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The Slug Flow Behavior of Polyethylene Particles Polymerized by Ziegler-Natta and Metallocene Catalysts

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Abstract−We investigated the flow behavior of polyethylene particles polymerized by Ziegler-Natta catalyst and Metallocene catalyst. The employed polymer particles were linear low-density polyethylene (LLDPE), and average particle size was 600 μm. Different flow behavior of polymer particles in a fluidized bed was observed with different polymerization catalysts in the bubbling and slugging flow regimes. The flow behavior determined from the pressure drop fluctuation in the lower and upper section of the bed was analyzed with statistical methods.

Key words: Flow Behavior, Polyethylene Particle, Ziegler-Natta, Metallocene, Slug Flow

INTRODUCTION

A large portion of polyethylene has been manufactured in a gas-phase fluidized bed reactor that commonly employs Ziegler-Natta catalyst. Recently, new catalyst has been investigated for the good mechanical, chemical and processing properties of polyethylene resins. The homogeneous organometallic catalyst has advantages over Ziegler-Natta catalyst in the polymerization process for much easier control of co-monomers introduction and molecular weight distributions. After the first commercial scale success of Exxon's LDPE production with metallocene catalyst in 1991, several chemical companies produced the PE with metallocene catalyst since then. Nowadays, the metallocene catalysts are designed and tested as the improved catalyst for the manufacturing of polyethylene in the fluidized bed reactors. Since physical properties such as particle size distributions, particle shape and particle density are related to properties of the polymerization catalysts, the hydrodynamics of polymer particles in a fluidized bed polymerization reactor would be different with the catalyst type. Only a few researches have been carried the flow behavior of polymer particles in a fluidized bed [Jiang et al., 1994; Cho et al., 2000]. In general, the gas-phase olefin polymerization in the fluidized beds operated at the gas velocity of U_g= 3.0-6.0 U_{mf} and at these gas velocity ranges the flow regime would be bubbling and slugging regimes [Mcauley et al., 1994]. Therefore, it is essential to understand the slugging phenomena in the fluidized bed.

The objective of this study is to examine the flow behavior of polyethylene particles polymerized by the Ziegler-Natta catalyst (PE-ZN) and the Metallocene catalyst (PE-MT). From the pressure fluctuations signals in a fluidized bed, several statistical methods are employed to analyze the characteristics of flow regimes in conjunction with particle properties determined by different types of catalysts.

EXPERIMENTAL

The experimental test set-up is shown in Fig. 1. The fluidized

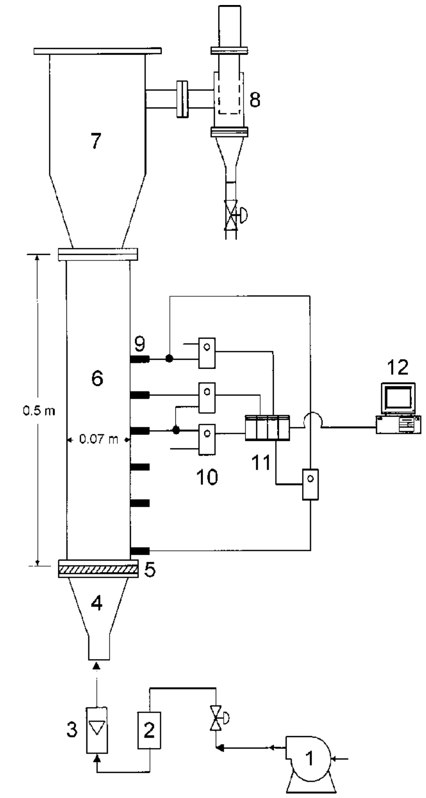

Fig. 1. Schematic diagram of experimental test set-up.

1. Blower	7. Disengaging section
2. Filter & Regulator	8. Cyclone separator
3. Rotameter	9. Pressure tap
4. Calming section	10. Pressure transducer
5. Distribution plate	11. A/D converter
6. Fluidization column	12. PC

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bed column was made of acrylic pipe of 0.07 m ID and 0.5 m in height and was connected to the cyclone. The disengaging section is located between the fluidized bed column and the cyclone as shown in Fig. 1 and was designed to simulate the dimensional similarity of commercial fluidized bed reactor of the Unipol process. Air is supplied from the compressor and flows to calibrated flow meter and is introduced to the bottom of the bed through the perforated distributor. The static bed height was 75% of the bed volume and it was about 0.37 m above the distributor. Three differential pressure transducers were mounted at the lower and upper section of the bed in order to measure local pressure drop in the bed, and the other one was employed to measure the pressure drop of the overall bed.

Table 1. Physical properties of polymer particles (LLDPE)

Properties	Polymer particle polymerized by	
	Metallocene cat.	Ziegler-Natta cat.
Particle diameter, d_p	0.554 m	0.542 m
Particle density, ρ_s	800 kg/m^3	750 kg/m^3
Particle bulk density, ρ_b	500 kg/m^3	350 kg/m^3
Voidage at incipient fluidization, ε_{mf}	0.43	0.48
Minimum fluidization velocity, U_{mf}	0.09 m/s	0.07 m/s

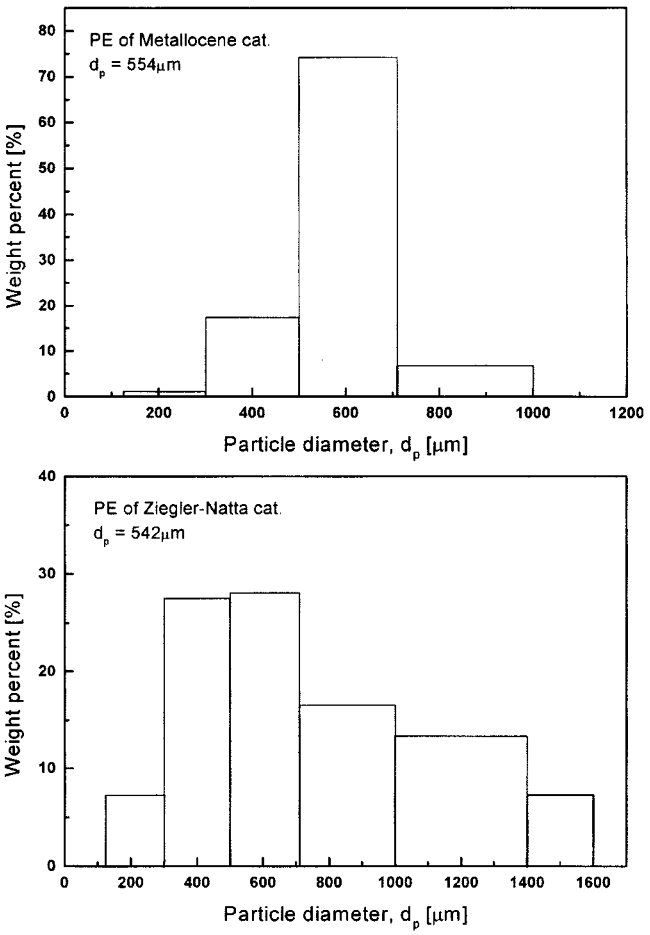

Fig. 2. Histogram of particle size distribution of polymer particles.

The lower section of the bed was defined where the pressure taps were located between the 0.14 m and 0.19 m above the distributor, and the upper section of the bed was defined where the pressure taps were located between 0.28 m and 0.33 m above the distributor. The overall pressure drop of the bed was measured through the pressure taps located between 5 cm and 0.40 m above the distributor. The measured pressure drops at the lower, upper and overall bed were transferred to a data acquisition unit and stored on a personal computer. The sampling rate of pressure drop was 100 Hz and sampling time was 80 seconds after the fluidized bed reached steady-state. Therefore, 8,000 pressure signals were collected for each run. The operating gas velocity covered the 1.2-5.0 U_{mf} ranges, and slug flow was observed for those gas velocity ranges.

The Hanwha Petrochemical Ltd, Korea, provided the LLDPE powders polymerized by Ziegler-Natta and Metallocene catalysts. The physical properties and the particle size distribution of LLDPE particles employed in this study are given in Table 1 and Fig. 2, respectively.

STATISTICAL ANALYSIS OF PRESSURE DROP SIGNALS

In order to analyze the time series of pressure drop fluctuation in a slugging fluidized bed, several classical statistical methods for signal were employed.

1. Average Absolute Deviation (AAD)

As a measure of the amplitude of the signal, the average absolute deviation of the signal from its average is used. As the probability distributions of the pressure fluctuation are not at all similar to the normal distribution, the linear measure of absolute deviation is considered to be a better measure than the standard deviation [Stappen et al., 1993].

$$\mathrm{AAD} = \frac{1}{N}\sum_{t=1}^{N}|x_t - \bar{x}| \tag{1}$$

2. Probability Density Function, Probability Distribution Function

For a continuous stationary random variable x(t), its probability density function $f_{x(t)}(x)$ and probability distribution function $F_{x(t)}(x)$ can be calculated as:

$$f_{x(t)}(x)\Delta x \equiv \lim_{T\to\infty}\frac{1}{T}\sum(\Delta T) \tag{2}$$

$$F_{x(t)}(x) \equiv \int_{-x}^{x} f_{x(t)}(x)dx \tag{3}$$

where T represents the total sampling time.

The probability density function itself showed the characteristic properties of the pressure fluctuations, and the distribution of measured signals and the probability distribution function is a cumulative function of probability density function [Fan et al., 1981].

RESULTS AND DISDUSSIONS

1. Incipient of Slug Flow

The pressure fluctuation signal measured in a fluidized bed gives a great deal of information in understanding the flow behaviors of

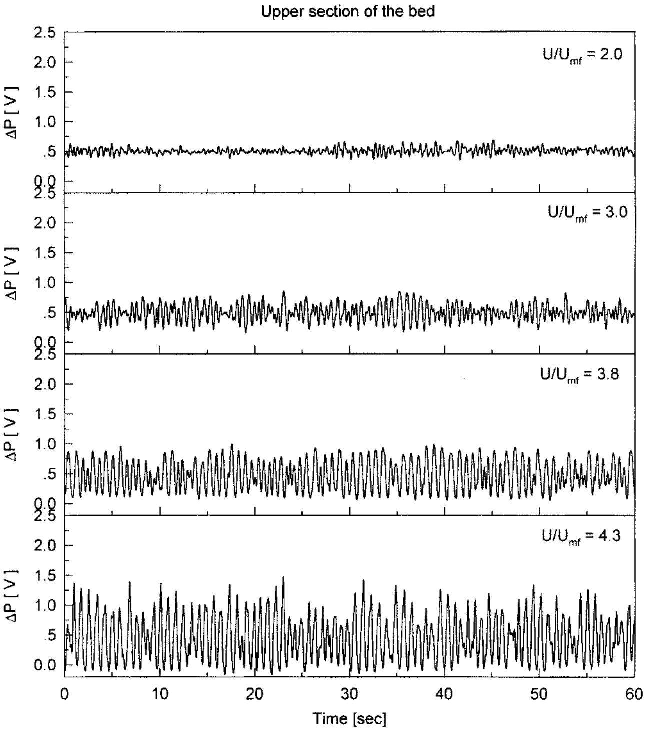

Fig. 3. Pressure fluctuation signals at different gas velocity for the particles of PE-ZN at the upper section of the bed.

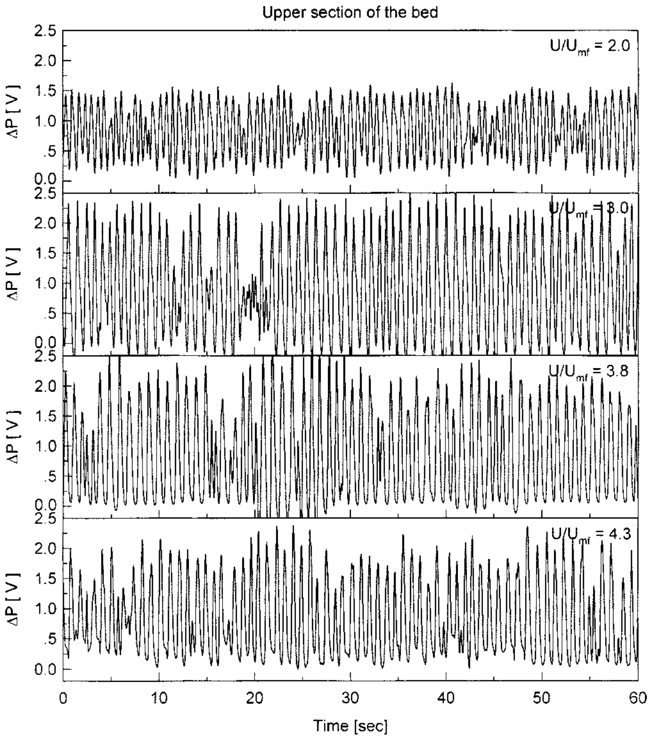

Fig. 4. Pressure fluctuation signals at different gas velocity for the particles of PE-MT at the upper section of the bed.

particle. Fig. 3 and Fig. 4 showed the pressure fluctuation measured in the upper section of the bed with particles of PE-ZN (polymerized by Ziegler-Natta catalyst) and particles of PE-MT (polymerized by Metallocene catalyst), respectively. For the operating gas

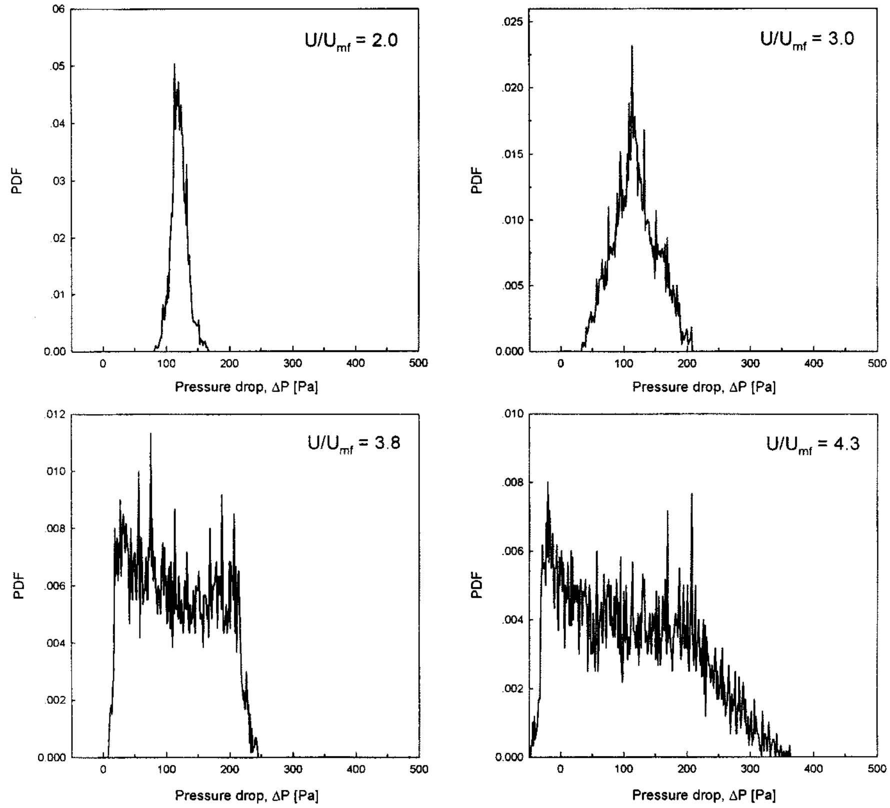

Fig. 5. Probability density function at different gas velocity for the particles of PE-ZN at the upper section of the bed.

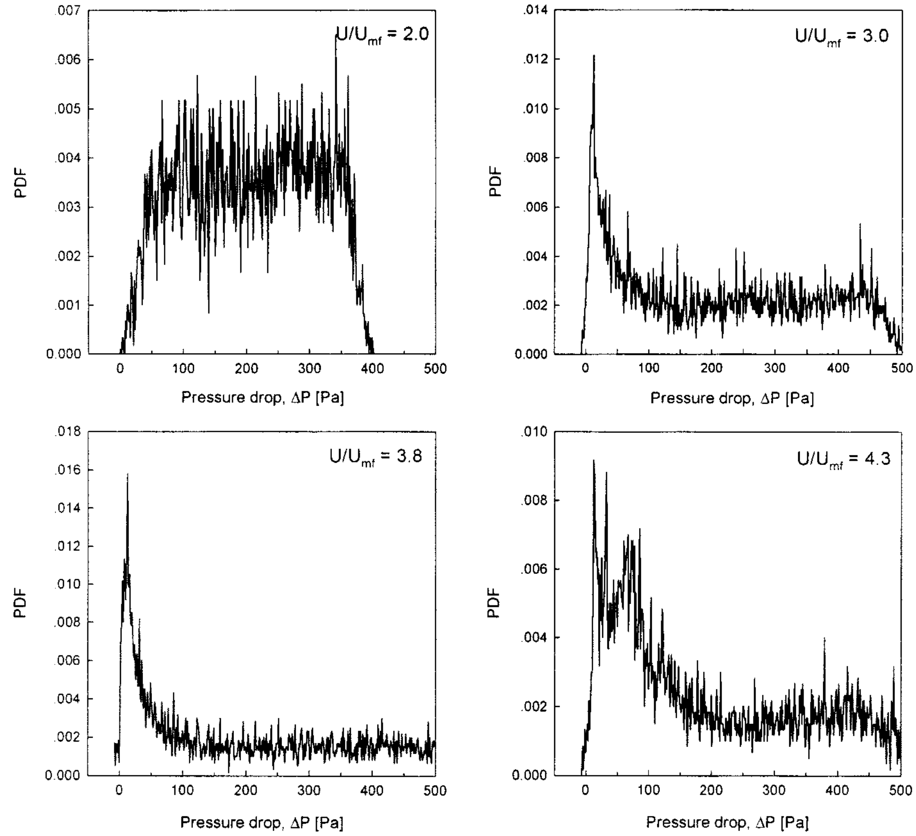

Fig. 6. Probability density function at the different gas velocity for the particles of PE-MT at the upper section of the bed.

velocity of U_g=2.0 U_{mf}–4.3 U_{mf}, we can easily see the different flow behavior of polymer particles with different polymerization catalysts. The polymer particles of PE-MT showed larger pressure fluctuations than that of polymer particles of PE-ZN. By comparison of Fig. 3 and Fig. 4, polymer particles of PE-MT approach the slugging flow regime at the lower gas velocity than the polymer particle of PE-ZN. It also showed that pressure fluctuations were very regular for PE-MT particles. One reason for this uniform periodic pressure fluctuation for PE-MT particles may be a result from the narrow particle size distributions. It is known fact that a powder with a wide size distribution fluidized more smoothly than a powder having a narrow size range. This implies less vibration of the bed and less tendency to slug due to smaller bubble sizes promoted by the wide size distribution.

In order to get more quantitative information for measured pressure fluctuation signals shown in Fig. 3 and Fig. 4, these signal data were converted to probability density function as shown in Fig. 5 and Fig. 6 for PE-ZN and PE-MT, respectively. The probability density function gives information on the dominant pressure drop during the fluidization [Fan et al., 1981] and when slugging occurred, the probability density function showed a wide spectrum of pressure drops due to alternating flow of solid and gas phase. Fig. 5 indicates that the polymer particle of PE-MT approached the slugging flow regime at the gas velocity of U_g=2 U_{mf}, while from Fig. 6, the polymer particles of PE-ZN showed the beginning of slugging at the gas velocity of U_g=3.8 U_{mf}. The superficial gas velocity for the onset of slugging was different for the particles of PE-ZN and PE-MT. From the data of the probability density function shown in Fig. 5 and Fig. 6, it was observed that the transition from bubbling to slugging regimes occurred at the higher gas velocity for the particles of PE-ZN in spite of similar particle size and density. The explanation for this phenomenon may result from the narrow particle size distribution and higher bulk density of particles of PE-MT. Therefore, probability density function can be another measure for the

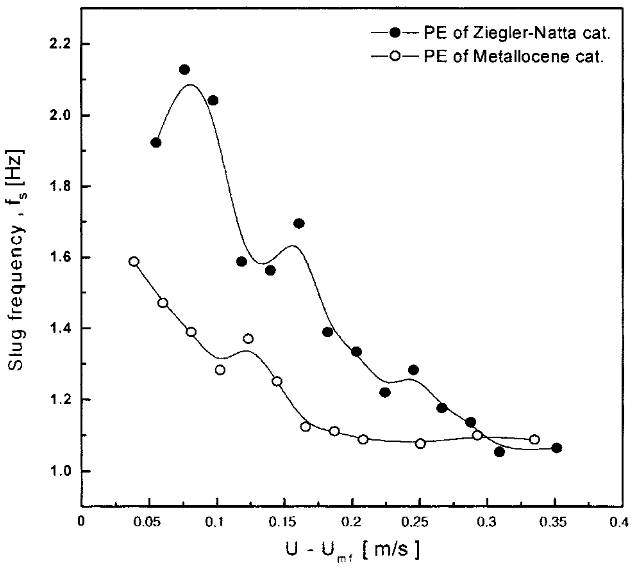

Fig. 7. Dominant slug frequency as a function of gas velocity for different polymer particles.

analysis of pressure signals from the fluidized bed.

2. Slug Frequency

The slug frequency for polymer particles of PE-MT and PE-ZN was measured from the pressure signals with different gas velocities and is shown in Fig. 7. As can be seen in Fig. 7, the slug frequency is found to decrease with an increase in gas velocity, and it appears to approach a limiting value of 1.0 Hz. Svoboda et al. [1984], Dimittia et al. [1997] and Satija and Fan [1985] also found that the dominant frequency was independent of gas velocity as the gas velocity increased for the Geldart B particles and Geldart D particles, respectively. For the Geldart B particle, the limiting frequency was 1.7 Hz [Svoboda et al., 1984] and 0.9 Hz for Geldart D particles [Dimittia et al., 1997; Sajita and Fan, 1985]. Therefore, it indicated that the limiting dominant frequency is dependent on particle type. At low gas velocity, the slug frequency of the particles of PE-ZT showed higher values than that of particles of PE-MT. From visual observation, we found that for the particles of PE-ZN, the shape of slug was axial slug, and for this type of slug it is known that the wall effect is less severe than for wall slug, so in this case the slug formed more frequently and easily broke-up. Therefore, the slug shape at the lower gas velocity results in the difference of slug frequency for the particles of PE-ZN and PE-MT.

The maximum slugging velocity, which represents the transition velocity from the slugging flow to the turbulent flow, was found to be U_g/U_{mf}=3.0 for the PE-MT and U_g/U_{mf}=5.3 for the PE-ZN. This means that PE-ZN has a wider slug regime than that of PE-MT. This phenomenon was also observed from the AAD values shown in Fig. 8. As can be seen, the absolute average deviation of pressure drop has the maximum value at U_g=3.0 U_{mf} for the particles of PE-MT and U_g=5.5 U_{mf} for the particles of PE-ZN. Therefore, this showed further evidence that particles of PE-ZN have a wider slug regime than particles of PE-MT.

The probability distribution function was employed to determine the mean of the fluctuating signal. Fig. 9 shows the cumulative probability distribution function obtained at the limiting slugging velocity in upper section of the bed. From Fig. 9, it was observed that the mean of the pressure drop, which can be found from the X-axis of the $F_{x(t)}$ (0.5), was 80 Pa for PE-ZT and 200 Pa for PE-MT. The explanation for the higher pressure drops in the slugging regime for PE-MT may come from the different slugging flow in the bed. From the previous discussions, we found that PE-MT has more periodic nature of slugging behavior and higher frequency of slug flow in the slugging regime for PE-ZN.

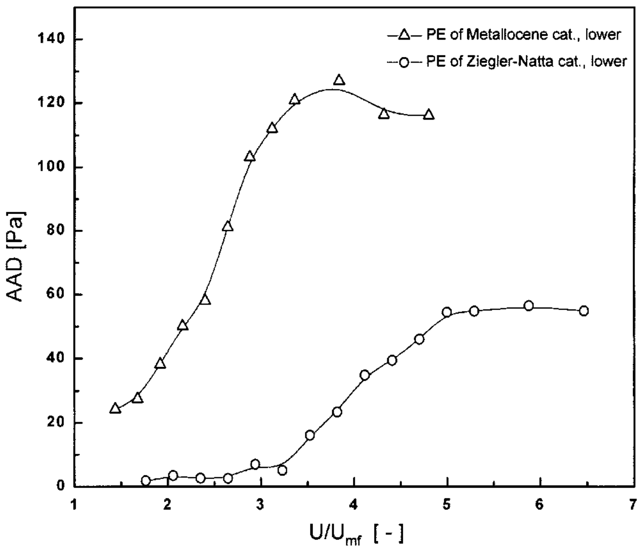

Fig. 8. Absolute average deviation (AAD) of pressure fluctuation at the lower section of the bed as a function of gas velocity for different polymer particles.

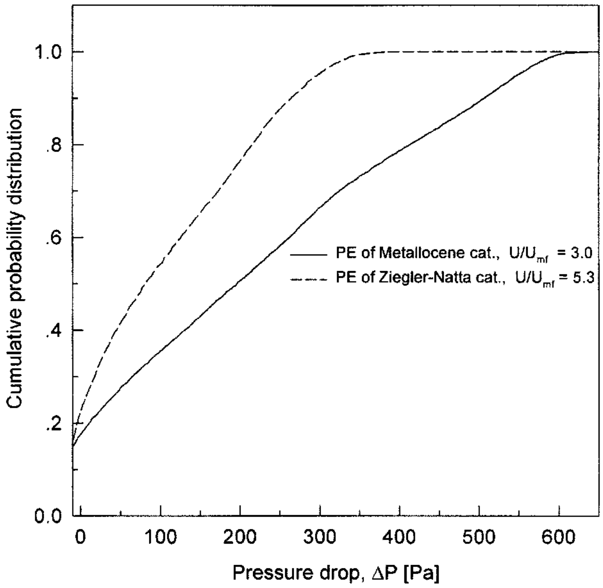

Fig. 9. Probability distribution function at the upper section of the bed for different polymer particles.

For a slugging bed, the pressure drop is a combination of particle-particle, particle-wall interaction and the energy required to accelerate a solid-slug to its terminal velocity. It was experimentally found that the pressure drop appeared to be largely due to the transformation and eventual dissipation of the potential energy developed by the rising solid slugs, and appeared to be independent of the extent of particle-particle and particle-wall frictional interactions [Chen et al., 1997]. Therefore, the high pressure losses for PE-MT results from the potential energy by the rising slugs, and the frequent frequency of slug flow required more energy for developing the slug. However, it is not clear at this point why the particles of PE-MT cause more frequent slugs and more periodic motions of slugs than the particles of PE-ZN in the slugging regime. We guessed that the physical properties and morphology of the LLDPE polymerized by different catalysts such as dielectric constant, particle size distribution, sphericity, and surface hardness may cause the different flow behavior in the slugging regime.

Future work requires that the effect of particle size distribution, dielectric constant, sphericity and particle surface property of polymeric particles on the flow behaviors should be the next research subject for the better understanding of slugging in the fluidized bed polymerization reactors.

CONCLUSIONS

The slug flow behavior of 0.55 mm polyethylene particles polymerized by Ziegler-Natta and Metallocene catalysts was investigated in a fluidized bed of 0.07 m ID and 0.5 m in height. The time series of pressure drop data during the slugging flow were analyzed through statistical methods.

The polymer particles of PE-MT showed larger pressure fluctuations than that of polymer particles of PE-ZN and also showed very uniform periodic pressure fluctuation during the slugging flow. The onset of slugging occurred at the gas velocity of U_g=3.8 U_{mf} for the particles of PE-ZN and U_g=2.0 U_{mf} for the particles of PE-MT. The slug frequency was found to decrease with an increase in gas velocity, and it approached to a limiting value of 1.0 Hz for both particles. However, at low gas velocity, more frequent slug flow was observed for the particles of PE-MT. The mean pressure drop during slugging flow was 80 Pa for particles of PE-ZN and 200 Pa for PE-MT. From this study it was concluded that in spite of similar particle size and particle density, the different slug flow behavior was observed due to different polymerization catalysts. This observed different slug flow behavior may result from the particle size distribution, particle bulk density, sphericity, particle hardness and so on.

NOMENCLATURE

f_s : dominant slugging frequency [Hz]
$f_{x(t)}(x)$: probability density function [-]
$F_{x(t)}(x)$: probability distribution function [-]
N : total sampling number [-]
U_g : superficial gas velocity [m/sec]
U_{mf} : minimum fluidization velocity [m/sec]
x_t : random variable [pa]
T : total sampling time [s]
ΔP : pressure drop [pa]

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