

# Adaptive Control of a Slim-type Reactor for Free Radical Polymerization of LDPE

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**ABSTRACT** - The adiabatic slim-type autoclave reactor for free radical polymerization of LDPE is represented by a two-compartment four-cell model, which is proven effective to predict the reactor behavior as well as the polymer properties. Since the temperature distribution along the reactor axis plays the central role for the properties of the polymer product, it is important in practice to regulate the temperature in each compartment. The present study aims for the application of the adaptive control algorithm not only in the period of start-up but also during the steady state operation. It is shown that the temperature control is significantly improved over the conventional PID-control and this also brings about a reduction of variations in the polymer properties. This study demonstrates the potential application of the adaptive controller for the control of the polymerization reactor operated under the adiabatic condition.

## INTRODUCTION

The process for high pressure polyethylene usually takes place in two different reactor systems ; that is, autoclave and tubular reactors. Ethylene is polymerized in the stirred autoclave via free radical mechanism using organic peroxides as initiators at temperatures ranging from 150 ~ 300°C and pressures from 1000 atm to 3000 atm. Conversion ranges normally between 10 and 20% and the reactor residence time varies from 10 to 60 seconds.

There are two basic types of the autoclave reactors : (1) highly backmixed compact reactor and (2) less highly mixed slim type reactor. The latter has an internally mounted motor for the stirrer and the length to diameter ratio falls in the range of 8~20. Reactors of this type can be compartmented into two or more zones and operated with appropriate temperature distribution in the reactor. It is used to produce narrow MWD resins which are well suited for film and injection molding application.

Among various objectives of the polymerization reactor

control, the most important one is the control of the polymer properties. For this purpose it is prerequisite to develop some method of on-line measurement and to estimate the parameters. The estimation of the temperature, conversion and molecular weight distribution should be based on a mathematical model. Therefore it is important to establish a relevant mathematical model for the reactor system.

Ponnuswamy et al.[13] examined a variety of problems related to the on-line measurement and the control of batch polymerization reactors. A Kalman filter has been applied by Schuler and Suzhen[14] to estimate the state of free radical polymerization reactor.

It is, however, next to almost impossible to estimate the properties of the polymer produced by the autoclave with a time-delay smaller than the residence time, which is usually less than one minute. Hence, it is necessary to analyze the variations of polymer properties accompanying the appropriate temperature control.

The present study aims for a systematic analysis of the variations in the polymer properties caused by the temperature control and for presenting a relevant temperature control strategy by which a more effective property control may be established.

## MODEL DEVELOPMENT

A deterministic description of the highly complicated physical and chemical processes in a polymerization reactor is based on the kinetic analysis of the polymerization mechanism. Here we shall adopt the free radical polymerization reaction mechanism[2] and thus the elementary reactions to be considered are initiation, propagation, termination, chain transfer to polymer, chain transfer to monomer, and backbiting reaction.

The slim-type reactor(Fig.1) to be treated here shall be represented by the two-compartment four-cell model

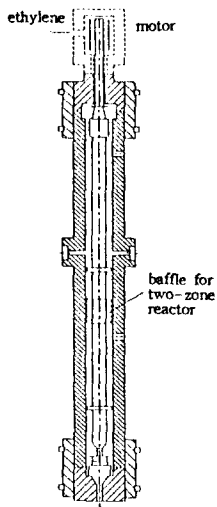


Fig. 1. ICI slim type autoclave.

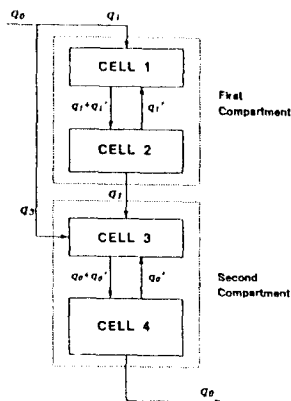


Fig. 2. Schematic diagram of the two-compartment four-cell model.

with back flow in each compartment. For the four-cell model shown schematically in Fig. 2, the mass and energy balances yield a set of ordinary differential equations which may be put in the form as follows :

$$V_i \frac{dC_j}{dt} = q_i C_{j,i} + q_i' C_{j,i+1} - \left( \sum_{k=1}^{i-1} q_k + q_i' + q_{i-1}' \right) C_j + \left( \sum_{k=1}^{i-1} q_k + q_{i-1}' \right) C_{j,i-1} + V_i r_{j,i}$$

$$\rho C_p V_i \frac{dT_i}{dt} = \rho C_p [q_i T_{i+1} + q_i' T_{i-1} - \left( \sum_{k=1}^{i-1} q_k + q_i' + q_{i-1}' \right) T_i + \left( \sum_{k=1}^{i-1} q_k + q_{i-1}' \right) T_{i-1}] + V_i r_{p,i} (-\Delta H_p) + P_i$$

The first subscripts in  $C_j$  and  $r_j$  represent the species in the order of  $I, M, G, G', G'', F, F',$  and  $F''$ , where  $I$  and  $M$  are the concentrations of initiator and monomer,  $G$  and  $F$  are the total concentrations of living and dead polymers, respectively, and the prime and the double prime denote the first and second moments. The second subscript  $i$  ( $i=1, 2, 3, 4$ ) indicates the cell number. Here  $T$  denotes the absolute temperature,  $r_p$  the polymerization rate, and  $P$  the rate of heat generation by agitation[12]. While  $C_j$  represents the concentration of the  $j$ -th species in the  $i$ -th cell, the expressions for  $r_j$  ( $j=1, 2, \dots, 9$ ) are given as follows :

$$r_I = -k_d I$$

$$r_M = 2fk_d I - k_p M G - k_{tm} M G$$

$$r_G = 2fk_d I - (k_{td} + k_{te}) G G'$$

$$r_{G'} = 2fk_d I + k_p M G - (k_{td} + k_{te}) G G'$$

$$+ k_{tm} M (G - G') + k_p (G F'' - G' F')$$

$$r_{G''} = 2fk_d I + k_p M (2G' + G) - (k_{td} + k_{te}) G G''$$

$$+ k_{tm} M (G - G'') + k_p (G F''' - G'' F')$$

$$r_F = k_{td} G^2 + \frac{k_{te}}{2} G^2 + k_{tm} M G$$

$$r_{F'} = (k_{td} + k_{te}) G G' + k_{tm} M G' + k_p (G' F' - G F'')$$

$$r_{F''} = k_{td} G G'' + k_{te} (G G'' + G'^2) + k_{tm} M G''$$

$$+ k_p (G'' F' - G F''')$$

$$r_P = k_p M G$$

In the above the pseudo-steady state assumption is applied for the free radical concentration and the closure technique by Hulbert and Katz[8] is used to obtain  $F''$ .

The initiators considered here are acetyl cyclohexanesulphonyl peroxide, ter-butyl peroxyvalate and ter-butyl peroxyacetate. The reaction rate constants are assumed to follow the Arrhenius expression and the associated parameters are given in Table 1, whereas other system parameters are given as  $\rho = 413$  g/l,  $C_p = 0.518$  cal/g·K,  $-\Delta H_p = 21400$  cal/gmol,  $f = 1$ ,  $V = 440$  l,  $P = 1200$  atm,  $T_f = 293.15$  K and  $q_0 = 18$  l/s.

TABLE 1. REACTION RATE CONSTANTS USED IN THIS STUDY.

Reaction	$k_0$ (l/mol·s or s <sup>-1</sup> )	E cal/mol
Initiation (tert-butyl peroxyacetate) (tert-butyl peroxyvalate) (Acetyl cyclohexane- sulphonyl peroxide)	1.396 × 10 <sup>13</sup> 2.112 × 10 <sup>12</sup> 1.309 × 10 <sup>19</sup>	30103 25308 33872
Propagation	1 × 10 <sup>6</sup>	6477-0.56P
Termination by combination by disproportionation	3 × 10 <sup>8</sup> 3 × 10 <sup>8</sup>	3950 3950
Chain transfer to monomer	3 × 10 <sup>4</sup>	9375-0.48P
Chain transfer to polymer	1 × 10 <sup>6</sup>	11778-0.48P
Backbiting	2.43 × 10 <sup>7</sup>	9717

## CONTROLLER

On-line determination of process parameters is central in adaptive control and it is an important part of a self-tuning regulator. In this study, we use the recursive least squares method which is frequently applied in conjunction with adaptive control. While the

PID-controller of both the velocity and position forms and the adaptive pole-placement controller are used during the start-up period, we employ not only the PID-controller but also the adaptive pole-placement controller during the steady state operation.

## RESULTS AND DISCUSSION

In Fig. 3 we present a bifurcation diagram drawn for the exit temperature, molecular weight and polydispersity in the second compartment when the feed temperature ( $T_f$ ) is chosen as the bifurcation parameter. The stable steady state branches corresponding to the actual operation are marked by arrows. The steady state multiplicity exists and the reactor system can have up to nine different temperatures. However, the steady state values of the molecular weight and polydispersity representing the polymer properties exist only for a certain range of temperature. Beyond the upper limit of this temperature range an abrupt increase of the polydispersity is observed. It is also noticed that the stable steady state branches for the molecular weight and polydispersity are located on the isola. Therefore, increasing the reactor temperature for the improvement of the productivity would bring about not only the occurrence of decomposition reaction but also an abrupt change of the polymer properties.

Figures 4 and 5 show the regions of different multiplicity patterns for which  $F_{I1}$  and  $F_{I2}$  are chosen as the bifurcation parameter. In Fig. 4 three different multiplicity patterns are observed in the plane of the feed temperature ( $T_{f1}$ ) and the residence time of the first compartment ( $\theta_1$ ). These are the varieties of double hysteresis, S-type and unique steady state. When the temperature of the first compartment is controlled, the multiplicity patterns for the state of the second compartment are classified into two varieties; i.e., simple S-type and unique steady state (See Fig. 5). This implies that the temperature control of the first compartment is more important.

In Fig. 6 variations in the polymer properties with the feed temperature are shown in the case of temperature control. It is clearly observed that the properties of the polymer are also controlled to some extent when the reactor temperature is controlled. In this case the reactor temperatures of individual compartments are controlled by manipulating the respective initiator feed rates. Figure 7 illustrates the bifurcation diagram when the initiator feed rates are manipulated for the temperature control. Here the feed temperature in Fig. 6 is increased or decreased by 10 K from the reference feed temperature ( $T_f = 293$  K) and the feed temperature is chosen as the bifurcation parameter. It is implied that if the reactor temperature is appropriately controlled, the changes in the operating

parameters would have little effect on the stability and the structure of the steady state.

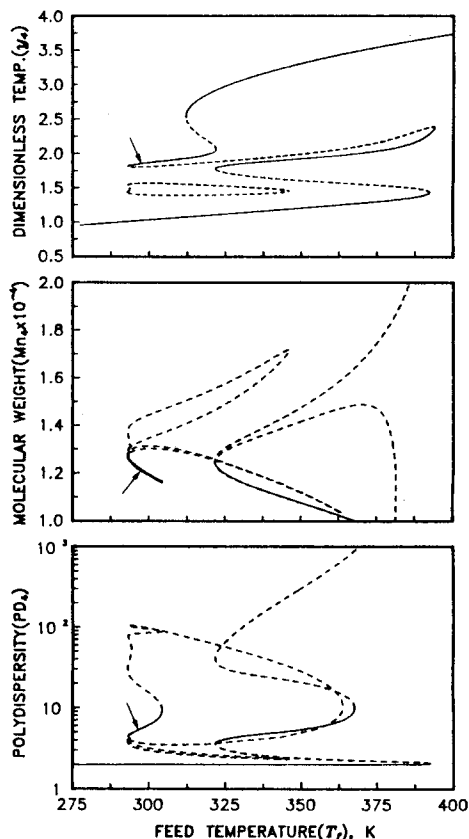


Fig. 3. Bifurcation diagram showing the steady state branches of temperature, molecular weight and polydispersity with the feed temperature ( $T_f$ ) as the bifurcation parameter.

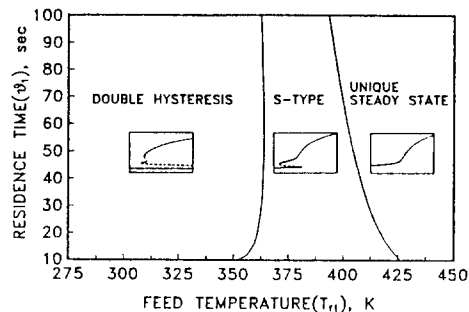


Fig. 4. Division of the  $(T_{f1}, \theta_1)$ -plane into regions of different multiplicity patterns with  $F_{I1}$  as the bifurcation parameter.

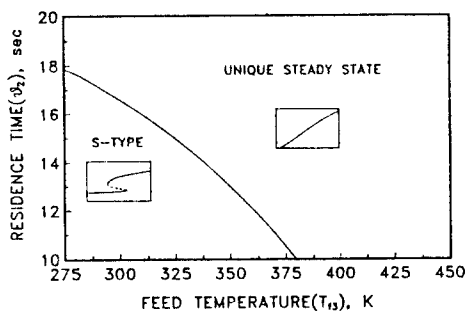


Fig. 5. Division of the  $(T_f, \theta_2)$ -plane into regions of different multiplicity patterns with  $F_f$  as the bifurcation parameter.

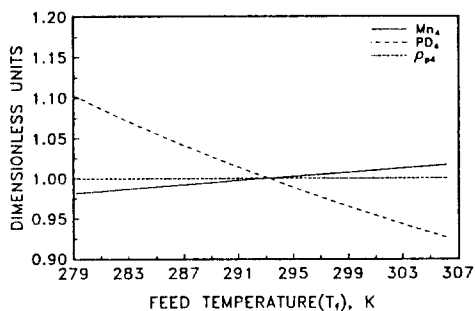


Fig. 6. Variations in polymer properties with the feed temperature in the case of reactor temperature control.

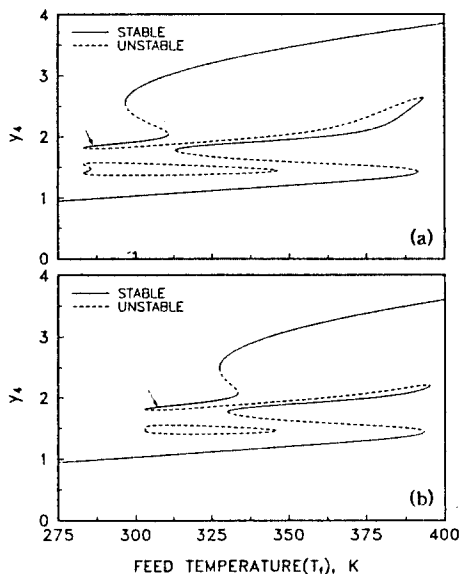


Fig. 7. Bifurcation diagrams showing the steady state branches of the exit temperature with the feed temperature  $(T_f)$  as the bifurcation parameter: (a)  $F_{f1} = 0.0102566$  and  $F_{f2} = 0.00614859$  mol/s; (b)  $F_{f1} = 0.0083402$  and  $F_{f2} = 0.00507107$  mol/s.

During the period of start-up, adoption of the adaptive controller is not allowed because the identification between the system and the model is just under way. Therefore, we use the adaptive controller after the parameter identification is accomplished to a certain extent. In Fig. 8 the variation in the model parameter is presented for three different initial values of the diagonal elements of the covariance matrix,  $P$ .

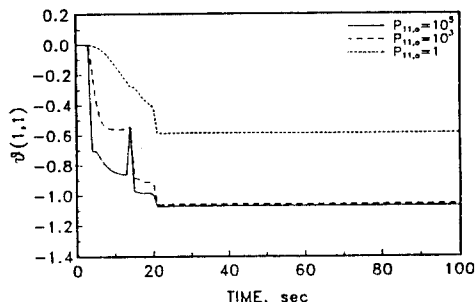


Fig. 8. Variations in the model parameter  $\theta(1,1)$  during the start-up procedure for three different initial values of covariance matrix  $P$ .

Figure 9 presents the response curves of the reactor temperature during the start-up procedure along with the required variations of the initiator feed rates,  $F_{f1}$  and  $F_{f2}$ . In this step the initiators of three different kinds are used within the low, middle and high temperature ranges, respectively. The arrow in the lower part of Fig. 9 indicates the time when the initiator is changed. The velocity form of the PID control algorithm is adopted until the injection of the high temperature initiator. It is noticed that the temperature control is significantly improved by using the adaptive pole-placement controller instead of the PID-controller when the reactor temperature approaches the steady value.

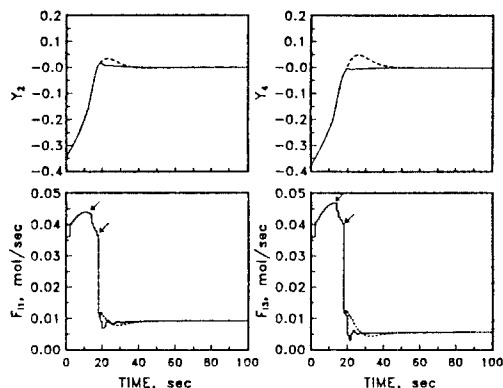


Fig. 9. Start-up procedure (— : PID + Pole-placement control, ··· : PID control).

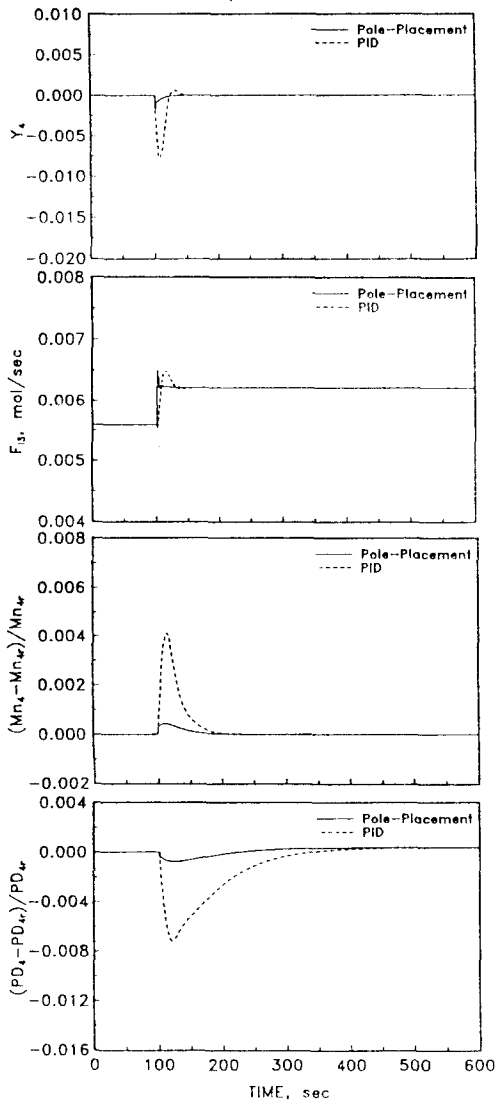


Fig. 10. Comparison between the performances of the PID and the pole-placement controller in case of 10% decrease in the initiator efficiency.

Figure 10 compares the performance of the adaptive pole-placement controller with that of the PID controller in case of 10% decrease in the initiator efficiency ( $f$ ). When the PID-controller is used, the temperature deviation is 0.8%. On the other hand, if the pole-placement controller is employed, deviations of the temperature and the polymer properties are negligible. Since, however, the required variation of the initiator feed rate shows a sharp increase to give an overshoot, actual implementation of this controller depends on the performance of the control valve. Figure 11 illustrates the variations in the polymer properties when the temperature of the second compartment is increased by 5%. The rate of change in

the molecular weight is almost the same as that in the polydispersity. It is noticed that, if the set point for the exit temperature is changed, the temperature control becomes quite satisfactory and the temperature reaches the steady state faster than the polymer properties.

In Fig. 12 the performance of the pole-placement controller is shown for the case of a step change in the set point for the exit temperature (duration=200 sec, max=+5%, min=-5%). When the pole-placement controller is applied, the temperature overshoot is eliminated. This illustration clearly demonstrates that, by predicting all the parameter values and applying them to the adaptive controller, a better reactor temperature control can be accomplished for the adiabatic polymerization reactor. Furthermore the deviations of the polymer properties can be reduced considerably.

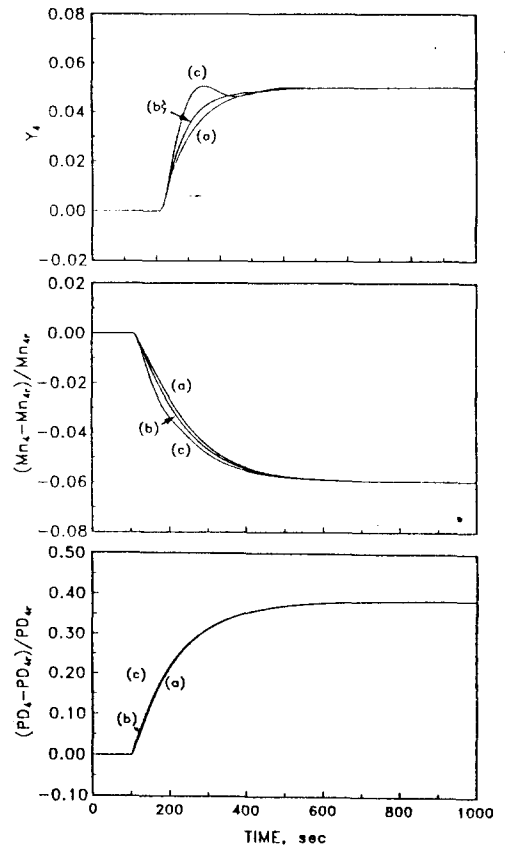


Fig. 11. Variations in the reactor temperature and the polymer properties in the second compartment for various values of  $\xi_m$ : (a) 0.9, (b) 0.7, (c) 0.4.

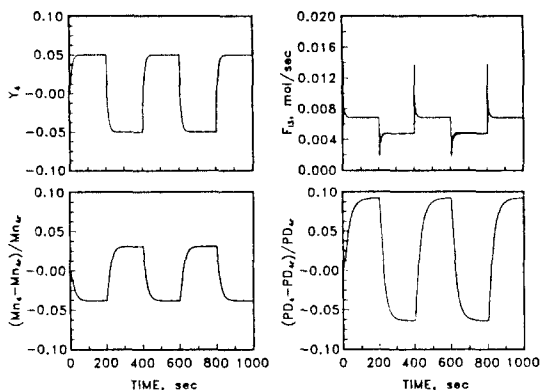


Fig. 12. Performance of the pole-placement controller (duration : 200 sec, period = 400 sec,  $u_{ref} = \pm 5\%$ ).

### CONCLUSIONS

The adaptive control strategy is evaluated by implementing it on a realistic model for the LDPE autoclave reactor. A simulation model is derived describing the polymerization of LDPE in a slim-type reactor. The adaptive pole-placement controller performs adequately when applied to the highly nonlinear system representing the LDPE autoclave reactor.

The adaptive pole-placement controller can be applied for the unmeasured disturbances as well as the measured ones, and in this case it is found that the deviations of polymer properties become negligible. In a servo problem, the temperature overshoot can be eliminated, and thus a better reactor temperature control can be accomplished by using the adaptive controller. In addition, the deviations of the polymer properties can be reduced considerably.

**ACKNOWLEDGEMENT** - The support of the Automation Research Center(ARC), a center of excellence designated by KOSEF, for this study is gratefully acknowledged.

### NOTATION

$C_p$  : Heat capacity of the reaction mixture[cal/g·°C]  
 $E$  : Activation energy[cal/mol]  
 $f$  : Initiator efficiency  
 $G$  : Living polymer concentration[mol/l]  
 $F$  : Dead polymer concentration [mol/l]  
 $F_1$  : Initiator feed rate[mol/sec]  
 $-\Delta H_p$  : Heat of polymerization[cal/mol]  
 $I$  : Initiator concentration[mol/l]  
 $k$  : Reaction rate constant[ $s^{-1}$  or  $l/mol \cdot s$ ]  
 $M$  : Monomer concentration[mol/l]  
 $M_n$  : Molecular weight  
 $P$  : Reactor pressure(atm)  
 $P_1$  : Heat of mixing[cal/sec]  
 $R_j$  : Living polymer species of chain length  $j$

$P_j$  : Dead polymer species of chain length  $j$   
 $q$  : Flow rate[l/s]  
 $T$  : Temperature[K]  
 $x$  : Dimensionless concentration  
 $Y$  : Dimensionless observed temperature  
 $y$  : Dimensionless temperature  
 $V$  : volume[l]

### Greek letters

$\lambda$  : Exponential forgetting factor  
 $\theta$  : Model parameter  
 $\theta_i$  : Residence time[sec]  
 $\rho$  : Density of the reaction mixture[g/l]

### Subscripts

$f$  : Feed condition  
 $i$  :  $i$ -th cell or chain length  
 $j$  : Chain length  
 $r$  : Reference  
 $1, 2, 3, 4$  : Cell number

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