

Estimation of Product Yield and Kinetic Parameters of Phenolic-Resin Pre-Polymer Synthesis using Acid and Base as Catalyst

*Uyigue, L. and Kubianga, E.O.

Department of Chemical Engineering, University of Port Harcourt, PMB 5323, Choba, Port Harcourt, Nigeria.
Corresponding Author: *Uyigue, L.

Abstract: In this paper, phenolic-resin polymerization was reviewed by placing emphasis on the influence of method of production and its operating conditions on the product yield and kinetics of phenol-formaldehyde pre-polymer synthesis. Batch and semi-batch techniques were used to synthesize novolac and resole resin pre-polymers using standardized phenol to formaldehyde mole ratios. The operating conditions for the reactions were varied in order to measure its influence on reaction performance and kinetics. The results obtained showed that yield of phenolic-resins generally increased with increasing catalyst concentration and reaction temperature. Optimum yield for novolac resin synthesized by batch process was 77.5 %; while that for novolac and resole resins synthesized by semi-batch processes were respectively 96.5 and 96.9 %. The propagation rate constant and rate of polymerization for novolac resins synthesized by batch process at 50 % catalyst concentration increased respectively from 0.000885 l/mols; 0.002166 mol/l/s to 0.005282 l/mols; 0.006902 mol/l/s even as reaction temperature increased from 40 to 100 °C. Similar trends were observed for other operating conditions. Also, the propagation rate constant and rate of polymerization for resole resin synthesized by semi-batch process increased respectively from 0.093×10^{-4} l/mols; 0.03 mol/l/s to 0.113×10^{-4} l/mols; 0.037 mol/l/s with decreasing reaction temperature and increasing catalyst concentration. Overall activation energy required for phenolic-resin pre-polymer synthesis lies between 30 and 40 kJ/mol

Keywords: Phenolic-resin pre-polymer, operating condition, kinetic parameter, synthesis technique and phenol-formaldehyde mole ratio

*corresponding author

Date of Submission: 29-09-2018

Date of acceptance: 14-10-2018

I. INTRODUCTION

Phenolic-resins have existed for several years now, but it has become irreplaceable because of the efficient characteristics of its products, commonly used as insulation/electrical materials, washing machine blades and molding powders (e.g. Bakelite or Formica or Micarta). Others are water soluble adhesives, varnishes, composite wood materials, industrial laminates etc. (Perez et al, 2007 and Nguyen et al, 2003). Basic raw materials for its production are phenol and formaldehyde. The latter is normally used in its monohydrate form called methylene glycol. Phenolic-resin products are of two types: novolac and resole. Novolac is produced under acidic condition with excess of phenol, while resole is produced under basic condition also with excess of formaldehyde (Bilmeyer, 2005).

Phenolic-resin synthesis is a complex process which is associated with loss of water; hence it is called condensation polymerization. The polymerization reaction is of two steps: pre-polymer synthesis and curing reaction. Novolac resin will normally be produced through methylation of phenol active positions and propagation of low hydroxymethylated phenol by electrophilic aromatic substitution into linear chains of methylene (or ether) bridged pre-polymer chain which is fusible and soluble in some solvent. In the same vein, resole resin is produced via a network of methylation and propagation reactions to forming mixtures of low and highly hydroxymethylated pre-polymer chains, which can be cured into an infusible and insoluble methylene (or ether) bridged resins (Gardziella et al, 2000).

The curing reaction involves gelation and vitrification processes, wherein resins of useful properties can be produced. Unlike resole, novolac resin may require an external curing agent (e.g. hexamethylene tetramine (HMTA)) normally introduced in a two-step process (Zhang et al, 1997). Note that the determination of a reliable kinetic data for phenolic-resin polymerization is a complicated exercise because of the occurrences of complex mixtures of products from the polymerization. In addition, it is also affected by reaction conditions, phenol-formaldehyde ratio, catalyst concentration (or pH), reaction temperature and degree of agitation (Atthajariyakul and Vanishseni, 2001).

In view of these challenges, many literature reports tends to focus on estimating the curing rate as a representative of the overall rate of polymerization of phenol-formaldehyde using simple kinetic expressions

which cannot be used for interpreting the propagation steps for wide ranged conditions, thereby leaving out the kinetics of the actual pre-polymer synthesis. For example, Biernath and Soane (1992) reported on the curing kinetics of epoxy-cresol-novolac; Krajnc et al (2000) reported on kinetic modeling of resole curing for industrial laminates production, while Lee et al (2003) studied the effect of activation energy on the curing behavior of resole- and novolac-type phenolic-resins. Also, Christjanson et al (2010) worked on the curing mechanism of resole phenol-formaldehyde resins.

Notable reaction routes for synthesizing phenolic-resin pre-polymers include simultaneous and parallel reactions. Others are consecutive and competitive propagation reactions. The challenge here is also in the determination of its kinetic parameters for which most reports are centered on in-line techniques which is acclaimed more reliable than the conventional experimental method. In this regard, Conner and Reeves (1999), and Mitsunaga et al (2000) had presented computational approaches for estimating kinetic parameters for phenol-formaldehyde pre-polymer reaction based on monomers atomic charges and transition state theory. The results obtained were observed to be consistent with other literature data as in Javitsas (1966) and Higuchi et al (1999), where phenolic-resin reaction rate constants were generally between 0.0113 and 0.054 l/mols.

Atthajariyakul and Vanishseni (2001) also reported on the kinetics of resole-type pre-polymer synthesis wherein rate equations and kinetic model formulations were established in line with a simultaneous reaction network proposed by Zavitsas (1966 and 1968). Values of seven kinetic parameters associated with the Zavitsas network were estimated and compared with other literature data. The rate constants for the reactions were observed to have increased as the reaction temperature and reagent concentration increases for all reaction steps.

Poljanšek and Krajnc (2005) performed an in-line monitoring of phenol-formaldehyde pre-polymer synthesis using method of attenuated total reflectance (ATR) in a Fourier transform infrared spectrometer (ReactIR 4000) equipped with light conduit and diamond-composite sensor. This technique measured the pre-polymer components and conversions as well as its dynamic concentration profiles. Kinetics data measured with this method agreed well with those determined by conventional experimental methods.

Grenier-Loustalot et al (1996) also studied the reactivity of substituted phenols using high-performance liquid chromatography and nuclear magnetic resonance spectroscopy to monitor the mechanism and kinetics of the reactivity of substituted phenols towards condensation reactions. Several factors were considered, for which para and ortho-positions in phenol favored high degree of substitution with methylene glycol group which in turn favors condensation of water molecules. Increased ionization constant of the phenol group causes increase in degree of substitution.

The focus of this present study is on phenolic-resin pre-polymer synthesis, vis-a-vis the effects of different synthetic methods, reaction temperature and catalyst concentration on its reactivity and kinetics. A simplified reaction mechanism is proposed for the competitive propagation of hydroxymethylated phenol by electrophilic aromatic substitution. The kinetic parameters for the pre-polymer's syntheses will be estimated based on experimental data. The curing reaction kinetics will however not be studied.

II. MATERIALS AND METHOD

2.1 Materials

The reagents used for this work are listed: formaldehyde (37 % w/w, Aldrich), phenol (90 % w/w, Aldrich), sulphuric acid (98 % w/w, BDH) and sodium hydroxide pellet (96 % w/w, Fisher). Sulphuric acid and sodium hydroxide were diluted and used as catalysts. Other materials and equipment used will be mentioned in the appropriate section.

2.2 Method

This section includes laboratory experiments for phenolic-resin synthesis, chemistry of phenolic-resin polymerization and kinetic parameter evaluation.

2.2.1 Synthesis of novolac-type resin

(a). Batch synthesis

Based on a phenol to formaldehyde mole ratio of 1:0.8, 80 ml of phenol liquid (90 % w/w), 33 ml of formaldehyde (37 % w/w) and 10 ml of sulphuric acid (50 % w/w) were added simultaneously into a 250 ml three-necked round bottom flask (fitted with a reflux condenser and a thermometer) and having its base placed on the cavity of a thermally controlled heating mantle operating at 40 °C and suspended by a clamp-retort stand apparatus. The flask was frequently agitated until a highly viscous consistency was formed. The viscous liquid was dried in an automated vacuum dryer to remove residual moisture. This liquid is called novolac-type pre-polymer. The reaction time and weight of product recovered were recorded. This procedure was also repeated for other reaction temperature (60, 80 and 100 °C) and concentration of catalyst (60, 70 and 80 %). The number of times for which the synthesis was repeated for different operating conditions were labeled as experimental runs A to N.

(b). Semi-batch synthesis

Using the same reactor assembly, and phenol to formaldehyde ratio of 1:0.8 as in section 2.2.1(a), 33 ml of formaldehyde (37 % w/w) was added drop-wise (or titrated) with the aid of a burette into a mixture of 80 ml of phenol liquid (90 % w/w) and 10 ml sulphuric acid (50 % w/w) contained in the flask at 89 °C amidst agitation. The reaction time and weight of product recovered was recorded. This procedure was repeated for other operating temperature (83, 80, 78 and 63 °C) and catalyst concentration (60, 65, 70 and 80 % w/w). Experimental runs for this section were labeled O to S.

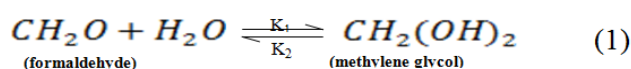
2.2.2 Synthesis of resol-type resin

A semi-batch method was also applied. 80 ml of phenol liquid (90 % w/w) and 10 ml sodium hydroxide (10 % w/w) were simultaneously added into the same reactor assembly mentioned in section 2.2.1(a). At 94 °C, 51 ml formaldehyde (37 % w/w) was added drop-wise (or titrated) based on a phenol-formaldehyde mole ratio of 0.8:1. The mixture was frequently agitated until solid resin was produced. The resin was recovered by drying using vacuum drier. Reaction time and weight of resin produced were recorded. This procedure was repeated for other reaction temperature (86, 82 and 81 °C) and catalyst concentration (20, 30 and 40 % w/w), while T to W were labeled as experimental runs for this section.

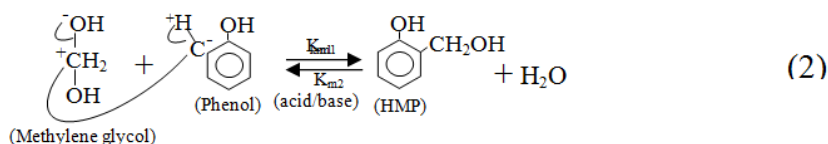
2.2.3 Chemistry of the phenolic-resin polymerization

(a). Hydration and Methylation step

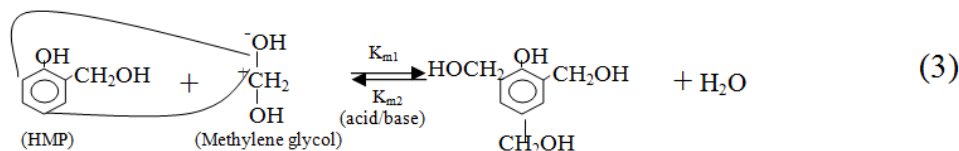
The first step is the hydration of formaldehyde which is an equilibrium reaction that favors the formation of methylene glycol.



where K_1 , K_2 and $K=K_1/K_2$ are rate and equilibrium constants for hydration of formaldehyde. The second step is the protonation of methylene glycol via electrophilic aromatic substitution activated by a catalyzed medium, for which the formation of hydroxymethylene phenol (HMP) and release of water is promoted.



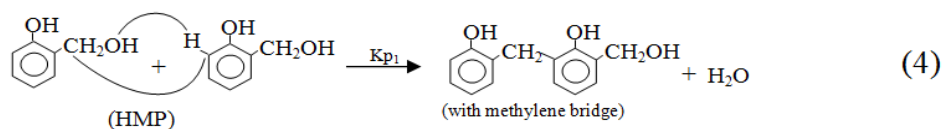
Where, k_{m1} , k_{m2} and $K_m=K_{m1}/K_{m2}$ are the rate and equilibrium constants for methylation. Excess formaldehyde will promote further hydroxymethylation in phenol free positions or active sites (in ortho and para positions) as shown in eq. 3.



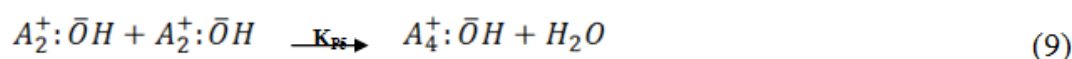
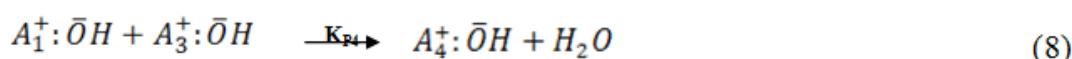
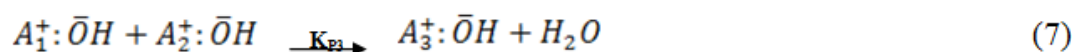
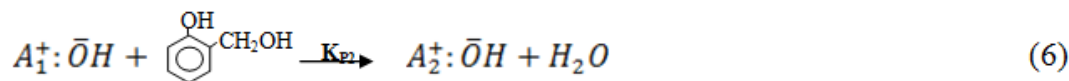
This is a condensation reaction step in which water molecule is eliminated.

(b). Propagation reaction step

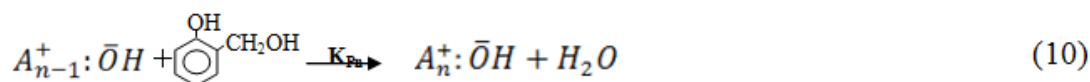
Several independent and competitive propagation reactions occur in this step with much of HMP molecules being consumed by electrophilic aromatic substitution and protonation, to cause continuous elimination of water. The propagation chain can be linear or networked depending on the number of free active positions in the phenol. Methylene group in the propagation acts as bridge between the phenol groups as shown in eq. 4.



Further propagation of methylene bridged phenol may continue in this independent order: eq. 6 to 10, where A_i^+ = Active methylene bridged phenols, and i = Strength (or number) of methylene bridges ranging from 1, 2, 3,.....,n.



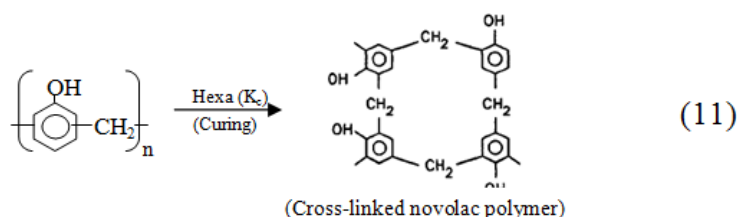
⋮



Where K_{Pi} ($i = 1, 2, 3 \dots n$) = Rate constants for propagation. Water is a by-product in the propagation step. It can be removed from the product by direct drying or through an open reactor process operating at near (or above) the boiling point of water.

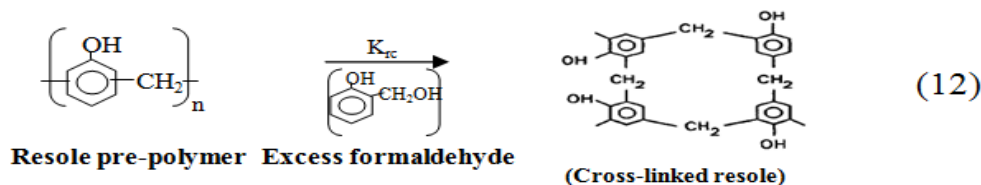
(c). Curing reaction step

The curing reaction step for novolac resin polymerization does not exist because of insufficient formaldehyde which serves as internal linking or bridging agent. For most applications, novolac pre-polymer is chemically blended with other external bridging agents (e.g. hexamethylene tetramine $[(\text{CH}_2)_6\text{N}_4]$) to form methylene bridged phenolic-resin (see eq.11).



Where K_c = Rate constant for curing (or cross-linking).

The curing step for resole resin polymerization is different from that of novolac, because further polymerization may be evident in other positions of activation in its aromatic ring (i.e. ortho or para). At temperatures above 60 °C, excess formaldehyde (or methylene glycol) cross-link with the propagation chain to form complex branched polymer called resole resin. Also, in resole curing step, the degree of methylene-bridging is much higher than the methylene-ether-bridging. This configuration depends strongly on curing temperature and catalyst concentration (or pH).



2.2.4 Kinetic expressions for phenolic-resin polymerization

Procedures for the kinetic parameters evaluation were generally the same for both novolac and resole pre-polymers.

(A). Hydration and methylation steps

The equilibrium constant, K, for hydration of formaldehyde is expressed below in eq.13 as:

$$K = \frac{k_1}{k_2} = \frac{[CH_2(OH)_2]}{[CH_2O][H_2O]} \quad (13)$$

Given that the concentration of distilled water at neutral point and 25 °C is a constant; Eq. (13) can be re-expressed as,

$$K[CH_2O] = [CH_2(OH)_2] \quad (14)$$

Also, the equilibrium constant for methylation, K_m is given as,

$$K_m = \frac{k_{m1}}{k_{m2}} = \frac{[HMP]}{[\phi-OH][CH_2(OH)_2]} \quad (15)$$

(B) Propagation reaction step

Rate expressions for some independent and competitive phenolic propagation reactions were considered for this step as presented:

$$-\frac{d[HMP]}{dt} = K_{P1}[HMP][HMP] + K_{P2}[A_1^+:\bar{O}H][HMP] \quad (16)$$

$$-\frac{d[A_1^+:\bar{O}H]}{dt} = K_{P2}[A_1^+:\bar{O}H][HMP] + K_{P3}[A_1^+:\bar{O}H][A_2^+:\bar{O}H] + K_{P4}[A_1^+:\bar{O}H][A_3^+:\bar{O}H] \quad (17)$$

$$-\frac{d[A_2^+:\bar{O}H]}{dt} = -K_{P2}[A_1^+:\bar{O}H][HMP] + K_{P3}[A_2^+:\bar{O}H][A_1^+:\bar{O}H] + K_{P5}[A_2^+:\bar{O}H]^2 \quad (18)$$

$$-\frac{d[A_3^+:\bar{O}H]}{dt} = -K_{P3}[A_1^+:\bar{O}H][A_2^+:\bar{O}H] + K_{P4}[A_1^+:\bar{O}H][A_3^+:\bar{O}H] \quad (19)$$

$$-\frac{d[A_4^+:\bar{O}H]}{dt} = -K_{P4}[A_1^+:\bar{O}H][A_3^+:\bar{O}H] - K_{P5}[A_2^+:\bar{O}H][A_2^+:\bar{O}H] \quad (20)$$

:

:

$$-\frac{d[A_{n-1}^+:\bar{O}H]}{dt} = -K_{Pn-1}[A_{n-1}^+:\bar{O}H][HMP] \quad (21)$$

The rate of polymerization, r_p is obtained by summing the different rates of propagation i.e. Eqs. (16) - (21) to give eq. 22.

$$K_{P1}[HMP][HMP] + K_{P2}[A_1^+:\bar{O}H][HMP] + K_{P3}[A_1^+:\bar{O}H][A_2^+:\bar{O}H] + K_{P4}[A_1^+:\bar{O}H][A_3^+:\bar{O}H] + \dots \dots \dots + K_{Pn-1}[A_{n-1}^+:\bar{O}H][HMP] \quad (22)$$

Assuming equal concentration of reactants and stable strength of propagation, such that,

$$K_{P1} = K_{P2} = K_{P3} = \dots K_{Pn} = K_P \quad (23)$$

For which the concentrations of the intermediate species become,

$$[A_1^+:\bar{O}H] = [A_2^+:\bar{O}H] = \dots = [A_{n-1}^+:\bar{O}H] = [HMP] \quad (24)$$

Then eq. 25 will become,

$$-r_p = nk_p[HMP][HMP] = k_p^I[HMP] \quad (25)$$

Where, n = average chain length of the phenolic-resin pre-polymer and $k_p^I = nk_p[HMP]$.

Thus, combining eqs. 14 and 15 and substituting into eq. 25 will give,

$$-r_p = k_p^I K_m K [\phi-OH] [CH_2O] \quad (26)$$

Assuming equimolar reactant system and constant density process for which formaldehyde and phenol are respectively the limiting reactants for novolac and resole synthesis, eq. 26 will be rewritten as,

$$-r_p = k_p^I K_m K [CH_2O]_0^2 (1 - X_p)^2 \quad (\text{Novolac}) \quad (27)$$

and

$$-r_p = k_p^I K_m K [Q-OH]_0^2 (1 - X_p)^2 \quad (\text{Re sole}) \quad (28)$$

Therefore, eqs. 27 and 28 gives the respective rate of polymerization for novolac and resole resin pre-polymer, where k_p^I , K_m and K are respectively the rate constant for propagation, equilibrium constants for methylation and hydration.

2.2.5 Kinetic parameters evaluation

(a). Activation Energy

The activation energy for the polymerization can be obtained from Arrhenius equation in eq. 29.

$$k_p^I = A e^{\left(\frac{-E}{RT}\right)} \quad (29)$$

Where, k_p^I = rate constant for propagation, A= frequency factor, E= activation energy, R= gas constant and T= temperature. Activation energy for the polymerization is calculated using eq. 30.

$$E = RT \ln\left(\frac{A}{k_p^I}\right) \quad (30)$$

The frequency factor, A is calculated from bimolecular gas-collision theory as presented in eq. 31.

$$A = \left(\frac{\sigma_1 + \sigma_2}{2}\right) \frac{N}{10^3} \sqrt{8\pi kT \left(\frac{1}{m_1} + \frac{1}{m_2}\right)} \quad (\text{Levenspiel, 1999}) \quad (31)$$

Where, N= Avogadro constant, mol⁻¹; σ_1 and σ_2 = collision or molecular diameters respectively for phenol and formaldehyde, Å (or m); m_1 and m_2 = molecular weight/N respectively for phenol and formaldehyde, g; k = Boltzmann constant, J/K; T= temperature, K.

(b). Rate constant for propagation

The rate constant for propagation, k_p^I for phenolic-resin's polymerization is measured using eqs.32 and 33, by subjecting eq.26 to integration based on the limits: $X_p \geq 0$ and $t \geq 0$, where X_p and t are respectively the overall conversion and reaction time for phenolic-resin polymerization.

$$\frac{X_p}{1 - X_p} = [CH_2O]_0 K_p^I K_m K t \quad (\text{for Novolac}) \quad (32)$$

$$\frac{X_p}{1 - X_p} = [Q-OH]_0 K_p^I K_m K t \quad (\text{for Re sole}) \quad (33)$$

Where, $[CH_2O]_0$ and $[Q-OH]_0$ = initial concentrations of formaldehyde and phenol, mol/l.

(c). Mass of water released

The amount of water released from the polymerization of phenol and formaldehyde is measured from material balance calculation as shown in eq.34 below.

$$m_{\frac{H_2O}{2}} = m_{(\phi-OH + CH_2O)_2} - \left[m_{(\text{phenolic resin})} + m_{(\text{unconverted reactants})} \right] \quad (34)$$

Where, m_{H_2O} = mass of water released, g; $m_{(\phi-OH+CH_2O)}$ = mass of reactants (phenol + formaldehyde); $m_{\text{phenolic-resin}}$ = mass of product (phenolic-resin), g; $m_{(\text{unconverted reactants})}$ = mass of unconverted phenol + formaldehyde.

III. RESULTS AND DISCUSSION

3.1 Yield of phenolic-resins polymerization

The yield of novolac resins synthesized from batch and semi-batch processes were generally observed to have increased with increasing reaction temperatures (40 - 100 °C) and catalyst concentrations (50 - 80 % w/w) for the given experimental runs A to N. For the batch process, 66.2 and 76 % were respectively obtained as minimum and maximum yield for novolac resin for the given operating conditions (Table 1 and Figure 1). Also evident is reduction in mass of water released from the same process as reaction time reduces over the reaction temperature range of 40 to 100 °C. For instance, at fixed catalyst concentration of 50 % w/w, the reaction time and mass of water released reduced respectively from 23 mins; 41.04 g to 6 mins; 29.99 g. These trends were replicated in all the experimental runs as shown in Figure 2, indication that reaction temperature and catalyst concentration greatly affects the amount of water released in a novolac resin polymerization.

Table 1: Yield of novolac resin and mass of water released from batch process at different temperature and catalyst concentration.

Experimental run	Catalyst conc. (%w/w)	Reaction temperature (°C)	Reaction time, t (mins)	Yield of novolac (%)	Mass of water released (g)
A	50	40	23	66.2	41.04
B		60	16	69.6	36.91
C		80	8	73.3	32.42
D		100	6	75.3	29.99
E	60	40	15	69.2	37.4
F		60	8	71.8	34.24
G		80	5	74.6	30.84
H		100	2	77.3	27.56
I	70	40	6	71.2	34.97
J		60	3	74.3	31.2
K		80	2	76.4	28.66
L		100	1	77.5	27.32
M	80	40	2	74.3	31.21
N		60	<1	75.9	29.26

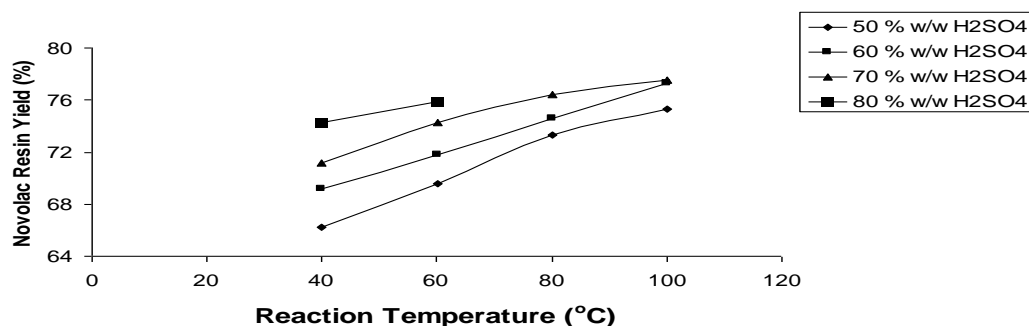


Figure 1: Plots of yield of batch synthesized novolac resin versus reaction temperature

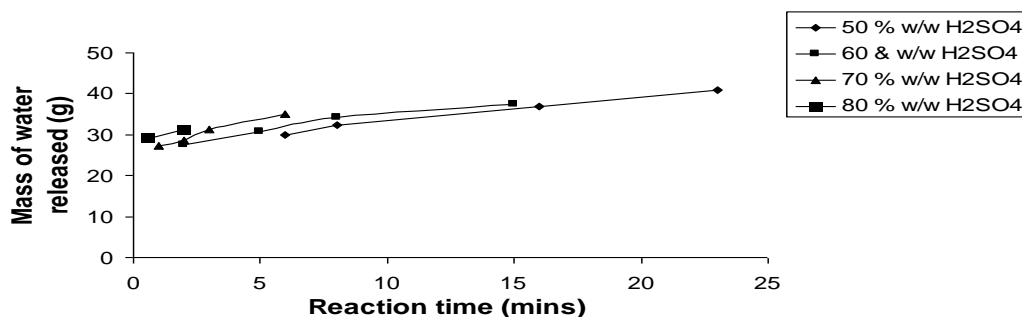


Figure 2: Plots of mass of water released from the novolac resin batch process versus the reaction time

The semi-batch process also showed significant increase in yield of novolac resin at increased reaction temperature and catalyst concentration for the different experimental runs: O to S, when compared with the batch process. Thus, maximum yield of 96.5 % for novolac resin was obtained at 80 % w/w acid catalyst concentration and 63 °C reaction temperature, while a minimum yield of 67.1 % was obtained at 50 % w/w acid catalyst concentration and at reaction temperature of 89 °C (Table 2). The higher yield of novolac resins evident in the semi-batch process as against the batch process was attributed to the enough contact time between formaldehyde and phenol as provided by the drop-wise addition of formaldehyde into the reactor. This also explains the reduction in mass of water released in the semi-batch process as in Table 2.

Table 2: Yield of novolac resin and mass of water released from semi-batch processes at different reaction temperature and catalyst concentration

Experimental run	Catalyst Conc. (%w/w)	Reaction temperature (°C)	Reaction time, t (mins)	Yield of novolac (%)	Mass of water released (g)
O	50	89	53	67.1	39.95
P	60	83	45	77.3	27.56
Q	65	80	39	83.1	20.52
R	70	78	30	94.8	6.31
S	80	63	18	96.5	4.25

In the case of resole resin synthesis, NaOH was used as catalyst, yet high yield of resole resins were obtained for the different experimental runs: T to W. Changes in catalyst concentration and reaction temperature did not have meaningful effect on the resole resin yield, because the resole resin's yield were almost constant for all the experimental runs. It only increased by 1.04 % even as the base catalyst concentration and reaction temperature changes respectively: 10 to 40 % w/w and 94 to 81 °C (Table 3). Similar trend was also observed for water released. Reason for this trend may be due to the characteristic curing reaction step associated with resole resin synthesis often caused by excess formaldehyde. Therefore, optimum condition for resole resins production would be at base catalyst concentration of 40 % w/w and reaction temperature of 81 °C.

Table 3: Yield of resole resin and mass of water released from semi-batch processes at different reaction temperature and catalyst concentration

Experimental run	Catalyst Conc. (%w/w)	Reaction temperature (°C)	Reaction time, t (mins)	Yield (%)	Mass of water released (g)
T	10	94	156	95.9	4.98
U	20	86	148	96.2	4.61
V	30	82	141	96.6	4.13
W	40	81	132	96.9	3.76

3.2 Kinetic parameters of phenolic-resin polymerization

The hydration of formaldehyde step was observed to be a fast reaction for both processes. This could be attributed to the low steric hindrance observed around the carbon centre for the methylene group in the formaldehyde, hence the equilibrium constant K, for hydration of formaldehyde for batch and semi-batch processes were obtained as 2 and 200. The low value of equilibrium constant for methylation step, K_m for both

batch and semi-batch processes (i.e. $K_m = 0.06$ and 0.068) also showed slow rate of methylation of the phenol group, which is probably due to steric repulsion by neighboring hydrogen atom or due to low bond energy of atom. Similar factors were adduced by Grenier-Loustalot et al (1996) to have affected the degree of substitution or reactivity of the phenol group.

Actual polymerization of phenolic-resins is evident in the competitive propagation step which follows a second order rate law, and it is also the step where much of the monomers are consumed. The strength and speed of the propagation step are measured by the propagation rate constant (k_p^I) and the rate of polymerization (r_p). Consequently, at catalyst concentration of 50 % w/w, wherein the reaction temperature varied from 40 to 100 °C, the k_p^I and r_p also increased in a corresponding order: 0.000885 l/mols; 0.002166 mol/l.s to 0.005282 l/ml.s; 0.006902 mol/l.s (Table 4). Similar trend was also observed for other batch of novolac resins synthesized with catalyst concentrations fixed at 60, 70 and 80 % w/w respectively, thus, it indicating that the kinetics of batch synthesis of novolac resin was highly influenced by catalyst concentration and temperature. This inference is corroborated by the works of Higuchi et al, (1999), Athajariyakul and Vanishseni (2001) where phenolic-resin reaction rate constants fell within similar range of values and were seen to also increase as reaction temperature increases.

Table 4: Kinetic parameters for novolac synthesis by batch process using sulphuric acid as catalyst

Experimental run	Reaction time, t (mins)	Reaction temperature (°C)	Propagation rate constant, K_p^I (l/mols) x 10^4	Rate of polymerization, r_p (mol/l.s) x 10^4
A	23	40	8.85	21.66
B	16	60	14.88	29.44
C	8	80	35.67	54.47
D	6	100	52.82	69.02
E	15	40	15.57	31.64
F	8	60	33.09	56.36
G	5	80	61.06	84.38
H	2	100	177.00	195.36
I	6	40	42.83	76.1
J	3	60	100.18	141.73
K	2	80	168.27	200.74
L	1	100	358.08	388.28
M	2	40	150.28	212.59
N	0.8	60	409.26	509.12
* Hydration and methylation equilibrium constants: $K = 2$, $K_m = 0.06$				
**Initial concentration of Phenol, $(Q-OH)_0 = 10.25$ mol/l				
***Initial concentration of Formaldehyde, $(CH_2O)_0 = 13.36$ mol/l				

For novolac and resole resins synthesized by semi-batch process, k_p^I and r_p for both syntheses increased with decreasing reaction temperature and increasing catalyst concentration. For novolac synthesis, both k_p^I and r_p respectively increased from 0.036×10^{-4} l/mols; 0.0086 mol/l.s to 1.14×10^{-4} l/mols, 0.27 mol/l.s even as the reaction temperature decreases from 89 to 63 °C at increased catalyst concentration of 50 to 80 % w/w (Table 5). Similar trend was also evident for the semi-batch resole resin synthesis (Table 6). This trend is at variance to Athajariyakul and Vanishseni (2001) wherein phenolic-resin rate constant increases with increasing reaction temperature. Thus, difference in method of synthesis may probably be the cause.

Table 5: Kinetic parameters for novolac synthesis by semi-batch process using sulphuric acid as catalyst

Experimental run	Reaction time, t (mins)	Reaction temperature (°C)	Propagation rate constant, K_p^I (l/mols) x 10^4	Rate of polymerization, r_p (mol/l.s) x 10^4
O	53	89	0.036	85.68
P	45	83	0.072	168.5
Q	39	80	0.12	280.74
R	30	78	0.57	1353.13
S	18	63	1.14	2687.74
* Hydration and methylation equilibrium constants: $K = 200$, $K_m = 0.086$				
**Initial concentration of Phenol, $(Q-OH)_0 = 10.25$ mol/l				
***Initial concentration of Formaldehyde, $(CH_2O)_0 = 13.36$ mol/l				

Table 6: Kinetic parameters for resole resins synthesis by semi-batch process using sodium hydroxide as catalyst

Experimental run	Reaction time, t (mins)	Reaction temperature (°C)	Propagation rate constant, K_p^1 (l/mols) x 10 ⁴	Rate of polymerization, r_p (mol/l/s)
T	156	94	0.093	0.030
U	148	86	0.083	0.027
V	141	82	0.094	0.031
W	132	81	0.113	0.037
* Hydration and methylation equilibrium constants: $K = 200$, $K_m = 0.086$				
**Initial concentration of Phenol, $(Q-OH)_0 = 10.25$ mol/l				
***Initial concentration of Formaldehyde, $(CH_2O)_0 = 18.41$ mol/l				

Activation energy for novolac resin synthesis was observed to increase with increased reaction temperature. For instance, at catalyst concentration of 50 % w/w, the activation energy for novolac resin synthesis increased from 24.4 to 30.5 kJ/mol even as reaction temperature increased from 40 to 100 °C (Table 7). This trend was also evident at catalyst concentrations of 60 and 70 % w/w, thus, indicating that lower catalyst concentration (< 50 % w/w) will favor reduction in activation energy for phenolic-resin synthesis.

Table 7: Activation energy for novolac resins synthesis using a batch process

Experimental run	Catalyst conc. (% w/w)	Temperature (°C)	Ratio of Arrhenius factor to propagation rate constant (A/k_p^1)	Activation Energy, E (kJ/mol)
A	50	40	11767.51	24.39
B		60	15100.15	26.64
C		80	16790.48	28.55
D		100	18900.26	30.54
E	60	40	353539.07	33.25
F		60	467959.99	36.15
G		80	540900.87	38.74
H		100	583148.51	41.17
I	70	40	157955.48	31.15
J		60	202608.55	33.83
K		80	241251.95	36.37
L		100	283428.18	38.93

IV. CONCLUSION

The yield and kinetics of phenolic-resin synthesis were strongly affected by two major factors: method of synthesis and operating conditions for reaction. Semi-batch syntheses favored higher yield of novolac and resole resins than batch syntheses. Yield of phenolic-resins syntheses generally increased with increasing catalyst concentration and reaction temperature for which 77.5 % was optimum for novolac resin synthesized by batch process, while 96.5% and 96.9 % were respectively optimum for novolac and resole resins synthesized by semi-batch process.

Kinetic expressions for both novolac and resole resins propagation follows a second order rate law. The propagation rate constant and rate of polymerization of phenolic-resins synthesized by batch process increases with increased reaction temperature, while that synthesized by semi-batch process increases with decreased reaction temperature. Overall activation energies required for phenolic-resin polymerization lies between 30 and 40 kJ/mol

SYMBOL AND ABBREVIATION

K = Equilibrium constant for hydration
 K_m = Equilibrium constant for methylation
 X_p = Conversion for phenolic-resin
 k_p^1 = Rate constant for propagation, l/mols
 r_p = Rate of polymerization, mol/l/s
E = Activation energy, kJ/mol
A = Frequency factor, kJ/mol

R = Universal gas constant, J/molK

m_{H_2O} = Mass of water released, g

A_i^+ = Active methylene bridged phenol chain

$[Q - OH]$ = Concentration of phenol, mol/l

$[HMP]$ = Concentration of hydroxyl methylene phenol, mol/l

ATR = Attenuated total reflectance

FT-IR = Fourier transform infrared

NMR = Nuclear Magnetic resonance

HMTA = Hexamethylene tetra-amine

REFERENCES

- [1]. Atthajariyakul, S. and Vanichseni, S. (2001) Development of a kinetic model for resole-type phenolic-resin formation. *Thammasat International Journal of Science and Technology*, 6(3): 12-18.
- [2]. Biernath, R.W. and Soane, D.S. (1992) Cure kinetics of epoxy cresol novolac encapsulants for microelectronics packaging. *Contemporary Topics in Polymer Science*, 7: 130-159.
- [3]. Billmeyer, F.W. (2005) *Textbook of polymer science*, 3rd edition, John Wiley and Sons Inc., Singapore.
- [4]. Conner, A.H. and Reeves, M.S. (1999) Reaction of formaldehyde at the ortho and para-positions of phenol: exploration of mechanisms using computational chemistry. *Adhesives Technical Interest Group Session: FPS annual meeting*: 483 – 487.
- [5]. Christjanson, P., Pehk, T., and Paju, J. (2010) Structure and curing mechanism of resole phenol-formaldehyde pre-polymer resins. *Proceedings of the Estonian Academy of Sciences*, 59(3): 225-232.
- [6]. Gardziella, A., Pilato, L.A. and Knop, A. (2000) *Phenolic-resins: chemistry, applications, standardization, safety and ecology*. Springer-Verlag Berlin Heidelberg.
- [7]. Grenier-Loustalot, M., Larroque, S., Grenier, P., and Bedel, D. (1996) Phenolic resins: self- condensation of methylolphenols in formaldehyde-free media. *Polymer*, 37(6): 955-964.
- [8]. Higuchi, M., Nohno, S. and Morita, M. (1999) Kinetics of the base-catalyzed hydroxymethylation of phenol. *In: International Contribution to Wood Adhesion Research*. A.W Christiansen and L.A. Pilato eds. Forest Products Society, Madison, WI: 101-107.
- [9]. Krajnc, M., Golob, J., Podrzaj, J. and Barboric, F. (2000) A kinetic model for resole curing in the production of industrial laminates. *Acta Chim. Slov.* 47: 99 - 109.
- [10]. Lee, Y.K., Kim, D.J., Kim, H.J. and Sokolov, J. (2003) Activation energy and curing behavior of resole- and novolac-type phenolic-resins by differential scanning calorimetry and thermogravimetric analysis. *Journal of Applied Polymer Science*, 89(10): 2589 – 2596.
- [11]. Levenspiel, O. (1999) *Chemical reaction engineering*, 3rd edition. John Wiley and Sons Inc. New York.
- [12]. Mitsunaga, T., Conner, A.H., and Hill, C.G. (2000) Reaction of formaldehyde with phenols: a computational chemistry study. *Proceedings on Wood Adhesives, Nevada*: 147-153.
- [13]. Nguyen, M.T., Kryachko, E.S. and Vanquickenborne, L.G. (2003) *The chemistry of phenols: general and theoretical aspects of phenols*, Z. Rappoport edition. John Wiley and Sons Ltd. England.
- [14]. Perez, J.M., Rodriguez, F., Alonso, M.V. and Echeverria, J.M. (2007) Characterization of a novolac resin substituting phenol by ammonium lignosulfonate as filler or extender. *Bio-Resources* 2(2): 270 -283.
- [15]. Poljanšek, I. and Krajnc, M. (2005) Characterization of phenol-formaldehyde pre-polymer resins by in line FT-IR spectroscopy. *Acta Chimica Slovenica*, 52: 238 –244.
- [16]. Zhang, X., Looney, M.G., Solomon, D.H. and Whittaker, A.K. (1997) The chemistry of novolac resins. *Polymer*, 38(23): 5835-5848.
- [17]. Zavitsas, A.A. (1968) Base-catalyzed hydroxymethylation of Phenol by aqueous formaldehyde. *Kinetics and Mechanism, Journal of Polymer Science: Part A-1*, 6: 2533 - 2559.
- [18]. Zavitsas, A.A. (1966) Kinetics of sodium hydroxide-catalyzed hydroxymethylation of phenol by formaldehyde, *Journal of America Chemical Society, Division of Organic Coatings and Plastics*, 26: 93 - 106.