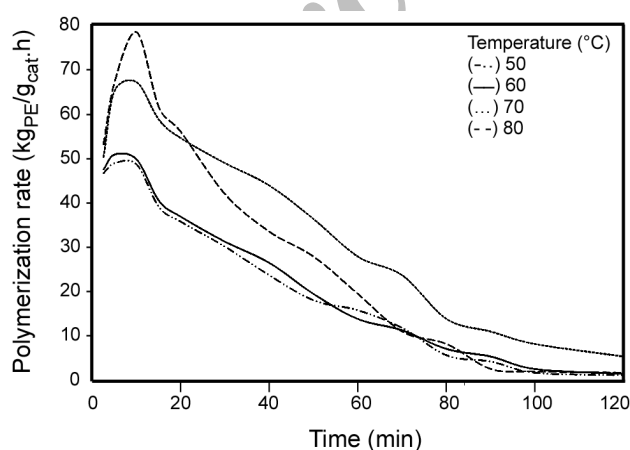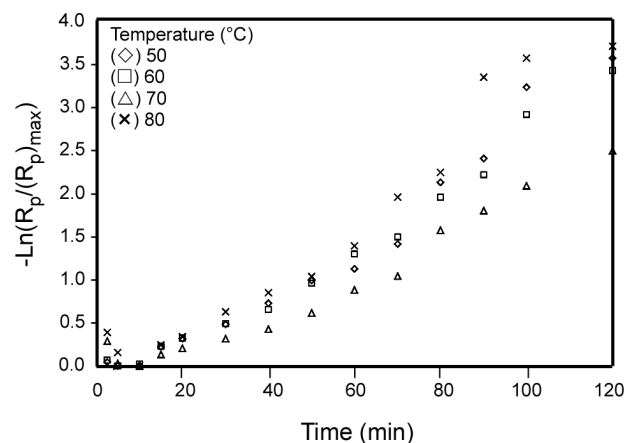Gas phase polymerizations were carried out at 15 bar

Figure 9. The effect of temperature on $-Ln(R_p/(R_p)_{max})$ of ethylene polymerization in gas phase at 15 atm.

pressure and low hydrogen concentration under very good heat transfer conditions while temperature varied between 40°C to 80°C. As shown in Figures 8 and 9, the reaction rate increased by increasing the temperature to maximum 80°C, and then it decreased by further increase in temperature. The maximum productivity occurred at 80°C, but at lower temperatures, especially at 40°C and 50°C, the catalyst needs time to reach its maximum activity. Figure 3 demonstrates the effect of different temperatures on the deactivation rate coefficient, k_d, in the gas phase polymerization of ethylene at 15 atm. As shown in this figure, the deactivation rate coefficient is decreased by increasing the temperature from 50°C to 70°C, though with further increase in temperature this coefficient is increased considerably.

Effect of Monomer Concentration
Gas phase polymerization of ethylene was carried out at 80°C by variation of monomer concentration in terms of partial pressure from 2 to 15 bar. Consequently, by increasing the partial pressure of monomer inside the reactor, the monomer concentration on the catalyst active centres is increased at the same time. At low concentration of monomer, a linear reaction rate was obtained but at higher pressures (concentration), there was a slight deviation from linearity as shown in Figures 10 and 11. Eqn (8) was fitted to the experimental data to find the deactivation rate coefficients, k_d. The variation of k_d with monomer partial pressure and concentration is shown

Figure 8. The effect of temperature on the rate of ethylene polymerization in gas phase at 15 atm.
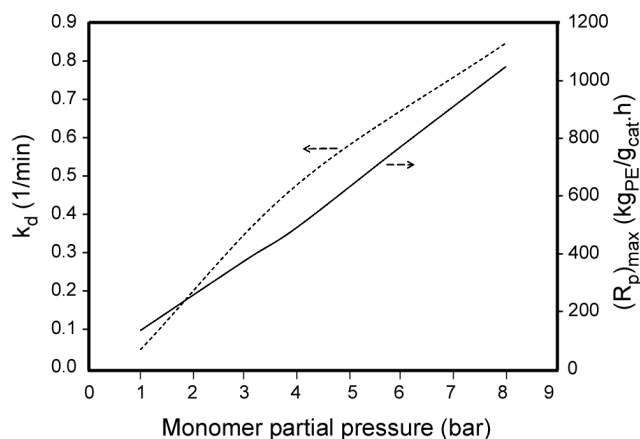
Figure 10. The effect of monomer partial pressure on $(R_p)_{max}$ and the deactivation rate coefficient, k_d, in slurry phase polymerization of ethylene at 80°C.

in Figures 10 and 11, respectively.

Kinetic Parameters in Slurry and Gas Phase Polymerizations of Ethylene

The reaction rate of polymerization is the main difference in gas and slurry phase polymerizations. One reason for this difference is the monomer concentration on the active centres. As mentioned earlier, it is expected that the mechanism for gas and slurry phase reactions to be the same. Therefore eqn (8) can be rearranged as:

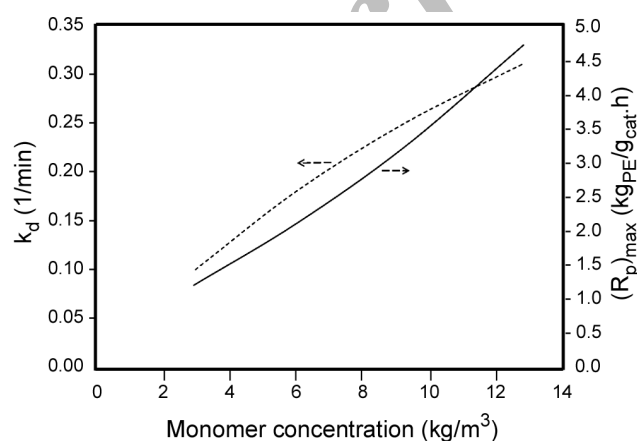$$(R_p)_{max} = k_{p_0} \cdot e^{-E_{ac}/RT} \cdot C_m \cdot C_{max}^0 \qquad (9)$$

Figure 11. The effect of monomer concentration on $(R_p)_{max}$ and the deactivation rate coefficient, k_d, in gas phase polymerization of ethylene at 15 atm.

Table 1. Comparison of the kinetic parameters in gas and slurry polymerizations of ethylene.

Parameter	Slurry phase	Gas phase
k_{d0} (min^{-1})	0.023	0.032
$E_{ac,p}$ (kJ/mol)	43	52
$k_{p0} \times C_{max}$ (m^3/h.g$_{cat}$)	7.6×10^8	6.4×10^7
E_{dac} (kJ/mol)	40.2	38.1

to give:

$$Ln\left(\frac{(R_p)_{max}}{C_m}\right) = Ln\left(k_{p_0} \cdot C_{max}^0\right) - \frac{E_{ac}}{RT} \qquad (10)$$

Therefore, the coefficients of kinetic parameters can be obtained by plotting ln $((R_p)_{max}/C_m)$ versus 1000/T. These parameters are compared in Table 1 for gas and slurry phase polymerizations of ethylene using a new heterogeneous MgCl$_2$ supported Z-N catalyst developed in BIPC. The catalyst activity and morphology [19] were improved against other catalysts such as BIPC PZ. As it is shown in this table, k_{d0} and E_{ac} are higher in gas phase polymerization, unlike E_{dac} and $k_{p0} \times C_{max}^0$ which are higher in slurry phase process. These parameters are very crucial for modelling and scale up of gas and slurry phase polymerizations of ethylene using the developed catalyst, particularly in a multi-step fluidized bed reactor developed by authors for gas phase polymerization of ethylene [18].

The Products in Gas and Slurry Phase Processes

Specifications of newly developed and a commercially available MgCl$_2$ supported Z-N catalysts are presented in Table 2. The activity of the developed catalyst was 1.5 times of the commercial catalyst at 80°C and pressure of 8 bar. This value increased to 1.7 at pressure of 15 bar at the same temperature in the gas phase process. The activity of PZ in gas phase process decreased to 12-15 kg$_{PE}$/g$_{cat}$ (33%) at 8-15 bar pressure. Thus the new catalyst exhibited a better performance in terms of the yield at low and intermediate pressures. Also, the exceptional perform-ance of the developed catalyst was observed at high pressures (15-30 bar) [18]. As it is mentioned earlier, higher molecular weight polymer with narrower

Table 2. Specifications of newly developed and commercially available MgCl$_2$ supported Ziegler-Natta catalysts.

Characteristics*		New MgCl$_2$ supported Z-N catalyst	Commercially available catalyst
Composition (mg/g$_{cat}$)	Ti	76	50
	Mg	120	160
Activity (kg$_{PE}$/g$_{cat}$)		28.10	18.2
Bulk density (g/mL)		0.29	0.28
MFI (g/10 min)		2.00	3.1
Non-Newtonian index		29.00	30.0
D$_{50\%}$ (μm)		310.00	160.0
PSD (wt%)	> 850 (μm)	2.5	6.4
	> 500 (μm)	7.0	7.2
	> 250 (μm)	58.1	12.4
	> 180 (μm)	16.4	12.4
	> 100 (μm)	10.1	42.5
	> 75 (μm)	3.2	12.2
	> 45 (μm)	2.5	6.6
	< 45 (μm)	0.2	0.4

$^{(*)}$ Polymerization conditions: Ti: 0.01 mmol/L, TEAl: 0.5 mmol/L, heptane: 500 mL, H$_2$ partial pressure: 4 kg/cm^2, total pressure: 6 kg/cm^2, temperature: 80°C.
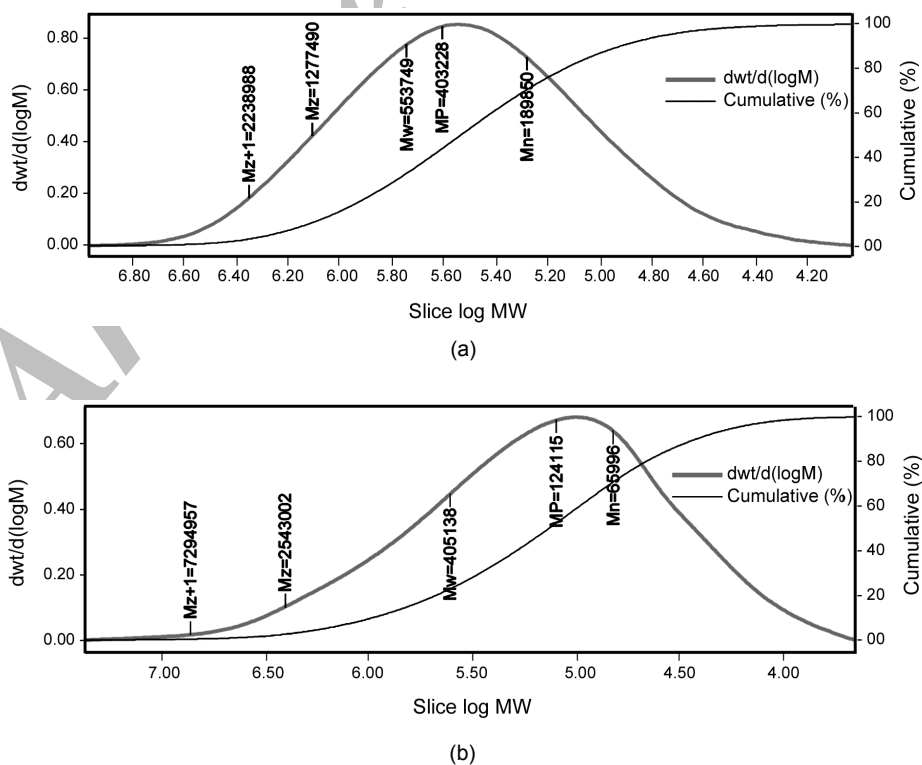

(a)

(b)

Figure 12. GPC of the polyethylene produced by the newly developed Ziegler-Natta catalyst at 80°C: (a) 15 bar pressure in gas phase process and (b) 8 bar pressure in slurry phase process.

Table 3. Molecular weight of polyethylene produced by the newly developed catalyst at 80°C.

Phase	Pressure (bar)	$\overline{M}_w$	$\overline{M}_n$	PDI
Gas	15	553749	189850	2.90
Slurry	18	405138	65996	6.13

distribution can be obtained in the gas phase process. This is also observed with the developed catalyst by comparing the slurry phase and gas phase polymerizations as shown in Figure 12. The molecular weight distribution in the gas phase process was narrower against the broad and bimodal distribution in the slurry phase. The molecular weight of the produced polymer and its distribution in the gas phase and slurry phase processes are also compared in Table 3. By increasing pressure from 8 bar in slurry phase process to 15 bar in gas phase process, the molecular weight increased by a factor of 1.36 with narrower distribution (2.9 vs. 6.13). The better morphology and narrower particle size distribution of the polymer produced with our newly developed catalyst at medium pressure indicate higher performance of this catalyst compared with commercially available catalysts.

CONCLUSION

Ethylene polymerization was carried out under different conditions of temperature, pressure and hydrogen concentration in slurry and gas phase processes using a new heterogeneous $MgCl_2$ supported Ziegler-Natta catalyst. It was found that these process variables have considerable effect on the rate of polymerization, deactivation of active sites of catalyst and kinetic parameters. A lower deactivation rate coefficient was obtained at higher concentration or partial pressure of hydrogen. The deactivation rate coefficient dropped by increasing the temperature to the maximum of 70°C, and it did increase beyond this temperature. The initial reaction rate of polymerization increased by increasing the reaction temperature to the maximum of 80°C, but it dropped to lower values in comparison with that of 70°C at longer reaction times exceeding 20 min. Also, important characteristics of the newly developed

catalyst were narrow particle size distribution of PE, higher performance and activity in the gas and slurry phase processes compared to a commercial catalyst.

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