



## Kinetic modeling of propylene homopolymerization in a gas-phase fluidized-bed reactor

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### ABSTRACT

A comprehensive mechanistic model describing gas-phase propylene polymerization is developed. The kinetics of polymerization is based on a multiple active site for Ziegler–Natta catalyst. The model considers the polymerization reaction to take place in both bubble and emulsion phases. The developed model was used to predict polymer production rate, number and weight average molecular weights, polydispersity index (PDI) and melt flow index (MFI). Results showed that by increasing the superficial gas velocity from 0.1 to 0.7 m/s the proportion of the polymer produced in the bubble phase increases from 7.92% to 13.14% which highlights the importance of considering the existence of catalyst in the bubble phase. Comparing the developed model with published models of the same reactor revealed that the polymer productivity will be higher using the new model at high catalyst feed rate.

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### 1. Introduction

Bubbling fluidized beds have extensively been studied over the past 50 years and a variety of models have been proposed to describe their steady-state and dynamic behavior [1–6]. The literature shows that the main objective of gas-phase olefin polymerization reaction engineering is to understand how the reaction mechanism, the physical transport processes, reactor configuration and reactor operating conditions affect the properties of the polymer product. In general, polymerization processes can be widely classified into homogeneous and heterogeneous. The homogeneous reactor comprises polymerization which is carried out in just one phase. In the heterogeneous systems, polymerization occurs in the presence of different phases, thus, inter-phase mass transfer, heat transfer and chemical reactions are important.

To describe the kinetic scheme of heterogeneous Ziegler–Natta catalyst, single, as well as multiple, catalyst active sites models have been proposed [7–9]. In this kinetic scheme the key elementary reactions have been established, which include formation of active centers, insertion of monomer into the growing polymer chains, chain transfer reactions, and catalyst deactivation. Most of the proposed mechanisms are based on information about polymerization rate, molecular weight distribution and active center concentrations.

A flow diagram of gas-phase polypropylene production process is shown in Fig. 1. As shown in this figure, Ziegler–Natta

catalyst and triethyl aluminum co-catalyst are charged continuously to the reactor and react with the reactants (propylene and hydrogen) to produce the polymer. The feed gas which comprises propylene, hydrogen and nitrogen, provides fluidization through the distributor, heat transfer media and supply reactants for the growing polymer particles. The fluidized particles disengage from unreacted gases in the disengaging zone. The solid-free gas is combined with fresh feed stream after heat removal and recycled back to the gas distributor. The monomer conversion per pass through the bed can vary from 2% to 5% and overall monomer conversion can be as high as 98% [10]. The polypropylene product is continuously withdrawn from near the base of the reactor and above the gas distributor. The unreacted gas is recovered from the product which proceeds to the finishing area of the plant.

Many researchers (e.g., [1,10–13]) have presented various models for gas-phase olefin polymerization in fluidized-bed reactors in order to investigate temperature control problems and to predict system stability. In this work, a dynamic multiple active sites model is presented to describe the kinetic behavior, production rate and molecular weight distribution of propylene homopolymerization, in an industrial-scale gas-phase fluidized-bed reactor. The present model focuses on characterizing the homopolymerization kinetics occurring at the multiple active sites of the catalyst.

### 2. Polymerization kinetics

Ability of the heterogeneous Ziegler–Natta catalysts to produce polymers with broad molecular weight distributions has

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**Nomenclature**

AlEt <sub>3</sub>	triethyl aluminum co-catalyst
A <sub>r</sub>	Archimedes number
B	moles of reacted monomer bound in the polymer in the reactor
B <sub>w</sub>	mass of resin in the reactor (kg)
d <sub>p</sub>	particle diameter (m)
F <sub>cat</sub>	catalyst feed rate (kg/s)
F <sub>in</sub> <sup>*</sup> (j)	molar flow rate of potential active sites of type j into the reactor
H <sub>2</sub>	hydrogen
I <sub>m</sub>	impurity such as carbon monoxide (kmol/m <sup>3</sup> )
j	active site type
k <sub>dl</sub> (j)	deactivation by impurities rate constant for a site of type j
k <sub>ds</sub> (j)	spontaneous deactivation rate constant for a site of type j
k <sub>f</sub> (j)	formation rate constant for a site of type j
k <sub>fh</sub> (j)	transfer rate constant for a site of type j with terminal monomer M reacting with hydrogen
k <sub>fm</sub> (j)	transfer rate constant for a site of type j with terminal monomer M reacting with monomer M
k <sub>fr</sub> (j)	transfer rate constant for a site of type j with terminal monomer M reacting with AlEt <sub>3</sub>
k <sub>fs</sub> (j)	spontaneous transfer rate constant for a site of type j with terminal monomer M
k <sub>h</sub> (j)	rate constant for reinitiation of a site of type j by monomer M
k <sub>hr</sub> (j)	rate constant for reinitiation of a site of type j by co-catalyst
k <sub>i</sub> (j)	rate constant for initiation of a site of type j by monomer M
k <sub>p</sub> (j)	propagation rate constant for a site of type j with terminal monomer M reacting with monomer M
M	monomer (propylene)
MFI	melt flow index (g/10 min)
$\bar{M}_n$	number average molecular weight of polymer (kg/kmol)
$\bar{M}_w$	weight average molecular weight of polymer (kg/kmol)
M <sub>w</sub>	monomer molecular weight (kg/kmol)
N <sup>*</sup> (j)	potential active site of type j
N(0, j)	uninitiated site of type j produced by formation reaction
N(1, j)	living polymer chain of type j with length one
N(r, j)	living polymer molecule of length r, growing at an active site of type j, with terminal monomer M
N <sub>d</sub> (j)	spontaneously deactivated site of type j
N <sub>dl</sub> (0, j)	impurity killed sites of type j
N <sub>dIH</sub> (0, j)	impurity killed sites of type j
N <sub>H</sub> (0, j)	uninitiated site of type j produced by transfer to hydrogen reaction
NS	number of active site types
P	pressure (Pa)
PDI	polydispersity index
PP	polypropylene
Q(r, j)	dead polymer molecule of length r produced at a site of type j
r	number of units in polymer chain
R	instantaneous consumption rate of monomer (kmol/s)
R(j)	rate at which monomer M is consumed by propagation reactions at sites of type j

Re <sub>mf</sub>	Reynolds number of particles at minimum fluidization condition
R <sub>p</sub>	production rate (kg/s)
R <sub>pb</sub>	bubble phase production rate (kg/s)
R <sub>pe</sub>	emulsion phase production rate (kg/s)
R <sub>v</sub>	volumetric polymer outflow rate from the reactor (m <sup>3</sup> /s)
t	time (s)
T	temperature (K)
U <sub>0</sub>	superficial gas velocity (m/s)
U <sub>mf</sub>	minimum fluidization velocity (m/s)
V	reactor volume (m <sup>3</sup> )
V <sub>b</sub>	volume of bubbles
V <sub>p</sub>	volume of polymer phase in the reactor (m <sup>3</sup> )
V <sub>pb</sub>	volume of polymer phase in the bubble phase (m <sup>3</sup> )
V <sub>pe</sub>	volume of polymer phase in the emulsion phase (m <sup>3</sup> )
X(n, j)	n <sup>th</sup> moment of chain length distribution for dead polymer produced at a site of type j
Y(n, j)	n <sup>th</sup> moment of chain length distribution for living polymer produced at a site of type j

*Greek letters*

δ	volume fraction of bubbles in the bed
ε <sub>b</sub>	void fraction of bubble for Geldart B particles
ε <sub>e</sub>	void fraction of emulsion for Geldart B particles
ε <sub>mf</sub>	void fraction of the bed at minimum fluidization
μ	gas viscosity (Pa s)
ρ <sub>g</sub>	gas density (kg/m <sup>3</sup> )
ρ <sub>s</sub>	polymer density (kg/m <sup>3</sup> )

long being recognized. There are two factors responsible for exhibiting this distribution. One factor is mass and heat transfer resistances that lead to a broadening of the molecular weight distribution. The other factor is existence of multiple sites where each type has its own relative reactivity. However, it has been shown that under most polymerization conditions, the effect of multiple active site types is more important than that of transport resistances [14,15]. The single-site kinetic model is not enough to describe the kinetic behavior, production rate and molecular weight distribution of propylene homopolymerization. Therefore, a two-type active site was considered in the present study.

Using a similar methodology to McAuley et al. [9], Kissin [16] and Carvalho de et al. [17], the following kinetic model was developed using Ziegler–Natta catalysts containing multiple active sites to describe the homopolymer production rate, molecular weight and its distribution. Throughout this section, the index *j* refers to the type of active site. Each site type is associated with different rate constants for formation, initiation, propagation and chain transfer. The following reactions were considered for the Ziegler–Natta multi-site catalyst.

**2.1. Formation of active sites**

For a typical Ziegler–Natta catalyst potential active sites of type *j* on the catalyst particle and the co-catalyst react to form active sites [16]:



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