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Dynamic Simulation and Modelling of Bulk Polymerization of Ethylene Using Bi-functional initiators

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Abstract: A dynamic simulation and modelling of ethylene bulk polymerization in an autoclave reactor are presented in this paper, based on a kinetic model. This simulation is done for mono- and bi-functional initiators, and results show that application of the bi-functional initiators cause an increase in ethylene conversion. The presented model shows very good results for high temperature and low temperature, in comparison with experimental data in the literature.

Introduction

Polyethylene is a most widespread polymer worldwide, and numerous articles have been published about its physical properties, reaction mechanisms and process simulations.

Low density polyethylene (LDPE) produced under high pressure (82-276 MPa) and high Temperature (405-605 K) with a free radical initiator (such as peroxides and oxygen) [1-3], represents about 33% of the total volume of produced polyethylene [4]. Temperatures exceeding the range which was said, cause ethylene to decompose and are not recommended in practice.

The high pressure polymerization of ethylene is performed in two types of reactors: tubular and autoclave [5]. LDPE is produced in either a stirred autoclave or a tubular reactor; total domestic production, divided between the two systems at 45% for tubular and 55% for autoclave, is estimated to be 3.4 million metric tons per year [6]. Neither process has gained a clear advantage over the other [6]. The high pressure process is usually a bulk polymerization initiated by organic peroxide as an initiator.

Many scientists have tried to model and simulate the ethylene polymerization in high pressure autoclave reactors [7-12] and tubular reactors [13-16]. In spite of the recent visible success of Ziegler-Natta and metallocene type catalysts in polymerizing polyethylene in low temperature and pressure conditions [17], application of organic peroxides in production of LDPE at high pressure, remain substantially significant. Because the low conversion of ethylene in high pressure polymerization, we must find a new procedure for enhancing the low conversion in this type of process. One of these procedures is to investigate the effectiveness of initiators.

The chemistry and behaviour of organic peroxides used as initiators in free radical polymerization have been considered by many researchers. One of most important results of their investigations, are the change in decomposition rates of organic peroxides with change in the thermal conditions. For example, for the low temperature polymerization processes such as styrene or methyl methacrylates, a number of bi-functional peroxides were tested and analyzed, and the results with these bi-functional peroxides showed considerable enhancement in the conversion, [12, 18-20, 34]. The chemistry and kinetics of these organic peroxides and effects of these peroxides in the reaction rates, and effectiveness of products, were investigated in a series of publication by Luft and co-workers [21-25] and Scorah [34].

In this study, based on a kinetic model, a dynamic simulation and modelling for polymerization of ethylene with bi-functional initiators is presented.

Reaction Mechanism

The reaction mechanism adopted in the model presented below, consists of the well-known steps of initiation, propagation, termination, and transfer to monomer and to transfer agents. Mono-functional peroxides such as benzoyl and dioctanoyl have one oxygen-oxygen bond separating two identical or different organic groups. Under the thermal conditions oxygen bonds breaks up giving rise to two possible free radicals

$$R_1 - O - O - R_1 \xrightarrow{k_d} 2R_1 - \dot{O} \tag{1}$$

where R_1 is an organic group and k_d is the rate coefficients of initiator decomposition. These types of initiators use in industry, generally.

For bi-functional initiators we assumed the decomposition of initiators is unsymmetrical as shown below

$$R_1 - OO - R2 - OO - R_1 \xrightarrow{k_{d1}} R_1 - \dot{O} + \dot{O} - R2 - OO - R_1 \tag{2}$$

For notational convenience we can rewrite the Eq. (2) in the new form

$$I \xrightarrow{2k_{d1}} \dot{R}_{1in} + \dot{R}_{2in} \tag{3}$$

where $\dot{R}_{1in}$ is a primary initiator free radical, $\dot{R}_{2in}$ is a second initiator radical with one undecomposed peroxide and k_{d1} is the rate coefficient of initiators decomposition.

We assumed mechanism of bulk polymerization of ethylene with bi-functional initiators, as shown below

Initiation by bi-functional initiators

$$I \xrightarrow{2k_{d1}} \dot{R}_{1in} + \dot{R}_{2in}$$

$$\dot{R}_{1in} + M \xrightarrow{K_1} \dot{R}_1$$

$$\dot{R}_{2in} + M \xrightarrow{K_2} \dot{R}_1{}'$$

$$P_i' \xrightarrow{Kd2} \dot{R}_{1in} + \dot{R}_i$$

$$P_i'' \xrightarrow{Kd2} \dot{R}_{1in} + \dot{R}_i{}'$$

Thermal initiation

$$3M \xrightarrow{K_{th}} 2\dot{R}_{1in}$$

Propagation

$$\dot{R}_i + M \xrightarrow{Kp} \dot{R}_{i+1}$$

$$\dot{R}_i{}' + M \xrightarrow{Kp} \dot{R}_{i+1}{}'$$

Termination

$$\dot{R}_i + \dot{R}_j \xrightarrow{K_{tc}} P_{i+j}$$

$$\dot{R}_i + \dot{R}_j' \xrightarrow{K_{tc}} P_{i+j}'$$

$$\dot{R}_i' + \dot{R}_j' \xrightarrow{K_{tc}} P_{i+j}''$$

Transfer to monomer

$$\dot{R}_i + M \xrightarrow{K_{tfm}} P_i + \dot{R}_1$$

$$\dot{R}_i' + M \xrightarrow{K_{tfm}} P_i' + \dot{R}_1$$

β-scission to secondary radicals

$$\dot{R}_{i+1} + M \xrightarrow{K\beta} P_i + \dot{R}_{1in}$$

$$\dot{R}_{i+1}' + M \xrightarrow{K\beta} P_i' + \dot{R}_{1in}$$

Intermolecular transfer

$$\dot{R}_i \xrightarrow{K_b} \dot{R}_i$$

$$\dot{R}_i' \xrightarrow{K_b} \dot{R}_i'$$

Transfer to polymer

$$\dot{R}_i + P_p \xrightarrow{K_{fp}} P_i + \dot{R}_p$$

$$\dot{R}_i + P_p' \xrightarrow{K_{fp}} P_i' + \dot{R}_p$$

$$\dot{R}_i' + P_p \xrightarrow{K_{fp}} P_i + \dot{R}_p'$$

$$\dot{R}_i' + P_p' \xrightarrow{K_{fp}} P_i' + \dot{R}_p'$$

where in all relations, M, I, and P are monomer (ethylene), bi-functional initiator and polymer (polyethylene), respectively. Also $\dot{R}_i$ is regular radical, $\dot{R}_i'$ is macro-radical with one undecomposed peroxide and P_i is dead polymer molecule P_i' is dead polymer with one undecomposed peroxide and P_i'' is dead polymer with two undecomposed peroxides.

Dynamic Model for Autoclave CSTR Reactor

This dynamic model can be developed from the molar balances of all species available in the reaction mechanism.

By performing the molar balances on the growing radicals $\dot{R}_i$ and $\dot{R}_i'$, we can write their moments λ_m and λ_m' (m=0, 1, 2) by assuming pseudo-steady state hypothesis for these radicals. Mavridis and Kiparissides [29-30] and Yoon and Rhee [31] found little difference in the solution to the molecular weight distribution when pseudo-steady state hypothesis is relaxed. Moreover, in our simulations, when the pseudo-steady state hypothesis was relaxed the results were not significantly changed. The assumption makes the odes much easier to solve, as they become less stiff.

$$\lambda_0' = \frac{R_{in}' + 2 f_2 K_{d2} \mu_0''}{K_{tfm}[M] + K_\beta + K_b + K_{tc}\lambda_{to}} \tag{4}$$

$$\lambda_0 = \frac{R_{in} + (K_{tfm}[M] + K_\beta + K_b)\lambda_0' + f_2 K_{d2} \mu_0'}{K_{tc}\lambda_{to}} \tag{5}$$

$$\lambda_1 = \frac{R_{in} + (K_{tfm}[M] + K_\beta + K_b)\lambda_{to} + f_2 K_{d2} \mu_1' + K_p[M]\lambda_0 + K_{fp}(\mu_2 + \mu_2')\lambda_0}{K_{tc}\lambda_{to} + K_{tfm}[M] + K_\beta + K_b + K_{fp}(\mu_1 + \mu_1')} \tag{6}$$

$$\lambda_1' = \frac{R_{in}' + 2 f_2 K_{d2} \mu_1'' + K_p[M]\lambda_0' + K_{fp}(\mu_2 + \mu_2')\lambda_0'}{K_{tc}\lambda_{to} + K_{tfm}[M] + K_\beta + K_b + K_{fp}(\mu_1 + \mu_1')} \tag{7}$$

$$\lambda_2 = \frac{R_{in} + f_2 K_{d2} \mu_2' + K_p[M](2\lambda_1 + \lambda_0) + K_{fp}(\mu_3 + \mu_3')\lambda_0}{K_{tc}\lambda_{to} + K_{tfm}[M] + K_\beta + K_b + K_{fp}(\mu_1 + \mu_1')} \tag{8}$$

$$\lambda_2' = \frac{R_{in}' + 2 f_2 K_{d2} \mu_2'' + K_p[M](2\lambda_1' + \lambda_0') + K_{fp}(\mu_3 + \mu_3')\lambda_0'}{K_{tc}\lambda_{to} + K_{tfm}[M] + K_\beta + K_b + K_{fp}(\mu_1 + \mu_1')} \tag{9}$$

where R_{in} and R_{in}' are the initiation rates which are defined as

$$R_{in} = 2K_{th}[M]^3 + 2 f_2 K_{d1}[I] + f_2 K_{d2}(\mu_0' + 2\mu_0'') \tag{10}$$

$$R_{in}' = 2 f_1 K_{d1}[I] \tag{11}$$

The overall live radical concentration in the reaction mixture, λ_{to}, can be calculated by equation (12).

$$\lambda_{to} = \sqrt{\frac{R_{in} + R_{in}' + f_2 K_{d2}(\mu_0' + 2\mu_0'')}{K_{tc}}} \tag{12}$$

In the reactor the monomer and initiator are consumed simultaneously and we can write the consuming equations of these species, as shown below, respectively.

$$\frac{d([M])}{dt} = -R_p[M] + F_r([M]_f - [M])/V_r \tag{13}$$

$$\frac{d([I])}{dt} = -2K_{d1}[I] + F_r([I]_f - [I])/V_r \tag{14}$$

where R_p is the rate of polymerization.

$$R_p = K_p \lambda_{to} \tag{15}$$

In this model we assumed the reactor volume, pressure and temperature are constant.

We can write all of the moment equations as shown below.

$$\frac{d(\mu_0)}{dt} = K_{tc}\lambda_0^{\ 2}/2 + (K_{tfm}[M] + K_\beta + K_b)\lambda_0 - F_r\mu_0/V_r \tag{16}$$

$$\frac{d(\mu_1)}{dt} = K_{tc}\lambda_0\lambda_1 + (K_{tfm}[M] + K_\beta + K_b)\lambda_1 + K_{fp}((\lambda_1 + \lambda_1^{'})\mu_1 - \lambda_{to}\mu_2) - F_r\mu_1/V_r \tag{17}$$

$$\begin{aligned}\frac{d(\mu_2)}{dt} &= K_{tc}(\lambda_0\lambda_2 + \lambda_1^{\ 2}) + (K_{tfm}[M] + K_\beta + K_b)\lambda_2 + K_{fp}((\lambda_2 + \lambda_2^{'})\mu_1 - \lambda_{to}\mu_3) \\ &- F_r\mu_2/V_r\end{aligned} \tag{18}$$

$$\frac{d(\mu_0^{'})}{dt} = K_{tc}\lambda_0\lambda_0^{'} - K_{d2}\mu_0^{'} + (K_{tfm}[M] + K_\beta + K_b)\lambda_0^{'} - F_r\mu_0^{'}/V \tag{19}$$

$$\begin{aligned}\frac{d(\mu_1^{'})}{dt} &= K_{tc}(\lambda_0\lambda_1^{'} + \lambda_1\lambda_0^{'}) - K_{d2}\mu_1^{'} + (K_{tfm}[M] + K_\beta + K_b)\lambda_1^{'} \\ &K_{fp}((\lambda_1 + \lambda_1^{'})\mu_1^{'} - \lambda_{to}\mu_2^{'}) - F_r\mu_1^{'}/V_r\end{aligned} \tag{20}$$

$$\begin{aligned}\frac{d(\mu_2^{'})}{dt} &= K_{tc}(\lambda_2\lambda_0^{'} + 2\lambda_1\lambda_1^{'} + \lambda_0\lambda_2^{'}) - K_{d2}\mu_2^{'} + (K_{tfm}[M] + K_\beta + K_b)\lambda_2^{'} \\ &+ K_{fp}((\lambda_2 + \lambda_2^{'})\mu_1^{'} - \lambda_{to}\mu_3^{'}) - F_r\mu_2^{'}/V_r\end{aligned} \tag{21}$$

$$\frac{d(\mu_0^{''})}{dt} = K_{tc}\lambda_0^{'2} - 2K_{d2}\mu_0^{''} \tag{22}$$

$$\frac{d(\mu_1^{''})}{dt} = K_{tc}\lambda_0^{'}\lambda_1^{'} - 2K_{d2}\mu_1^{''} \tag{23}$$

$$\frac{d(\mu_2^{''})}{dt} = K_{tc}(\lambda_0^{'}\lambda_2^{'} + \lambda_1^{'2}) - 2K_{d2}\mu_2^{''} \tag{24}$$

Several authors have used the closure technique of Hulburt and Katz [26], although this method may not be completely suitable for polyethylene produced in high pressure [32]. This technique will be evaluated as a possible closure method. By this method, we can calculate the third moments as below:

$$\mu_3 = \frac{\mu_2}{\mu_0\mu_1}(2\mu_0\mu_2 - \mu_1^{\ 2}) \tag{25a}$$

$$\mu_3^{'} = \frac{\mu_2^{'}}{\mu_0^{'}\mu_1^{'}}(2\mu_0^{'}\mu_2^{'} - \mu_1^{'2}) \tag{26a}$$

One of the other closure techniques which are recommended for polyethylene is the log-normal distribution closure technique. Molecular weight distributions of produced polyethylene at high pressure tend to be log-normal distribution [33]. For this reason we can assume that distribution is log-normal, and derive the third moments as discussed in ref [32]. The results are:

$$\mu_3 = \mu_0 (\mu_2 / \mu_1)^3 \tag{25b}$$

$$\mu_3' = \mu_0' (\mu_2' / \mu_1')^3 \tag{26b}$$

Zabisky et al. [32], proposed a new mixed closure technique which is geometric average of methods of Hulburt and Katz (HK) and the log-normal (LN) distribution. This geometric technique has showed very good agreement with reactor experimental data [32]. By means of this geometric mean closure technique, we can obtain the third moments as below:

$$\mu_3 = \sqrt{\mu_{3,Hk}\mu_{3,LN}} \tag{25c}$$

$$\mu_3' = \sqrt{\mu_{3,Hk}' \mu_{3,LN}'} \tag{26c}$$

where in these two equations, $\mu_{3,Hk}$ and $\mu_{3,Hk}'$ has been obtained from equations (25a) and (26a) by Hulburt and Katz method. $\mu_{3,LN}$ and $\mu_{3,LN}'$ has been obtained from equations (25b) and (26b) by log-normal distribution technique.

The simultaneous solution of the system of algebraic equations, (4)-(12), and differential equations, (13)-(24), necessary to simulate the process is achieved by the application of a numerical method. For solving this problem, we use the ode15s function in MATLAB software, which work based on Gear's method [27] and is explained by Shampine and Reichelt, completely [28]. The set of equations is stiff because the dynamics associated with changes in some intermediate species are very fast compared to the dynamics associated with the other states in the model. After solution of this problem, all moments of radicals and polymer concentration distributions along with the monomer and initiator concentrations for every time increment, are obtained. From these values the conversion and molecular weight averages development with time are calculated as

$$X(t) = \frac{[M]_0 - [M](t)}{[M]_0} \tag{27}$$

$$\overline{M}_n = \frac{M_{wm}\left(\mu_1(t) + \mu_1'(t) + \mu_1''(t) + \lambda_1(t) + \lambda_1'(t)\right)}{\left(\mu_0(t) + \mu_0'(t) + \mu_0''(t) + \lambda_0(t) + \lambda_0'(t)\right)} \tag{28}$$

$$\overline{M}_w = \frac{M_{wm}\left(\mu_2(t) + \mu_2'(t) + \mu_2''(t) + \lambda_2(t) + \lambda_2'(t)\right)}{\left(\mu_1(t) + \mu_1'(t) + \mu_1''(t) + \lambda_1(t) + \lambda_1'(t)\right)} \tag{29}$$

where M_{wm} is the monomer molecular weight.

Results and Discussion

In this model we assumed that free radical polymerization of ethylene initiated by a bi-functional initiator in an isothermal autoclave reactor in which the reaction mixture is perfectly mixed. In this work for the parameters $[M]_f, [I]_f, F_r$, the values of 2 mol/lit, $[I]_0$, and V_r / τ were used, respectively. For using the data from Seidl and Luft [22], we assumed a small reactor of 15 ml which operated at 1700 bar pressure. As discussed in the Brandolin et al. [15], the values of kinetic parameters significantly vary in the literature; in this study all of the kinetic parameters are renewed by the existed experimental data available in the literature. These parameters are available in the Tab.1. Values of kinetic parameters for the initiators are available in the Tab. 2.

Tab. 1. Numerical values of parameters used in model calculations

Parameter	Unit	Values
K_{th}	l^2/mol^2s	$5.99\times10^3\exp(-1.44\times10^5/T-0.11)$
K_p	l/mols	$5.45\times10^5\exp(-8.33\times10^3/T+0.27)$
K_{tc}	l/mols	$4.34\times10^8\exp(-7.23\times10^3/T+0.15)$
K_{tfm}	l/mols	$1.2\times10^5\exp(2.85\times10^5/T+1.99)$
K_β	1/s	$1.4\times10^9\exp(-3.82\times10^3/T+0.96)$
K_{fp}	l/mols	$1.8\times10^9\exp(-1.86\times10^4/T-1.54)$
K_b	1/s	$3.25\times10^5\exp(-1.48\times10^4/T-0.49)$

Tab. 2. Decomposition rate constants of peroxide initiators.

Initiators	K_{d1}	K_{d2}
Dioctanoyl peroxide	$2.29\times10^{14}\exp(-5.96\times10^4/T-3.67)$	0
2,2-bis(tert-Butylperoxy)-butane)	$1.81\times10^{16}\exp(-8.38\times10^4/T-2.35)$	$6.04\times10^{17}\exp(-8.3\times10^4/T-0.02)$
2,5-Dimethyl hexane- 2-t-butylperoxy-5-perpivalate	$1.81\times10^{16}\exp(-8.52\times10^4/T-1.98)$	$6.04\times10^{17}\exp(-8.67\times10^4/T-1.21)$

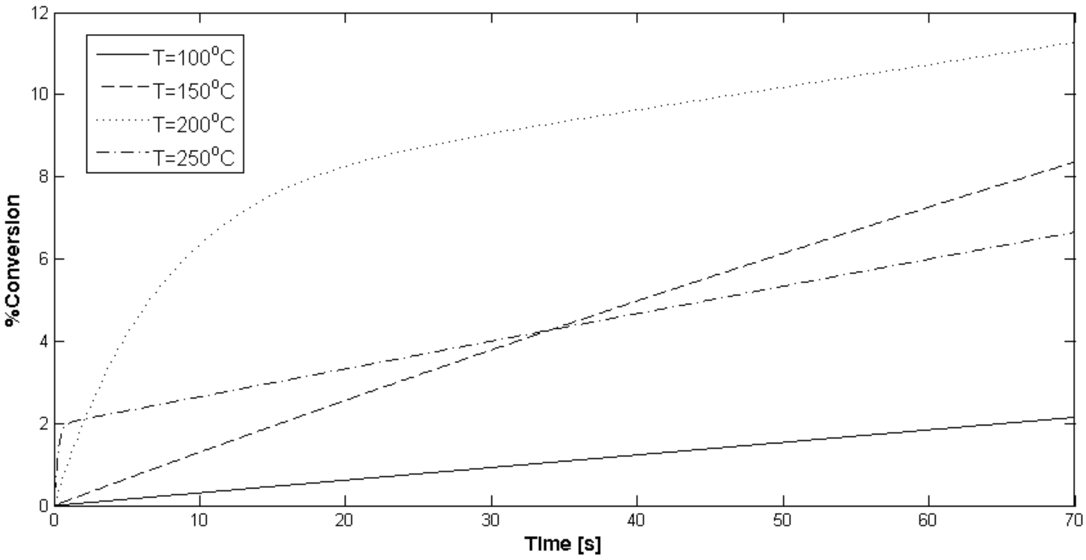

Fig. 1. Predictions of ethylene conversion vs. time for different temperature, for bulk polymerization of ethylene by dioctanoyl peroxide.

We solve this problem by the three closure techniques (Hulburt and Katz, log-normal, and geometric mean average) which are presented in equations (25) and (26).

For a given residence time, ethylene conversion has been plotted in Fig. 1. Fig. 1 shows the change of ethylene conversion with change in time for some temperatures. Conversion profiles rise for increasing temperature up to 150°C.

For higher temperatures, the polymerization rate is very rapid in the beginning of the polymerization and reaches a final conversion value lower than that obtained with 150^{o}C (The type of closure technique did not have any significant effect in the results of Fig. 1).

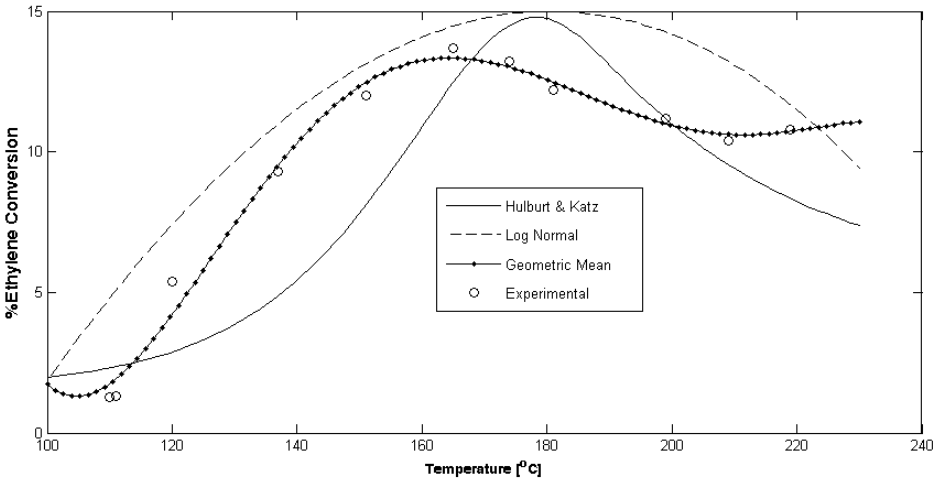

Fig. 2. Predictions of ethylene conversion vs. temperature, for bulk polymerization of ethylene by dioctanoyl peroxide. $[I]_0 = 41\times10^{-6} mol/m^3, \tau = 65s$ (Data from Luft et al. [21]).

In Fig. 2, the results of simulation for polymerization of ethylene by Dioctanoyl peroxide as a mono-functional initiator are shown. As can be seen in Fig. 2 the best results have been obtained by the geometric mean closure technique. The conversion of ethylene in this case, remains very low, for moderate reaction temperature about 105 ^{o}C, after this region, the conversion increases to about 14% at about 160 ^{o}C. Above this temperature the conversion decreases. This behaviour has been observed experimentally by Luft et al. [21], and gets confirmed by this model. Experimental data for polymerization of ethylene by bi-functional initiators at high pressure are very rare. Only work in this area has been done by Luft and Seidl [24] and Luft and Dorn [25]. As can be seen in Fig. 3 the best results have been obtained by the geometric mean closure technique. Fig. 3 shows the results of simulation for polymerization of ethylene by 2,2-bis (tert-butylperoxy)-butane as a bi-functional initiator. As shown in Fig. 3 the maximum conversion of ethylene reaches 15% at about 280^{o}C and then decreases after this region. Fig. 4 shows the results of simulation for polymerization of ethylene by [2,5-dimethylhexane-2-t-butylperoxy-5-perpivalate] as an another initiator. In this case by geometric mean closure technique, the maximum conversion of ethylene reaches about 33% at temperature about 275^{o}C.

$[I]_0 = 41\times10^{-6} mol/m^3, \tau = 65s$

This behaviour is better shown in the Fig. 2 which shows the ethylene conversion vs. temperature for residence time of 65s by three closure techniques.

The presented model predicts results very well for bi-functional initiators, for all range of temperatures, and is in agreement with experimental data. One of the most important results of this model is the ability of prediction of the region of maximum conversion. Obtained results show that the increase only a quarter of bi-initiators, in comparison with mono-functional initiators, is required to yield twice the maximum ethylene conversion. As can be seen in Figs. (2) – (4), the geometric mean averages of Hulburt and Katz and log-normal distribution which had presented by Zabisky et al. [32], Fits the experimental data very well in all range of temperatures. These results are with agreement by the results of Zabisky et al [32].

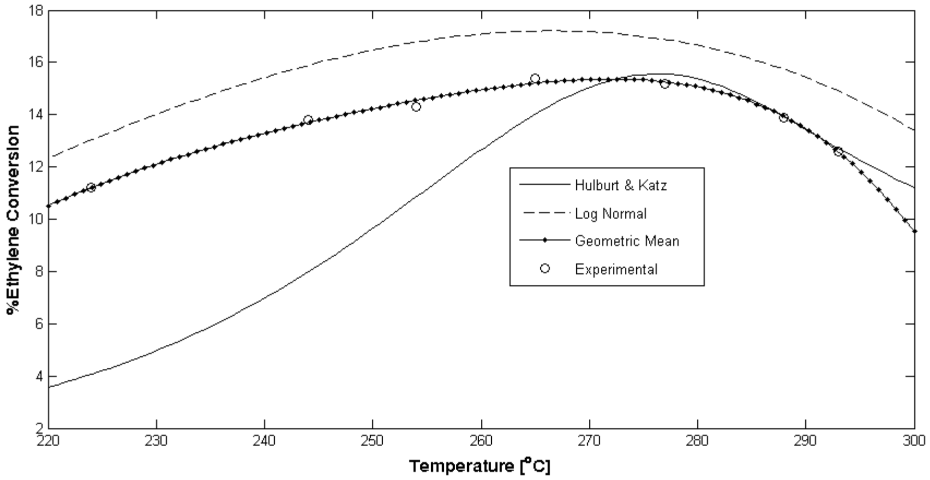

Fig. 3. Predictions of ethylene conversion vs. temperature, for bulk polymerization of ethylene by 2,2-bis (tert-butylperoxy)-butane. $[I]_0 = 10 \times 10^{-6} mol/m^3, \tau = 40s$ (Data from Luft and Seidl [24]).

Fig. 5 shows the average molecular weights of polyethylene produced by 2,2-bis (tert-butylperoxy)-butane and [2,5-dimethylhexane-2-t-butylperoxy-5-perpivalate] as initiators by the geometric mean closure technique. Results fit data very well.

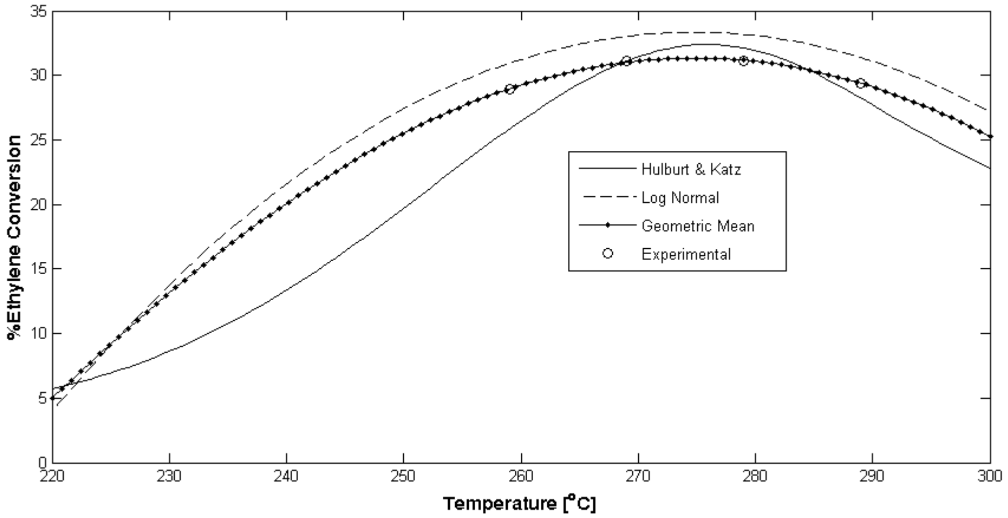

Fig. 4. Predictions of ethylene conversion vs. temperature, for bulk polymerization of ethylene by [2,5-dimethylhexane-2-t-butylperoxy-5-perpivalate]. $[I]_0 = 25 \times 10^{-6} mol/m^3, \tau = 40s$ (Data from Luft and Dorn [25]).

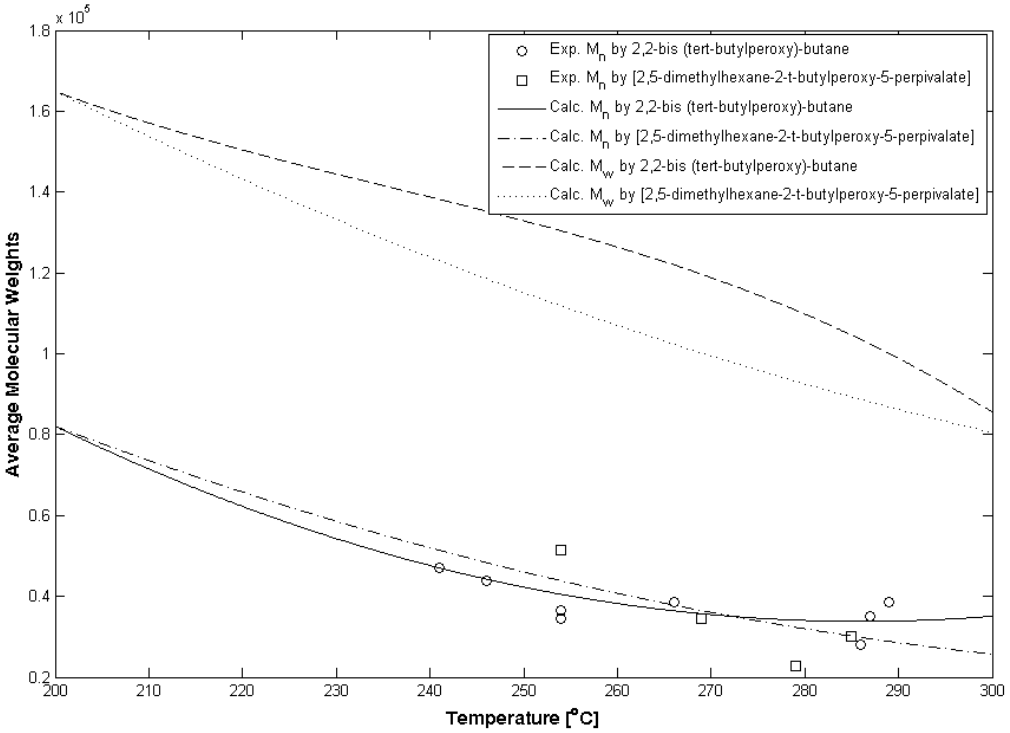

Fig. 5. Comparison between the calculated and experimental average molecular weights of polyethylene produced by 2,2-bis (tert-butylperoxy)-butane and [2,5-dimethylhexane-2-t-butylperoxy-5-perpivalate] $[I]_0 = 25 \times 10^{-6} mol/m^3, \tau = 40s$ (Data from Luft and Seidl [24]).

Conclusions

In the presented work, a dynamic simulation for bulk polymerization of polyethylene at high pressure by bi-functional initiators was done, by a kinetic model. The results of model were compared with available experimental data in the literature, for one mono- and two bi-functional initiators. The obtained results showed that the type of closure technique for calculation of the third moments, have important effect on the precision of the results. In this work the geometric mean average of Hulburt and Katz and log-normal distributions, showed the best results when compared with experimental data.

The model predicted herein can predict the behaviour of high pressure bulk polymerization of ethylene, very well.

Nomenclature

f_1	Efficiency of first part of initiator radical
f_2	Efficiency of second part of initiator radical
$[I]$	Initiator Concentration [mole/l]
$[I]_f$	Initiator Concentration in feed [mole/l]
K_b	Rate constant for backbiting reaction [1/s]

K_β	Rate constant for β-scission reaction
K_d	Decomposition rate constant for mono-functional Initiator [1/s]
K_{d1}	Decomposition rate constant of first part of bi-functional peroxide, [1/s]
K_{d2}	Decomposition rate constant of second part of bi-functional peroxide, [1/s]
K_p	Rate constant for propagation, [l/mol. s]
K_{fp}	Rate constant transfer to polymer, [l/mol. s]
K_{tc}	Rate constant for termination, [l/mol. s]
K_{th}	Rate constant for thermal initiation, [l/mol s]
K_{tfm}	Rate constant for transfer to monomer, [l/mol s]
$[M]$	Monomer concentration, [mol/l]
$[M]_f$	Monomer concentration in feed, [mol/l]
$\overline{M}_w$	Weight average molecular weight of polymer, [gr/mol]
$\overline{M}_n$	Number average molecular weight of polymer, [gr/mol]
P_i	Dead polymer concentration, [mol/l]
P_i'	Dead polymer concentration, with one second part of initiator
P_i''	Dead polymer concentration with two parts of initiators' radicals
F_r	Total flow rate of reactants in reactor, [l/s]
R_{in}	Rate of initiation with first part of initiators' radicals
R_{in}'	Rate of initiation with second part of initiators' radicals
R_i	Radical of chain length i
R_j	Radical of chain length j

R_i'	Macroradical of chain length i with first part of initiator's radical
R_j'	Macroradical of chain length i with second part of initiator's radical
R_p	Rate of polymerization, [mol/l s]
t	Time, [s]
T	Temperature, [K]
V_r	Reactor Volume, [l]
λ_i	Moments of live polymer radicals (i=0, 1, 2)
λ_i'	Moments of live polymer radicals with a part of initiator's radical (i=0, 1, 2)
λ_{to}	Total concentration of radicals, [mol/l]
μ_i	Moment of P (i=0, 1, 2, 3)
μ_i'	Moment of P' (i=0, 1, 2, 3)
μ_i''	Moment of P'' (i=0, 1, 2)
τ	Reactor Residence time, [s]

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