Computer Model for Tubular High-Pressure Polyethylene Reactors

A computer model was developed for tubular high-pressure polyethylene reactors. Plug flow and absence of axial mixing were assumed. Emphasis was placed on realistic modeling of the reaction kinetics and the variation of physical properties along the reaction coordinate. A good simulation of axial temperature profiles, conversion, molecular weights, molecular weight distribution, and transport properties along the reaction coordinate is believed to have been achieved. The model can be extended readily to cases where radial diffusion is significant.

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SCOPE

A computer model was developed for tubular high-pressure polyethylene reactors. Simplifications (plug flow, absence of axial mixing) were made which are shown to be justifiable in high throughput reactors. However, the steady state free radical approximation was not made, and variations in the density and viscosity of the fluid along the reaction coordinate were taken into account explicitly. Emphasis was placed on realistic kinetics including long chain branching, use of the best rate constants available, and realistic simulation of all physical properties along the reaction coordinate. Temperature profiles, monomer and initiator conversion, the number average molecular weight ($\overline{M}_n$), and the molecular weight distribution (MWD) were calculated for a typical set of operating conditions as they might exist in a simple, high throughput reactor. The response of the model to changes in operating variables and kinetic constants was then examined. The model can be extended readily to simulate reactors with multiple initiator or monomer injection and to reactors in which laminar conditions prevail in the high conversion zone.

CONCLUSIONS AND SIGNIFICANCE

This model permits a calculation, for any point along the reaction coordinate, of transport properties, the first several moments of the radical and polymer size distributions, and of long chain branching. Considerable insight is therefore gained into the kinetics of this most important vinyl polymerization, as carried out under commercial conditions, and into the physical properties of the product. The reaction is found to be rapid, and the concentration of the active intermediates (radicals) is larger by about two orders of magnitude than that encountered in the much more familiar isothermal case, where the steady state approximation for the free radicals is normally made.

Because the reaction is exothermic and the rate of initiation has a large positive temperature coefficient, the polymerization reaction accelerates rapidly after a certain rate of initiation has been achieved. The temperature profile is therefore S-shaped between the reactor inlet and the point at which the maximum temperature is reached, with the appearance of a point of inflection at which the reaction may be said to take off. Beyond that point, little heat is exchanged with the environment, and only limited control can be exerted over the course of the reaction. To a first approximation, therefore, conversion and polymer properties are determined by the size and location of the temperature interval available for polymerization. Changes in conversion which can, nonetheless, be brought about by changes in reactor design and operating variables, such as jacket temperature, wall heat transfer coefficient, or reactor diameter, are shown to be of a magnitude which is commercially significant.

Under design and operating conditions applicable to a high throughput reactor, with a single initiator used, and in the absence of downstream injection of initiator or monomer (monomer conversion of about 10%), the model predicts Reynolds numbers of greater than 200 000 throughout the reaction zone, in justification of the plug flow assumption. It is not necessary to assume polymer deposits on the walls or new types of side reactions, not observed at radical concentrations typical for the isothermal case, to account for the behavior of the reactor and the wide MWD of the product.

Nearly all low-density polyethylene (LDPE) is made in stirred autoclaves or in tubular reactors at high pressures. This paper discusses a computer model for tubular polyethylene reactors and some of the results obtained with it. The main objective was to develop a model which would permit a realistic calculation of conversion of ethylene to polymer and of the first three moments of the molecular weight distribution (MWD) under typical operating conditions.

Earlier modeling of the same process has been discussed by Mullikin et al. (1965), Schoenemann and Thies (1970, 1972), Marano (1974), and Agrawal and Han (1975), who used various physical assumptions and mathematical techniques.

The model of Mullikin et al. is an analog computer model, designed primarily to simulate conversion and properties related to short chain branching, such as poly-

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mer density. The publication of Schoenemann and Thiess neither formulates the basic equations to be solved in detail nor lists the design, physical, or kinetic parameters used in the calculations. An explicit comparison of their model and ours is therefore not possible. Marano's model appears to be similar to ours in many respects; again, a detailed comparison is not possible because of only partial specification of mathematical techniques and parameters. Nonetheless, it is clear that many of the major physical assumptions made and results reported by these authors are similar to those to be reported here.

The model of Agrawal and Han, on the other hand, is the only one discussed in sufficient detail to permit an explicit comparison with our model. One of the major differences between the two models arises from the fact that Agrawal and Han study explicitly the effect of axial mixing on reactor performance. We believe the effect of axial mixing to be unimportant or, at any rate, to merit neglect, in a first model designed to portray major process and product characteristics. The reasons for this are as follows. The operating pressures of polyethylene plants tend to be well above the upper critical solution pressure of the system polyethylene-ethylene, as measured under nonflow conditions (Ehrlich, 1965); although this is not necessarily the case under conditions of high shear (Ver Strate and Philippoff, 1974), and, since complications in the long chain branching mechanism not taken into consideration in our model may indeed lead to polymer deposits on the reactor walls under some conditions (Kinkel, 1972), it seems appropriate to view the reaction as taking place in a single supercritical phase (Ehrlich and Mortimer, 1970). Pulsing of reactors should therefore not be necessary to avoid the inevitable consequences presumed to arise from the buildup of a viscous, polymer rich phase; indeed, tubular polyethylene reactors can be operated continuously without pulsing. In any case, the introduction of pressure pulses is unlikely to generate Peclet numbers low enough to lead to substantial axial mixing over a significant section of the reaction zone. The Peclet number shown by Agrawal and Han to be necessary for such effects to be significant is about 100; the Peclet number calculation for the present model, with a diffusion constant of 10^{-7} cm^2/s used in the place of the dispersion index D, yields 10^{14}. It is unlikely that even a more realistic value of D can bring the Peclet number into the proper range.

The other major difference results from the fact that Agrawal and Han address themselves primarily to the case of substantial heat transfer from the reactor to the environment throughout the reaction zone. To the best of our knowledge, most tubular polyethylene reactors are operated under conditions such that the polymerization is very rapid and nearly adiabatic throughout most of the reaction zone. There also appear to be major differences in the methods of calculating the molecular weight distribution in the two models.

Since our model, therefore, differs in important respects from the only other digital computer model available in the open literature in sufficient detail for use by others, an explicit description of the model, together with a specification of parameters and results, seems appropriate.

THE REACTION MECHANISM

It is well known that many of the physical properties of polyethylene are determined by the number of short-chain branches and, possibly, also by their structure and distribution (Raff and Doak, 1965). Results with a Monte Carlo model used to simulate short chain branching in LDPE have been reported earlier. (Wu et al., 1972). Other properties of LDPE are influenced by the MWD which depends largely on the degree of long chain branching (chain transfer to polymer), a mechanism which can be formulated independently of that for short chain branching. The latter is therefore not included in our model. In order to avoid further complications, we also neglect mutual chain termination by disproportionation and chain transfer to modifier. The contribution of both of these reactions is, at present, difficult to assess, and their inclusion would serve no special purpose. The reaction mechanism is as follows (Ehrlich and Mortimer, 1970):

Initiation

$$I \xrightarrow{\alpha} 2R_1(0) \tag{1}$$

Propagation

$$R_i(x) + M \xrightarrow{\beta} R_i(x+1) \tag{2}$$

Termination
by combination

$$R_i(x) + R_j(y) \xrightarrow{\gamma} P_{i+j-1}(x+y) \tag{3}$$

by therml degradation

$$R_i(x) \xrightarrow{\epsilon} P_i(x) + R_1(0) \tag{4}$$

(β-scission)
Chain transfer to polymer

$$R_i(x) + P_j(y) \xrightarrow{y\xi} P_i(x) + R_{j-1}(y) \tag{5}$$

DEVELOPMENT OF THE EQUATIONS

Molar balances on all components in the system can be readily written from the stoichiometric Equations (1) to (5). These equations are similar to those developed by Saidel and Katz (1968) but include the additional effect of variable density and hence a variable velocity in the reactor.

The overall mass balance is

$$\frac{d}{dz}(\rho v) = 0 \tag{6}$$

$$\frac{dv}{dz} = -\frac{v}{\rho}\frac{d\rho}{dz} \tag{7}$$

where $d\rho/dz$ can be evaluated in terms of dT/dz and dm/dz from the physical property equations.

Molar balances then yield

on initiator

$$\frac{d(iv)}{dz} = -\alpha i \tag{8}$$

on monomer

$$\frac{d(mv)}{dz} = -\beta m \lambda_{00} \tag{9}$$

From this point on, the development closely parallels that of Saidel and Katz (1968), who adapted their earlier work (Katz and Saidel, 1967) to include the effect of long chain branching. Molar balances were also made on each radical and polymer species present; then the double moments

$$\lambda_{mn} = \sum_i i^m \int x^n r_i(x)\, dx \tag{10}$$

$$\mu_{mn} = \sum i^m \int x^n p_i(x)\, dx \tag{11}$$

TABLE 1. MODEL EQUATIONS

$$\frac{di}{dz} = -\left(2\alpha i + \frac{dv}{dz}\right) \Big/ v$$

$$\frac{dm}{dz} = -\left(\beta m\,\lambda_{00} + m\frac{dv}{dz}\right) \Big/ v$$

$$\frac{d\lambda_{mn}}{dz} = \Big\{ n\beta m\lambda_{m,n-1} + 2\alpha i\,\delta_{no} - \gamma\lambda_{00}\lambda_{mn} - \epsilon\lambda_{mn} + \epsilon\lambda_{00}\delta_{mo}$$

$$+ \xi\{\lambda_{00} \sum_{j=0}^{m} \binom{m}{j} \mu_{j,n+1} - \mu_{01}\lambda_{mn}\} - \lambda_{mn}\frac{dv}{dz}\Big\} \Big/ \quad v$$

$$\frac{d\mu_{mn}}{dz} = \Big\{ \gamma/2 \sum_{j=0}^{m}\sum_{k=0}^{j}\sum_{i=0}^{n} \quad (-1)^{m-j}\binom{m}{j}\binom{i}{k}\binom{n}{i}$$

$$\lambda_{ki}\lambda_{j-k,n-1} + \epsilon\lambda_{mn} + \xi\,(\lambda_{mn}\mu_{01}$$

$$- \lambda_{00}\mu_{m,n+1}) - \mu_{mn}\frac{dv}{dz}\Big\} \Big/ \quad v$$

$$\frac{dT}{dz} = \frac{10^{-3}}{\rho v C_p}\{(-\Delta H)\,\beta m\lambda_{00} + \frac{4}{D}U\,(T_w - T)\}$$

where the equations also satisfy the macroscopic molar balances on initiator and monomer

$$v_o i_o = (\lambda_{00}/2 + \mu_{00} + i)v$$

$$v_o m_o = (\lambda_{01} + \mu_{01} + m)v$$

and the initial conditions

$$v = v_o \quad i = i_o \quad m = m_o \quad \lambda_{mn} = 0 \quad \mu_{mn} = 0 \quad \text{at } z = 0$$

The number average and weight average degrees of polymerization $\overline{X}_n$ and $\overline{X}_w$ and the mean number of branches $\overline{X}_b$ are obtained in the usual manner:

$$\overline{X}_n = (\lambda_{01} + \mu_{01})/(\lambda_{00} + \mu_{00})$$

$$\overline{X}_w = (\lambda_{02} + \mu_{02})/(\lambda_{01} + \mu_{01})$$

$$\overline{X}_b = (\lambda_{10} + \mu_{10})/(\lambda_{00} + \mu_{00})$$

were defined. The differential equations for the radical and polymer species were each multiplied by $i^m\ x^n$ and summed over all numbers of branch points and integrated over all chain lengths to derive differential equations for the moments, the R.H.S. of which were identical to those derived by Saidel and Katz, except for the addition of terms of the type $-(\mu_{mn}/v)\ (dv/dz)$ for the variable density. The moment equations as initially written depend on higher order moments owing to the dependence of the long chain branching reaction on the length of the polymer chain being activated. This requires a moment closure method in order to solve the set of equations sequentially. The closure method used was that of Hulburt and Katz (1964) without modification. This method assumes that the chain length distribution can be represented as a truncated series of Laguerre polynomials by using a gamma distribution weighting function chosen so that the coefficients of the second and third terms are zero. In this work it was assumed that use of three terms was sufficient, since Saidel and Katz had found only a small difference between solutions of three terms and those of four terms (Saidel and Katz, 1968). The authors are aware that Bamford and Tompa (1954) claimed that up to ten terms are necessary (but they used an exponential weighting function which was less appropriate) and that, as Jackson, Small, and Whitely (1973) pointed out, there is no proof that the series is uniformly convergent and thus may not necessarily be terminated when two successive approximations are considered close enough. The set of equations to be solved is given in Table 1.

SOLUTION

The set of equations to be solved is very stiff, first during the development of the radical concentrations which occurs relatively rapidly and second when the reactor becomes almost adiabatic after the temperature exceeds a takeoff point of about 180°C. Accordingly, an adaptation of an Adams-Moulton predictor corrector method developed by Gear (1971) for stiff equations was used for integration. This method automatically adjusts step size and order of the integrating algorithm to optimize computer time. Computations were performed on a CDC 6400 by using 80 s of CP time per simulation.

A set of reference initial conditions was chosen which was thought to be typical for a process with a single initiator, with monomer and initiator addition at the reactor inlet only.

Several of the reference conditions were then varied, a single variable being altered for each run, while all others were set at the reference condition. In this way the effect of changing initial and operating conditions was determined. As the rate of long chain branching had not been determined experimentally, it was also assumed to be a variable, so that the effect of this particular mechanism could be evaluated.

RATE CONSTANTS AND PHYSICAL PROPERTIES

The reaction rate constants and their temperature dependencies are listed in Table 2, and the physical properties of the mixture are defined by the equations in Table 3. For a discussion of the reaction mechanism and the magnitudes of the rate constants chosen, the reader may consult a recent review (Ehrlich and Mortimer, 1970).

TABLE 2. REACTION RATE CONSTANTS

The reaction rate parameters are listed so as to conform to equations of the type $\Phi = \Phi_o \exp(-E_\Phi/RT)$ and are expressed in units of l mole, s, and in cal/mole.

	α	β	γ	ϵ	ξ
Φ_o	1.6×10^{16}	2.95×10^{7}	1.60×10^{9}	2.72×10^{11}	9.0×10^{5}
E_Φ	38 400	7 091	2 400	20 000	9 000

Comments: The value of α is that recommended for di-t-butyl peroxide which is the initiator chosen for this problem.

The parameter $\beta\gamma^{-1/2}$ has been obtained from experiment at 130°C and chosen to correspond to a uniform reaction pressure of 2 000 atm (Ehrlich and Mortimer, 1970). The rate constants ϵ and ξ, which have an important, if not dominant, effect on $\overline{X}_n$ and $\overline{X}_w$, respectively, are less well known than $\beta\gamma^{-1/2}$ and are treated as adjustable parameters and assigned values so as to generate polyethylene with a molecular weight and MWD typical of LDPE. The estimates of all activation energies, except E_ϵ, may be considered to be fairly reliable.

All values of E_Φ correspond to activation energies which are taken to be pressure independent, except E_β, which includes a pressure correction The value of E_β at 1 atm. is 8,200 cal/mole

TABLE 3. PHYSICAL CONSTANTS

$\Delta H = -21\,400$

$\rho_m = 0.00125\ [0.358(473\text{-}T) + 398.9] = 0.710 - 4.475 \times 10^{-4}T^*$

(Michels and Geldermans, 1942)

$V_p = 1.16\ [1 + 4.3 \times 10^{-4}(T - 423)] = 0.949 \times 4.988 \times 10^{-4}T^*$

(Parks and Richards, 1949)

$\eta_o = 1.98 \times 10^{-4} + 1.15 \times 10^2/T^{2*}$

(Carr et al., 1955)

$\log_{10}\eta_r = 0.0313\mu_{01}{}^{3/2}/\mu_{oo}{}^{1/2\dagger}$

$\eta_s = \eta_r\eta_o$

$\rho_s = \{1 + (V_p - V_m)\ M_o + 0.028\}/V_p$

$w_m = 0.028\ M_o/\rho_s$

$C_p = 0.518\ w_m + (1.041 + 8.3 \times 10^{-4}T)w_p$

(Michels et al., 1946; Hellwege et al., 1962)

$K = 5.0 \times 10^{-4}\ w_m + 3.5 \times 10^{-4}\ w_p$

(Eiermann et al., 1965)

$U^{-1} = h_i{}^{-1} + h_w{}^{-1}$

$h_i = \dfrac{KNu}{D}$

$Nu = 0.026\ Re^{0.8}\ Pr^{0.33}$

(turbulent region)

$Nu = 0.116\ (Re^{2/3} - 125)\ Pr^{0.33}\ [1.0 + (D/L)^{2/3}]$

(transition region)

(for higher conversion reactors)

(switch from turbulent to transition at $Re = 10\,000$)

* Assuming a reactor pressure of 2 000 atm.

† This relation is obtained from the equations $\log \eta_r = bc[\eta]$ and $[\eta] = k\,\overline{X}_n{}^{0.5}$, where b and k are constants, $[\eta]$ is the intrinsic viscosity of the polymer in $(g/100\ cm^3)^{-1}$, and c the polymer concentration in g/100 cm³. Both equations represent crude approximations of experimental data (Ehrlich and Woodbrey, 1969; Trementozzi, 1957), adequate for the purpose, and allow one to take into consideration the effect of the molecular weight of the polymer on the transport properties.

RESULTS

We have chosen as our reference reactor one having a 5 cm diameter and an ethylene throughput of about 50 000 Kg/hr. The reactor pressure was assumed to be 2 000 atm, and the pressure drop across the reactor was neglected. The other reference conditions are listed in Table 4, together with the dependent variables: monomer conversion (c_M), number average degree of polymerization (X_n), MWD ($\overline{X}_w/\overline{X}_n$), number average of branches (X_b), and peak temperature ($T_{\max}$).

Table 5 lists results brought about by a change from the reference condition of the single independent variable listed in the first column of the table. Figures 1 to 9 show plots of some of the dependent variables as a function of axial distance along the reactor or as a function of conversion.

TABLE 4. REFERENCE CONDITIONS

Independent variables

$T = 100°\text{C}$

$[m_o] = 19.41\ \text{moles}/l$

$[I]_o = 2.0 \times 10^{-4}\ \text{moles}/l$

$V_o = 1\,500\ \text{cm/s}$

$D = 5.08\ \text{cm}$

$T_j = 180°\text{C}$

$\xi_o = 9.00 \times 10^5\ l\ \text{mole}^{-1}\ \text{s}^{-1}$

$E_\xi = 9\,000\ \text{cal/mole}$

$h_o = 0.025\ \text{cal cm}^{-2}\ \text{s}^{-1}\ °\text{C}^{-1}$

Dependent variables

C_M (% monomer converted)	$\overline{X}_n$	$\overline{X}_w$	$\overline{X}_w/\overline{X}_n$	$\overline{X}_b$	$T_{\max}$ (°C)
9.98	582	5 174	8.89	1.151	294.4

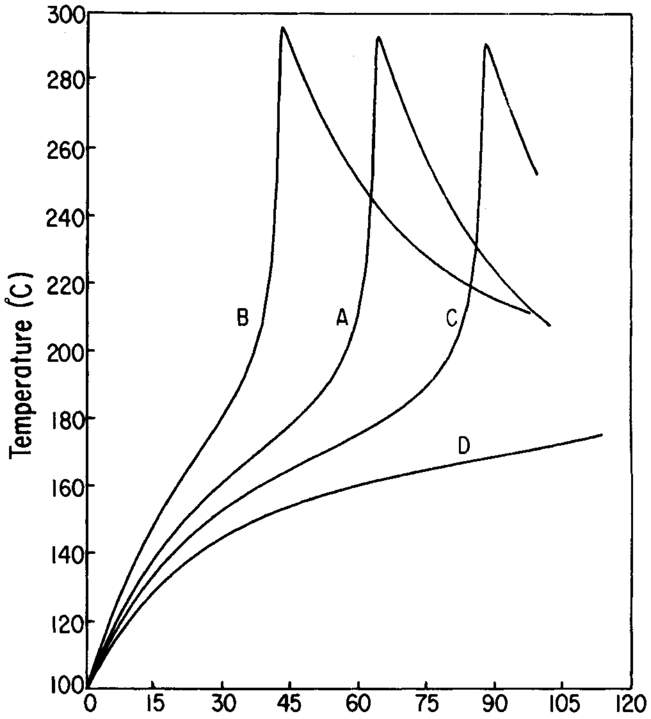

Fig. 1. Dependence of reactor temperature on axial position for the following values of the jacket temperature:

A: $T_j = 180°C$ (reference condition)
B: $T_j = 200°C$
C: $T_j = 170°C$
D: $T_j = 160°C$

TABLE 5. CHANGE FROM REFERENCE CONDITIONS*

	C_M	$\overline{X}_n$	$\overline{X}_w$	$\overline{X}_w/\overline{X}_n$	$\overline{X}_b$	$T_{\max}$
Ref. cond.	9.98	582	5 174	8.89	1.151	294.4
$h_w = 0.045$	10.43	603.0	4 711	7.81	1.163	292.1
$h_w = 0\,015$	9.90	576.2	5 956	10.34	1.148	294.8
$T_j = 200°C$	8.83	510.0	3 667	7.18	1.119	296.6
$T_j = 190°C$	9.29	535.0	4 210	7.87	1.130	295.1
$T_j = 170°C$	11.18	643.8	7 096	11.02	1.185	292.2
$T_j = 160°C$			Reaction incomplete			
$D = 10.16$	9.93	571	6 383	11.18	1.148	296.5
$D = 3.00$	10.52	611	4 754	7.77	1.167	291.1
$\xi_o = 1.8 \times 10^6$	9.99	579.8	10 057	17.35	1.30	294.4
$\xi_o = 0$	10.00	579.4	2 914	5.03	1.00	294.4
$[I_o] = 2.5 \times 10^{-4}$	10.29	528	5 118	9.68	1.143	299.7
$[I_o] = 1.5 \times 10^{-4}$	9.63	656	5 247	7.80	1.161	287.1

* The first column lists the independent variable which has been changed from the reference condition.

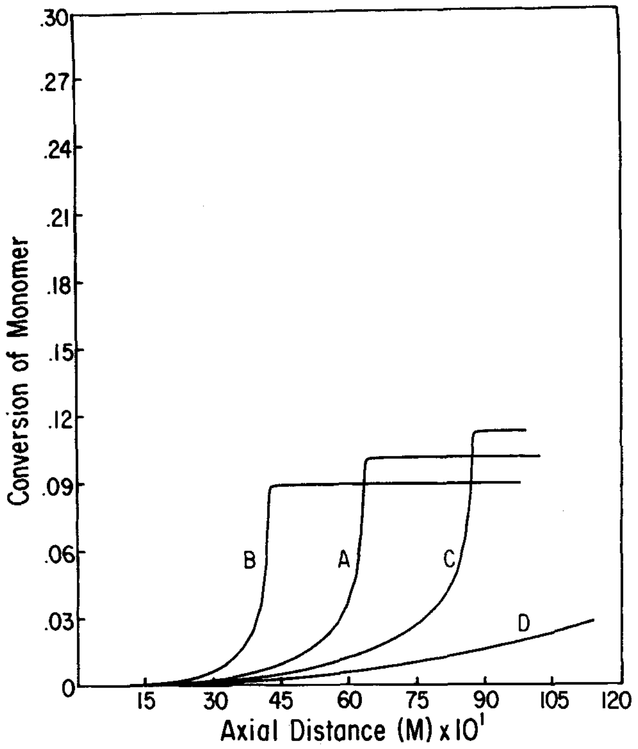

Fig. 2. Dependence of monomer conversion on axial position for the following jacket temperatures:

A: T_j = 180°C (reference condition)
B: T_j = 200°C
C: T_j = 170°C
D: T_j = 160°C

Reaction conditions and initiator concentration were chosen such that a peak temperature of about 300°C was achieved in the reactor. (A limit of approximately this magnitude must be imposed in order to avoid explosive decomposition of the ethylene.) Tables 4 and 5 and Figure 1 show that a minimum jacket temperature of approximately 170°C is required for the reaction to be completed within the assigned reactor length, and Figure 2 shows that the reaction is virtually complete at the point at which the maximum reactor temperature is reached. The initiator is, of course, also exhausted at this point.

It is clear from Figures 1 and 2 that for some jacket temperature between 160° and 170°C, the reaction proceeds almost isothermally at a controlled but very slow rate, requiring enormous reactor lengths for adequate conversion. In contrast, at T_j = 200°C a residence time of about 40 s is required for a conversion of about 9%. Conversion increases from 8.83 to 11.18% as the jacket temperature is lowered from 200° to 170°C (Table 5).

Such a change, occurring as it does in a high volume process, is of substantial commercial significance. An increase in reactor diameter results in a slight decrease in conversion. These changes, although very significant, are limited by the almost adiabatic character of the reaction zone when the jacket temperature is high enough for takeoff and are associated with a relative insensitivity of the reaction to certain design and operating variables. Among the latter, one finds the initial initiator concentration $[I_o]$ (Table 5). Although moderate changes in h_w have a modest effect on conversion, the preheat time is changed, and thus there is a larger change in the location of the hot spot of the reactor ($T_{\max}$). This latter effect (shown in Figure 3) can occur as h_w decreases owing to fouling of the inner tube surface by high molecular weight polymer. Figure 3 may, therefore, be viewed as picturing a progressive downstream displacement of the reaction zone

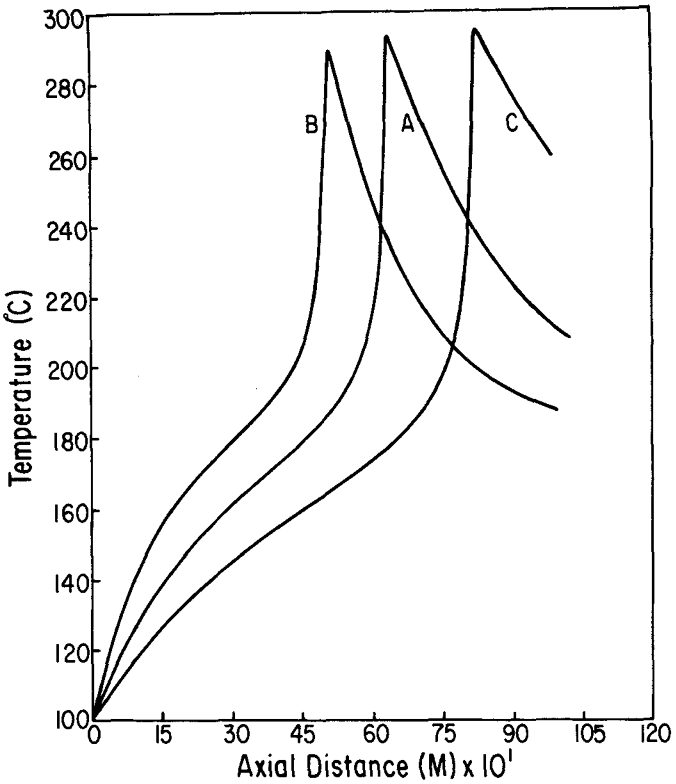

Fig. 3. Dependence of reactor temperature on axial position for the following values of the wall heat transfer coefficient:

A: h_w = 0.025 cal cm^{-2} s^{-1} °K^{-1} (reference condition)
B: h_w = 0.045 cal cm^{-2} s^{-1} °K^{-1}
C: h_w = 0.015 cal cm^{-2} s^{-1} °K^{-1}

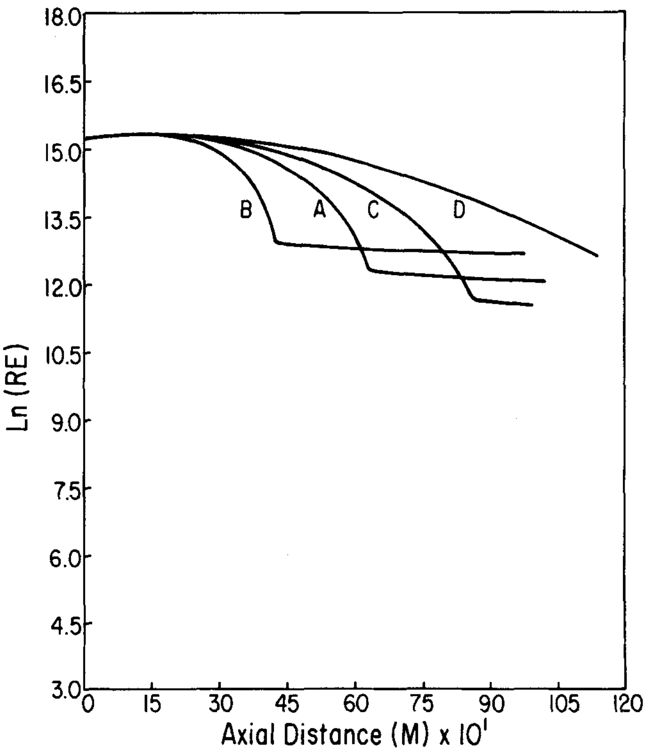

Fig. 4. Natural logarithm of Reynolds number vs. axial position for the following jacket temperatures:

A: T_j = 180°C (reference condition)
B: T_j = 200°C
C: T_j = 170°C
D: T_j = 160°C

as the inner surface of the reactors is fouled by polymer deposition or the cooling jacket is fouled owing to an external source. Since, to a first approximation, conversion is proportional to the temperature interval available for

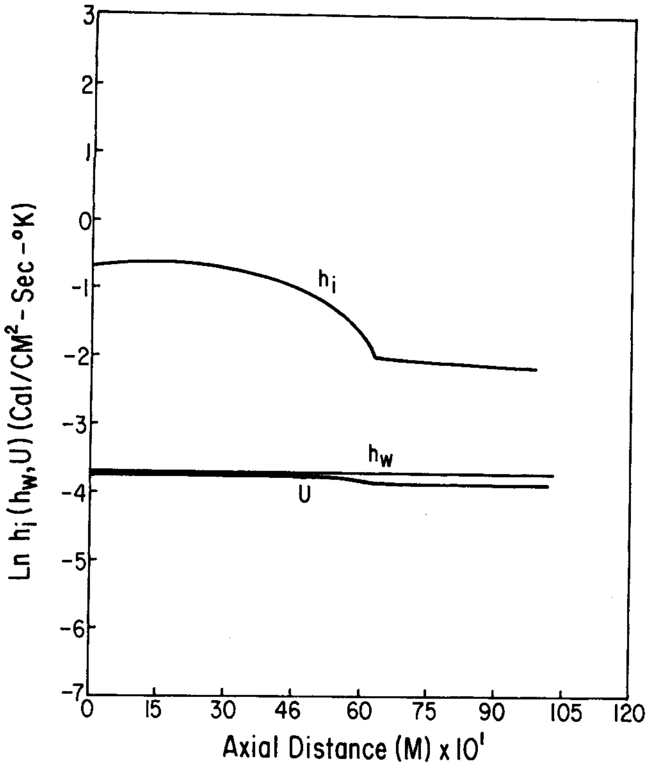

Fig. 5. Natural logarithm of heat transfer coefficients vs. axial position (reference conditions)
A: h_i inside film coefficient
B: h_w wall coefficient
C: U overall heat transfer coefficient

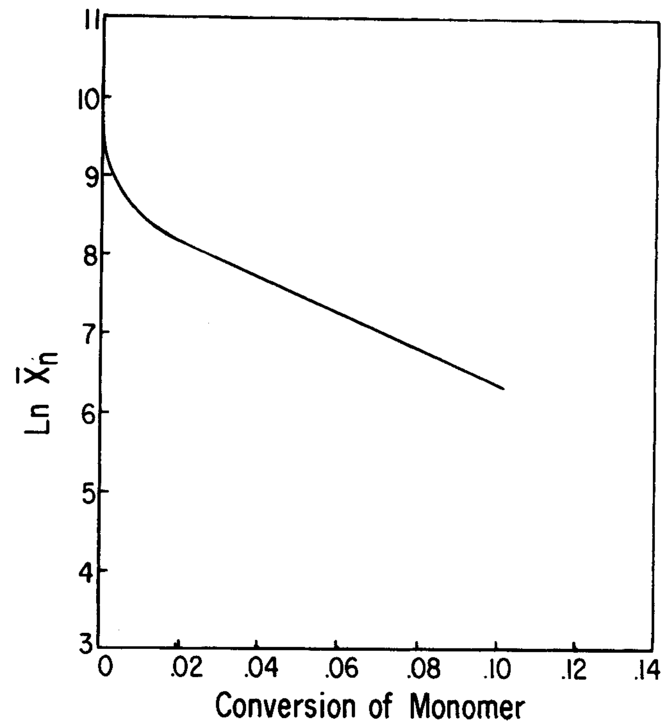

Fig. 6. Natural logarithm of number average degree of polymerization vs. monomer conversion, reference condition.

polymerization, use of a more active initiator, of multiple initiators, or downstream injection of initiator and/or cold ethylene represents major ways of increasing conversion.

In the adiabatic reaction zone, conversion and temperature increase rapidly; the combined effect on viscosity is that it also increases rapidly which causes the Reynolds number to dip sharply as the reaction is concluded. However, as the final Reynolds number for the reference run is 220 000, the flow regime is turbulent throughout (Figure 4). The sharply declining Reynolds number causes the inside film heat transfer coefficient to decline sharply also, but heat transfer is controlled mainly by h_w (which includes the external film resistance, fouling resistance on both surfaces, and the tube wall resistance) during warm-up, and h_i is only influential at substantial conversions (Figure 5). As already noted, tubular polyethylene reactors are operable at conversions of 20% or higher through use of devices like injection of cold ethylene and/or use of more than one initiator. Under such conditions, laminar flow may occur in the high conversion zone even in high-throughput reactors, and this may require a modification of the model.

Throughout nearly the entire reaction, the number average degree of polymerization decreases with temperature, and hence with conversion, in part because the activation energy for one of the termination steps, reaction (4), is greater than that for propagation, and in part because the radical population increases sharply with temperature and conversion throughout most of the reaction (Figure 6). At extremely low conversion, however, where not even a quasi steady state approximation for the free radical concentration would be valid, the molecular weight increases with conversion, leading to a sharp peak in $\overline{X}_n$ with temperature at less than 0.01% conversion. The ascending branch of Figure 6 is therefore barely visible on our plot, and a function which has a sharp maximum appears as a monotonically declining one. [The high molecular weight material made at very low conversion, if not eliminated by modifier or other means, may be a source of reactor fouling (Kinkel, 1972).]

The MWD broadens with conversion, as expected, partly as a consequence of the fact that the rate of long chain branching is assumed to be proportional to the weight concentration of polymer [Equation (5)]. Note that $\overline{X}_w/\overline{X}_n$ rises even at very low conversion, substantially above 1.5, the value characteristic of an isothermal reaction with termination by combination only (Figure 7). Figure 7 also shows that this is true even in the absence of long chain branching. The rather wide MWD is therefore only partly caused by long chain branching; another major contribution arises from the high temperature dependence assumed for the β-scission termination step. However, even in the absence of these two side reactions, $\overline{X}_w/\overline{X}_n$ exceeds 1.5

TABLE 6. MAGNITUDE OF LOWER MOMENTS DURING THE REACTION

T (°C)	C_M (% monomer converted)	C_I (% initiator converted)	$\gamma_{00} \times 10^8$	$\lambda_{01} \times 10^4$	$\lambda_{10} \times 10^8$	$\mu_{00} \times 10^4$	μ_{01}	$\mu_{02} \times 10^4$	$\mu_{10} \times 10^4$	$\overline{X}_n$	$\overline{X}_w$	$\overline{X}_b$
210.0	3.54	13.98	39.6	9.51	51.9	2.87	0.694	0.608	3.36	2 417	8 765	1.17
226.2	4.85	25.52	67.7	12.49	90.8	5.30	0.956	0.741	6.28	1 803	7 758	1.18
251.0	6.75	51.75	129.2	16.17	173.8	11.37	1.34	0 886	13.44	1 179	6 617	1.18
275.9	8.60	85.17	157.9	14.01	210.7	21.99	1.72	0.987	25.64	783	5 734	1.17
288.9	9.75	98.22	81.8	6.28	109.1	30.28	1.93	1.027	35.00	636	5 334	1.15

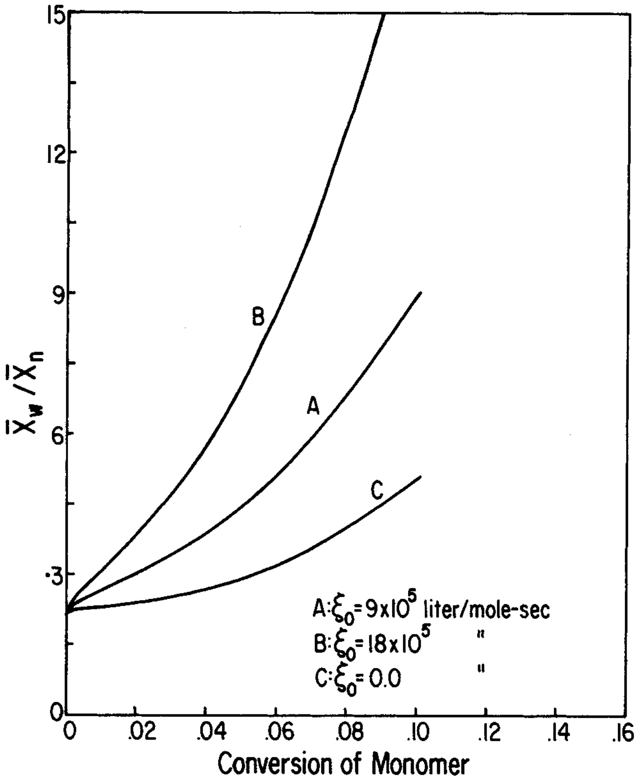

Fig. 7. Ratio of weight average to number average degree of polymerization as a function of conversion for different rates of long chain branching.

A: $\xi_0 = 9 \times 10^5$ *l* mole^{-1} s^{-1} (reference condition)
B: $\xi_0 = 18 \times 10^5$ *l* mole^{-1} s^{-1}
C: $\xi_0 = 0.0$

owing to the temperature dependence of α, β, and γ (Figure 8). A decrease in h_w broadens the MWD, a change that could be brought about by reactor fouling (Figure 9).

It is of interest to note that the model would predict number average molecular weights which are approximately one order of magnitude too large if the β-scission reaction, characterized by rate constant ϵ, is omitted. Among all the reaction steps of the model, the latter is the only one that may be considered to be controversial (Ehrlich and Mortimer, 1970). The magnitude of ϵ was chosen to generate values of $\overline{X}_n$ known to be typical of LDPE. The failure of the model to predict the correct molecular weights in the absence of that step thus provides proof for the presence of β-scission or of some other type of chain transfer reaction which controls the molecular weight.

One special benefit of the present method is that it permits the calculations of the first several moments of monomer and radical distributions anywhere along the reaction coordinate. Table 6 shows these moments, as well as monomer and initiator conversion and some other parameters at several points where the reaction is most rapid. We note that λ_{00}, the total radical concentration, equals about 2×10^{-6} moles/l at the point at which the reaction is most rapid. This is by two orders of magnitude greater than normally encountered in steady state isothermal vinyl polymerizations. It has been suggested that the high radical concentrations presumed to be present at high temperature and pressure in polyethylene reactors might lead to side reactions not encountered in the isothermal case (Gaylord, 1971). Although the authors know of no convincing evidence that this is so, the possibility cannot be precluded, and the present calculations allow one to make a good estimate of the magnitude of the radical concentration in tubular polyethylene reactors which can be compared with that characteristic of CSTR reactors.

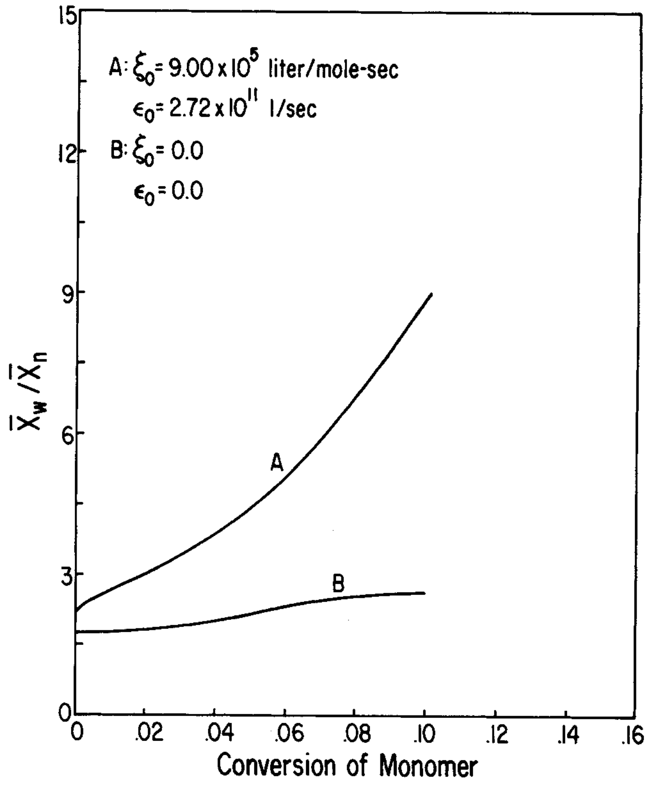

Fig. 8. Ratio of weight average to number average degree of polymerization in the absence of long chain branching and β-scission:

A: $\epsilon_0 = 2.72 \times 10^{11}$ $\xi_0 = 9 \times 10^5$ moles *l*$^{-1}$ s^{-1} (reference condition)
B: $\epsilon_0 = 0$, $\xi_0 = 0$

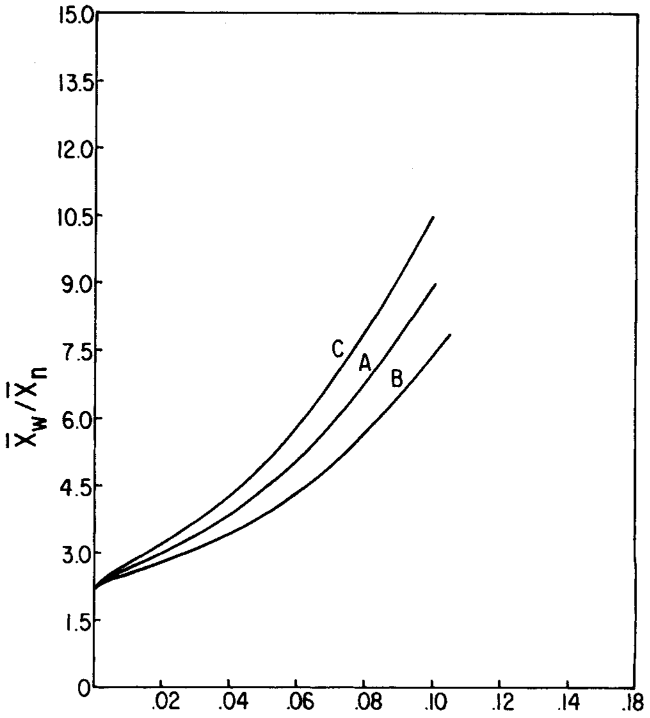

Fig. 9. Ratio of weight average to number average degree of polymerization as a function of conversion for the following wall heat transfer coefficients (reference conditions):

A: $h_w = 0.025$ cal cm^{-2} s^{-1} °C^{-1}
B: $h_w = 0.045$ cal cm^{-2} s^{-1} °C^{-1}
C: $h_w = 0.015$ cal cm^{-2} s^{-1} °C^{-1}

VALIDITY OF MODEL

The axial temperature profile calculated is qualitatively similar to that obtained by Mullikin et al. (1965), Schoenemann and Thies (1970), Marano (1974), and under some conditions, by Agrawal and Han (1975). It is characteristic of an exothermic rapidly accelerating reaction which is quenched by depletion of one of the reactants (initiator). It is well known that these characteristics fit the tubular polyethylene process, as it is normally carried out. The conversions calculated are also known to be quite typical for such a process, in the absence of modifications designed to increase the conversion, such as use of multiple initiators and/or multiple injections of monomer or initiator. Indeed, the conversions calculated here do not exceed greatly the adiabatic limit. (A conversion of 8.2% is calculated by assuming an adiabatic reaction between the temperature limits of 180° and 300°C.)

The results provide only partial support for the numerical values of the rate constants chosen. Although the residence times calculated are certainly correct (assuming a reactor length of 1 000 m with a 200 m hot zone, the total residence time is 67 s with 13 s in the hot zone), these values are not very sensitive to $\beta\gamma^{-1/2}$. The results appear to support the conclusion, made on the basis of other evidence (Ehrlich and Mortimer, 1970), that the molecular weight is controlled by a chain transfer step, here assumed to be the β-scission reaction, characterized by rate constant ϵ. In the absence of that reaction, the model predicts molecular weights which are much too high.

The results for $\overline{X}_n$, $\overline{X}_b$, and $\overline{X}_w/\overline{X}_n$ cannot be used to support details of the long chain branching mechanism or the mathematical techniques chosen to calculate the higher moments of the MWD, since the rate constant for long chain branching ξ was chosen so as to generate values of $\overline{M}_w/\overline{M}_n$ known to be typical for LDPE. In fact, the corresponding values of $\overline{X}_b$ are lower than those predicted according to some recent models for long chain branching (Jackson et al., 1973; Small, 1972, 1973; Mullikin and Mortimer, 1970, 1972).

MODIFICATIONS OF MODEL

The model can be modified readily to include the effect of radial mass transfer resistance for low throughput/high conversion reactors, such as pilot scale reactors, where the final flow regime might be expected to be laminar. Work is proceeding on this development. The computation time would be reduced considerably if the quasi steady state approximation could be made for the radical concentration. Such a simplification would make the model more attractive for process optimization studies. These modifications will be explored in a following paper (Howell, 1976).

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NOTATION

C_p = specific heat, cal g^{-1}
ΔH = enthalpy of reaction, cal(mole monomer)$^{-1}$
h_i = inside film heat transfer coefficient, cal $cm^{-2}s^{-1}$ $°K^{-1}$
h_w = wall heat transfer coefficient (includes fouling and outside film resistances), cal $cm^{-2}s^{-1}°K^{-1}$
I = initiator species
i = initiator concentration, moles l^{-1}
K = thermal conductivity, cal $cm^{-1}s^{-1}°K^{-1}$
M = monomer species
M_o = molecular weight of monomer
m = monomer concentration, moles l^{-1}
Nu = Nusselt number
P = polymer species (terminated radical)
Pr = Prandtl number
$p_i(x)$ = concentration of polymer species of chain length x with i branches, moles monomer l^{-1}
R = radical species
Re = Reynolds number
$r_j(y)$ = concentration of radical species of chain length y with j branches
T = temperature of reacting fluid (°K) or as indicated
T_j = temperature in the jacket (°K) or as indicated
U = overall heat transfer resistance, cal $cm^{-2}s^{-1}°K^{-1}$
V_m = specific volume of monomer, cm^3g^{-1}
V_p = specific volume of polymer, cm^3g^{-1}
v = velocity, cm s^{-1}
w_m = weight fraction of monomer
z = axial distance from reactor inlet, cm or as indicated
D = reactor diameter, cm or as indicated
w_p = weight fraction of polymer
$\overline{X}_n$ = number average degree of polymerization
$\overline{X}_w$ = weight average degree of polymerization
$\overline{X}_b$ = average number of long chain branches per molecule
$(x)(y)$ = chain length

Greek Letters

$\alpha,\beta,\gamma,\epsilon,\xi$ =reaction rate constants (see Table I)
δ_{mo} = kronecker delta
λ_{mn} = radical moment [defined by Equation (10)], moles l^{-1}
μ_{mn} = polymer moment [defined by Equation (11),] moles l^{-1}
η_o = monomer viscosity, poise
η_r = relative viscosity $\left(\dfrac{\text{solution viscosity}}{\text{solvent viscosity}}\right)$
η_s = solution viscosity, poise
ρ_m = monomer density, g cm^{-3}
ρ_s = solution density, g cm^{-3}

Subscripts

i,j = number of long chain branches
m = monomer
o = condition at reactor inlet
p = polymer
s = solution

LITERATURE CITED

Agrawal, S., and C. D. Han, "Analysis of the High Pressure Polyethylene Tubular Reactor with Axial Mixing," *AIChE J.*, 21, 449 (1975).

Bamford, C. H., and H. Tompa, "The Calculation of Molecular Weight Distributions from Kinetic Schemes," *Trans. Faraday Soc.*, 50, 1097 (1954).

Carr, N. L., J. D. Parent, and R. E. Peck, "Viscosity of Gases and Gas Mixtures at High Pressures," *Chem. Eng. Progr. Symposium Ser. No. 16*, 51, 91 (1955).

Ehrlich, P., "Phase Equilibria of Polymer—Solvent Systems at High Pressures Near Their Critical Loci. II. Polyethylene-Ethylene," *J. Polymer Sci.*, A3, 131 (1965).

———, and G. A. Mortimer, "Fundamentals of the Free Radical Polymerization of Ethylene," *Advan. Polymer Sci.*, 7, 386 (1970).

Ehrlich, P., and J. C. Woodbrey, "Viscosities of Moderately Concentrated Solutions of Polyethylene in Ethane, Propane and Ethylene," *J. Appl. Polymer Sci.*, 13, 117 (1969).

Eiermann, K., "Modellmässige Deutung der Wärmeleitfahigkeit von Hochpolymeren," *Koll. Z.*, 201, 3 (1965).

Gaylord, N. G., "Proposed Participation of Excited Monomer in the Free Radical-Catalyzed High Pressure, High Temperature Polymerization of Ethylene," *J. Macromol. Sci., Chemistry*, **5**, 1015 (1971).

Gear, C. W., Comm. "The Automatic Integration of Ordinary Differential Equations," *A.C.M.*, **14**, 3 (1971).

Hellwege, K. H., W. Knoppf, and W. Wetzel, "Spezifische Wärme von Polyolefinen und einigen anderen Hochpolymeren im Temperaturbereich von 30°C—180°C," *Koll. Z.*, **180**, 126 (1962).

Howell, J. A., Unpublished (1976).

Hulburt, H. M., and S. Katz, "Some Problems in Particle Technology," *Chem. Eng. Sci.*, **19**, 555 (1964).

Jackson, R. A., P. A. Small, and K. S. Whiteley, "Prediction of Molecular Weight Distributions in Branched Polymers," *J. Polymer Sci.*, **A1**, **11**, 1781 (1973).

Katz, S., and G. M. Saidel, "Moments of the Size Distribution in Radical Polymerization," *AIChE J.*, **13**, 319 (1967).

Kinkel, K., "Some Aspects of High Pressure Polymerization of Ethylene in Technical Units," Paper presented before Tenth Annual Meeting, European High Pressure Research Group, Strasbourg, (Apr., 1972).

Marano, J., "Modelling of Polymer Reactors. The Non-Isothermal Free-Radical System," Seminar presented at Northwestern University, Evanston, Ill. (Feb. 25, 1974).

Michels, A., and M. Geldermans, "Isotherms of Ethylene Up to 3,000 Atmospheres Between 0°C and 150°C," *Physica*, **9**, 967 (1942).

————, and R. S. DeGroot, "Thermodynamic Properties of Ethylene Under Pressure Up To 3,000 Atmospheres and Temperatures Between 0°C and 150°C, Tabulated as Functions of Density," *ibid.*, **12**, 105 (1946).

Mullikin, R. V., and G. A. Mortimer, "Another Look Out Long-Chain Branching," *J. Macromol. Sci.—Chem.*, A4, 1495 (1970).

————, "Long-Chain Branching Under Conditions of Non-Uniform Branching Probability, *ibid.*, A-6, 1301 (1972).

Mullikin, R. V., P. E. Parisot, and N. L. Hardwicke, "Analog Computer Studies of Polyethylene Reaction Kinetics," Paper presented at 58th AIChE Annual Meeting, Philadelphia, Pa (Dec. 5-9, 1965).

Parks, W., and R. B. Richards, "The Effect of Pressure on the Volume, Thermodynamic Properties and Crystallinity of Polythene," *Trans. Faraday Soc.*, **45**, 203 (1949).

Raff, R. A. V., and K. W. Doak, *Crystalline Olefin Polymers*, Part I., Wiley, New York (1965).

Saidel, G. M., and S. Katz, "Dynamic Analysis of Branching in Radical Polymerization, *J. Polymer Sci.*, **A-2**, **6**, 1149 (1968).

Schoenemann, K., and J. Thies, "Calculation of High Pressure Polyethylene Reactors for Polymers of Definite Structure and Properties," Tenth Annual Meeting, European High Pressure Research Group, Strasbourg (Apr., 1972); "The Calculation of High Pressure Polyethylene Reactors by Means of a Model Comprehending Molecular Weight Distribution and Branching of the Polymer," 1st International Symp. Chem Research. Eng., Carnegie Inst., Washington, D.C. (1970).

Small, P. A., Effects of Long-Chain Branching on Distribution of Degree of Polymerization," *Polymer*, **13**, 536 (1972).

————, Effects of Long-Chain Branching on Distribution of Degree of Polymerization: 2," *ibid.*, **14**, 524 (1973).

Trementozzi, Q. A., "Effect of Long-Chain Branching on Some Solution Properties of Polyethylene," *J. Polymer Sci.*, **23**, 887 (1957).

Ver Strate, G., and W. Philippoff, "Phase Separation in Flowing Polymer Solutions," *ibid.*, *B.* (*Polymer Letters*) **12**, 267 (1974).

Wu, P. C., J. A. Howell, and P. Ehrlich, "Monte Carlo Simulation of Structure of Low-Density Polyethylene," *Ind. Eng. Chem. Prod. Res. Develop.*, **11**, 352 (1972).

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Optimal Design of Pressure Relieving Piping Networks by Discrete Merging

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Refinery relief-header network design can be optimized by a new discrete optimization technique which requires no rounding of decision variables, no initial guesses for the solution, and no artificial termination criteria; it produces parametric solutions when the optimum is attained. The method is also faster and more compact than the alternative continuous optimization methods.

SCOPE

Pressure relieving piping networks are widely employed as a safety measure in refineries and chemical complexes. The optimal design of such a system calls for the minimization of equipment cost while maintaining conditions of maximal flows and safe pressure limits. The constrained minimization is to be attained by selecting a discrete diameter for each of the pipe sections. A typical network may contain up to several hundred such pipe sections connected to scores of process vessels and units.

The most obvious formulation of this problem [Equations (5) to (7)] limits the maximum network size to about 100 pipe sections on a CDC 6400 computer by using gradient projection methods of nonlinear programming. Murtagh (1972) proposed a dual formulation which resulted in substantial reduction of computing time and storage. However, the drawback common to all continuous optimization techniques is that the solution must be rounded to the nearest standard pipe sizes, a procedure which raises the specter of nonoptimal size selection. Moreover, the applicability of these methods depends on the specific forms of the objective functions and constraints.

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