European Symposium on Computer Aided Process Engineering – 15
L. Puigjaner and A. Espuña (Editors)

Mathematical Modeling of Ethylene Polymerization with Ziegler-Natta Catalyst

S.M. Ghafelebashi Zarand[a1*], S. M. M. Mortazavi[b],
[a]Polymer Group, Research and Technology, National Petrochemical Company, Tehran, Iran
[b]Iran Polymer and Petrochemical Institute, Tehran, Iran

Abstract

Slurry polymerization of ethylene with Ziegler-Natta Catalysts was modeled with help combination of both polymeric multigrain (PMGM) and polymeric multilayer (PMLM) as developed by Gupta and Soares & Hamielec theories, respectively. In this study, kinetics scheme considered completely including: activation site, initiation, propagation, chain transfer to monomer, transfer to cocatalyst, transfer to chain transfer agent, spontaneous transformation, deactivation and reactions with impurities. To run the simulation some assumptions were made some important examples of which include: fragmentation phenomena in catalyst were considered, all of ingredients and temperature were uniform, single site and multi site active centers of catalysts were used in simulation. Active site concentration inversely was related to polyethylene molecular weights, as active site concentration of catalysts increased then number average molecular weight (N_n) was decreased. One of the important additives in polyolefins polymerization is cocatalyst where with increasing cocatalyst concentration, N_n of polyolefins decreased. Hydrogen currently used as chain transfer agent and N_n inversely related to hydrogen concentration. Polydispersity index increased with increasing active center types, then single site catalysts or metallocene were used to polymerize narrow molecular weight distribution.

Keywords: Mathematical Modeling, Slurry Polymerization, Ziegler-Natta Catalysts, Polyethylene

1. Introduction

Polyethylene and polypropylene grades have developed over years as the dominant polymers used in many industries such as, automotive, pipe, cable and other applications [1]. It is estimated that in the year 2005 about 65 million tons will be produced, which makes up over 55 percent of all plastics. It is well known that polyolefins are produced using Ziegler-Natta Catalysts in homogeneous, heterogeneous and colloidal forms, and Phillips type catalysts which known free radical polymerization type of olefins.Ziegler-Natta Catalysts are structured by transition metals of groups IV-VIII and metal alkyl with metal of groups I-III. In industrial, titanium salts and alkyl aluminum used, respectively [2].

1-Author to whom correspondence should be addressed: m.ghafelebashi@npc-rt.ir

Ray suggested that these are three scales for modeling of transition metal catalyzed olefin polymerization including: macroscale for reactor phenomena, microscale for microstructural properties and mesoscale concerns these two scales of polyolefins [2].
There are three main models for polymer particle growth in Ziegler-Natta catalyst system consisting: solid core model [4], polymeric flow model [4] and multi grain model [3]. In this model catalysts are fragmented and make a continuous phase. Ray suggested multigrain model to account for the molecules weight characteristics of heterogeneous catalyzes olefin polymerization [3]. Polymer particle growth generally modeled based on polymeric multigrain (PMGM) and polymeric multilayer (PMLM) were developed by Gupta [5] and Soares & Hamielec studies [6], respectively. In this study slurry polymerization of ethylene with Ziegler-Natta catalysts was modeled with help combination of PMGM and PMLM theories.

2. Model Description

2.1 Kinetic Scheme

A complete kinetic representation of olefin polymerization in slurry phase and using Ziegler-Natta catalysts has been developed based on polymeric multilayer (PMLM) kinetic.Complete kinetic scheme are summarized in Table I, including: activation site, initiation, propagation, chain transfer agent (hydrogen as chain transfer agent), spontaneous transformation (such as β-hydride elimination), deactivation and reaction with impurities in reaction media.

Table I. Kinetics Prameters used in Modeling

Site formation	$n^*(j)+C \longrightarrow n(0,j)$	$kf(j)$
Initiation	$n(0,j)+M_i \longrightarrow n_i(1,j)$	$ki_i(j)$
Propagation	$n_i(r,j)+M_k \longrightarrow n_k(r+1,j)$	$kp_{ik}(j)$
Transfer to monomer	$n_i(r,j)+M_k \longrightarrow n_k(r,j)+Q(r,j)$	$ktm_{ik}(j)$
Transfer to cocatalyst	$n_i(r,j)+C \longrightarrow n_2(1,j)+Q(r,j)$	$ktC_i(j)$
Transfer to hydrogen	$n_i(r,j)+H_2 \longrightarrow n_H(0,j)+Q(r,j)$ $n_H(0,j)+C \longrightarrow n_2(1,j)$	$kH_i(j)$ $kH_A(j)$
B-hybride elimination Deactivation	$n_i(r,j) \longrightarrow n_H(0,j)+Q(r,j)$ $n_i(r,j) \longrightarrow n_d(j)+Q(r,j)$ $n_H(0,j) \longrightarrow n_d(j)$ $n(0,j) \longrightarrow n_d(j)$	$Kts_i(j)$ $kd_s(j)$ $kd_s(j)$ $kd_s(j)$
Impurities	$n_i(r,j)+I \longrightarrow n_{dlH}(0,j)+Q(r,j)$ $n_H(0,j)+I \longrightarrow n_{dlH}(0,j)$ $n(0,j)+I \longrightarrow n_{dI}(0,j)$ $n_{dlH}(0,j) \longrightarrow n_H(0,j)+I$ $n_{dI}(0,j) \longrightarrow n(0,j)+I$	$KdI(j)$ $KdI(j)$ $KdI(j)$ $ka(j)$ $ka(j)$

In the kinetic equation of Table I , parameters defined as follows:
n^*: potential active site of catalyst, n: live polymer chains, chemically bonded to the active metal center of catalyst, Q: dead or terminated polymer chains, M: Monomer molecules, C: Catalyst, H_2: Hydrogen as a chain transfer agent in reaction media, I: Impurities. The subscript j indicates active site type, k and i are type of monomers either

chemically bonded to active centers or free in the reaction media and finally r is the chain length of the polymers chain. Chain transfers to monomer (kfm) and B-hydride elimination (kB) are two pathways to form the unsaturated terminal groups in polyethylene [6]. These double bonds can produce the branched structure or long chain branching (LCB). In this study LCB was not considered, its one of the most important assumption in this simulation. The long chain branching produced in polyethylene and free radical polymerization were investigated by using the Monte Carlo simulation method on the basis of the random sampling technique [7].

The partial differential equations are used to calculate of reactant concentration and moments to estimation of final properties of polyethylene such as molecular weight and other characteristics.

2.1 Simulation Assumptions

Some important assumptions include:

All of primary particles were spherical. Catalyst fragmentation phenomena were considered. All of ingredients in reactor and temperature were considered uniform. Multi and single-site active centers of catalysts were used in this simulation. Rate constants of initiation equals with rate constants of propagation. Pressure and temperature were constant. Slurry polymerization of ethylene with Zeigler-Natta catalysts was simulated using parameters as described in Table II [6].

Table II. Parameters for simulation of Ziegler-Natta Catalyzed Ethylene Polymerization in slurry phase using (PMLM)[13].

Units	Value	Parameter
$cm^2 s^{-1}$	10^{-5}-10^{-6}	D_{1_butene}
$cm^2 s^{-1}$	10^{-5}-10^{-6}	$D_{ethylene}$
$mol\ lit^{-1}$	0.13	$[M]_{1\_butene}$
$mol\ lit^{-1}$	0.5-4	$[M]_{ethylene}$
$mol\ \ lit^{-1}$	0.1-0.001	C^*
$lit\ (mol.\mathrm{s})^{-1}$	95-5000	k_{p1_butene}
$lit\ (mol.\mathrm{s})^{-1}$	95-5000	$k_{p\,ethylene}$
cm	0.001-0.01	R_0

Primary particle diameter was discretised into radial shells, N_s, at initial time reaction. By increasing of N_s, volume of calculations was increased. Based on the expressions and material balances for all of the ingredients in reactor and molecular weight equations as shown algorithm in Figure (1) solute with numerical techniques.

3. Results and Discussion

3.1 Concentration of catalyst

Catalyst concentration related with active site concentration directly. Figure (2) shows relative between catalyst concentration and number average molecular weight (in versus

catalyst concentration, 0.1, 0.01 and 0.001). With increasing of active site concentration, number of polymeric chain are increased, than N_n was decreased as shown in Figure (2) [6].

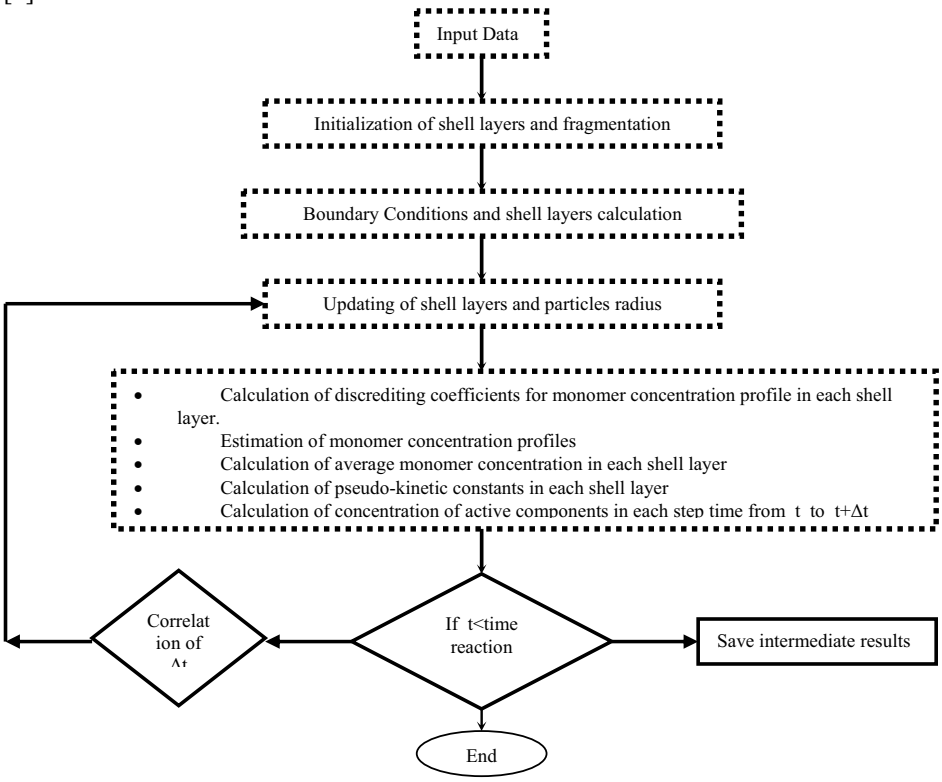

Figure (1) Numerical Algorithm of Ethylene Polymerization with Ziegler-Natta Catalysts

3.2 Cocatalyst concentration

One of the interesting results in study is the cocatalyst concentration effect on the rate of polymerization and final properties of polyolefins. Figure (3) shows rate of polymerization versus cocatalyst concentration.

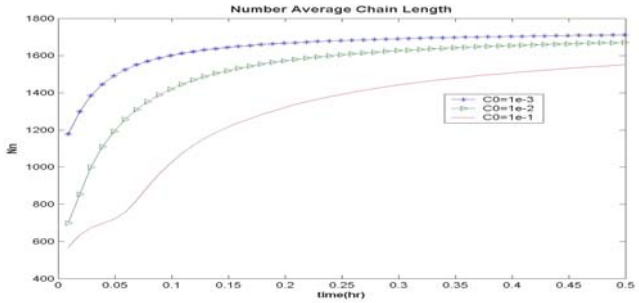

Figure (2) Effect catalyst concentration on N_n

As predicted in Figure (3), time attended to maximum rate of reaction decreased with increasing of cocatalyst concentration [6]. Depending of average molecular weight with cocatalyst concentration show in Figure (4). Number average molecular weight of

polyethylene decreased with increasing of cocatalyst concentration because concentration of active site simultaneously increased [6].

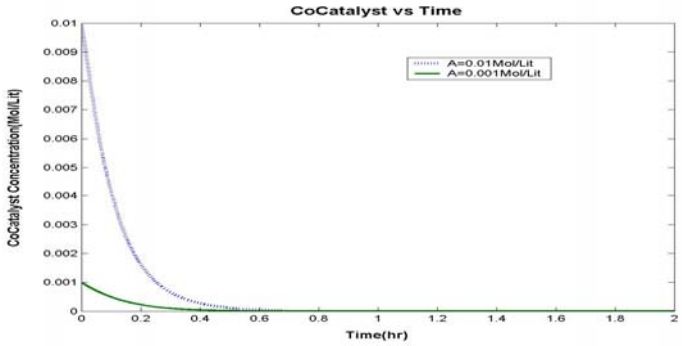

Figure (3) Effect of cocatalyst concentration on rate of polymerization

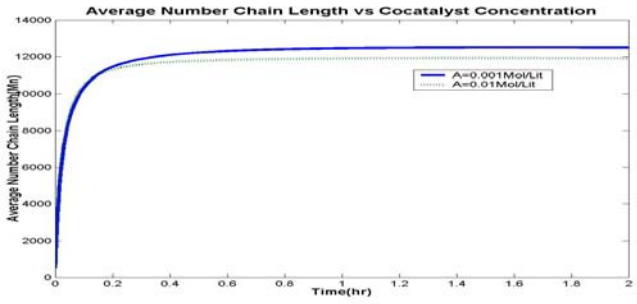

Figure (4) Effect of cocatalyst concentration on number average molecular weight

3.3 Hydrogen concentration Effect

Hydrogen currently used as chain transfer agent in olefin polymerization especially in ethylene and propylene polymerization. Figure (5) shows variation of number average molecular weight with hydrogen concentration. N_n inversely related to hydrogen concentration and number average molecular weight decreased [6].

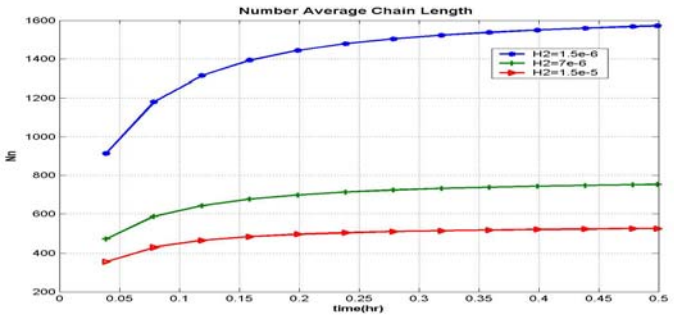

Figure (5) Effect of Hydrogen concentration on number average molecular weight

3.4. Type of Active Center Effects

Number and types of active center of catalysts influence on final properties of polyolefins such as average molecular weight and polydispersity index. Figure (6)

shows the effects of number of active center on PDI. When single site catalyst such as metallocene was used, polydispersity index reach about two and indicated narrow molecular weight distribution. PDI increased with increasing of active center[6], when active sites are equal 2 PDI reached about 3.5 and show broader molecular distribution versus single site catalyst. PDI reached about 7 with increasing of type of site.

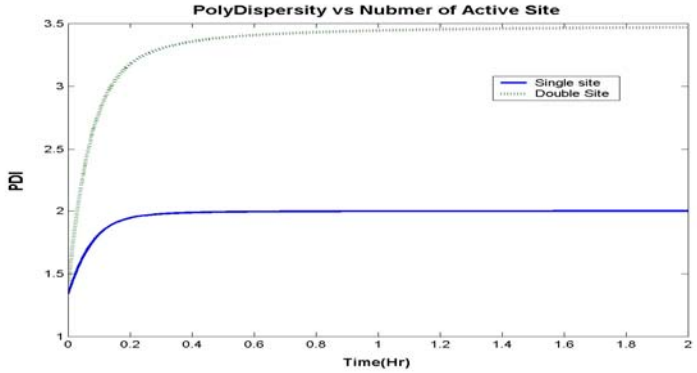

Figure (6) Effect of number active center on PDI

4. Conclusions.

Slurry polymerization of ethylene simulated with help combination of both polymeric multi grain (PMGM) and polymeric multilayer (PMLM) model. In this study parameters affected in olefin polymerization are as follows:

Increasing number of active center decreased number average molecular weight, time attended to maximum rate of reaction decreased with increasing of cocatalyst concentration, number average molecular weight of polyethylene decreased with increasing of cocatalyst concentration, number average molecular weight decreased with increasing hydrogen concentration, PDI increased with increasing type of active center.

5. References

[1] Salamone.J.C.Poymericmaterials Encyclopedia, 3, 10-13, 1996.

[2] L. L. Bohn, "Ethylene polymerization process with a highly active Ziegler-Natta catalyst:1.Kinetics" POLYMER, 19, 553-561, 1978.

[3] R. A. Hutchinson, C. M. Chen, W. H. Ray, " Polymerization of olefins through Heterogeneous catalysis X: Modeling of particle growth and morphology", Journal of Applied Polymer Science, 44, 1389-1414, 1992.

[4] W. R. Schmeal, J. R. Street, "Polymerization in expanding catalysts", AIChE J., 17 (5), 1189-1197,1971.

[5] P. Sarkar, S. K. Gupta, "Simulation of propylene polymerization: an efficient algorithm", Polymer, 33 (7),1477-1485,1992.

[6]] J. B. P. Soares, A. E. Hamielec, "General dynamic mathematical modeling of heterogeneous Ziegler-Natta and Metallocene catalyzed copolymerization with multiple site types and mass and heat transfer resistances", Polym. Reac. Eng., 3(3), 261-324,1995.

[7] S. M. Ghaflebashi Zarand, S.Pourmahdian, F. Afshar Taromi, B. Dabir, " Modeling of Styrene/Butadiene Co- polymerization in Emulsion with Monte Carlo Simulation ", Chem. Eng. Technol., 26, 969-974 ,2003.