

Heat transfer efficiency in PEBC synthesis

V V Pliushchev¹, O S Kharitonova², M A Nazarova¹, V V Bronskaya¹,
G V Manuyko¹, R S Shaikhetdinova¹, G A Aminova¹ and D S Balzamov³

¹Department of Technology of Engineering Materials, Kazan National Research Technological University, Karl Marx St., 68, Kazan, 420015, Russia

²Department of Chemical Technology of Petroleum and Gas Processing, Kazan National Research Technological University, Karl Marx St., 68, Kazan, 420015, Russia

³Department of Power Supply of Enterprises and Energy Resource Saving Technologies, Kazan State Power Engineering University, Krasnoselskaya St., 51, Kazan, 420066, Russia

E-mail: olga.220499@mail.ru

Abstract. The kinetics of propylene and ethylene copolymerization in a fluidized bed reactor is considered. Dynamic reactor model based on material balance of monomers, copolymer and copolymerization kinetics has been developed in order to obtain predicted data on monomer flow, copolymer concentration under different process conditions. The complex two-phase model is presented based on two models: well-mixed and two-phase model. The profiles of concentrations and temperatures in microparticles are obtained, and the average concentrations and temperatures at the active sites of the catalyst are determined. The dependences of temperature on the height of the fluidized bed of the reactor at different gas incoming velocity and at different temperature of the monomer input are obtained. Mathematical model that is basis of creating expert control complex of PEBC synthesis process and allow to make quantitative connection between technological parameters of reactors which allows to control technological mode with the acceptable accuracy is presented. Experiment catalytic system is microspheric titanium trichloride (MS-TiCl₃) and co-catalyst-diethylaluminum chloride.

1. Introduction

Propylene-ethylene block copolymer (PEBC) is an inexpensive, environmentally friendly product. Since the opening of new ion-coordinating catalysts, production has been rapidly developing. The demand for the production of Propylene-Ethylene Block Copolymer (PEBC) is related to the value of the properties of this material: high strength, stress cracking resistance in aggressive environments, heat resistance, frost resistance, low specific weight, ability to pass ultraviolet rays and absorb radioactive radiation, good dielectric properties. Carrying out copolymerization of polypropylene and ethylene in the gas phase on complex organometallic catalysts allows to significantly simplify and improve the technology of production of PEBC in the result of the elimination or significant reduction of solvent consumption, the elimination of polymer washing and drying operations, and solvent regeneration. The elimination of polymer washing stage in the gas-phase process is achieved by maximizing the use of catalyst.

A fluidized bed reactor is one of the most common industrial reactors for producing polyolefins and copolymers of olefins due to good mixing of particles, excellent possibilities of heat and mass transfer [1]. The analysis of literature showed the prospects of synthesis of propylene copolymers us-



ing a number of modern catalysts for obtaining both traditional and new polymer materials with a set of thermophysical and physico-chemical properties [2-8]. Consistent processes of homo- and copolymerization of olefins allow to regulate the composition, molecular mass characteristics, properties and supermolecular structure of polyolefins, to obtain modified polyolefins with a set of properties. There is a perforated grille for uniform distribution of the fed ethylene in the lower part of reactor and there is an extended zone designed to reduce gas speed and absorb the bulk of polyethylene in the upper part. The heat removal of the reaction is carried out by ethylene cooled in the circulating circuit heat exchanger. The technological scheme provides for automatic feeding of catalyst, monomer, comonomer, hydrogen and automatic discharge of polymer with the use of logical control systems.

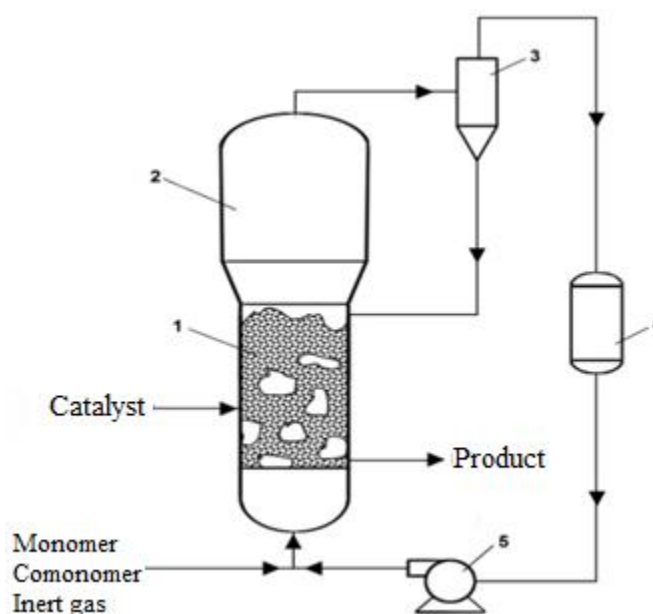


Figure 1. Diagram of ethylene gas phase polymerization in the catalyst fluidized bed: 1 - reaction zone; 2 - separation zone; 3 - cyclone; 4 - heat exchanger; 5 - compressor.

However, today there are a number of technological problems, the main of which is the heat sink. Since the polymerization reaction is highly exothermic, the localized overheating points and, as a result, an abnormality of the fluidization regime may be formed with insufficient heat dissipation. The complexity of modeling such a process consists in the need to take into account many interactions between phases. A distinctive feature of considered gas-phase polymerization is that this system does not involve the gas phase in the polymerization zone. Polymerization occurs in the boundary layer between the solid catalyst and the polymer matrix, which swells due to monomers during polymerization. The role of the gas phase is to transport monomers, mix polymer particles and remove the reaction heat. These problems cannot be solved without the apparatus of mathematical modeling [9-16].

2. Materials and Methods

The mathematical model proposed by K B McAulie, J P Taibot and T J Harris was taken for solving problems [1]. The complex two-phase model is based on two models: well-mixed and two-phase model, according to which some assumptions were introduced:

1. A fluidized bed consists of two phases (bubble phase and continuous phase);
2. The reaction occurs only in the continuous phase in the minimal fluidization regime;
3. The excess gas passes through the bubble phase layer.
4. Bubbles grow only to the maximum stable size. Because bubbles reach their maximum size at the base of the layer, they are assumed to have the same size. They pass through the layer with a constant speed, heat and mass transfer coefficients are average in the height of the layer.
5. The continuous phase acts in perfect mixing mode.

6. Radial gradients of concentration and temperature can be neglected, as the bubbles are distributed evenly over the bottom.
7. There is a slight resistance to heat and mass transfer between the gas and the solids in the continuous phase. This assumption is true when the catalyst particles are small enough and the catalyst activity is not very high.
8. Average particle size is used and particle agglomeration is not considered in the model.

It is assumed that the activation of catalyst instantaneously occurs, the speed constant value for each stage does not depend on the chain length, the polymer chain activity depends on a last monomer added to the active centre of the polymeric chain. The chain transfer reaction is assumed to occur through the active chain reaction with hydrogen. The copolymerization reaction mechanism can be presented as the following kinetic scheme. $\text{TiCl}_4/\text{MgCl}_2 + \text{PEEB} + \text{AlR}_3$ (PEEB -para-ethoxy-ethylbenzoate) is used as the catalyst.

According to the kinetic scheme the kinetic equations were offered:

$$r_{C^*} = -k_i^1 M_1 \cdot C^* - k_i^2 M_2 \cdot C^* - k_d \cdot C^* + k_{tr}^1 P^* [H_2] + k_{tr}^2 Q^* [H_2] \quad (1)$$

$$r_{M_1} = -k_i^1 C^* M_1 - k_p^{11} P^* M_1 - k_p^{21} \cdot Q^* M_1 \quad (2)$$

$$r_{M_2} = -k_i^2 C^* M_2 - k_p^{12} P^* M_2 - k_p^{22} \cdot Q^* M_2 \quad (3)$$

$$r_{P^*} = -k_i^1 C^* M_1 + k_p^{21} Q^* M_1 - k_p^{12} \cdot P^* M_2 - k_{tr}^1 P^* [H_2] - k_d^1 P^* \quad (4)$$

$$r_{Q^*} = -k_i^2 C^* M_2 + k_p^{12} Q^* M_2 - k_p^{21} \cdot Q^* M_1 - k_{tr}^2 Q^* [H_2] - k_d^2 Q^* \quad (5)$$

$$r_{H_2} = -k_{tr}^1 P^* [H_2] - k_{tr}^2 Q^* [H_2] \quad (6)$$

where $P^* = \sum_{S=1}^{\infty} \sum_{n=1}^{\infty} P_{S,n}^*$, $Q^* = \sum_{S=1}^{\infty} \sum_{n=1}^{\infty} Q_{S,n}^*$.

Dependencies of speed constants on temperature are represented by Arrhenius equation [6]:

$$k = k_0 e^{-E/RT} \quad (7)$$

Propylene, ethylene and hydrogen are fed into the fluidization reactor and the polymerization reaction is initiated:

- 1) The monomer concentration in the reactor is homogeneous and changes only over the copolymerization time.
- 2) The pressure influence in the reactor on the copolymer density is not taken into account.
- 3) The diffusion effect of reagents between phases is ignored. It means that the reaction system in the fluidization reactor is considered as a pseudohomogeneous phase.

The material balance equation for catalyst particles in the fluidization reactor is as follows:

$$V_0 \frac{dC^*}{dt} = G_{solid} / M_{solid} - QC^* + r_{C^*} V_0 \quad (8)$$

Similar equations can be obtained for propylene, ethylene, active polymeric chains, hydrogen and the solids copolymer phase:

$$V_0 \frac{dM_1}{dt} = \frac{G_{M_1}^{input}}{M_{M_1}} - QM_1 + r_{M_1} V_0 \quad (9)$$

$$V_0 \frac{dM_2}{dt} = \frac{G_{M_2}^{input}}{M_{M_2}} - QM_2 + r_{M_2} V_0 \quad (10)$$

$$V_0 \frac{dP^*}{dt} = -QP^* + r_{P^*} V_0 \quad (11)$$

$$V_0 \frac{dQ^*}{dt} = -QQ^* + r_{Q^*} V_0 \quad (12)$$

$$V_0 \frac{d[H_2]}{dt} = \frac{G_{H_2}^{input}}{M_{H_2}} - Q[H_2] + r_{H_2} V_0 \quad (13)$$

$$m \frac{dW}{dt} = G^{input} W^{input} - \frac{m}{V_0} QW + V(r_{M_1} M_{M_1} M_1 + r_{M_2} M_{M_1} M_2) V_0 \quad (14)$$

The molar volume of gas mixture in the reactor is determined by the formula (15):

$$V = \frac{1}{M_1 + M_2} \quad (15)$$

The material balance equations for a fluidized bed reactor are given by:

$$\frac{dm}{dt} = G^{input} - \frac{m}{V_0} Q \quad (16)$$

The investigated two-phase model is represented by the system of material and thermal balances (17)-(21):

$$C_{bc} = C_c + \exp \frac{K_{bc} H}{U_b} \frac{U_b}{K_{bc} H} \quad (17)$$

$$U_c \frac{C_0 - C_c}{H} - Q \frac{C_c}{V_c \rho_p} - k_{p0} e^{\frac{E_a}{RT_0}} \quad (18)$$

$$C_c X_{kt} \rho_p \frac{1 - \varepsilon_{mf}}{\varepsilon_{mf}} + \Delta K_{bc} \frac{C_{bc} - C_c}{(1 - \Delta)} \varepsilon_{mf} = 0 \quad (19)$$

$$T_{bc} = T_c + (T_0 - T_c) \left(U_b \frac{c_{pg}}{H_{bc} H} \right) \quad (20)$$

$$\begin{aligned}
& AU_c(1-\Delta)C_0\varepsilon_{mf}c_{pg}(T_0-T_c)+c_{pg}k_{bc}(c_b-c_c)V_b(T_{bc}-T_c)+ \\
& +H_{bc}V_b(T_{bc}-T_c)+\Delta Hk_{p0}\exp_c\frac{-E}{RT_0}C_c*X_{kt}\rho_p\frac{1-\varepsilon_{mf}}{\varepsilon_{mf}}=0
\end{aligned} \tag{21}$$

where T_0 temperature of the incoming gas, c_{pg} heat capacity of the gas phase, ρ_p density PEBC, U_b bubble phase velocity, U_c reaction rate in a solid medium, H reactor height, K_{fc} mass transfer coefficient of boundary layer in solid phase, K_{bc} mass transfer coefficient from bubble phase to continuous phase, H_{bc} heat transfer coefficient from the bubble phase to the continuous phase, ε_{mf} void content in layer at minimum fluidization rates, T_c temperature in the continuous phase, V_c volume of the continuous phase, C_b concentration of the gaseous monomer in the bubble phase, C_c concentration of the gaseous monomer in the continuous phase.

The system is supplemented with equations for finding the average values of concentration and temperature of the monomer, as well as equations of material and heat balances for a single bubble (22)-(25):

$$\bar{C}_b = C_c + \exp \frac{Kbc * H}{Ub} \frac{U_b}{K_{bc}H} \tag{22}$$

$$\bar{T}_b = T_c + (T_0 - T_c) \left(\frac{U_b C_{pg}}{H_{bc}H} \right) \left(1 - \exp \frac{-Hbc * H}{Ub * H} \right) \tag{23}$$

$$T_b = T_c + \exp \frac{Hbc * H}{Ub * Cb * cpg} \tag{24}$$

$$C_b = C_c + \exp \frac{Kbc * H}{Ub} \tag{25}$$

where Cb concentration of gaseous monomer in the bubble phase, Cc concentration of gaseous monomer in the continuous phase, Hbc heat transfer coefficient from the bubble phase to the continuous phase, H reactor height, Ub velocity of the bubble phase, c_{pg} heat capacity of the gas phase, T_0 temperature of the incoming gas, Tc temperature in the continuous phase.

3. Results

Equations (1)-(15) make up a dynamic model of propylene and ethylene copolymerization reaction, by which we determine the molar volume of gas mixture, concentration of monomer and solid phase in the fluidized bed reactor. The values of kinetic constants depend not only on the catalytic system composition, technological conditions of the copolymerization process, but also on used mathematical model so it is necessary to be identified them. Calculations using identified parameters $k^1_i = 5 \cdot 10^{-5} \text{ m}^3/(\text{mol} \cdot \text{s})$, $k^2_i = 1 \cdot 10^{-4} \text{ m}^3/(\text{mol} \cdot \text{s})$, $k^{11}_p = k^{21}_p = 5 \cdot 10^{-5} \text{ m}^3/(\text{mol} \cdot \text{s})$, $k^{12}_p = k^{22}_p = 1 \cdot 10^{-4} \text{ m}^3/(\text{mol} \cdot \text{s})$, $k^1_{tr} = k^2_{tr} = 1.6 \cdot 10^{-4} \text{ m}^3/(\text{mol} \cdot \text{s})$, $G_{M1}^{\text{enter}} = 252 \text{ kg/h}$, $G_{M2}^{\text{enter}} = 176 \text{ kg/h}$, $G_{H2}^{\text{enter}} = 45.7 \text{ kg/h}$ (figure 2,3) are carried out according to the presented model.

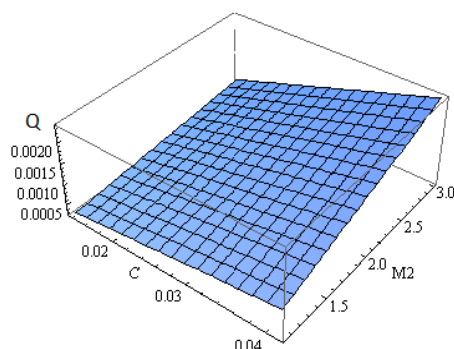


Figure 2. Dependence of active copolymer chains concentration (with the ethylene end link) on concentration of catalyst and ethylene at identified parameters.

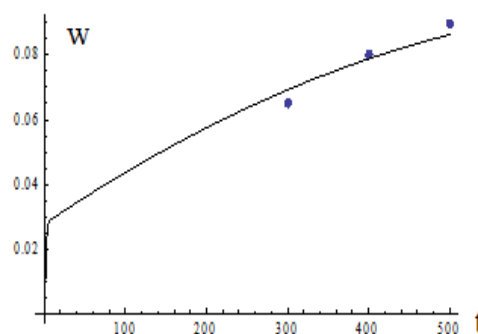


Figure 3. Dependence of a part of the solid copolymer phase on the residence time in the reactor (points — experiment, line — model calculation).

The dependences of temperature on the height of the fluidized bed of the reactor at different gas incoming velocity and at different temperature of the monomer input are obtained.

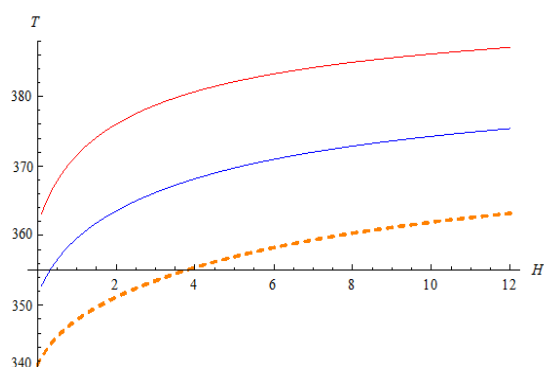


Figure 4. Dependence of the monomer temperature on the height of the continuous phase in the device at $T_0 = 340$, $T_{01} = 350$, $T_{02} = 360$, $C_0 = 20$ kg/m³, $U_0 = 0.34$.

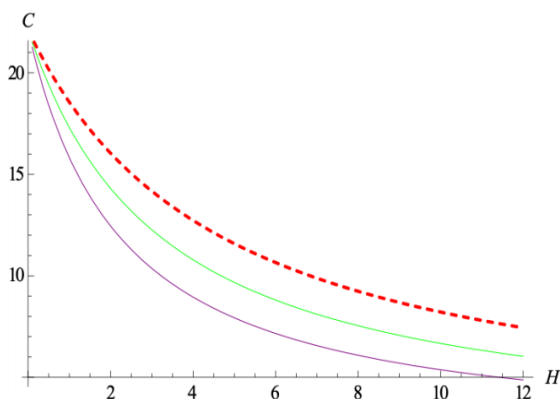


Figure 5. Dependence of monomer concentration on the height of the bubble phase in the apparatus at $T_0=340$, $T_{01}=350$, $T_{02}=360$, $C_0=20$ kg/m³, $U_0=0.34$.

The system of equations of the two-phase model was solved by Runge-Kutta method. Profiles of concentrations and temperatures in microparticles were obtained, as well as the average concentrations and temperatures at the active catalyst centers were determined.

4. Discussion

There is a tendency of increase of active copolymer chains concentration with increase of concentration of monomers and catalyst (figure 2). Kinetic constants, the comparison of the experiment and calculated values of a part of the solid copolymer phase in the reactor are obtained as a result of parametric identification and presented in figure 3. It was also revealed as a result of modeling that the increase of hydrogen concentration leads to an increase of the ethylene links addition speed. A dynamic

reactor model has been developed to predict the speed of consumption of monomer and hydrogen over time during propylene and ethylene copolymerization in a fluidized bed reactor. According to the results of simulation it was established that the predicted data on monomer flow, copolymer concentration and slurry density under different technological conditions are consistent with the experimental data.

5. Conclusion

The presented profiles show the nature of the change in concentration and temperature in microparticles due to monomer diffusion and chemical reaction. Monomer concentration decreases because of the monomer consumption and temperature increases due to exothermic nature of ethylene polymerization. That is because of the need to take into account many parameters when describing heterogeneous systems, the mathematical model of ethylene gas phase polymerization process will be supplemented by equations taking into account the influence of growth polymeric particles on the nature of the flow structure and changes in catalyst activity.

To obtain high-quality PEBC in the framework of the existing technological process, it is possible to ensure conditions of synthesis, containing up to 30% of the mass. elastomeric component, with a yield of at least 20% of PEBS, increasing the efficiency of the reactor heat removal system in order to reduce the maximum copolymerization temperature to an acceptable level.

Designation

C — concentration of deactivated catalyst [mol/m³], C* = concentration of active catalyst [mol/m³], G_{M1}^{enter}-mass propylene flow [kg/s], G_{M2}^{enter}-mass ethylene flow [kg/s], G_{H2}^{enter} -mass hydrogen flow [kg/s], G^{enter}-mass flow of materials [kg/s], G_s-mass flow of solid particles [kg/s], [H₂] -hydrogen concentration [mol/m³], k¹_i- propylene chain initiation speed constant [m³/ (mol⁰s)], k²_i - ethylene chain initiation speed constant [m³/ (mol⁰s)], k¹¹_p-constant of addition speed of propylene to the chain with the propylene end link [m³/ (mol⁰s)], k²¹_p-constant of addition speed of propylene to the chain with the ethylene end link [m³/ (mol⁰s)], k¹²_p - constant of addition speed of ethylene to the chain with the propylene end link [m³/ (mol⁰s)], k²²_p-constant of addition speed of ethylene to the chain with the ethylene end link [m³/ (mol⁰s)], k¹_{tr} - constant of chain transfer (with the propylene end link) to hydrogen [m³/ (mol⁰s)], k²_{tr}- constant of chain transfer (with the the ethylene end link) to hydrogen [m³/ (mol⁰s)], k¹_d-chain break constant (with the propylene end link) [m³/ (mol⁰s)], k²_d-chain break constant (with the ethylene end link) [m³/ (mol⁰s)], k_d-constant of deactivation speed of active catalyst [m³/ (mol⁰s)], m-total mass of a mixed system in a fluidized bed reactor [kg], M₁ = propylene concentration [mol/m³], M₂ = ethylene concentration, P^{*}_{s, n}-active copolymer chain (with the propylene end link) containing s propylene links and n ethylene links [mol/m³], P_{s, n}-dead copolymer chain [mol/m³], Q^{*}_{s, n} -active copolymer chain (with the ethylene end link) containing s propylene links and n ethylene links [mol/m³], Q_{s, n}-dead copolymer chain [mol/m³], R-gas constant, r_{C*}-active catalyst flow speed [mol/m³ s], r_{M1}- propylene flow speed [mol/m³ s], r_{M2}-ethylene flow speed [mol/m³ s], r_{p*}-growth speed of active chains (with the propylene end link) [mol/m³ s], r_{Q*}-growth speed of active chains (with the ethylene end link) [mol/m³ s], r_{H2}- hydrogen flow speed [mol/m³ s], T-temperature [K], V₀-effective reactor volume [m³], W-part of the solid phase in the reactor, M_{M1} -molar mass of propylene [kg/kmol], M_{M2} -molar mass of ethylene [kg/kmol], M_{solid} -molar mass of catalyst [kg/kmol], M_{gas} - the molar mass of gas mixture [kg/kmol].

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