The Effect of Phenol/Formaldehyde Ratio on the Char Yield from Phenolic Resins

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Synopsis

An idealized mechanism for the carbonization of phenolic resins was adopted and an equation was derived for the char yield. In simplified cases this was shown to be a function giving a maximum of 67.9% at a 1:1 formaldehyde/phenol molar ratio, falling rapidly at lower and slowly at higher ratios. In experimental verification, the alkali-catalyzed reaction of phenol and formaldehyde at various molar ratios was studied and the resulting resins were characterized and carbonized. The char yields were found to correspond well with predictions, with a maximum of about 67.2% in the region of 1.1:1 formaldehyde/phenol molar ratio.

INTRODUCTION

The nonoxidative pyrolysis of phenolic resins is a common process in the manufacture of carbon bodies, since these resins are versatile materials which can be used in many forms (e.g., foams, impregnants in laminates) and are reported to give good char yields.

Several authors[1-4] have given these yields as being in the range of 50%–55%, but more recent reports[5-7] have cited yields of over 60% and our preliminary studies gave results of 65%–70%. This communication develops a theoretical approach to the maximum char yield from a pure phenol–formaldehyde resin and shows by experimental studies of a series of resins the applicability of the equations so derived.

In this approach considerable use has been made of the pyrolysis mechanism invoked by Madorsky[4] and amplified considerably by Parker and Winkler.[8] These authors postulate homolytic scission of the carbon–carbon bond connecting terminal phenolic rings to the main chain as the initiating step at 300°C and the only one in which aromatic carbon atoms are lost from the polymer. Above 500°C, methylene linkage atoms and hydroxylic oxygen atoms are also lost. Free methylol groups would also be lost and, effectively, the char would comprise only the carbon atoms in all phenol rings other than those terminating chains. At temperatures up to 400°C, Conley and co-workers[10] have proposed an oxidative mechanism which produces a similar fragment pattern to that of Parker and

Winkler.[8] At higher temperatures, Conley[10] postulates ring scission and rearrangement to condensed systems with loss of ring carbon atoms.

The composition of commercial phenolic resins is not generally disclosed and may be altered from time to time. Consequently, it was necessary in the present study to prepare a series of resins from phenol and formaldehyde in various ratios using sodium hydroxide as catalyst.

THEORETICAL

The condensation of phenol and formaldehyde may be catalyzed either by base or acid, as follows:
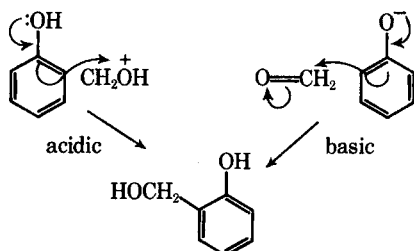
Formation of such a phenolic alcohol (the introduction of a methylol substituent) is generally accepted as the first step in phenol–formaldehyde condensations. Thereafter (a) a further introduction of methylol substituents is possible, (b) condensation may occur between the phenolic alcohol and more phenol to form a methylene ($-CH_2-$) bridge:
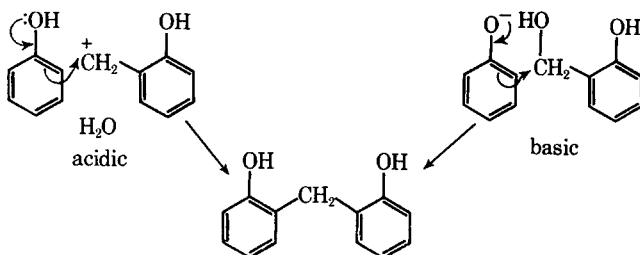
These two reactions are competing and their relative rates depend on the mole ratio of formaldehyde to phenol and on the catalyst used. Their combined effect is to produce long-chain or highly branched molecules, or a completely crosslinked resin, possibly with some free methylol substituents:
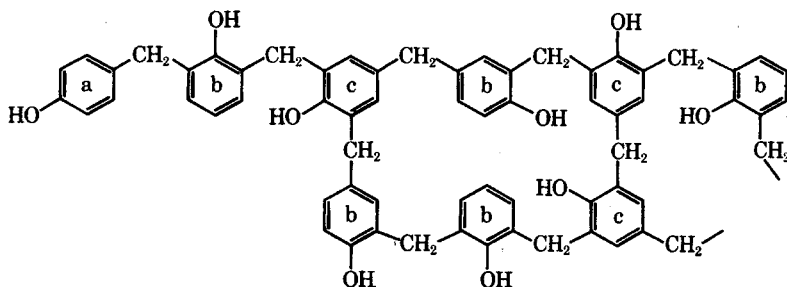
Condensation is possible between two methylol substituents to form a dibenzyl ether linkage, $-CH_2-O-CH_2-$, which however loses formaldehyde on heating to revert to a methylene bridge.

Three classes of phenolic rings may be distinguished: (a) pendant or "attached" rings (those carrying only one methylene bridge) which may also carry one or two free methylol substituents; (b) bridging rings (those carrying two methylene bridges) which may carry only one free methylol substituent; (c) crosslinking rings (those carrying three methylene bridges) which are fully o- and p-substituted and cannot carry free methylol substituents.

The Theoretical Char Yield

Let the mole fraction of attached rings be a, the mole fraction of bridging rings be b, and the mole fraction of crosslinking rings be c. By definition

$$a + b + c = 1 \tag{1}$$

and further

$$0 \leq (a, b, c) \leq 1 \tag{2}$$

Let the average number of free methylol groups per attached ring be n and the average number of free methylol groups per bridging ring be m. By definition

$$n \leq 2, m \leq 1 \tag{3}$$

Each methylene bridge is shared by two rings and is derived from one molecule of formaldehyde precursor. Each free methylol group is also derived from one molecule of formaldehyde.

Thus F moles of formaldehyde are used per mole of phenol, where

$$F = 3c/2 + b(1 + m) + a(\tfrac{1}{2} + n) \tag{4}$$

$$= (c + b + a) + c/2 - a/2 + bm + an,$$

i.e., from eq. (1)

$$F = 1 + (c - a)/2 + bm + an \tag{4a}$$

or

$$c - a = 2(F - 1) - 2(bm + an) \tag{4b}$$

If $F > 1.5$, then $c - a > 1 - 2(bm + an)$. Since, from eq. (2), $c - a \not> 1$,

$$(bm + an) > 0 \tag{5}$$

If $F < 1$, then $c - a < -2 (bm + an)$. Hence from eqs. (2) and (3), $c - a < 0$, or

$$a > c, \text{ i.e., } a > 0 \tag{6}$$

Equations (5) and (6) imply respectively that a resin prepared with more formaldehyde than 3:2 will always contain some free methylol groups and that one prepared with less formaldehyde than 1:1 can never be completely linked, i.e., will contain discrete molecules.

The average empirical gram formula unit of the resin will contain $(a + b + c)$ moles of phenolic rings, $(a/2 + b + 3c/2)$ moles of methylene bridges, and $(m + n)$ moles of methylol groups.

Average empirical formula unit is $(a + b + c)$ C_6H_6O + $(a/2 + b + 3c/2)$ C + $(m + n)$ CH_2O because every addition of a methylol group or formation of a methylene link entails removal of one H atom from a ring, i.e.,

$$\text{average unit} = (a + b + c)94 + (a/2 + b + 3c/2)12 + (m + n)30$$

$$= 94 + (F - bm - an)12 + (m + n)30$$

from eqs. (1) and (4)

$$= 94 + 12F + m(30 - 12b)$$

$$+ n(30 - 12a) \text{ gram atoms} \quad (7)$$

TABLE I
Some Parameters of Phenolic Resins Relating to Char Yields

F	$94 + 12F$	a (minimum)	c(from 4b)	$72(1 - a)$	%, Y_c
1.5	112.0	0	1.0	72.0	64.3
1.4	110.8	0	0.8	72.0	64.9
1.3	109.6	0	0.6	72.0	65.7
1.2	108.4	0	0.4	72.0	66.4
1.1	107.2	0	0.2	72.0	67.2
1.0	106.0	0	0	72.0	67.9
0.9	104.8	0.2[a]	0	57.6	55.0
0.8	103.6	0.4[a]	0	43.2	41.7
0.7	102.4	0.6[a]	0	28.8	28.1

[a] From (4b) with $c = 0$.

If attached rings, linking groups, and methylol and hydroxyl side groups are lost on pyrolysis, the average empirical gram formula unit of char will contain $(b + c)$ moles of phenolic ring residues essentially stripped of hydrogen atoms, i.e., it will contain

$$72(b + c) \text{ gram atoms} \quad (8)$$

Hence, from eqs. (1), (7), and (8),

$$\text{char yield } Y_c = 72(1 - a)/[94 + 12F + m(30 - 12b) + n(30 - 12a)]$$

$$(9)$$

Since from eq. (2) (12*b*, 12*a*) < 30, char yield is at a maximum when *m*, *n*, and *a* are minimized. This implies, from eq. (5),that $m = n = 0$ if $F \leq 1.5$; and, from eq. (6), that $a = 0$ if $F \geq 1$. When $m = n = 0$

$$Y_c = 72(1 - a)/(94 + 12F) \tag{9a}$$

Values of Y_c (maximum) derived from eq. (9a) are shown in Table I.

It is unlikely that the exact situation shown in Table I would be experimentally attainable, assuming as it does that $m = n = 0$ and (in the high char yield region $F = 1.0 - 1.5$) $a = 0$. In particular, the maximum char yield of 67.9% at $F = 1$ would require $b = 1$, i.e., unbranched chains closed upon themselves.

As a practical 1:1 resin would contain a certain proportion of attached and crosslinking rings, i.e., would be a branched novolak, its char yield would be lower than predicted theoretically and the peak Y_c value would be expected at F somewhat greater than 1.0.

EXPERIMENTAL

Resin Preparation

In the present work, which was restricted to water-soluble liquid resoles, the distillation stage which normally follows condensation was omitted.

A number of syntheses were carried out in which the molar ratios were: formaldehyde, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5 moles; phenol 1.0 mole.

The resins were prepared using the following procedure: Laboratory-grade phenol (4 moles, 376 g) was weighed into a tared 1-liter reaction flask and the required quantity of A.R. formaldehyde solution was weighed in. (Note: 1 mole CH_2O = 81 g 37%–40% solution.) Sodium hydroxide solution (72.8 cc $\equiv$ 3.008 g NaOH) was added, followed by 2 g of glass beads. The flask with contents was reweighed to obtain the total weight of starting materials and the mixture was stirred with a glass rod until a clear colorless solution resulted. The flask was fitted with a thermometer which dipped into the liquid and a reflux condenser. The complete apparatus was then lowered into an oil bath at 125°C, until the level of oil was slightly above the level of the flask contents. The temperature of the reaction mixture rose steadily, the rate becoming more rapid at about 81°C. Refluxing occurred at about 85°–87°C and the temperature rose rapidly to 97°C, remaining constant for about 10 min and falling to 96°C after 21 min at which point the entire apparatus was removed from the oil bath, with cooling water still circulating. The flask contents consisted of a low-viscosity, pale yellow, one-phase resinous liquid.

After 20 hr the reflux condenser was removed from the flask assembly, which was then weighed. In practice the weight loss during the reaction was 0–4 g, about 1–3 g of water being condensed on the flask lid.

Characterization of Resoles

Properties which were determined in order to characterize the resoles were as follows:

(a) Water Tolerance: The quantity of added water which just gives permanent cloudiness, as a percentage of resole weight.

(b) Formaldehyde Content: Uncombined formaldehyde as a percentage of initial formaldehyde weight.[9]

(c) Viscosity: Paint Research Station bubble viscometer method.

(d) Specific Gravity: Float hydrometer method.

(e) Solids Content (100°C): The residue after heating 5.0 g of resole for 48 hr at 100°C as a percentage of the resole weight.

(f) Solids Content (150°C): The residue after heating 5.0 g of resole for 48 hr at 100°C followed by heating for 48 hr at 150°C as a percentage of the resole weight.

A table of the properties of some of the resoles produced is given in Table II.

TABLE II
Properties of Phenol–Formaldehyde Resoles

	Formaldehyde/phenol (molar) ratio					
	1:1	1.1:1	1.2:1	1.3:1	1.4:1	1.5:1
Water tolerance, %	135.2	151.0	201.5	232.1	161.4	204.7
Formaldehyde content, %	3.8	4.8	8.4	10.85	9.7	10.05
Viscosity, poise	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
Specific gravity, g/cm³	1.115	1.117	1.115	1.117	1.120	1.120
Solids content (100°C), %	51.6	52.8	51.6	51.3	51.0	51.1
Solids content (150°C), %	49.3	49.7	48.3	46.9	46.4	46.4

Curing Cycle

Because the yield of carbon is calculated using the starting weight of cured resin as a basis, it was important to establish a reliable cure schedule which would give reproducible yields of cured resin. The aim was to find a curing cycle which would produce the maximum elimination of volatiles without degradation of the polymer, i.e., which would result in the formation of a stable resite as a basis for carbonization. Preliminary trials showed that a weight of resole of the order of 5 g was required to obtain a coherent sample throughout the entire curing and carbonizing process. These quantities were curable in air at an initial temperature of 100°C without disintegration and attained constant weight in a reasonable time. Successive postcuring in air at 150°C and 200°C resulted in further small weight losses, constant weight being attained at 150°C after periods varying from 30 to 260 hr, and at 200°C after 70–150 hr. Further curing in air at 250°C, however, resulted in degradation of the samples, a continuous loss in weight being observed.

The behavior of a typical resole sample on curing is shown in Table III. A further 144 hr of cure at 200°C increased the loss to 2.525 g. The figures show that an initial cure for a period of 48 hr at 100°C, followed by a further period of 48 hr at 150°C, results in over 96% of the total weight loss which could be obtained at 200°C. A cure cycle of 48 hr at 100°C followed by 48 hr at 150°C was therefore adopted for production of resites as a basis for carbonization.

TABLE III
Cure Schedule Results[a]

Initial cure at 100°C:				
Total period of cure, hr	24	48	192	
Total loss in wt, g	2.315	2.345	2.355	(constant wt)
Total loss in wt, % of resole wt	45.80	46.52	46.63	
Total loss in wt, % of loss at constant wt	98.28	99.56	100	
Postcure at 150°C:				
Total period of cure, hr	24	48	120	
Total loss in wt, g	0.070	0.085	0.105	(constant wt)
Total loss in wt, % of resole wt	1.38	1.69	2.08	

[a] Weight of sample 5.040 g.

Carbonization

Studies by Parker and Winkler[3] indicate that a temperature of at least 800°C is required in order to produce carbon from phenolic resins in an inert environment. In the current work, the resites in the form of discs approximately 35 mm in diameter and 2–3 mm thick and weighing 2.3–2.5 g were placed in stainless steel dishes on a seven-tiered rack in a vertical stainless steel tube. They were heated in a slow stream of argon to an indicated temperature of 1000°C, being then held at this temperature for at least 1 hr, followed by cooling under argon. Temperature distribution measurements showed that at an indicated temperature of 1000°C, the lowest actual temperature attained in the tube was 920°C.

A number of resite samples were carbonized by the above method, and typical carbon yields are given in Table IV. These results indicate that

TABLE IV
Carbon Yields from Phenol–Formaldehyde Resins

Formalde-hyde/phenol molar ratio	Carbon weight, %			
	sample 1	sample 2	sample 3	average
1:1	64.45	62.22	62.49	63.05
1.1:1	68.26	66.71	66.53	67.17
1.2:1	66.45	67.50	65.98	66.64
1.3:1	68.28	67.51	67.79	67.86
1.4:1	65.30	65.72	65.89	65.64
1.5:1	65.01	64.37	65.15	64.84

the maximum carbon yield is obtained in the range 1.1:1 to 1.3:1 (formaldehyde/phenol molar ratio).

DISCUSSION

Figure 1 shows a graph of Y_c against F, derived from eq. (9a) above, with the experimentally determined carbon yields (Table IV) superimposed. The close agreement of the two sets of figures is a confirmation of the validity of the theoretical treatment. In particular, the postulated shift of Y_c (maximum) to an F value greater than 1.0 is borne out by the observed data: Y_c (maximum) probably occurs in the region of $F = 1.1$,
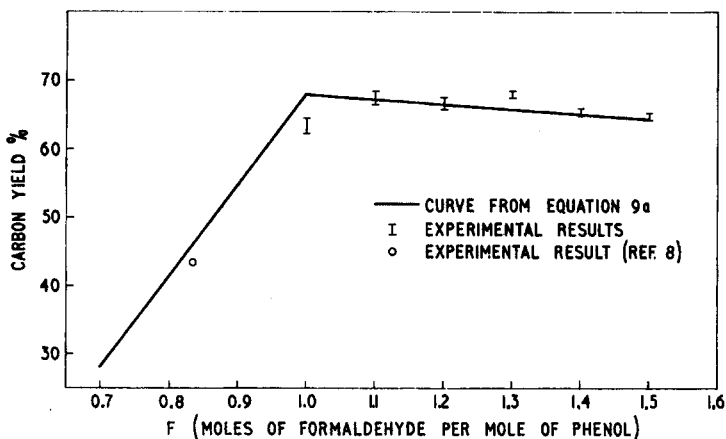

Fig. 1. Theoretical and observed carbon yields from phenol–formaldehyde resins: (———) curve from eq. (9a); (I) experimental results; (O) experimental results obtained from Parker and Winkler.[8]

with a value of 67.2%. The high carbon yield at $F = 1.3$ is anomalous in view of the departure from the theoretical line at this point compared with the close agreement at other points. The validity of the theoretical treatment in the novolak ($F < 1$) region is supported by the experimental result of Parker and Winkler,[8] which is also shown on the graph.

CONCLUSIONS

Water-miscible phenol–formaldehyde resoles have been prepared with formaldehyde/phenol ratios from 1:1 to 1.5:1 by a simple process. The resoles could be cured by heating to give resites which were stable in air at 200°C but which oxidized at 250°C.

When carbonized in argon at 1000°C, the yields of carbon agreed closely with those predicted from a consideration of model resin structures. The optimum carbon yield of 67.2% occurred at a formaldehyde/phenol molar ratio of 1.1:1.

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