Batch and continuous reactors for the production of novolacs

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(*Received* 31 *December* 1980; *revised* 6 *April* 1981)

The behaviour of batch and continuous reactors for the production of standard novolacs is discussed theoretically. A kinetic model valid from low to high formaldehyde conversions is used Results show the influence of the formaldehyde/phenol molar ratio as well as the stated formaldehyde conversion on the composition of the resulting novolac. For the limit of complete segregation, a series of three ideal stirred tanks are shown adequate for the continuous industrial production, at total mean residence times equivalent to those of batch reactors. The influence of partial micromixing is discussed

Keywords Kinetics, formaldehyde; phenol; novolacs; batch reactor; continuous reactor; micromixing

INTRODUCTION

Although the production of standard novolacs is usually carried out in batch reactors, reported continuous processes are beginning to find industrial applications[1,2]. A discussion concerning the prediction of yield and molecular distributions in continuous reactors[3,4], for the particular case of novolacs, may prove to be useful.

In order to enable the prediction of the evolution of molecular species in the acid-catalysed phenol–formaldehyde condensation, a suitable kinetic scheme, valid from the beginning of reaction to the final stages (high formaldehyde conversions) is necessary. One of such schemes, which showed a reasonable agreement with experimental results, is the following[5]:

$$P_i + F \xrightarrow{k_a} Q_i \qquad (1)$$

$$P_j + Q_i \xrightarrow{k_c} P_{i+j} \qquad (2)$$

where P_i and Q_i are novolac i-mers (Q_i has a methylolated ring), and F is formaldehyde, as is shown in *Figure 1*. The phenolic OH is plotted directly linked to the aromatic ring to show that either o and p positions may be used to generate methylene linkages or methylolated products. Neither P nor Q structures are necessarily linear for $i > 3$.

The first step in the reaction mechanism is the addition of formaldehyde to phenol or any high mer to give a methylol group. The second step is the condensation of the methylolated product with any j-mer.

The specific rate constants, k_a and k_c, can be calculated as the product of the corresponding rate constants per unit reaction site (k'_a and k'_c) and the total number of reaction sites S_i in the P_i structure:

$$k_a = k'_a S_i \qquad (3)$$

$$k_c = k'_c S_i \qquad (4)$$

$S_1 = 3$ (o,o' and p positions of the phenolic ring) (5)

$$S_i = 4 + \theta(i-2) \quad , \quad i \geq 2 \qquad (6)$$

The four exterior reaction sites are considered as completely available for the reaction. Interior sites, including those corresponding to eventual branches, are less reactive than their exterior counterparts. The factor θ, less than unity, in equation (6) accounts for this fact. Kinetic parameters take the following values for the production of standard novolacs[5]:

$$(k'_c/k'_a) \sim 8 \quad , \quad \theta \sim 0.125.$$

RESULTS AND DISCUSSION

Batch reactors

The kinetic scheme described by equations (1) and (2) leads to the following molar balances:

$$-dP_1/dt = k'_a 3P_1 F + k'_c 3P_1 \sum_{j=1}^{\infty} Q_j \qquad (7)$$

$$-dP_i/dt = k'_a S_i P_i F + k'_c S_i P_i \sum_{j=1}^{\infty} Q_j - k'_c \sum_{j=1}^{i-1} S_j P_j Q_{i-j}, i \geq 2 \qquad (8)$$

$$-dQ_i/dt = k'_c Q_i \sum_{j=1}^{\infty} S_j P_j - k'_a S_i P_i F \qquad (9)$$

$$-dF/dt = k'_a F \sum_{j=1}^{\infty} S_j P_j \qquad (10)$$

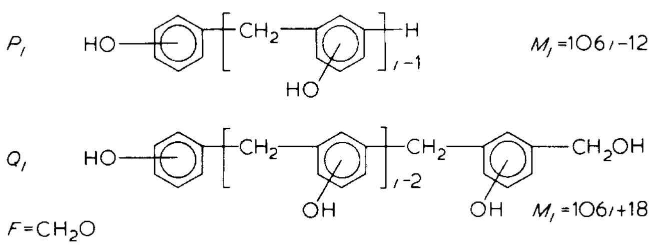

Figure 1 Monomers and polymers involved in the reaction scheme

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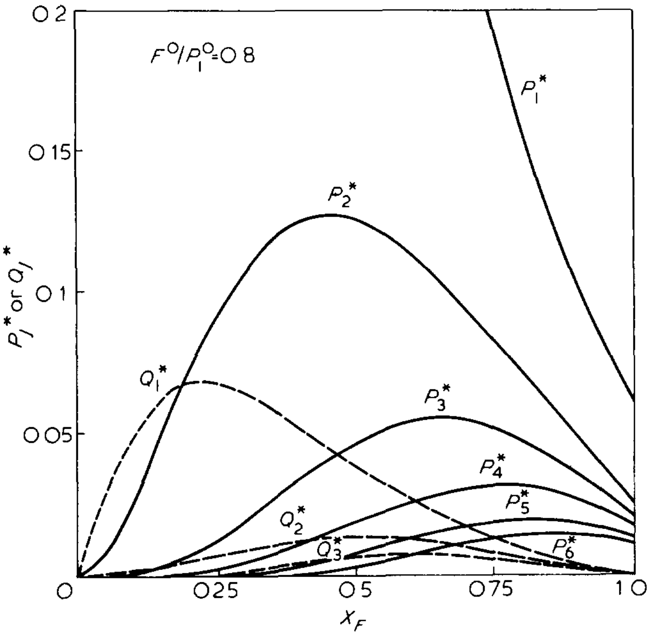

Figure 2 Evolution of molecular species during the production of a novolac in a batch reactor

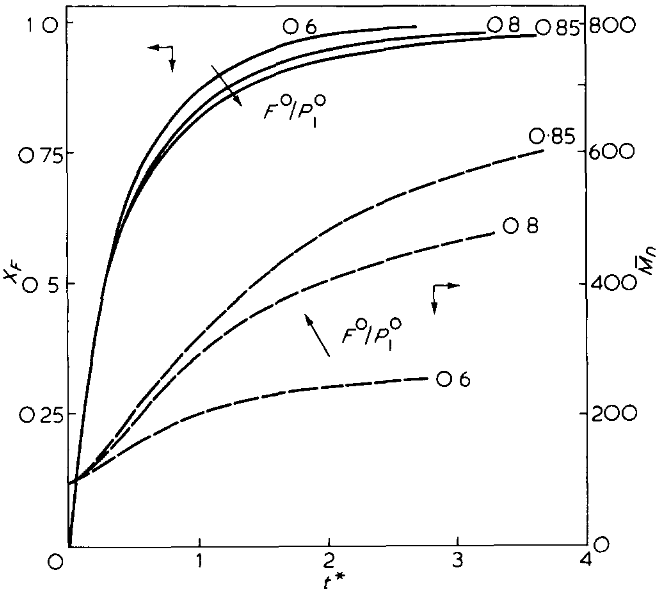

Figure 3 Formaldehyde conversion and number average molecular weight as a function of the reaction time in a batch reactor, for different formaldehyde/phenol initial molar ratios

Equations (8) to (10) were numerically solved by reducing the system to a finite J number of j-mers, and checking that:

$$\sum_{j=1}^{J} j(P_j+Q_j) \rightarrow P_1^0 \qquad (11)$$

for all the formaldehyde conversion range (P_1^0 is the initial molar concentration of phenol). A value of $J=40$ proved to be satisfactory.

Calculations were performed in terms of the following dimensionless variables and parameters:

$$t^* = k_a'P_1^0 t \quad , \quad P_j^* = P_j/P_1^0 \quad , \quad Q_j^* = Q_j/P_1^0$$

Figure 2 shows the evolution of P_j^* and Q_j^* as a function of formaldehyde conversion, for $F^0/P_1^0=0.8$. All the j-mers go through a maximum concentration for a given formaldehyde conversion, except free phenol which shows a sharp concentration decrease during the final stages of polymerization. The only Q_j^* species which appears at a significant extent is monomethylol phenol. However, the concentration of methylolated products is practically negligible for the final product. *Figure 3* shows the variation of formaldehyde conversion, x_F, and number average molecular weight:

$$\bar{M}_n = \left\{106 + \sum_{j=1}^{40}(18Q_j^* - 12P_j^*)\right\} \Bigg/ \left\{\sum_{j=1}^{40}(P_j^* + Q_j^*)\right\} \qquad (12)$$

as a function of reaction time, for different formaldehyde/phenol initial molar ratios (neglecting the Q_j^* concentrations gives practically the same $\bar{M}_n$). Novolacs with molecular weights ranging from 400–600 result from F^0/P_1^0:0.8–0.85 and $x_F>0.9$–0.95. These are standard conditions of the industrial practice. On the other hand, attaining formaldehyde conversions greater than 0.97–0.98 requires long reaction times, which may be uneconomical. The selected final conversion limits the molecular weight of the resulting product.

Figure 4 illustrates the weight distribution of the j-mers:

$$w_j = [P_j^*(106j-12) + Q_j^*(106j+18)]/$$

$$[106 + \sum_{j=1}^{40}(18Q_j^* - 12P_j^*)] \quad , \qquad (13)$$

for two formaldehyde/phenol initial molar ratios and a formaldehyde conversion, $x_F=0.98$. Increasing F^0/P_1^0 leads to a broader distribution with a definite maximum for a 5 or 6-mer.

Continuous reactors

In order to model the continuous reactor, the mixing characteristics must be first discussed. The appearance of

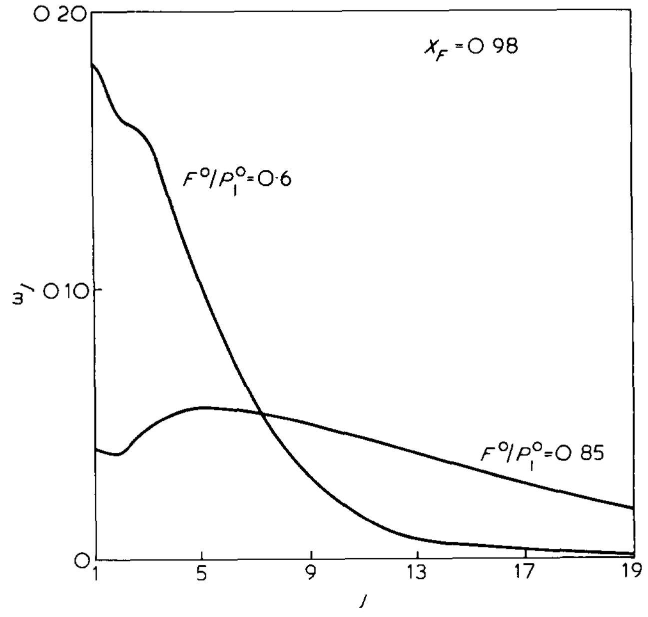

Figure 4 Weight distribution for a novolac obtained in a batch reactor with different formaldehyde/phenol initial molar ratios

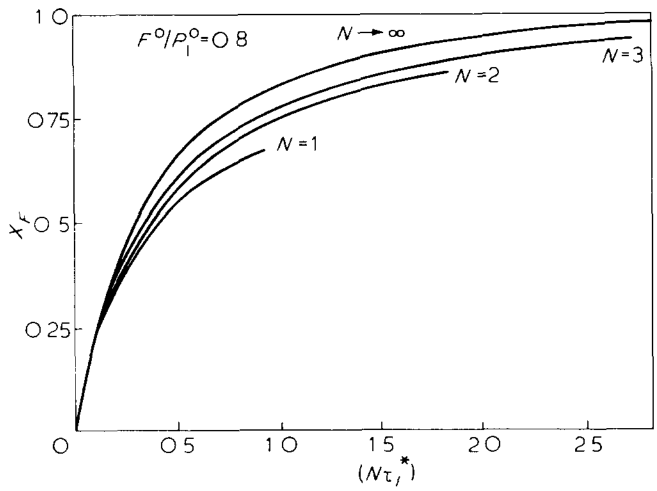

Figure 5 Formaldehyde conversion vs. total mean residence time for a polymerization carried out in a series of *N* ideal stirred tanks

two phases (water and polymer) at medium formaldehyde conversions and the high viscosity of the reacting mixture enable us to infer that actual mixing will be closer to macro rather than micromixing. For this case of segregated flow, the concentration of the j-mers at the reactor outlet in steady state, is given by:

$$P_j = \int_0^\infty P_j(t)|_{\mathrm{batch}} E(t)\,\mathrm{d}t \tag{14}$$

$$Q_j = \int_0^\infty Q_j(t)|_{\mathrm{batch}} E(t)\,\mathrm{d}t \tag{15}$$

$$F = \int_0^\infty F(t)|_{\mathrm{batch}} E(t)\,\mathrm{d}t\ , \tag{16}$$

where $E(t)$ is the residence time distribution for the actual reactor.

The series-of-stirred tanks model may be used to simulate the polymerization reactor by N ideal stirred tanks in series. The total volume of the tanks is the same as the volume of the actual reactor. Thus, for a given flow rate the total mean residence time is also the same. The $E(t)$ function for this model is given by[6]:

$$E(t) = \frac{(t/\tau_i)^{N-1}\exp(-t/\tau_i)}{\tau_i(N-1)!}\ , \tag{17}$$

where τ_i is the mean residence time in each tank.

On the other hand, the series-of-stirred tanks disposition is indeed used for the continuous polymerization of novolacs[1,2]. However, the parameter N to be used in equation (17) is the equivalent number of ideal stirred tanks which gives the same residence time distribution than the actual arrangement.

Equations (14) to (16) were numerically solved for $N = 1, 2$ and 3. *Figure 5* shows the formaldehyde conversion as a function of the total dimensionless mean residence time,

$$N\tau_i^* = N\,\mathrm{k}'_a P_1^0 \tau_i$$

and $F^0/P_1^0 = 0.8$. The curve for $N \to \infty$ represents a plug flow reactor or a batch process (making $t^* = N\tau_i^*$). Finite N values give rise to a smaller conversion than batch reactors for the same mean residence time. Also, the molecular weight distribution is broader in the former case, since it essentially averages many batch molecular weight distributions at various conversions[4].

A series of three ideal stirred tanks seems to be a reasonable alternative giving formaldehyde conversions, $x_F > 0.9$ at total mean residence times equivalent to the corresponding to batch reactors. *Figure 6* shows the molecular distribution which results from a series of three ideal stirred tanks, using a formaldehyde/phenol molar ratio, $F^0/P_1^0 = 0.85$, and a formaldehyde conversion, $x_F = 0.924$, attained at a total mean residence time, $(N\tau_i^*) = 2.7$. The resulting number average molecular weight is $\bar{M}_n = 411$, which is typical for commercial novolacs containing all the unreacted phenol. Thus, this arrangement seems plausible for the industrial production. For example, the Euteco Continuous Process[1,2] uses a series of two stirred tank reactors. However, their length to diameter ratio makes them more like plug flow reactors than conventional stirred tanks. The equivalent N is surely greater than two.

Let us now mention the influence of a partial degree of micromixing. For reaction orders greater than one, as is the present case, the micromixing is prejudicial[7]. In order to illustrate this effect, molar balances for a single stirred tank reactor in the limit of complete micromixing may be stated:

$$(P_1^0 - P_1)/\tau = \mathrm{k}'_a 3P_1F + \mathrm{k}'_c 3P_1 \sum_{j=1}^{\infty} Q_j \tag{18}$$

$$-P_i/\tau = \mathrm{k}'_a S_i P_i F + \mathrm{k}'_c S_i P_i \sum_{j=1}^{\infty} Q_j - \mathrm{k}'_c \sum_{j=1}^{i-1} S_j P_j Q_{i-j}\ ,\ i \geqslant 2 \tag{19}$$

$$-Q_i/\tau = \mathrm{k}'_c Q_i \sum_{j=1}^{\infty} S_j P_j - \mathrm{k}'_a S_i P_i F \tag{20}$$

$$(F^0 - F)/\tau = \mathrm{k}'_a F \sum_{j=1}^{\infty} S_j P_j \tag{21}$$

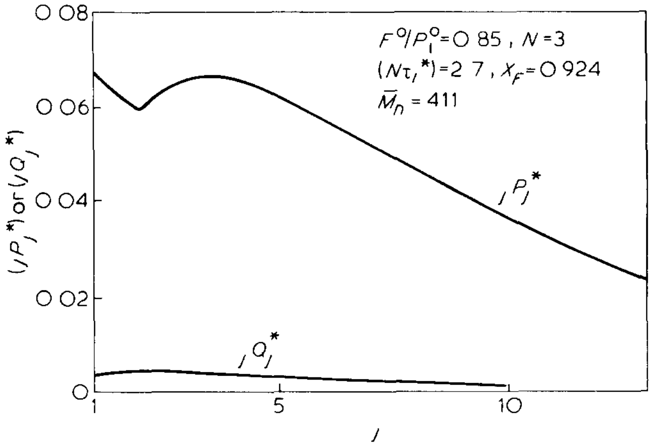

Figure 6 Molecular distribution for a novolac obtained in a series of three stirred tanks, at a total mean residence time close to the corresponding to the batch production for the same formaldehyde/phenol initial molar ratio

Equations (18) to (21) were numerically solved for a formaldehyde/phenol molar ratio $F^0/P_1^0 = 0.8$ and a dimensionless mean residence time, $\tau^* = 0.5$. Results showed a formaldehyde conversion, $x_F = 0.49$ and a remaining free phenol concentration, $P_1^* = 0.462$. For the corresponding segregated flow reactor, *Figure 5* shows $x_F = 0.55$ and $P_1^* = 0.392$. As expected, the performance of the segregated reactor is better. However, from these results one may infer that a partial degree of micromixing should not alter considerably results valid for the limit of completely segregated flow.

CONCLUSIONS

The behaviour of batch and continuous reactors for the production of standard novolacs has been simulated. The influence of the formaldehyde/phenol initial molar ratio and the formaldehyde conversion degree, on the characteristics of the resulting novolac was analysed. Results showed monomethylol phenol to be the only methylolated product present in significant concentrations; however, it disappeared at high formaldehyde conversions. A series of three ideal stirred tanks, operating at total mean residence times equivalent to those of batch reactors, was shown adequate for the continuous production of a typical novolac.

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