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Integrated Product-Process Design Approach for Polyethylene Production

Yang Yang, Xiong Zou*, Fan Xiao, Hongguang Dong

School of Chemical Engineering, Dalian University of Technology, NO.2 Linggong Road, 116024, Dalian, P.R.China
zouxiong@mail.dlut.edu.cn

Because polymer is a mixture composed of many repeat units, the properties of polymer with same repeat unit vary in different molecular weight distribution (MWD). MWD, in a sense, could be regarded as the formulation of polymer, producing tailored polyethylene (PE) with specified quality targets contains not only process design, but also formulated product design. Product design and process design problems were always solved separately in previous work, which led to a suboptimal solution. In this work, an integrated method for ethylene polymerization in solution with Ziegler-Natta catalyst is proposed to obtain optimal feed conditions and volume of reactor when polymer properties such as glass transition temperature and melt index are specified. In the proposed framework, MWD is found to be the key variable in the interplay between product design and process design. This optimization model is solved through nonlinear programming by maximizing profit which considers product revenue, material and reactor cost, and an illustrative example is presented to demonstrate the validity and advantages of the proposed approach.

1. Introduction

Being faced with environmental, economic, and social sustainability problems, precise synthesis of chemical products still lacks systematic method (Thomé and Scavarda, 2015). As an example, polymer, as one of the most common products in chemistry field, has been widely used in many fields such as medical treatment, mechanical engineering and so on because of its diversity and high-quality performance, and it even replaces metal and glass in some fields. So many attempts have been made to solve the problem about modelling the polymerization process and searching for polymer structure-property relationship to get target polymer with desired properties. The key to solving this problem is to find the relationship among polymer properties, polymer structure and process parameters, which can be easily found in previous work of process and product design. In process modelling, as molecular weight distribution (MWD) of final polymer can be obtained easily by giving operating conditions such as temperature, pressure and catalyst because polymer scientists have always been studying reaction mechanism of polymerization, much work has been done to calculate MWD of polymer and even inverse problem has been done to find the best MWD. Embiruçu et al. (2000) established a detailed model to predict final properties by describing the polymerization mechanism and the mass, energy, and momentum balance equations for reactors, and the results of calculation fit plant data well. This problem can also be solved through optimization techniques, Pontes et al. (2008) developed a method which can efficiently solve the inverse problem to determine optimal feed composition for continuous ethylene polymerization in order to produce tailored polyethylene (PE) resins with specified quality targets. Furthermore, C. Zhang et al. (2016) even considered the optimal reactor network synthesis of polymerization process after giving detailed information of MWD. In polymer design modelling, after Van Krevelen and Te Nijenhuis (2009) classified polymer properties which can be calculated using group contribution method, Satyanarayana et al. (2009) proposed a complete model to find target polymer candidates which meets properties demand by introducing computer aided molecular design. Pavurala and Achenie (2014) also extended into oral drug delivery after analysing the properties needed. Polymer product design models are being increasingly completed by effort of chemical scientists. As research continues, it is obvious that different from normal molecular product, polymer product design contains not only repeat unit design, but also polymer formulation design. This is because even though the repeat unit of polymer is fixed, MWD can also influence its

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properties. Therefore, searching for optimal MWD to match target properties in the same repeat unit of polymer is also one part of polymer product design.
However, process design and product design are always treated separately. It is unavoidable that designing process after product design will usually fall in to a suboptimal strategy. L. Zhang et al. (2016) threw light on design of chemical-based product and emphasized the importance of integration between process and product design. Recently, more and more scientists focus on this topic, attempt has been made but this methodology is not yet industrially applied in polymer design. In polymer product-process integration, although many kinds of MWD can match target properties, optimal MWD should be determined as it is related to feed composition and operation conditions. So MWD is a really important structure parameter to connect the two parts as it is not only the result calculated by process model, but also the input value in property predicting model. In this work, we demonstrate the product-process integrated models and apply into ethylene polymerization. After giving target polymer properties such as glass transition temperature, process parameters such as feed formulation and volume of reactor can be optimized through this methodology. In these models, polymerization mechanism and property prediction models are described, a case study is also presented by considering the cost of material and reactor to show the feasibility of this model and then followed with conclusion.

2. Process description and model

2.1 Polymerization process

The polymerization processes we discuss here consists of several continuous stirred-tank reactors (CSTR). Ethylene slurry polymerization with Ziegler–Natta catalyst system is applied in this work, and the feed composition is made up of monomer (ethylene), hydrogen, solvent (usually hexane), catalyst and co-catalyst. The kinetic mechanism of this process is summarized in Table1 (C Zhang et al., 2016). The catalyst is titanium tetrachloride ($TiCl_4$) with triethyl aluminium ($Al(C_2H_5)_3$) as the co-catalyst.

Table 1: Polymerization kinetic mechanism

Reaction Type	Descriptions	Kinetic Rate Constant
Activation	$C_p(j)+A \rightarrow P_0(j)$	$k_{aA}(j)$
Initiation	$P_0(j)+M \rightarrow P_1(j)$	$k_i(j)$
Propagation	$P_n(j)+M \rightarrow P_{n+1}(j)$	$k_p(j)$
Transfer to monomer	$P_n(j)+M \rightarrow P_1(j)+D_n(j)$	$k_{tM}(j)$
Transfer to hydrogen	$P_n(j)+H_2 \rightarrow P_0(j)+D_n(j)$	$k_{tH}(j)$
Transfer to cocatalyst	$P_n(j)+A \rightarrow P_0(j)+D_n(j)$	$k_{tA}(j)$
Transfer β-hydride	$P_n(j) \rightarrow P_0(j)+D_n(j)$	$k_t(j)$
Deactivation	$P_n(j) \rightarrow C_d(j)+D_n(j)$	$k_d(j)$
	$P_0(j) \rightarrow C_d(j)$	$k_d(j)$

where $C_P(j)$, $P_0(j)$, $C_d(j)$ are the potential active site, active site and deactivated site of catalyst $TiCl_4$ at the jth active site. A is co-catalyst $Al(C_2H_5)_3$, M is monomer, H_2 is hydrogen, $D_n(j)$, $P_n(j)$ are the dead and living polymer chain of length n at the jth active site, j represents the index of active sites, and $k_{aA}(j)$, $k_i(j)$, $k_p(j)$, $k_{tM}(j)$, $k_{tH}(j)$, $k_{tA}(j)$, $k_t(j)$, $k_d(j)$ are the kinetic rate constants of every reaction at the j th active site.
For different temperatures in reactor, the Arrhenius equation Eq(1) is used to determine the kinetic rate

$$k = k_0 \cdot \exp\left[-\frac{E_a}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)\right] \tag{1}$$

where k represents for the kinetic rate constants $k_{aA}(j)$, $k_i(j)$, $k_p(j)$, $k_{tM}(j)$, $k_{tH}(j)$, $k_{tA}(j)$, $k_t(j)$, $k_d(j)$, k_0 is the pre-exponential kinetic rate constant, E_a is the activation energy, R is the universal gas constant, T is the reaction temperature, and T_{ref} is the reference temperature.
According to Table 1, an overall kinetic rate constant K_{TD} is defined for transfer and deactivation

$$K_{TD}(j) = k_{tM}(j)[M] + k_{tH}(j)\left([H_2]\right)^{0.5} + k_{tA}(j)[A] + k_t(j) + k_d(j) \tag{2}$$

where [M], [H_2], [A] is the concentration of the species in the reactor.

For living and dead chain of length n=1, the reaction rate $r_{P_1(j)}$, $r_{D_1(j)}$ can be written as Eq(3) and Eq(4):

$$r_{P_1(j)} = k_i(j)[M][P_0(j)] + k_{tM}(j)[M]Y^0(j) - k_p(j)[M][P_1(j)] - K_{TD}(j)[P_1(j)] \quad (3)$$

$$r_{D_1(j)} = K_{TD}(j)[P_1(j)] - k_{tM}[M][P_1(j)] \quad (4)$$

For n$\geqslant$2, the equations of reaction rate $r_{P_n(j)}$, $r_{D_n(j)}$ can be written as Eq(5) and Eq(6):

$$r_{P_n(j)} = \left(k_p(j)[M]([P_{n-1}(j)] - [P_n(j)])\right) - K_{TD}(j)[P_n(j)] \quad (5)$$

$$r_{D_n(j)} = K_{TD}(j)[P_n(j)] \quad (6)$$

For high molecular weight polymers like HDPE, as the chain length can reach nearly 10^5, extensive calculation will be needed to get MWD information. To avoid this, the method of moments is applied to calculate every size of the chain length distribution with considerably less effort. This method is enough for calculating average molecular weight. The rth moment μ^r of the given distribution function f(n) is showed in Eq(7).

$$\mu^r = \sum_{n=1}^{\infty} n^r f(n) \quad (7)$$

In this situation, the rth moments of living and dead polymer at the jth active site $Y^r(j)$, $X^r(j)$, equations can be written as follows.

$$Y^r(j) = \sum_{n=1}^{\infty} n^r \left[P_n(j)\right] \quad (8)$$

$$X^r(j) = \sum_{n=1}^{\infty} n^r \left[D_n(j)\right] \quad (9)$$

So for the zeroth, first and second moments of the living and dead polymer chains, the reaction rate of them can be presented below.

$$r_{Y^0(j)} = k_i(j)[M]\left[P_0(j)\right] + k_{tM}(j)[M]Y^0(j) - K_{TD}(j)Y^0(j) \quad (10)$$

$$r_{X^0(j)} = K_{TD}(j)Y^0(j) - k_{tM}(j)[M]\left[P_1(j)\right] \quad (11)$$

$$r_{Y^1(j)} = k_i(j)[M]\left[P_0(j)\right] + k_p(j)[M]Y^0(j) + k_{tM}(j)[M]Y^0(j) - K_{TD}(j)Y^1(j) \quad (12)$$

$$r_{X^1(j)} = K_{TD}(j)Y^1(j) - k_{tM}(j)[M]\left[P_1(j)\right] \quad (13)$$

$$r_{Y^2(j)} = k_i(j)[M]\left[P_0(j)\right] + k_{tM}(j)[M]Y^0(j) + k_p(j)[M]\left(2Y^1(j) + Y^0(j)\right) - K_{TD}(j)Y^2(j) \quad (14)$$

$$r_{X^2(j)} = K_{TD}(j)Y^2(j) - k_{tM}(j)[M]\left[P_1(j)\right] \quad (15)$$

Besides, for potential active sites, active and deactivated sites, reaction rate of them can be written as follows

$$r_{C_P(j)} = -k_{aA}(j)[A][C_P(j)] \quad (16)$$

$$r_{P_0(j)} = -k_i(j)[M][P_0(j)] - k_d(j)[P_0(j)] + k_{aA}(j)[A][C_P(j)] + \left(k_{tH}(j)([H_2])^{0.5} + k_{tA}(j)[A] + k_t(j)\right)Y^0(j) \quad (17)$$

$$r_{C_d(j)} = k_d\left([P_0(j)] + Y^0(j)\right) \quad (18)$$

2.2 Mass balance

To simplify the models, mass balances in reactor are developed taking into account the assumption that only one phase exist in the reactor, which means that no gas phase and no phase equilibrium equations are considered in this work. Mass balances for each species are written as follows.

$$\left([M]_{in} * F_{in}\right) - \left([M] * F\right) = \sum_{j=1}^{Ns}\left(k_i(j)\left[P_0(j)\right] + \left(k_p(j) + k_{tM}(j)\right)Y^0(j)\right)[M] * V \tag{19}$$

$$\left([H_2]_{in} * F_{in}\right) - \left([H_2] * F\right) = \sum_{j=1}^{Ns} k_{tH}(j)[H_2]^{0.5} Y^0(j) * V \tag{20}$$

$$\left([C_6H_{14}]_{in} * F_{in}\right) - \left([C_6H_{14}] * F\right) = 0 \tag{21}$$

$$[A]_{in} * F_{in} - [A] * F = \sum_{j=1}^{Ns}\left(k_{aA}(j)\left[C_P(j)\right] + k_{tA}(j)Y^0(j)\right)[A] * V \tag{22}$$

$$\left[C_P(j)\right]_{in} * F_{in} - \left[C_P(j)\right] * F = -r_{C_P(j)} * V \tag{23}$$

$$\left[C_d(j)\right]_{in} * F_{in} - \left[C_d(j)\right] * F = -r_{C_d(j)} * V \tag{24}$$

$$\left[P_0(j)\right]_{in} * F_{in} - \left[P_0(j)\right] * F = -r_{P_0(j)} * V \tag{25}$$

$$Y^r_{in}(j) * F_{in} - Y^r(j) * F = -r_{Y^r(j)} * V \quad r = 0,1,2 \tag{26}$$

$$X^r_{in}(j) * F_{in} - X^r(j) * F = -r_{X^r(j)} * V \quad r = 0,1,2 \tag{27}$$

where Ns represents the number of active sites in catalyst, in this work the parameter is set to 5. F_{in} and F are the feed and product flow rate of reactor, respectively. V is the volume of reactor.

Average molecular weights have an enormous influence on the final polymer quality, and they are also the important parameters to predict polymer properties. Polydispersity, PDI, is usually used to represent the width of MWD. The numerical and weight average molecular weights, M_n and M_w, and PDI can be calculated with Eq(28), Eq(29) and Eq(30), mw is the molar mass of ethylene, 28.4 g/mol.

$$Mn = \frac{\sum_{j=1}^{Ns}\left(Y^1(j) + X^1(j)\right)}{\sum_{j=1}^{Ns}\left(Y^0(j) + X^0(j)\right)} * mw \tag{28}$$

$$Mw = \frac{\sum_{j=1}^{Ns}\left(Y^2(j) + X^2(j)\right)}{\sum_{j=1}^{Ns}\left(Y^1(j) + X^1(j)\right)} * mw \tag{29}$$

$$PDI = \frac{Mw}{Mn} \tag{30}$$

And the mass flow rate of PE can be calculated in Eq(31) using $Y^1(j)$ and $X^1(j)$:

$$W_{PE} = mw * F * \left(\sum_{j=1}^{Ns} Y^1(j) + X^1(j)\right) \tag{31}$$

3. Property prediction model

The quality of the polymer product mainly depends on its property. Glass transition temperature (T_g), which is defined as the boundary between glassy state and rubbery state, has always been an important factor to measure the quality of polymer product. The most widely utilized empirical expression of T_g is shown below (Van Krevelen and Te Nijenhuis, 2009):

$$T_g = T_g(\infty) - \frac{K_g}{M_n} \tag{32}$$

In Eq(32), $T_g(\infty)$ is the limiting value of T_g when M_n reaches its infinity. K_g is an additional empirical parameter which is also usually obtained by fitting equation to experimental data for a given polymer. For polyethylene, the value of $T_g(\infty)$ is 176 K, and K_g's value is 15,000 K g/mol.
The melt index (MI), another important property, is defined as the amount of polymer weight extruded during a 10-min test at specified conditions, thus it is inversely related to the weight average molecular weight. Here we use an empirical model (Embiruçu et al., 2000) to represent the melt index, which is given by

$$MI = \alpha_1 \cdot (M_w)^{-\beta_1} \tag{33}$$

where α_1 and β_1 are empirical constants. For PE resin, the values are 4.195×10^{19} and -3.9252, respectively.

4. Optimization problem

The objective function is then given by

$$\Phi = \left[a \cdot W_{PE} - \left(b_M W_M + b_{H_2} W_{H_2} + b_C W_C + b_A W_A \right) \right] \cdot t - cV \tag{34}$$

Eq(34) defines the objective function to maximize profit Φ, where a, b_M, b_{H2}, b_C, b_A, is the price of PE, monomer, hydrogen, catalyst, co-catalyst, respectively, W_{PE}, W_M, W_{H2}, W_C, W_A is the mass flow rate of each species, t represents for production time, c is a constant related to the price of reactor. So the purpose of this function is not only to determine suitable feed policies, but also to introduce important process parameters, volume, which costs a lot in polymer production.

5. Case study

In this study, three examples are presented to demonstrate the result of integrated product-process optimization, where one CSTR is used to produce PE, and the method considers not only the proportion of feed, but also the cost of reactor volume. It is noted that as phase equilibrium equations are not introduced because of simplification, feed flow rate of solvent will not be shown in the result. The temperature in reactor is set to 358.15K
This optimization study aims to produce polyethylene with the following polymer properties:
$0.139 < MI < 0.157$,
$175\ K < T_g < 175.5\ K$.
And qualitatively coherent values are employed for PE sales prices, raw material cost (Pontes et al., 2008), and reactor volume cost. These constants can be found in Table 2.
Results are demonstrated in Table 3. Example 1 shows the result where feed fraction is fixed using data from Meng et al. (2013), the objective of this one is to find the minimum reactor volume. Volume of reactor is fixed in example 2 to find the optimal proportion of feed which makes the whole profit maximize, and this is also the way used in Pontes et al. (2008). However, in example 3, neither feed nor volume is fixed, which aims to find the optimal feed fraction and volume of reactor to maximize the final profit.
As we can see in Table 3, increasing volume of the reactor will yield more PE product when the quality of product is fixed. So there must be a trade-off between the cost of raw material and reactor volume. The result of optimization with feed fraction and volume performs better than that of only feed fraction or only reactor volume.

Table 2: PE sales price, raw material cost and reactor volume cost

Parameters	Unit	Value
a	\$/kg	0.9549
b_M	\$/kg	0.58
b_{H2}	\$/kg	318.3
b_C	\$/kg	742.7
b_A	\$/kg	212.2
t	h	8000
c	\$/L	220

Table 3: Result data in feed-fixed example (example 1), volume-fixed example (example 2) and optimization example (example 3)

Variables	Unit	Example 1	Example 2	Example 3
Monomer feed	kmol/h	1075.2192	1079.5644	1079.6112
Hydrogen feed	kmol/h	4.014	0.2952	0.2736
Catalyst feed	kmol/h	0.0016	0.06264	0.0537
Co-catalyst feed	kmol/h	0.4824	0.0756	0.0612
Reactor volume	L	5595.214	60000	18392.793
M_n	g/mol	30000	30000	30000
M_w	g/mol	160000	160000	160000
T_g	K	175.5	175.5	175.5
MI	g/10 min	0.1569	0.1569	0.1569
PDI	-	5.333	5.333	5.333
PE output	kg/hr	1775.9592	7401.1716	4436.9856
Profit per year	American dollar	2553020	1650330	4685200

6. Conclusion

Integrated process-product design models for PE slurry polymerization with Ziegler–Natta catalyst system are presented. In this optimization technique, after giving target polymer properties, operation conditions are determined considering the whole cost, which is much more effective than traditional experimental test. In the process part, polymerization mechanism is introduced to calculate MWD, mass balances are proposed where feed flow rate can be calculated. As for product part, structure-property relationships are applied as property constraints, where MWD can be obtained by given target polymer properties. Compared with the previous optimization models containing a set of continuous/discrete differential-algebraic equations (Pontes et al., 2008), the new models consist of nonlinear programming equations, which can be solved more efficiently. The following case study demonstrates the advantages in product-process integration considering not only feed formulation, but also the important process parameter, reactor volume. These models will help develop new PE resin in an optimal and effective way, compared to the traditional step by step method, and this methodology can be applied into other polymer production process once knowing the polymerization mechanism, which means a versatile tool.

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