Kinetics of Hydroxymethyl Phenols Formation by In-Line FTIR Spectroscopy

Ida Poljanšek, Blaž Likozar, Matjaž Krajnc

Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, SI-1001 Ljubljana, Slovenia

ABSTRACT: The kinetics of phenol–formaldehyde pre-polymers catalyzed by sodium hydroxide at various temperatures was studied. Several reactions were conducted with different phenol to formaldehyde as well as phenol to sodium hydroxide molar ratios. The React-IR system was used to monitor the reaction as well as to determine residual free phenol and formaldehyde.

The changes in the concentrations of phenol and formaldehyde with the reaction time were determined. The value of the concentration of the hydroxide ion, [OH$^-$], was obtained by measuring the pH value of reaction mixture. The concentration of the hydroxide ion, [OH$^-$], expressed as a function of reaction time, was fitted by the six-order polynomial to the experimental data. On the basis of the proposed reaction scheme the kinetic model was developed.

The kinetic parameters were obtained by adjusting the experimental evolution of phenol and formaldehyde during the synthesis. Using this method the changes in the concentrations of five species of hydroxymethyl phenols with the reaction time was also been calculated. The activation energy and preexponential factor have been calculated for individual reactions. The accuracy of the kinetic model was confirmed by comparing experimental concentration profiles of formaldehyde and phenol with the calculated ones for different molar ratios. The experimental tendencies are in agreement with the results of the model. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 878–888, 2007

Key words: phenol–formaldehyde resins; kinetics; ReactIR; kinetic model

INTRODUCTION

The vital nature of phenolic resins in a diversity of applications attests to its present day importance within a spectrum of industries. They are indeed irreplaceable materials for selective high technology applications offering high reliability under severe circumstances.[1–3] One of the most used procedures for modified PF synthesis is the two step polymerization process, by which the 2,4,6-trihydroxymethyl phenol (THMP) is formed in the first step. Temperature and pH conditions under which reactions of phenols with formaldehyde are carried out have a profound effect on the characteristics of the resulting products.[4–6] In this step of formaldehyde addition to phenol, where different hydroxymethyl phenols are formed, the molar ratio between phenol and formaldehyde is of crucial importance.[7–9] Mono-, di-, or tri- hydroxymethyl phenols are synthesized with a molar excess of formaldehyde ($1 < F/P < 3$) under alkaline conditions at low temperatures (below 60°C) and they are stable at room temperatures, but are transformed into three-dimensional, crosslinked, insoluble, and infusible polymers by the application of heat.[10,11] Condensation reactions between hydroxymethyl phenols or condensation with phenol are negligible below 60°C and at high pH values. To clarify the complicated relationship between the phenol ring and formaldehyde functional group the present work is focused on the kinetic study of the formation of hydroxymethyl phenols.

The composition of phenol–formaldehyde prepolymers depends on the monomer ratio, type and amount of the catalyst, reaction conditions (temperature), and residual free monomers, therefore the determination of reliable kinetic data for hydroxymethyl phenols formation is complicated.[12–24] Because of the relatively difficult identification of reaction products it is not surprising that the reported kinetic data differ considerably.[14] To study the complex structures and kinetics of phenol–formaldehyde, many analytical techniques have been used such as high performance liquid chromatography,[5,24] IR spectroscopy,[25–29] ^{1}H and ^{13}C-NMR spectroscopy,[7,10,15,25,30] gel permeation chromatography,[30] and differential scanning calorimetry.[30] The influence of catalyst type on the reaction mechanism and kinetics has also been investigated,[4,31] as well as the influence of variable formaldehyde to phenol ratios before the crosslinking step.[32] Modragon and coworkers[5] analyzed the first step of the condensation reaction under controlled conditions: 80°C, formaldehyde to phenol

ratio 1 : 1.8, and initial pH value 8.0. Recently, Manfredi et al.[17] have presented the model of the synthesis of a resol-type phenolic resin at constant temperature and at constant pH value with different formaldehyde to phenol molar ratios. Riccardi et al.[18] have applied the model of Manfredi et al.[17] to study the influence of some of the other synthesis parameters on the kinetic scheme. Because of the lack of comprehensive information on phenol–formaldehyde reactions under very alkaline conditions in a wide range of pH values as well as in a wide range of temperatures and with different phenol to formaldehyde ratios, we chose to study the structural and kinetic differences between the prepolymers synthesized under different conditions. Authors in earlier kinetic studies neglected to consider the role of NaOH,[13] but Higuchi et al.[14] have developed a rate equation involving the concentration of the hydroxide ion which changes with the change in reaction composition. In their work the changes in the concentration of the hydroxide ion, phenol, formaldehyde, and products with the reaction time were described by computer simulation. Literature review reveals that kinetics of phenol–formaldehyde reactions were not studied in a wide range of temperature, catalysts concentration, and different phenol to formaldehyde ratio. Therefore a comprehensive kinetic study of the reaction of formaldehyde with phenol has been done. The influence of the molar ratio between phenol and formaldehyde as well as phenol to sodium hydroxide molar ratios on the phenol–formaldehyde prepolymers synthesis and on the composition of the synthesized product was investigated. In present work the model of Higuchi et al.[14] was adopted. However, the concentration of the [OH$^-$] ions was measured using pH values. The developed kinetic model was used to determine the concentrations of different components. The calculated concentrations were compared to the experimentally measured values of the concentrations of phenol and formaldehyde. Individual phenol and formaldehyde conversions and prepolymer composition changes as a function of time were determined by in-line ATR-FTIR spectroscopy when the condensation reaction was carried out.[25–31]

EXPERIMENTAL

Materials

Phenol (99+ %), 37% formaldehyde aqueous solution and sodium hydroxide (98%) were used. All the chemicals were supplied by Aldrich.

Synthesis of hydroxymethyl phenols

Hydroxymethyl phenols were synthesized in a 500 mL batch reactor fitted with a reflux condenser, a

mechanical stirrer, a digital thermometer, and an IR probe. Several batch condensations of phenol and formaldehyde were conducted at 30, 40, 50, and 60°C. Reaction vessels were heated to the same reaction temperature. Different hydroxymethyl phenols (Table I) were prepared with different amounts of the catalyst (0.1, 0.5, 0.8, and 1 mol of NaOH) and with different F/P ratios of 2.0, 2.5, and 3.0. The recipes used are shown in Table I.

All resins were prepared by the reaction of the required amounts of phenol (90% solution in water) with varying amounts of formaldehyde (37% solution in water, Merck) in the presence of the catalyst. First, 1 mol of phenol in aqueous solution (90% solution in water) and the required amounts of NaOH dissolved in water were charged into a reactor vessel. The sodium hydroxide solution was added to obtain reactive sodium methylolphenate and to adjust the pH value. The content was stirred and cooled because of the exothermic reaction. Varying amounts of formaldehyde (2.0, 2.5, and 2.5 mol) in aqueous solution were added at once in the reactor. After adding the formaldehyde solution the reactor content was heated to the four chosen reaction temperatures 30°C, 40°C, 50°C, and 60°C. The reaction was carried out for 6 h and the experiments were monitored by the in-line FTIR-ATR spectroscopy. The first spectra were collected after formaldehyde

TABLE I
Reaction Conditions of Hydroxymethyl Phenols Synthesis, Molar Ratio of Phenol, Formaldehyde, and NaOH at $t = 0$ and Temperature of Reaction Synthesis

Type of HMP	n phenol (mol)	n NaOH (mol)	n formaldehyde (mol)	T (°C)[a]
PF1/01/2/50	1.0	0.1	2.0	50
PF1/05/2/50	1.0	0.5	2.0	50
PF1/08/2/50	1.0	0.8	2.0	50
PF1/1/2/50	1.0	1.0	2.0	50
PF1/01/2.5/50	1.0	0.1	2.5	50
PF1/05/2.5/50	1.0	0.5	2.5	50
PF1/08/2.5/50	1.0	0.8	2.5	50
PF1/1/2.5/50	1.0	1.0	2.5	50
PF1/01/3/50	1.0	0.1	3.0	50
PF1/05/3/50	1.0	0.5	3.0	50
PF1/08/3/50	1.0	0.8	3.0	50
PF1/1/3/50	1.0	1.0	3.0	50
PF1/1/2/30	1.0	1.0	2.0	30
PF1/1/2.5/30	1.0	1.0	2.5	30
PF1/1/3/30	1.0	1.0	3.0	30
PF1/1/2/40	1.0	1.0	2.0	40
PF1/1/2.5/40	1.0	1.0	2.5	40
PF1/1/3/40	1.0	1.0	3.0	40
PF1/1/2/60	1.0	1.0	2.0	60
PF1/1/2.5/60	1.0	1.0	2.5	60
PF1/1/3/60	1.0	1.0	3.0	60

[a] Temperature at which we started to collect mid FTIR spectra of the condensation components.

addition. The samples for determining free formaldehyde and residual phenol content were withdrawn from the reaction vessel at selected reaction-time intervals. Afterwards, the resin is used as it is or it is neutralized.

FTIR spectroscopy

A ReactIR™ 4000 reaction analysis system equipped with a light conduit and DiComp (diamond composite) insertion probe was used to collect mid-FTIR spectra of the condensation components. The reaction mixture spectra of PF resin run were collected every 3 min for a total of 180 min in the wavenumber range between 4000 and 650 cm^{-1}. The spectra were recorded at a resolution of 8 cm^{-1} with 128 scans for each spectrum. These spectra were used to calculate the amounts of free phenol and free formaldehyde and to some extent the hydroxymethyl phenols composition. At the end of the synthesis the traditional titration method for determining free formaldehyde was carried out as well as gas chromatography to determine the residual phenol content.[27]

Kinetic model

According to the hydroxymethylation of phenol in aqueous alkaline media, the reaction scheme was predicted as shown in Figure 1. The initial reaction mixture comprises of phenol, NaOH, and formaldehyde. Phenol reacts with formaldehyde to form *ortho*- or *para*- monohydroxymethyl phenol; *ortho*, *para*-, or *ortho*, *ortho*- dihydroxymethyl phenol; and finally THMP. Seven reactions take place consecutively and competitively during the hydroxymethylation of phenol in aqueous alkaline media, where k_1, k_2, k_3, k_4, k_5, k_6, and k_7 are the stepwise rate constants for the formation of *ortho*- or *para*- monohydroxymethyl phenol; *ortho*, *para*-, or *ortho*, *ortho*- dihydroxymethyl phenol; and finally THMP, respectively. The dehydroxymethylation reactions have been neglected. Each individual reaction has been assumed to be of the second order, i.e., first order with respect to each reaction component, to the concentration of the total free formaldehyde, and to the respective phenolic anion. The initial addition reaction of formaldehyde with phenol is faster than the subsequent condensation reaction between substituted phenol rings. Below 60°C and at high pH, the condensation reaction between hydroxymethyl phenols or condensation with phenol is negligible. Hydroxymethyl phenols are initially the predominant intermediate compounds. Therefore, the appearance and disappearance of each component in the system can be expressed as a function of time by eqs. (1)–(7).
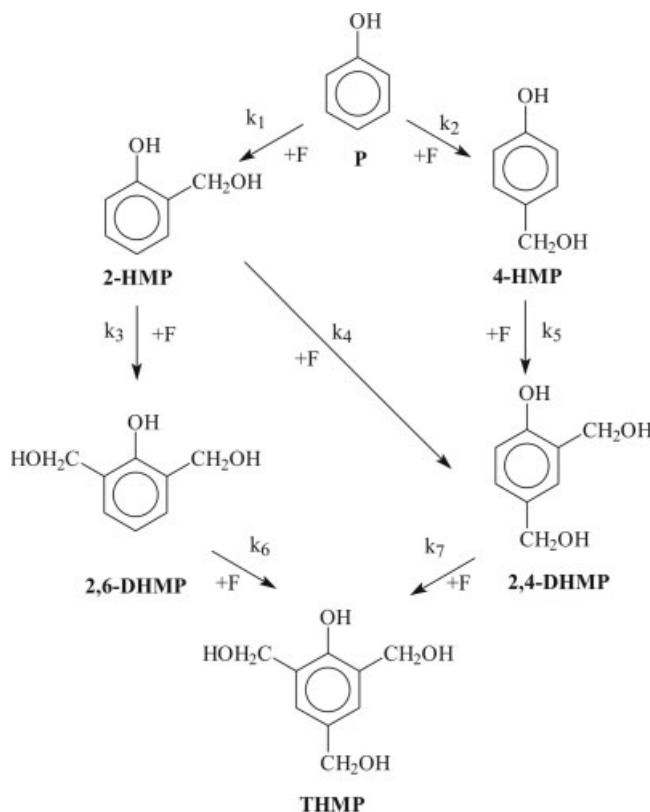
Figure 1 Reaction scheme for addition of formaldehyde to phenolic ring in aqueous alkaline media.

$$d[F]/dt = -((2^*k_1 + k_2)^*[F]^*[P^-]$$
$$+ (k_3 + k_4)^*[F]^*[2-HMP^-]$$
$$+ 2^*k_5{}^*[F]^*[4-HMP^-] + k_6{}^*[F]^*[2,6-DHMP^-]$$
$$+ k_7{}^*[F]^*[2,4-DHMP^-] \quad (1)$$

$$d[P]/dt = -(2^*k_1 + k_2)^*[F]^*[P^-] \quad (2)$$

$$d[2-HMP]/dt = 2^*k_1{}^*[F]^*[P^-]$$
$$- (k_3 + k_4)^*[F]^*[2-HMP^-] \quad (3)$$

$$d[4-HMP]/dt = k_2{}^*[F]^*[P^-]$$
$$- 2^*k_5{}^*[F]^*[4-HMP^-] \quad (4)$$

$$d[2,6-DHMP]/dt = k_3{}^*[F]^*[2-HMP^-]$$
$$- k_6{}^*[F]^*[2,6-DHMP^-] \quad (5)$$

$$d[2,4-DHMP]/dt = k_4{}^*[F]^*[2-HMP^-]$$
$$+ 2^*k_5{}^*[F]^*[4-HMP^-] - k_7{}^*[F]^*[2,4-DHMP^-] \quad (6)$$

$$d[THMP]/dt = k_6{}^*[F]^*[2,6-DHMP^-]$$
$$+ k_7{}^*[F]^*[2,4-DHMP^-] \quad (7)$$

T (°C)	pK_w
30	13.8330
40	13.5348
50	13.2617
60	13.0171

The differential equations involve the concentration of the ionic form of each phenolic component. Freeman and Lewis[13] used 1 mol of NaOH per mol of phenol in order that all phenolic components were in the anion form. The ionic concentrations can be calculated in terms of the sums of the concentrations of dissociated and undissociated phenols. Knowing the different acid ionization constants [dissociation constants, eqs. (8)–(13)] of the hydroxymethyl phenols at 25°C and the concentration of hydrogen ion $[H^+] = K_w/[OH^-]$ it has become possible to investigate the kinetics of the reaction under more realistic conditions with only the catalytic amount of NaOH (Table II). K_w is the equilibrium constant of the autodissociation reaction of water, called the ion product of water.

$$[H^+][P^-] = K_{a1}[PH] \qquad (8)$$

$$[H^+][2 - HMP^-] = K_{a2}[2 - HMPH] \qquad (9)$$

$$[H^+][4 - HMP^-] = K_{a3}[4 - HMPH] \qquad (10)$$

$$[H^+][2, 6 - DHMP^-] = K_{a4}[2, 6 - DHMPH] \qquad (11)$$

$$[H^+][2, 4 - DHMP^-] = K_{a5}[2, 4 - DHMPH] \qquad (12)$$

$$[H^+][THMP^-] = K_{a6}[THMPH] \qquad (13)$$

In eqs. (8)–(13), [PH], [2-HMPH], [4-HMPH], [2,6-DHMPH], [2,4-DHMPH], [THMP] represent the concentrations of corresponding undissociated phenols, whereas the K_{a1}–K_{a6} depict the dissociation constants of the six components.[1,14] To be formally correct and applicable to the general case, the concentration of undissociated phenol should be expressed as [PH] = [P]–[P$^-$], where [PH] is the concentration of undissociated phenol, [P$^-$] of dissociated phenol, and [P] is the concentration of the total amount of phenol. The same should be adapted to the other phenols. To detect the involvement of different reacting species arising from the higher acid strength of

the hydroxymethyl phenols generated, the value of the concentration of hydroxide ion, [OH$^-$], was obtained by measuring the pH value of the reaction mixture, which decreases as the reaction proceeds. The concentration of the hydroxide ion, [OH$^-$], expressed as a function of the reaction time, was fitted by the six-order polynomial to the experimental data. On the basis of the proposed reaction scheme the kinetic model was written down (Fig. 1). A set of seven simultaneous differential equations which involve the concentration of the hydroxide ion was obtained by combining eqs. (1)–(7) and eqs. (8)–(13). To solve the set of proposed kinetic equations the Rosenbrock algorithm was employed. The kinetic parameters were obtained by adjusting the experimental evolution of phenol and formaldehyde during the synthesis by means as a multiple parameter regression. Using this method the changes in the concentrations of five species of hydroxymethyl phenols with the reaction time may be calculated.

The activation energy and preexponential factor have been calculated for individual reactions. The accuracy of the mathematic model was confirmed by comparing experimental concentration profiles of formaldehyde and phenol with the calculated ones (using the estimated kinetic parameters) for different molar ratios. The experimental tendencies are in agreement with the results of the model.

RESULTS AND DISCUSSION

ATR-FTIR spectrometry was utilized to monitor the reaction of phenol with formaldehyde at 30, 40, 50, and 60°C. In-line data acquisition was performed by immersing the transmission probe directly into the reactor. Assignment of the characteristic peaks of phenol and formaldehyde was done using the previously collected spectra of both reactants in aqueous solution. The spectra of phenol and formaldehyde solutions are presented in Figure 2. The assignment of characteristic peaks was done on the basis of relevant literature and of our previous experimental work.[33,34] These signals were helpful in identifying the components of the condensation reaction of phenol and formaldehyde. We do have to emphasize that the literature assigned absorption bands to the various chemical groups did vary, as might be expected.[34]

The peak at 1370 cm^{-1} which corresponded to the phenol O—H in plane bend (observable in Fig. 3) diminished with the increasing concentration of base catalyst, because of the sodium hydroxide addition and the sodium methylolphenate formation.

The normalized phenol–formaldehyde resin spectra at the wavelengths in the range of interest for the PF resin synthesis are shown in Figure 4. As shown
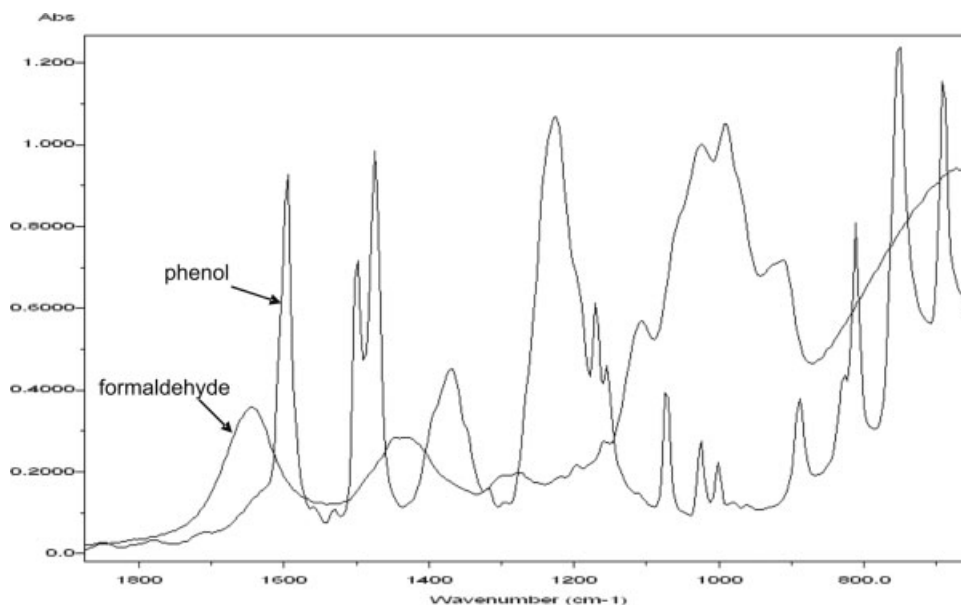
Figure 2 FTIR specta at the wavelengths in the range of interest for phenol and formaldehyde.

in Figure 4, the characteristic peaks of phenol at 1594, 1498, 1224, 1170, 999.7, and 748.8 cm^{-1} diminished with increasing reaction time, while the absorbance bands of C—O stretch and single bond C—O stretching vibrations of the hydroxymethyl groups at 1154 and 1058 cm^{-1}, respectively, increased.[31] The peaks at 1594 and 1498 cm^{-1} corresponded to the C=C aromatic ring vibrations. The peaks at 1224 and 1170 cm^{-1} corresponded to the C—C—O asymmetric stretch and C—H in plane deformations, respectively, while the 999.7 and 748.8 cm^{-1} peaks belonged to the C—H out of plane vibrations. The formaldehyde aqueous solution was added into the reactor at the beginning of

the process, therefore the characteristic peaks of methylene glycol C—O, O—H, and C—H bends at 1108 cm^{-1}, 1023 cm^{-1}, and 992 cm^{-1} were observed in the first spectrum, respectively, (Fig. 4). After the reactor content was heated to the preferred temperature a sharp decrease of phenol and formaldehyde peaks was observed as a result of the reaction.

At the beginning, the characteristic peak of the formaldehyde at 911 cm^{-1} decreased with increasing reaction time and at the temperature of 60°C slightly increased because of the conversion of hydroxymethyl groups into methylene bridges with the loss of formaldehyde and water. The absorbances for other characteristic groups were less observable
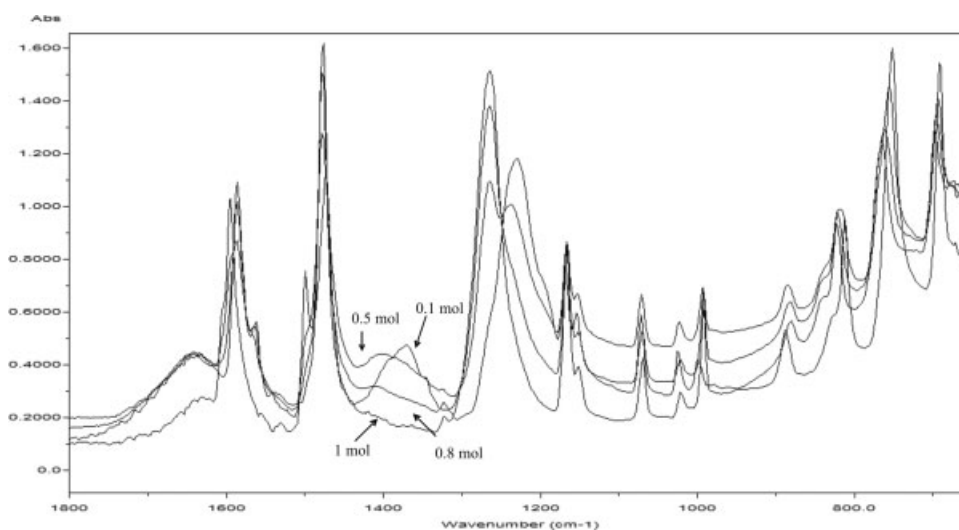

Figure 3 FTIR specta at the wavelengths in the range of interest for phenolate (0.1 mol of NaOH, 0.5 mol of NaOH, 0.8 mol of NaOH, 1 mol of NaOH per 1 mol of phenol).
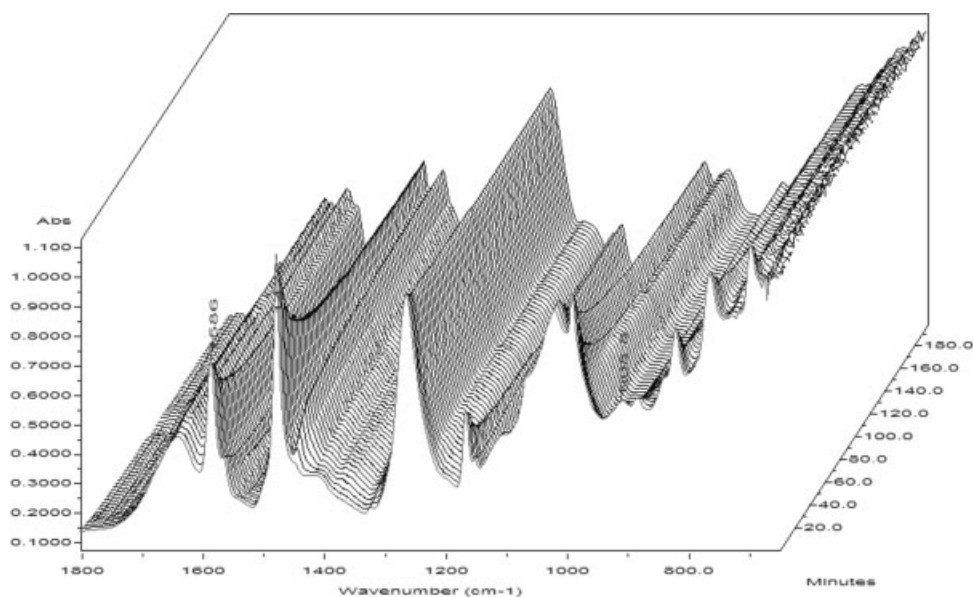
Figure 4 Reaction profile shows significant changes as the addition of formaldehyde to phenol (molar ratio FF1/1/2 at 50°C) occurs in range of 1800 cm^{-1}–650 cm^{-1}.

because they overlapped with other absorbances of the product. It can be observed (Fig. 4) that an additional peak occurred at 1610 cm^{-1}. This peak was attributed to C=C band vibrations of the product aromatic ring. In the phenol–formaldehyde resin spectrum additional characteristic signal of hydroxymethyl group C—H bend at 1478 cm^{-1} was present.

The changes in the concentrations of phenol and formaldehyde with the increasing reaction time were determined. A plot of the disappearance of phenol and formaldehyde at different temperatures as well as at different concentrations of base catalyst is shown in Figures 5 and 6, respectively. Figures 5 and 6 present the time evolution of phenol and formaldehyde consumption determined by means of the in-line IR measurements. The traditional titration method for determining free formaldehyde was carried out as well as gas chromatography to determine the residual phenol content. The calculated residual phenol content of final products was compared with those observed by GC. In spite of the different principle of measurements the agreement between the results is satisfactory. The consumption of monomers (phenol and formaldehyde) during the reaction was estimated by calculating the ratio between the absorbance at 1594 cm^{-1} (phenol) and the absorbance at 911 cm^{-1} (formaldehyde) at reaction time t and the corresponding peaks at the start of the polymerization reaction ($t = 0$). The in-line end values of the formaldehyde consumption (conversion) agreed well with those from the off-line traditional titration method. The concentration profiles for phenol in the synthesis of hydroxymethyl phenols at different temperatures as well as at different concentrations of

base catalyst agreed with the well known theory that in the synthesis of hydroxymethyl phenols the pH value of the reaction mixture has a great influence as well as does the temperature (Figs. 5 and 6). As the concentration of base catalyst increases, the rate of consumption of formaldehyde and phenol also increases, but only until the defined pH value is reached. After this limit the changes in the rate of consumption of formaldehyde and phenol were minimal and can be neglected in spite of the higher concentration of base catalyst. The influence of the pH value of the reaction mixture on the rate of consumption of formaldehyde and phenol was significant when 0.5 mol of NaOH per 1 mol of phenol is used instead of 0.1 mol of NaOH per 1 mol of phenol. Further increase in the pH value (0.8 mol of NaOH and 1 mol of NaOH per 1 mol of phenol) did not have an influence on the rate of consumption of formaldehyde and phenol (Fig. 6). The influence of the reaction temperature prevailed over the influence of the pH value of the reaction mixture. Besides, at higher temperatures the consumption of phenol and formaldehyde is higher.

In Table III the relative positional reaction rates in the phenol–formaldehyde reaction under alkaline conditions are shown where ortho substitution is set as unity.[4] It is more reasonable to compare the relative reaction rates. The rate constant of each entity is obtained by combining the reactivity ratio of each position related to the *ortho*-hydroxymethylene phenol kinetic constant value. This constant is obtained from the reaction between formaldehyde and the free ortho position of phenol. The reaction constants were collected on the basis of relevant
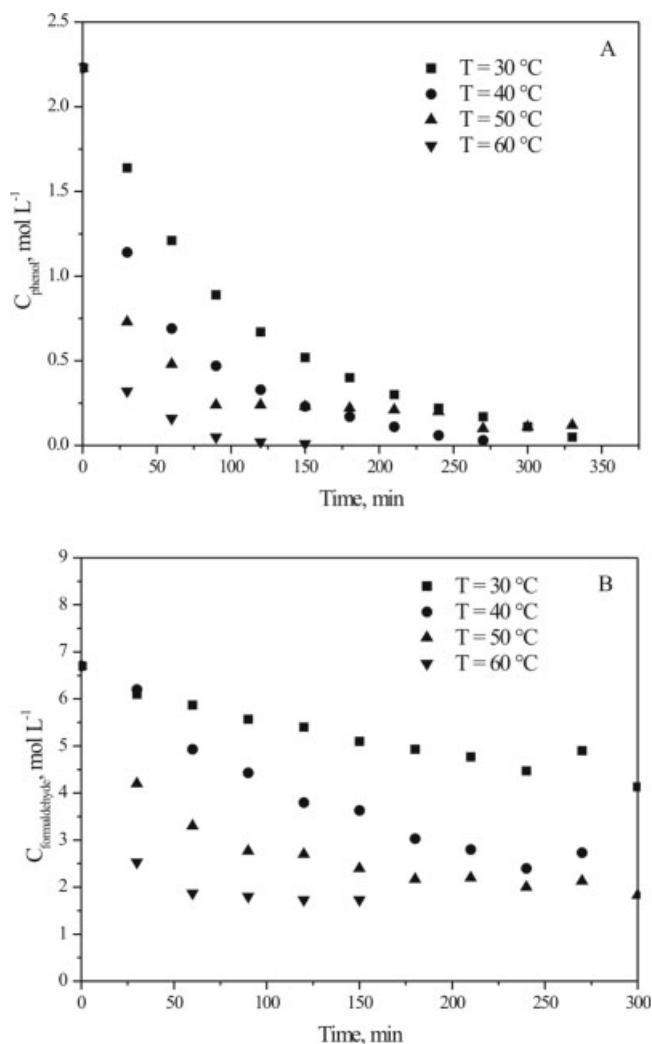
Figure 5 Concentration profile of phenol (A) and formaldehyde (B) for the synthesis of hydroxymethyl phenols at different temperatures for molar ratio phenol : formaldehyde = 1 : 3 with 1 mol of NaOH.

4-hydroxymethyl phenol especially 2,6-dihydroxymethyl phenol has a great affinity for formaldehyde addition. Table IV shows the calculated constant reaction values for addition reactions, expressed in L mol^{-1} s^{-1}, at different temperatures.

Concentrations of hydroxymethyl phenols synthesized under different conditions were compared to study the influence of the amount of catalyst and formaldehyde to phenol ratio on the constants of the formaldehyde addition to a free reactive position. At a higher concentration of base catalyst the reaction rate of 4-hydroxymethyl phenol formation is higher (Fig. 7), the concentration and the position of the maximum of 4-hydroxymethyl phenol increased. The reaction rate of 2-hydroxymethyl phenol formation slightly increased at higher amounts of catalyst, but on the other hand the concentration of 2-hydroxymethyl phenol diminished because of the higher reaction rate of further addition of formaldehyde to
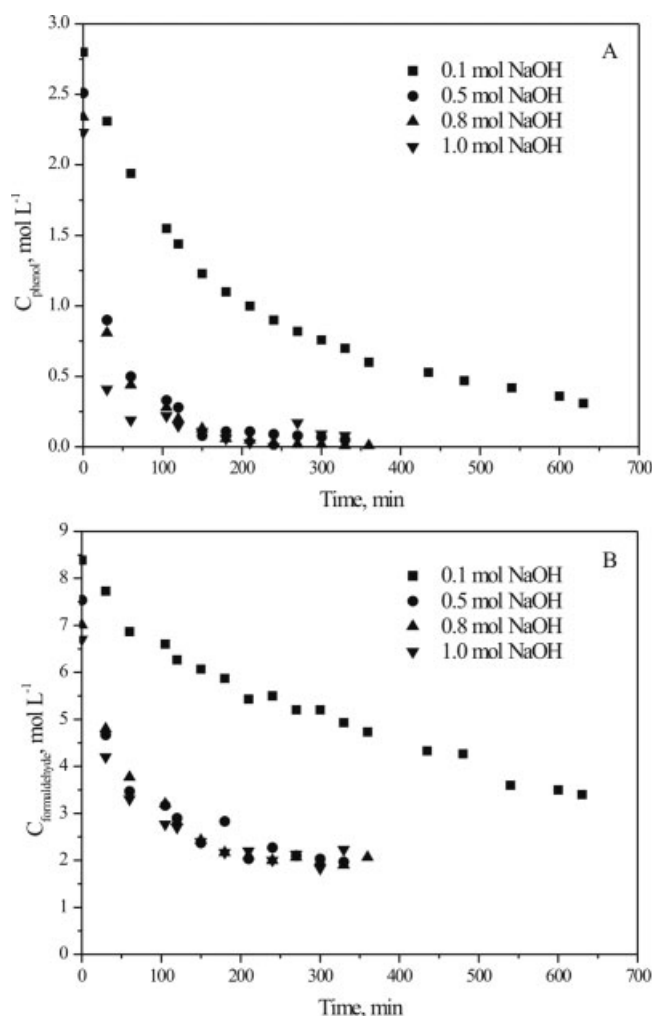

Figure 6 Concentration profile of phenol (A) and formaldehyde (B) for the synthesis of hydroxymethyl phenols at different concentration of base catalyst at 50°C for molar ratio phenol:formaldehyde = 1 : 3.

literature[13,21,22] and compared with the reaction constants obtained from our experimental work. As might have been expected there are considerable discrepancies among the kinetic data.

From the determined kinetic data several conclusions can be made. First, the para position in the phenol nucleus has greater affinity for formaldehyde addition than the ortho position. Nevertheless, the reaction rate of 2-hydroxymethyl phenol is higher because of the fact that two ortho positions are available. Influence of the electron attracting hydroxymethyl group was observed for 4-hydroxymethyl phenols, whereas the influence of the ring-deactivating hydroxymethyl group for 2-hydroxymethy phenol can be neglected. 2-Hydroxymethyl phenol is much more reactive than 4-hydroxymethyl phenol. Furthermore, 2,4-dihydroxymethyl phenol and 2,6-dihydroxymethyl phenol were more reactive than

TABLE III
Relative Positional Reaction Rates in the Phenol–Formaldehyde Reaction Under Alkaline Conditions, Ortho Substitution Set as Unity[14]

Reaction	Relative reaction rates				
	Freeman and Lewis[13] (1954) (30°C)	Minami and Ando[19] (1956) (40°C)	Zsavitsas and Beaulieu[20] (1967) (30°C)	Eapen and Yeddanapalli[22] (1968) (30°C)	Calculated, model, this work (40°C)
P + F → 2-HMP	1.00	1.00	1.00	1.00	1.00
P + F → 4-HMP	1.18	2.08	1.09	1.46	1.79
2-HMP + F → 2,6-DHMP	1.66	1.08	1.98	1.70	1.79
2-HMP + F → 2,4-DHMP	1.39	2.58	1.80	3.80	1.05
4-HMP + F → 2,4-DHMP	0.71	0.83	0.79	1.02	0.44
2,6-DHMP + F → THMP	7.94	3.25	3.33	4.54	7.03
2,4-DHMP + F → THMP	1.73	1.25	1.67	1.76	1.89

a free reactive position to form 2,4-dihydroxymethyl phenol and 2,6-dihydroxymethyl phenol. Relative reactivities for para substitution show greater pH sensitivity than those for ortho, due to the different transition states and different intermediates during the two types of substitution.

Formaldehyde to phenol ratio had an increasing effect on *para*-hydroxymethyl phenols but on the other hand had a decreasing effect on *ortho*-hydroxymethyl phenols at the catalyst amount of the 0.1 mol per 1 mol of phenol. The higher the formaldehyde to phenol ratio, the higher the amount of *para*-hydroxymethyl phenols was, whereas the amount of *ortho*-hydroxymethyl phenols was lower (Fig. 8) due to the further addition reaction of formaldehyde to a free reactive position. At higher concentrations of the catalyst i.e., 1 mol of NaOH per 1 mol of phenol, the molar ratio had a decreasing effect on the *ortho*- and *para*-hydroxymethyl phenols, causing the amount of *ortho*- and *para*-hydroxymethyl phenols to decrease as the F/P molar ratio increased (Fig. 9) because of the nature of competitive reactions. On the other hand the higher formaldehyde to phenol ratio had an increasing effect on the concentration of the final product, indicating that more of 2,4,6-THMP was formed as the reaction proceeds (Fig. 10). The reaction rate of 2,4,6-THMP increased with the increasing molar ratio between F/P. Formaldehyde to phenol ratio had a higher increasing effect

on the reactivity of second step reactions, where *para*-hydroxymethyl phenols and *ortho*-hydroxymethyl phenols reacted with additional molecules of formaldehyde. The addition reaction rate increases with the formaldehyde to phenol molar ratio.

In Figure 11 the concentration profiles for phenol, formaldehyde, and the reaction product were generated by the use of our kinetic model with the calculated kinetic data for the hydroxmethly phenols synthesis with the phenol/formaldehyde ratio 1/2.5 and 1 mol of NaOH at the reaction temperature of 40°C. The decrease of free phenol and on the other hand, the increase of mono-hydroxymethyl (2-HMP and 4-HMP), as well as the formation of di-(2,4-DHMP and 2,6-DHMP) and THMPs mono-hydroxymethyl phenols increased and then decreased due to the formation of dihydroxymethyl phenols and THMPs. The reaction rate of the formation of THMPs increased when the mono-hydroxymethyl groups reached the maximum. In the first 150 min the concentration of mono-hydroxymethyl groups increased and afterwards, when dihydroxymethyl phenols and THMPs were formed, the concentration started to decrease. The concentration of formaldehyde began to decrease from the beginning of the experiment. For the synthesis of hydroxymethyl phenols with the phenol/formaldehyde 1/2.5 ratio and 1 mol of NaOH at the reaction temperature of 40°C the concentration of free formaldehyde decreased

TABLE IV
Constant Rates for Addition Reactions

|	Freeman and Lewis[13] (1954) (30°C)	Calculated, model (30°C)	Calculated, model (40°C)	Calculated, model (50°C)	Calculated, model (60°C)
k_1 (L mol^{-1} s^{-1})	10.5×10^{-6}	11.4×10^{-6}	12.5×10^{-6}	23.2×10^{-6}	102.8×10^{-6}
k_2 (L mol^{-1} s^{-1})	6.2×10^{-6}	9.3×10^{-6}	11.2×10^{-6}	36.4×10^{-6}	58.6×10^{-6}
k_3 (L mol^{-1} s^{-1})	8.7×10^{-6}	5.7×10^{-6}	11.2×10^{-6}	26.5×10^{-6}	80.2×10^{-6}
k_4 (L mol^{-1} s^{-1})	7.3×10^{-6}	3.6×10^{-6}	6.6×10^{-6}	14.1×10^{-6}	60.2×10^{-6}
k_5 (L mol^{-1} s^{-1})	7.5×10^{-6}	1.3×10^{-6}	5.5×10^{-6}	32.0×10^{-6}	43.2×10^{-6}
k_6 (L mol^{-1} s^{-1})	41.7×10^{-6}	34.5×10^{-6}	43.9×10^{-6}	95.3×10^{-6}	159.4×10^{-6}
k_7 (L mol^{-1} s^{-1})	9.1×10^{-6}	7.3×10^{-6}	11.8×10^{-6}	20.9×10^{-6}	42.7×10^{-6}
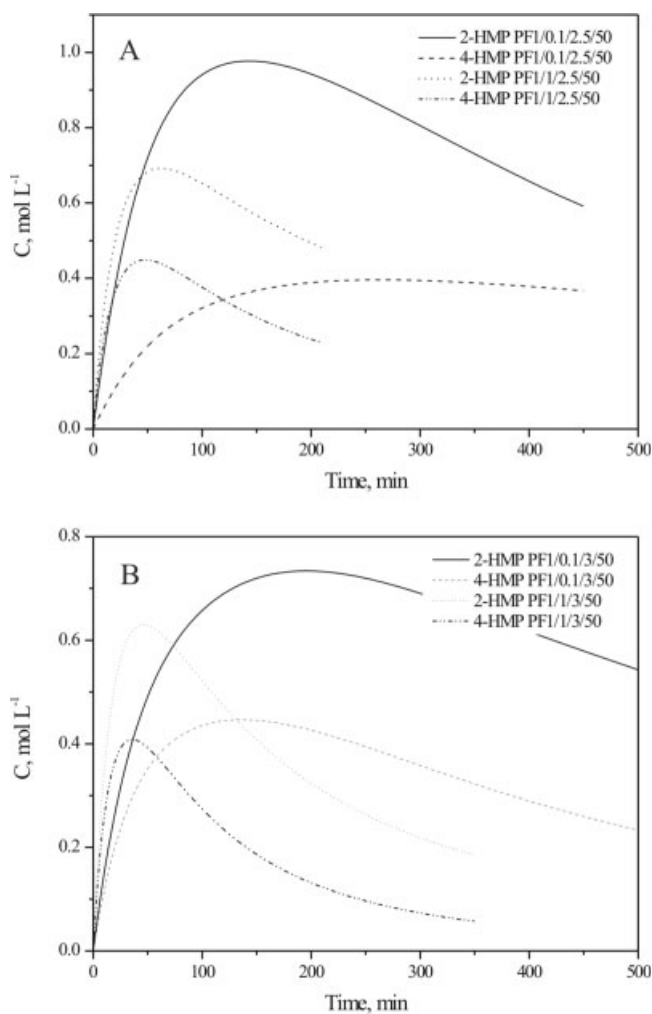
Figure 7 Concentration profile of 2-hydroxymethyl phenol and 4-hydroxymethyl phenol at the synthesis with different concentration of base catalyst at 50°C for molar ratio phenol : formaldehyde = 1 : 2.5 (A) and for molar ratio phenol : formaldehyde = 1 : 3 (B).
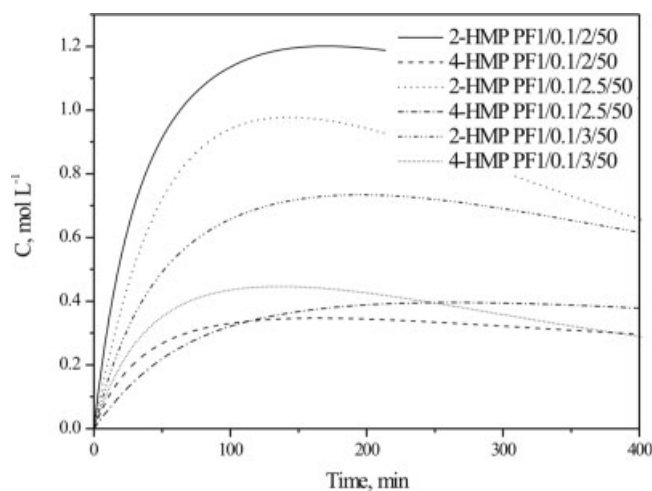
Figure 8 Concentration profile of 2-hydroxymethyl phenol and 4-hydroxymethyl phenol at the synthesis with different phenol to formaldehyde molar ratio and 0.1 mol of NaOH at 50°C.

from 6.14 mol/L to 2.93 mol/L at the end of the experiment. The in-line end values of the formaldehyde consumption agreed well with those from the off-line traditional titration method.

The activation energy (E_a) and frequency factor (A) were calculated from the linear plots of log k versus $1/T$. The calculated activation energy values for all the addition reactions together with literature values are presented in Table V. According to the reaction scheme, seven reactions take place consecutively and competitively during the hydroxymethylation of phenol in aqueous alkaline media, where E_{a1}, E_{a2}, E_{a3}, E_{a4}, E_{a5}, E_{a6}, and E_{a7} are the stepwise activation energies for the formation of *ortho-* or *para-* monohydroxymethyl phenol; *ortho, para-,* or *ortho, ortho-*dihydroxymethyl phenol; and finally THMP. The values show that variations in E_a are in the expected direction (Table V), the energy requirement for ortho

addition of formaldehyde to phenol has a higher energy requirement than the para addition reaction. The highest activation energy was found for the ortho addition reaction in 4-HMP, but on the other hand the lowest activation energy was calculated for the para and ortho addition reaction of formaldehyde to 2,6-DHMP and 2,4-DHMP, respectively. Values obtained in this work differ from those previously reported, especially for E_{a6} and E_{a7}.[13,18]

The consumption of phenol and formaldehyde may be calculated from the kinetic model by using optimized kinetic parameters. The accuracy of the kinetic model was confirmed by comparing experi-
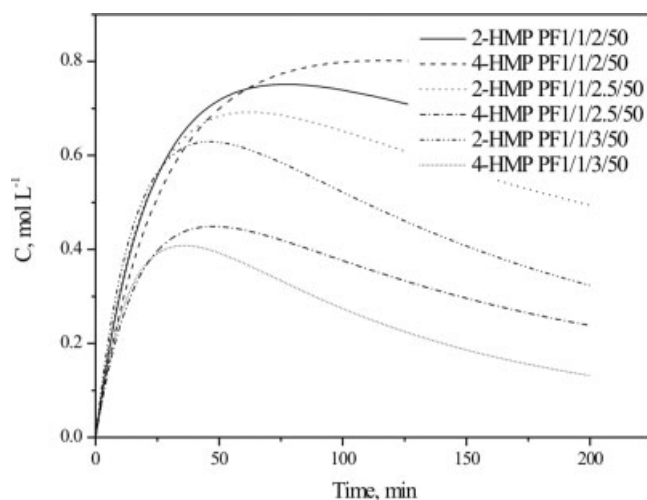

Figure 9 Concentration profile of 2-hydroxymethyl phenol and 4-hydroxymethyl phenol at the synthesis with different phenol to formaldehyde molar ratio and 1 mol of NaOH at 50°C.
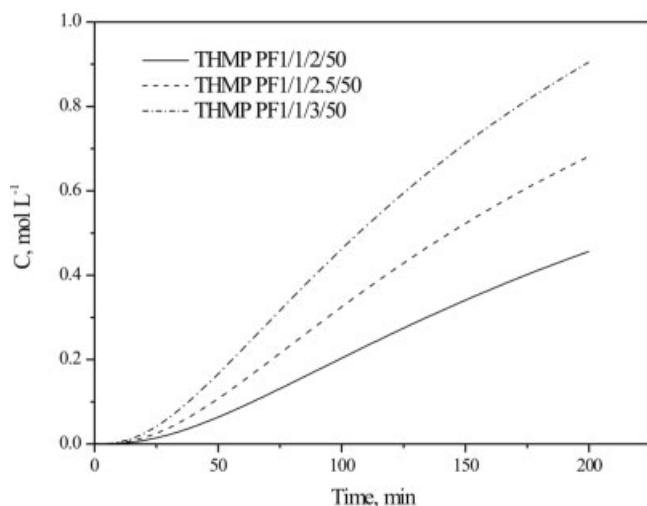
Figure 10 Concentration profile of 2,4,6-trihydroxymethyl phenol (THMP) at the synthesis with different phenol to formaldehyde molar ratio and 1 mol of NaOH at 50°C.

TABLE V
Activation Energies of Addition Reactions

Constant k_i	$E_{act.}$ (kJ mol^{-1}) Riccardi et al.[18] (2002)	$E_{act.}$ (kJ mol^{-1}) This work	k_0 (L mol^{-1} s^{-1}) This work
K_1	89.1	91.3	2.2×10^{10}
K_2	91.7	71.7	1.0×10^{7}
k_3	98.5	85.3	1.9×10^{9}
k_4	88.2	95.7	6.3×10^{10}
k_5	99.0	103.5	1.0×10^{12}
k_6	91.5	55.9	9.2×10^{4}
k_7	92.2	55.7	2.3×10^{4}

mental concentration profiles of formaldehyde and phenol with the calculated ones (using the estimated kinetic parameters) for different molar ratios of phenol to formaldehyde 1/2 in 1/3 and 1 mol of NaOH at reaction temperatures of 30°C, 40°C, 50°C in 60°C, as well as for reactions with a molar ratios of phenol to formaldehide 1/2, 1/2.5 in 1/3 and with 0.1 mol; 0.5 mol in 0.8 mol of NaOH at the reaction temperature of 50°C. The comparison of the calculated and experimental data representing the consumption of phenol and formaldehyde is illustrated in Figure 12. Concentrations of formaldehyde obtained by traditional titration method are presented. In general,
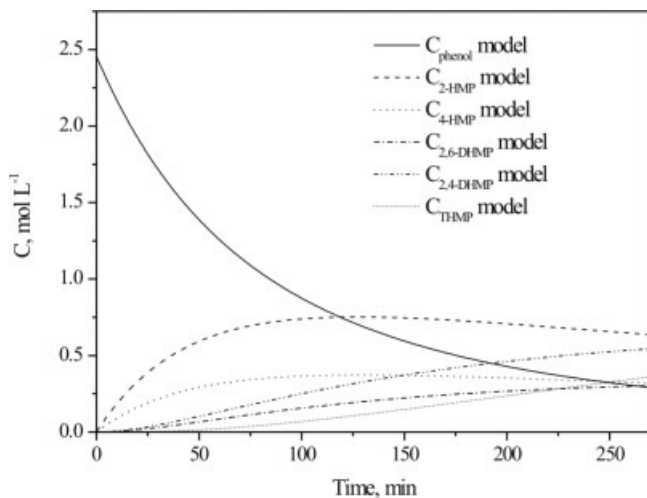
there is a fair agreement between the predicted and experimental values of the phenol and formaldehyde consumption for all the different molar ratios as well as for different molar concentrations of catalyst. On the other hand small discrepancies between predicted and experimental values of conversion were observed at higher temperatures (50°C and 60°C) where methylene-ether and methylene bridges can be formed to some extent, which was not incorporated in the kinetic model.

CONCLUSIONS

In-line FTIR-ATR spectroscopy was found to be a successful and informative analytical tool for determining individual phenol and formaldehyde conversions as well as intermediate and final product composition. The characterization of the chemical structure of hydroxymethyl phenols is very complex because of the many closely related isomers available. These prepolymers contain many active
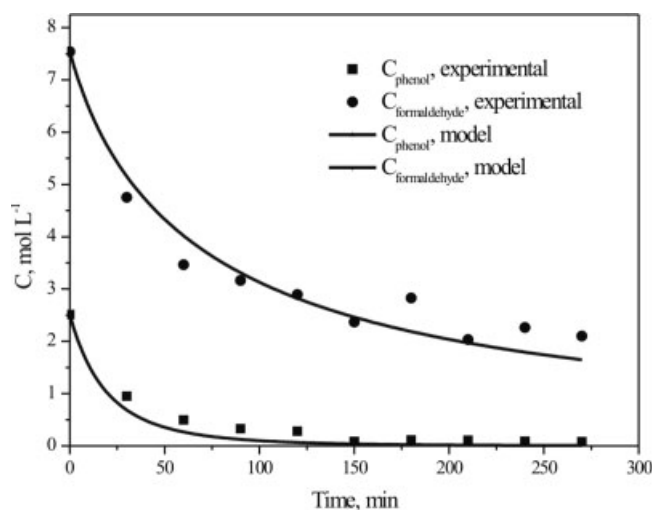

Figure 11 The concentration profiles for phenol (P), formaldehyde (F), 2-HMP, 4-HMP, 2,6-DHMP, 2,4-DHMP, and THMP during PF synthesis with phenol to formaldehyde molar ratio of 1 : 2.5 and 1 mol of NaOH at reaction temperature of 40°C.

Figure 12 The concentration profiles for phenol (P), formaldehyde (F) during PF synthesis with phenol to formaldehyde molar ratio of 1 : 3 and 0.5 mol of NaOH at reaction temperature of 50°C.

hydroxymethyl groups. It was observed that the structure of the PF resin depends on the initial molar ratio of F/P, temperature, and pH value. Different hydroxymethyl phenols were synthesized at four different temperatures (30, 40, 50, and 60°C) with different amounts of catalyst (0.1, 0.5, 0.8, and 1 mol of NaOH) and with different F/P ratios of 2.0, 2.5, and 3.0. It was observed that the intermediate product was actually a mixture of different hydroxymethyl phenols.

The semiempirical kinetic model for the prediction of phenol and formaldehyde conversion during the formation of hydroxymethyl phenols was developed in a relatively wide temperature range as well as in a wide pH range. The model incorporates the concentration of the hydroxide ion, [OH⁻], which has been shown to be an important parameter for controlling the composition of different hydroxymethyl phenols. The greater pH sensitivity in relative reactivities for para substitution than those for ortho was observed with the increase in the concentration of the hydroxide ion, [OH⁻], due to the different transition states and different intermediates during the two types of substitution. The increase in formaldehyde to phenol ratio increases the reactivity of second step reactions, where *para*-hydroxymethyl phenols and *ortho*-hydroxymethyl phenols reacted with additional molecules of formaldehyde. The kinetic model does not take into account the formation of methylene-ether bridges and methylene bridges. The modeling results may be used for the characterization of the addition reaction process of formaldehyde to phenol studied as well as for the prediction of the addition reaction behavior in a relatively wide temperature range, at different formaldehyde to phenol molar ratios and in a wide pH range. By comparing the model and experimental results it can be assumed that the mechanism of seven reactions, which take place consecutively and competitively during the hydroxymethylation of phenol in aqueous alkaline media, is a complex process with several intermediary steps. Through the development of the kinetic model of hydroxymethylation of phenol some insight into the mechanism of specific addition reactions has been gained.

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