I. Troch, F. Breitenecker, eds. ISBN 978-3-901608-35-3

DYNAMIC MODELING AND SIMULATION OF LOW DENSITY POLYETHYLENE PRODUCTION - A COMPARATIVE STUDY

I. Disli[1], A. Kienle[1,2]
[1]Institut für Automatisierungstechnik, Otto-von-Guericke-Universität Magdeburg,
[2]Max-Planck-Institut für Dynamik komplexer technischer Systeme, Magdeburg

Corresponding author: A. Kienle, Institut für Automatisierungstechnik, Otto-von-Guericke Universität Magdeburg, Universitätsplatz 2, D-39106 Magdeburg, achim.kienle@ovgu.de

Abstract. This study deals with the modelling and simulation of low density polyethylene (LDPE) production. LDPE is one of the most widely produced polymers which appears in the form of simple goods in our everyday life (e.g. food and pharmaceutical packaging, carrier bags). It is produced in a complex industrial process which takes place under extreme operating conditions (at pressure of ca. 2000-3000 bar) and may lead to nonlinear dynamics due to highly exothermic addition polymerization reactions. In principle, the process is represented by a distributed system with an external coordinate (the reactor length > 1000m) and various internal coordinates (the chain length of the polymer molecules, short and long chain branching and the number of double bounds), which can have strong effect on product properties. In this contribution a detailed reference model is introduced and possible model simplifications are discussed systematically from an on-line optimization and control point of view.

1 Introduction

Low density polyethylene (LDPE) is one of the most widely produced polymers which appears in the form of simple goods in our everyday life (e.g. food and pharmaceutical packaging, carrier bags). It is produced in a complex industrial process which takes place under extreme operating conditions (at pressure between 2000-3000 bar). It can show intricate nonlinear dynamic behaviour due to the high exothermicity of the chemical reaction in combination with some internal recycle loops [7, 8], which requires some stabilizing control.

Usually, such a plant receives the raw materials from upstream processes which may cause load changes in the LDPE plant. It is important to maintain the product quality in the face of such load changes. Furthermore, in such a plant, typically more than 15 different grades of product with different product properties (density, melt flow index etc.) may be produced. In order to follow frequently changing market demands it is necessary to follow an optimum grade transition policy during manufacturing different polymer while maintaining a profitable operation. These issues emphasize the significance of control tasks for the LDPE plant and subsequently the significance of suitable process models which can be employed for control purposes. First attempts on optimization based control were based on steady state models only [4]. However more recently it is possible to use dynamic optimization methods within the framework of nonlinear model predictive control (NMPC) based on dynamic models. Although first steps have been made in this direction [9], the size of the mathematical model arising from the distributed nature of the LDPE plant remains a challenging issue.

The objective of this study is to provide a benchmark model of the LDPE plant with a reasonable model size which can be useful for optimal control approaches. Therefore first a detailed reference model developed in our group [2, 1] is reviewed and then possible model simplifications are introduced systematically. The reference model of the LDPE plant is represented by a distributed system with an external coordinate (the reactor length > 1000 m) and various internal coordinates (the chain length of the polymer molecules, short and long chain branching and the number of double bounds), which can have strong effect on product properties. This model describes the heat transfer in detail in addition to including material recycles, both of which are shown to have influence on the plant dynamics. The experience gained on the process via reference model is used to make necessary model simplifications. The simulation with the suggested simple model are carried out to analyse the effects of heat transfer, the types of initiators and modifier on the state profiles and product properties. Results of the simple and reference models are compared and conclusions are drawn.

1.1 Process description

The flow diagram of the process, which is shown in Figure 1, includes a tubular reactor, some peripheral units such as compressors, separators, heat exchangers, mixers, two recycle streams. The tubular reactor of ethylene polymerization (i.e. LDPE production) operates under high pressures between 2000 and 3000 bar. Reactor temperature along the reactor varies between 400 K and 600 K. Such a reactor is usually very long (> 1000 m) and has a small diameter with a large ratio of length to diameter such as 25000. The feed stream to the reactor consists of high purity ethylene as monomer and a suitable modifier (chain transfer agent). Most often a mixture of peroxides is used as initiator and fed at four injection points along the reactor. Feed stream to the reactor is first preheated then

its pressure is raised to the required value through the compressors. The addition polymerization reactions shown in Table 1 are initiated by decomposition of initiators around the injection positions.

Typically ethylene polymerization is highly exothermic such that the heat released during the process is required to be removed partially by cooling jackets . Right after each initiator injection point there exist four cooling jackets. Furthermore, in order to keep the reactor temperature below the allowed maximum value, the conversion in the reactor is kept low by adjusting the initiator flow rates in addition to using the available cooling capacity. The polymer product, LDPE, is withdrawn from the last separator whereas the unreacted ethylene and modifier are recycled from both separators to the inlet of the reactor to be mixed with the fresh feed.

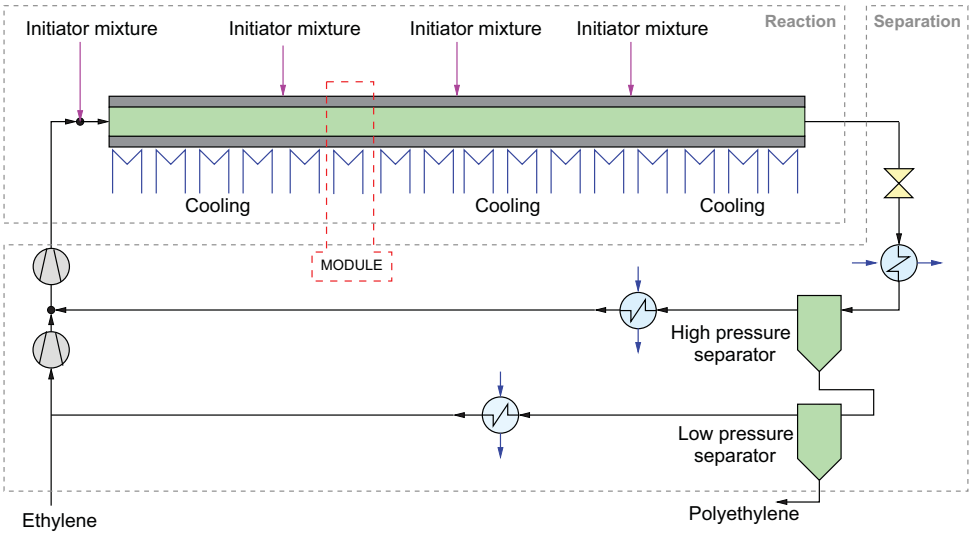

Figure 1: Flow diagram of LDPE plant

2 Reference model

A detailed reference dynamic model of the LDPE production plant has been developed in our group [2, 1]. The process is represented by a distributed system with an external coordinate (the reactor length of 2 km) and various internal coordinates (the chain length of the polymer molecules, short and long chain branching and the number of double bounds), which can have strong effect on product properties.

In the reactor it is assumed that : (i) ethylene-polyethylene mixture is homogeneous; (ii) there exist only liquid phase flowing in plug-flow mode without axial mixing; (iii) physical properties are function of temperature, pressure and composition; (iv) quasi-stationary pressure dynamics is valid; (v) a detailed reaction mechanism is considered. In peripheral units quasi-stationary energy balance and well mixed fluids are assumed. The chemical reactions of free radical addition polymerization are shown in Table 1. The polymer product, LDPE, includes polymer molecules of different chain lengths. It is necessary that the chain length distribution of the product should be described. For this purpose, the method of moments is used by including only the first 3 moment balances of dead and live polymer molecules.

The tubular reactor is represented by 16 modules in series. Each module comprises a part of reactor and a countercurrent coolant cycle around it. The model describes the heat transfer in detail in addition to including material recycles, both of which are shown to have influence on the plant dynamics. Model equations based on momentum, mass and energy balances are summarized for one reactor module as follows:

$$Reactor: \quad \frac{\partial x_i}{\partial t} + \upsilon(z,t)\frac{\partial x_i}{\partial z} = \sum_{j=1}^{J} \nu_{ij} r_j, \qquad 0 < z < L for i = 1,....,NC \tag{1}$$

$$\rho c_p \left(\frac{\partial T}{\partial t} + \upsilon(z,t)\frac{\partial T}{\partial z} \right) = \sum_{j=1}^{J} (\Delta H_r)_j r_j - U_{Wi}(T - T_W) \tag{2}$$

$$\frac{\partial P}{\partial z} = -\frac{1}{2}\zeta \frac{\dot{m}^2}{\rho(z,t).d} \tag{3}$$

$$Wall: \quad \rho_W c_{pW} \left(\frac{\partial T_W}{\partial t} + \beta(z,t)\frac{\partial^2 T_W}{\partial z^2} \right) = U_{Wi}(T - T_W) - U_{Wo}(T_W - T_C) \tag{4}$$

$$Coolant\ cycle: \quad \rho_C c_{pC} \left(\frac{\partial T_C}{\partial t} + \beta(z,t)\frac{\partial^2 T_C}{\partial z^2} \right) = U_{Wo}(T_W - T_C) - U_{ex}(T_C - T_{amb} \tag{5}$$

Main reactions		Side reactions	
Initiation		Chain transfer	
Initiator decomposition	$I_2 \xrightarrow{k_d} 2I^*$	*to Monomer*	$R_n + M \xrightarrow{k_{tr,M}} P_n + R_1$
Chemical initiation	$I^* + M \xrightarrow{k_i} R_1$	*to Polymer*	$R_n + P_m \xrightarrow{k_{tr,P}} P_n + R_{sec,m}$
Thermal initiation	$3M \xrightarrow{k_{th}} 2R_1 + M$	*to Modifier*	$R_n + X \xrightarrow{k_{tr,X}} P_n + R_X$
		Initiation	$R_X + M \xrightarrow{k_{p,X}} R_1$
Propagation	$R_n + M \xrightarrow{k_p} R_{n+1}$	Back biting	$R_n \xrightarrow{k_{bb}} R_n$
Termination		Propagation of secondary radicals	
by Combination	$R_n \xrightarrow{k_{bb}} R_n$		$R_{sec,n} + M \xrightarrow{k_{p,sec}} R_{n+1}$
by Disproportionation	$R_{sec,n} + M \xrightarrow{k_{p,sec}} R_{n+1}$	β-scission	$R_{sec,n} \xrightarrow{k_\beta} P_{n-k} + R_k$

Table 1: Reaction mechanism : I represents the initiator, I^* is the initiator radical, M is the monomer, R is the growing or live polymer radical, P is the dead polymer, n and m denote the degree of polymerization.

Where z is the axial coordinate; L is the total length of a reactor section and t is the time; υ is the axial velocity of the reaction fluid; ν is the stoichiometric coefficient; j is the index for reaction; r is the rate of reaction; ΔH_r is the heat of reaction; $\dot{m}$ is the mass flow through the cross section of the tubular reactor with diameter d ; ρ, C_p, U are density, heat capacity and heat transfer coefficient at different layers. The state vector x_i represents weight fraction of monomer, initiators, modifier, and related radicals, moments of living and dead polymer chains. The state vectors T, T_W, T_C, T_{amb}, represent temperatures of reaction fluid, reactor wall, cooling medium and ambient air respectively.

The balance equations for one reactor module result in a set of 30 partial differential and algebraic equations (PDAE's). The peripheral units are represented by differential algebraic equation systems (DAE). The simulation of the dynamic behaviour of the process is done within the flow-sheet simulation package DIVA [6]. As a priory to that the PDAE system is transformed to a DAE system by using the adaptive method of line with finite difference scheme.After discretization of the spatial coordinate (60 grid points for one module) the final DAE system consists of approximately 30000 dynamic and state variables [1] .

This model was validated successfully by showing very good agreement with steady state data available from industrial partners. The steady state temperature and conversion profiles are shown Figure 2. Häfele et al. [1] further studied the influence of the heat transfer through reactor wall and the influence of material recycles on the plant dynamics. It has been shown that: (i) the heat transfer through thick reactor wall dominates the time constant of the reactor; (ii) by including the material recycles the time constant is significantly increased and in some cases they give rise to intricate nonlinear behaviour.

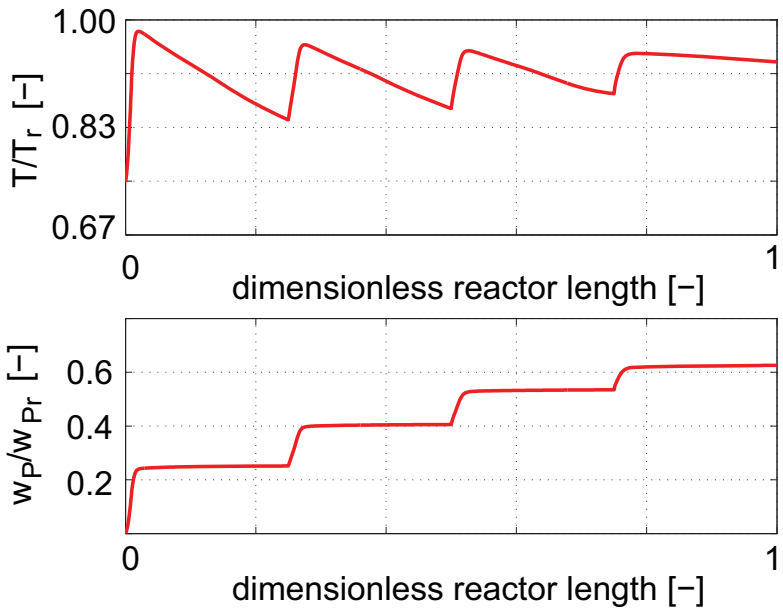

Figure 2: Detailed model - Dimensionless steady state temperature and conversion profiles along the reactor.

In general, the detailed model represents the steady state and dynamic behaviour of the industrial LDPE plant very well. However the size of the model is required to be reduced in order to carry out on-line optimization and control studies within a reasonable computation time. Therefore in the following section a simplified version of the LDPE plant model is proposed.

3 Simple model

The simple model of the LDPE plant is based on the mass and energy balances. Main simplifications are done on the plant flow-diagram, the reaction mechanism and the energy balance in addition to some other model assumptions.

Simplified plant flow-diagram

The simplified flow diagram of the LDPE plant is shown in Figure 3. It comprises a tubular reactor with four modules in series, one flash unit and one recycle stream. The operating conditions are the same as in the case of detailed model.

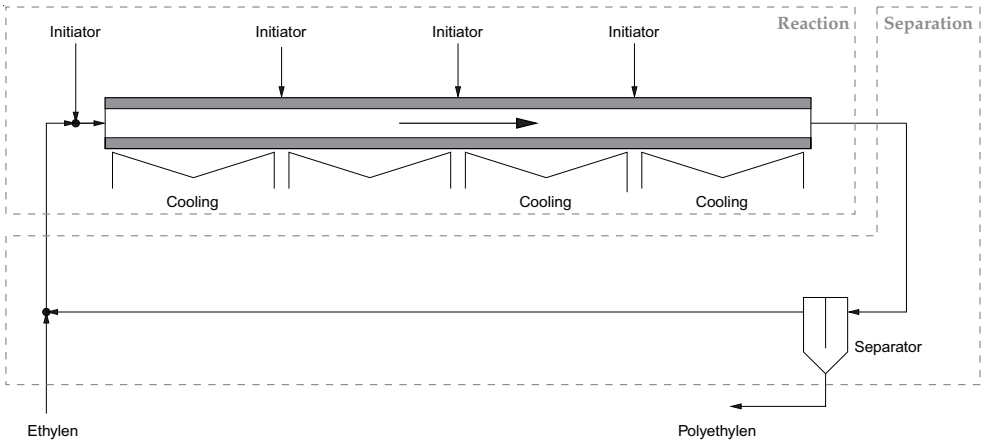

Figure 3: Simplified flow diagram of LDPE plant

Simplified reaction mechanism

The reaction mechanism of the simple model includes the main reactions which are highlighted in grey colour in Table 1 whereas the detailed plant model considers all reactions listed there. Kinetic parameters are given in Table 2 .

Simplified energy balance

It is assumed that (i) the overall heat transfer coefficient U has a constant value in each reactor module ; (ii) the cooling temperature T_c is constant along the whole cooling jacket. These lead to neglecting the energy balance equations on the coolant medium and the reactor wall side.

Additionally, the following assumptions hold: one phase (liquid) flow ; no axial dispersion (plug flow); constant pressure drop; constant physical properties; negligible time delay between peripheral units; constant temperature in the recycle; ideal separation in the flash unit. Mass and energy balances for both flash and mixer units are assumed to be quasi-stationary.

3.1 Model equations

The model equations for one reactor module, which comprises a part of the reactor between two initiator injection points and one counter current coolant cycle around it, are given as follows:

$$\frac{\partial C_i}{\partial t} + \upsilon \frac{\partial C_i}{\partial z} = \sum_{j=1}^{J} \nu_{ij} r_j, \qquad 0 < z < L for i = 1, ..., NC \tag{6}$$

$$\rho c_p \left(\frac{\partial T}{\partial t} + \upsilon \frac{\partial T}{\partial z} \right) = \sum_{j=1}^{J} (\Delta H_r)_j r_j - U(T - T_C) \tag{7}$$

The boundary conditions : $C_i(0,t) = C_{i,in}(t) \qquad T(0,t) = T_{in}(t)$
The initial conditions : $C_i(z,0) = C_{i,0}(z) \qquad T(0,t) = T_{in}(t)$

Initiation	
Init. decomposition	
$I_2 \xrightarrow{k_d} 2I^*$	$k_{dL} = 1.35 \times 10^{13} exp(\frac{-117476-0.2805\times10^{-5}P}{R_gT})^a \quad [m^3/s]$
	$k_{dH} = 2.89 \times 10^{14} exp(\frac{-138237-1.012\times10^{-5}P}{R_gT})^a \quad [m^3/s]$
Chemical initiation	
$I^* + M \xrightarrow{k_1} R_1$	$k_1 = k_p$
Propagation	
$R_n + M \xrightarrow{k_p} R_{n+1}$	$k_p = 5.88 \times 10^4 exp(\frac{-29704+2.325\times10^{-5}P}{R_gT})^b \quad [\frac{m^3}{kmol.s}]$
Termination	
by Combination	
$R_n + R_m \xrightarrow{k_{tc}} P_{n+m}$	$k_{tc} = 1.075 \times 10^6 exp(\frac{-1247+1.422\times10^{-5}P}{R_gT})^b \quad [\frac{m^3}{kmol.s}]$
by Disproportionation	
$R_n + R_m \xrightarrow{k_{td}} P_n + P_m$	$k_{td} = k_{tc}$

Table 2: Kinetic rate constants: ^{a} – Kim and Iedema [3], ^{b} – Lee and Marano [5]

The state vector C_i represents concentrations of monomer, initiators, modifier and related radicals, moments of living and dead polymer chains. The state vector T represents the reactor temperature. The method of moments is used to represent the progress of the reaction in terms of the leading moments of the chain length distribution of the "live" and "dead" polymer chains. These moments are defined by the following equations:

$$\lambda_i = \sum_{k}^{\infty} k^i [R_k] \qquad \text{and} \qquad \mu_i = \sum_{k=2}^{\infty} k^i [P_k] \tag{8}$$

where λ_i and μ_i are the i^{th} moments of the living polymer and the dead polymer chains respectively. 0^{th} moment corresponds to the total concentration of the polymer. 1^{st} and and 2^{nd} moments are used to characterize the molecular weight distribution, e.g. the number average chain length, *NACL*, which is also known as degree of polymerization, DP_n, and the polydispersity, *PD*.

$$NACL = \mu_1/\mu_0 \tag{9}$$

$$PD = (\mu_2\mu_0)/(\mu_1)^2 \tag{10}$$

If one is interested only in the stability control of the plant then the reactor model with 0^{th} moment is satisfactory. On the other hand, the product quality information (e.g. NACL and PD) is crucial for grade transition control problems. It requires to include at least 3 leading moments (0^{th}, 1^{st} and 2^{nd}) in the model equations. Accordingly the size of the model will increase.

The simple model formulation (with 3 leading moments) consists of a set of 14 PDAE per reactor module. After transforming this PDAE system into a DAE system, simulations are carried out within the flow-sheet simulation package DIVA [6]. The results of the simple model are presented in the following section.

3.2 Results

Results obtained from simulations of the simple model are presented for 4 different cases. In Case I, II and III, the effects of the overall heat transfer coefficient and the types of initiators on steady state profiles are shown. In these cases the reaction mechanism includes only the main reactions listed in Table 1. Case IV includes additionally the reaction related to the modifier consumption and aims to show the influence of modifier on product properties. The results obtained in each case are compared to those of the reference model.

Case I

In Case I, it is assumed that : (i) one type of initiator with a constant flow-rate is fed at each injection point; (ii) the heat transfer coefficient U has the same constant value in all four modules. The steady state profiles of temperature and concentration along the reactor are illustrated in Figure 4. The reference model profiles are represented by red solid lines, the state profiles of the simple model-Case I by blue dashed-dotted lines. Results of the Case I are qualitatively in agreement with the detailed model but there exists a large deviation from reference state profiles. This is not unexpected due to many simplifying assumptions made . In the next step these assumptions will be modified by considering the behaviour of the reference model.

Case II

In Case II, the effect of the heat transfer coefficient U on the steady state profiles is shown. The detailed model results indicate that U decreases along the reactor. Consequently, for the simple model, U will be specified at

a different mean value in each reactor module but in a decreasing manner through the end of the reactor. The assumption of using one type of initiator in each module is still valid. The resulting profiles of Case II are illustrated in Figure 4 by pink dashed lines. It can be noted that some improvement is obtained for the temperature profile of the simple model especially through the end of the reactor. However, a considerable large offset still remains between the states of simple and reference models.

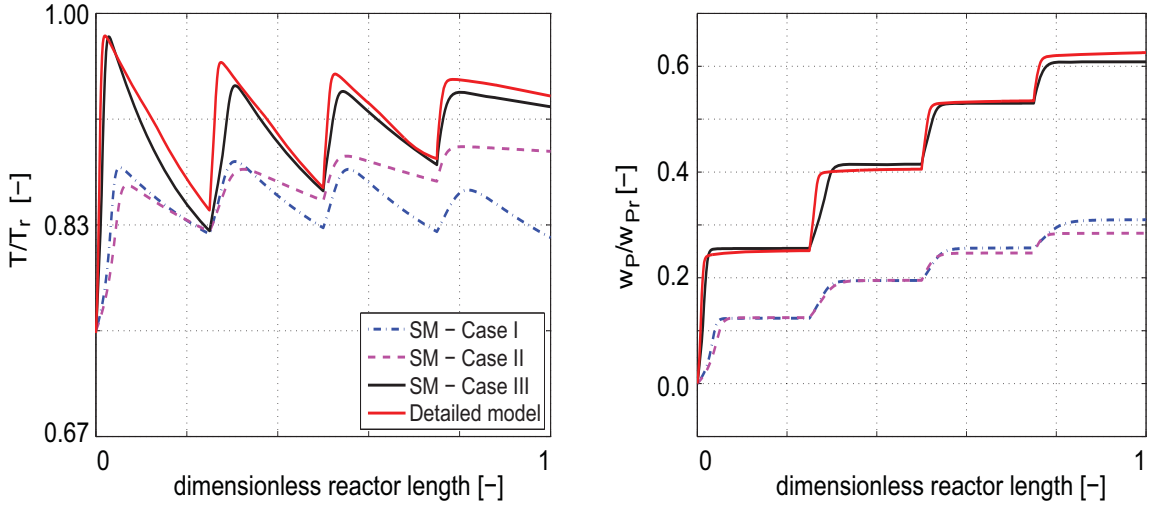

Figure 4: Dimensionless steady state temperature and conversion profiles along the reactor : Red continuous line - Detailed model; Dashed line - Simple model-I; Dashed and dotted line- Simple model-II; Black continuous line - Simple model-III

Case III

In Case III, a mixture of two types of initiators is used at each injection point, which is a more realistic approach. Additionally kinetic parameters of initiator decomposition reaction are taken from the reference model. The condition on the parameter U is the same as in Case II: U is kept constant at a different value in each reactor module. The results of Case III are demonstrated in Figure 4 by black solid lines. It is shown that almost perfect agreement is obtained quantitatively between the state profiles of simple and reference models.

At this point, a question arises about the product quality. Conversion, NACL and PD, are given in Table 3. Although the ethylene conversion approximately agrees for the reference model and the simple model (Case-III), there is a considerable deviation in NACL and PD values. This is due to neglecting all side reactions of the reaction mechanism up to this point. Side reactions have functions to stop a growing polymer chain or to cause branching along a polymer chain etc. In the next step, the most important side reaction will be consider in the reaction mechanism of the simple model.

Case IV

In Case IV, the conditions are the same as in Case III except that the reaction mechanism is extended by including the chain transfer reaction to the modifier which is responsible to regulate the chain length of the polymer molecules. The state profiles obtained in Case IV are the same as in Case III. Moreover, NACL and PD values are improved considerably (see Table 3) . Especially NACL with a realtive value of 0.99 is very close to that of the reference model.

	Conversion	NACL	Polydispersity
Simple model (Case III) (No modifier)	0.876	17.18	2.81
Simple model (Case IV) (With modifier)	0.876	0.99	0.49

Table 3: Product quality values relative to the reference model

As a result of these four case studies, it can be concluded that the simple model with the conditions applied in Case IV represents the LDPE production process reasonably well close to the reference states and product properties. It can be used in principle research for grade transition.

Model sizes

There may be some differences in the model sizes among the cases studied above. This depends on (i) the number of initiators - whether one type or a mixture of few types of initiators is used ; (ii) whether the modifier reaction is included or not. (iii) the number of leading moments included. However, any version of the simple models has a much smaller size then the reference model.

The comparison of the model sizes for reference and simple models are given in Table 4. The order of the ODAE system for the simple model-Case IV is 5600 which is reduced by a factor of 5 comparing to the order of 30000 in the case of reference model. If one is interested in only stability control of the plant, then one should use a simple model with only 0^{th} moments, which will result in a model with an order of 2400.

	Reference model [2, 1]	Simple model (Case IV)	Simple model (with 0^{th} moment)
Number of reactor module	16	4	4
Order of the PDAE system	30/module	14/module	6
Equidistant grid points	60/module	100/module	100/module
Order of the ODAE system	30000	5600	2400

Table 4: Comparison of model sizes

4 Conclusions

In this study a detailed reference model was introduced and possible model simplifications were discussed systematically from an on-line optimization and control point of view. The simulation with the suggested simple model were carried out to analyse the effects of the overall heat transfer coefficient, the types of initiators and modifier on the state profiles and product properties. The simple model was validated by comparing with the reference model. It was shown that the simple model which has a much smaller size than reference model works fine except some small deviations and has potential for stabilizing control studies. Considering that it also provides product properties at least in a qualitative way, the simple model can be used in principle research for grade transition control.

5 References

[1] M. Häfele, A. Kienle, M. Boll, and C.-U. Schmidt. Modeling and analysis of a plant for the production of low-density polyethylene. *Comput. Chem. Engng.*, 31:51–65, 2006.

[2] M. Häfele, A. Kienle, M. Boll, C.-U. Schmidt, and M. Schwibach. Dynamic simulation of a tubular reactor for the production of low-density polyethylene using adaptive method of lines. *J. Computational and Appl. Math.*, 183(2):288–300, 2005.

[3] D.-M. Kim and P. Iedema. Molecular weight distribution in low-density polyethylene polymerization ; impaxsct of scission mechanism in the case of a tubular reactor. *Chem. Eng. Sci.*, 59:2039–2052, 2004.

[4] C. Kiparissides, G. Verros, and J. MacGregor. Mathematical modeling, optimization and quality control of high-pressure ethylene polymerization reactors. *J. of Macromol. Sci.-Rev. Macromol.Chem. Phys.*, C33(4):437–527, 1993.

[5] K. Lee and J. Marano. Free-radical polymerization:sensitivity of conversion and molecular weights to reaction conditions. *ACS Symp.Ser.*, 104:221–251, 1979.

[6] M. Mangold, A. Kienle, K. Mohl, and E. Gilles. Nonlinear computation in diva - methods and applications. *Chem. Eng. Sci.*, 55:441–454, 2000.

[7] S. Pushpavanam and A. Kienle. Nonlinear behavior of an ideal reactor separator network with mass recycle. *Chem. Eng. Sci.*, 56:2837–2849, 2001.

[8] W. Ray and C. Villa. Nonlinear dynamics found in polymerization processes - a review. *Chem. Eng. Sci.*, 55:275–290, 2000.

[9] V. Zavala and C. Villa. Large-scale nonlinear programming strategies for the operation of low-density polyethylene tubular reactors. In *Proc. ESCAPE-18, Lyon, France*, pages 629–634, 2008.