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A STUDY OF FURFURYL ALCOHOL RESIN COMPONENTS BY GEL PERMEATION CHROMATOGRAPHY

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SUMMARY

Furfuryl alcohol resins contain a broad spectrum of compounds. A resin containing a high proportion of low molecular weight constituents has been prepared, and twelve compounds, five of which were previously unreported, have been separated from the resin and characterized. Both qualitative and quantitative gel permeation chromatographic data were obtained for a number of these compounds, and calibration curves have been prepared from the data. The gel permeation chromatographic technique was also used to study the reaction products formed by several of these compounds.

INTRODUCTION

Furfuryl alcohol polymerizes when catalyzed by acidic catalysts, amines, or γ -alumina to yield a complex liquid mixture of polyfurfuryl compounds which ultimately condense to a chemically inert solid¹⁻³. The rate and degree of polymerization can be controlled by regulation of the catalyst concentration, temperature, and reaction time.

The composition of liquid furfuryl alcohol resins, the condensation process, and the structure of thermoset resins have been studied extensively, but few investigators have applied chromatographic techniques to them. The first chromatographic study was conducted by SHONO *et al.*, who utilized paper chromatography⁴⁻⁶. These workers studied the effect of hydrogen ion concentration on the condensation rate and reported that the decrease in pH which occurs during the polymerization of furfuryl alcohol could be ascribed to the formation of levulinic acid. SHONO *et al.* also identified furfuryl alcohol, 5-furfurylfurfuryl alcohol, 5-(5-furfurylfurfuryl)furfuryl alcohol, difurfuryl ether, difurylmethane, 2,5-bis(hydroxymethyl)furan, and bis(5-hydroxymethyl-2-furyl)methane in resin systems prepared in their laboratory.

A second chromatographic study was conducted by BOQUIST *et al.*, who employed the gas chromatographic technique⁷⁻⁹. These investigators concluded that

the pyrolytic degradation of furfuryl alcohol resins occurs in three steps: (1) dehydration and decarboxylation, (2) carbon-carbon scission and disproportionation, and (3) dehydrogenation.

While studying the polymerization of furfuryl alcohol, WEWERKA utilized gel permeation chromatography (GPC) to analyze resins produced by using various catalysts¹⁰⁻¹¹. He concluded that the molecular weight distribution of the resins ranged from approx. 5,000 down to 100. WEWERKA also found that resins catalyzed with γ -alumina exhibited GPC peaks shifted to lower elution volumes than those catalyzed by other methods.

A study of furfuryl alcohol resins was initiated in this laboratory to separate and characterize individual components which could function as model compounds representative of various fractions of the resins. In the course of this work, twelve compounds were isolated from furfuryl alcohol resins; five of these were reported for the first time¹². Gel permeation chromatography was used extensively for determination of sample purity and, occasionally, for separations.

EXPERIMENTAL

Furfuryl alcohol resins were prepared in the laboratory with sulfuric acid catalyst and distilled into four fractions with boiling ranges of (A) 25-90°, (B) 99-110°, (C) 110-140°, and (D) 145° and higher. Individual components were then separated from the fractions by utilizing distillation, extraction, and various chromatographic techniques.

Furfuryl alcohol (I), difurylmethane (2,2'-methylene-difuran (IV)), and difurfuryl ether (2,2'-(oxydimethylene)difuran (VIII)) were isolated from fraction A. Fraction B contained 5-furfurylfurfuryl alcohol (II), 2,5-bis(5-furfuryl)furan (V), 5-furfuryl-2,2'-(oxydimethylene)difuran (IX), 2-methyl-5-(5-furfurylfurfuryl)furan (X), and 1,6-dihydroxy-2,2,6-trimethyl-4-heptanone (XII). Three compounds, 2,2'-methylenebis(5-furfurylfuran) (VI), 2,5-bis(5-furfurylfurfuryl)furan (VII), and 2-methyl-5-(5-furfurylfurfurylfurfuryl)furan (XI), were separated from fraction C. Fraction D yielded 2,2'-methylenebis(5-furfurylfuran) (VI) and 5-(5-furfurylfurfuryl)-furfuryl alcohol (III). Chemical formulas and numerical designations are given in Table I.

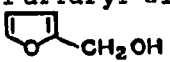
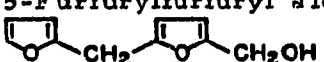



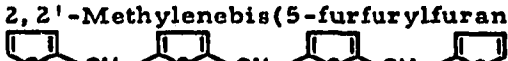


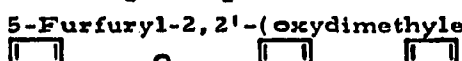
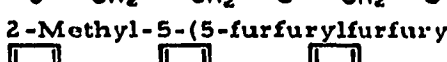
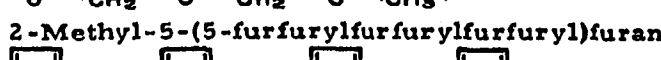
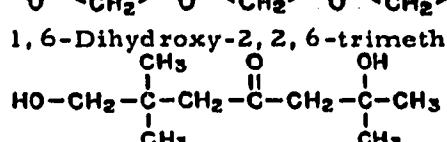
Details of resin preparation and fractionation, separation techniques, and the identification of compounds have been previously reported¹².

Gel permeation chromatography (GPC)

A Waters Associates Model 200 chromatograph was used to obtain gel permeation chromatograms. This instrument was equipped with five 4-ft. \times 3/8-in. Styragel columns which had maximum permeabilities of 500, 60, 45, 45, and 45 Å. A 5 ml siphon was used to collect fractions. The detector employed was a differential refractometer. Toluene at 80° was used as the eluent, and the sample flow rate was maintained at 1 ml/min. Initial experiments were performed with tetrahydrofuran and toluene at various temperatures to determine the optimum operating conditions. Sample concentrations varied from 0.2 wt.% to 6.0 wt.% for the pure compounds and up to 10 wt.% for the polymer. Material which did not dissolve in toluene at 80° was removed by filtration before the solution was injected onto the column. Injection

TABLE I

FURFURYL ALCOHOL RESIN COMPONENTS

No.	Compound	GPC peak Δ (ml)
I	Furfuryl alcohol 	-17.0
II	5-Furfurylfurfuryl alcohol 	4.5
III	5-(5-Furfurylfurfuryl)furfuryl alcohol 	21.0
IV	2, 2'-Methylenedifuran 	8.0
V	* 2, 5-Bis(5-furfuryl)furan 	24.0
VI	2, 2'-Methylenebis(5-furfuryl)furan 	36.0
VII	2, 5-Bis(5-furfurylfurfuryl)furan (VII) 	46.0
VIII	2, 2'-(Oxydimethylene)difuran (VIII) 	13.5
IX	* 5-Furfuryl-2, 2'-(oxydimethylene)difuran 	29.0
X	* 2-Methyl-5-(5-furfurylfurfuryl)furan 	29.0
XI	* 2-Methyl-5-(5-furfurylfurfurylfurfuryl)furan 	41.0
XII	* 1, 6-Dihydroxy-2, 2, 6-trimethyl-4-heptanone 	24.5

* New compounds.

times varied from 45 to 120 sec, depending on sample size. Refractometer response was linear, and resolution remained constant for the various sample sizes and injection times used.

Heat treatment of the polymer and components

Representatives of the major classes of compounds (alcohols, ethers, and polyfurfuryl furans) encountered in furfuryl alcohol resins were heated, and the reaction products were examined by GPC. In some experiments, the compounds were heated in air; in others, samples were degassed in vacuum ($\sim 10^{-5}$ Torr) and sealed in Pyrex

ampoules under vacuum or in argon. The samples were heated at 150 to 200° for times varying up to 24 h until some polymerization had occurred, but heating was discontinued before the sample had thermoset.

DISCUSSION

GPC of resin components

Gel permeation chromatography was used extensively in our work not only for separations but also to determine sample purity; samples which appear to be pure by other methods may contain sufficient impurities to show additional GPC peaks.

The normal calibration of the instrument was made using the polypropylene glycol standards supplied by Waters Associates and linear alkanes from C₁ to C₃₆. These compounds covered the linear portion of the curve as well as the nonlinear regions at the maximum and minimum pore volumes. As the pure compounds were isolated and their structures determined, an unsuccessful attempt was made to fit these compounds on the calibration curve. The hydroxymethyl substituted compounds were retained on the column considerably longer than the unsubstituted compounds. This effect was also observed for water, which eluted approximately seventy milliliters after nitrogen. The methyl substituted compounds eluted slightly earlier than expected based upon the elution time of the unsubstituted compounds. The unsubstituted compounds and the ethers formed a third curve. Apparently, the end group (methyl, hydrogen, or hydroxymethyl), in addition to size, is an important factor affecting the elution volume. This variation in elution of the three different types of compounds resulted in three calibration curves.

Calibration of the gel permeation chromatograph was carried out by using the twelve resin components and two additional compounds, 3-methyl furan and furan. The latter are not found in the resin but were included because they are the simplest members of their respective series. Some of the resin components were obtained only in mixtures; however, peak resolution and intensity were satisfactory in each case to distinguish the calibrating compound from its impurities. After the instrument was calibrated with the known compounds, the identification of new compounds could be verified from their positions on the calibration curves. In some cases, initial identification was made from the GPC curves and verified by other methods. The calibration curves are presented in Fig. 1.

Positions of GPC peaks are reported in Table I. The peak positions are expressed as the difference (Δ) between the peak position of the sample and that of the dissolved nitrogen, which provides a convenient internal standard since it appears in each chromatogram. This method was chosen because the Δ values are not sensitive to any changes in instrumentation or column packing. Compounds I and XII peak in the opposite direction from all others because the refractive index of their solutions is lower than that of the reference.

Fig. 2 shows a chromatogram of Varcum 8251, a commercial furfuryl alcohol resin (Reichhold Chemical Corporation), with its identifiable components labeled. The broad peak at approx. 115 ml corresponds with the higher molecular weight constituents which elute from the column first. Extrapolation of the front of this peak on the calibration curves indicates that this material has a molecular weight of $\sim 1,000$. Approximately five percent of the resin is insoluble in hot toluene. The

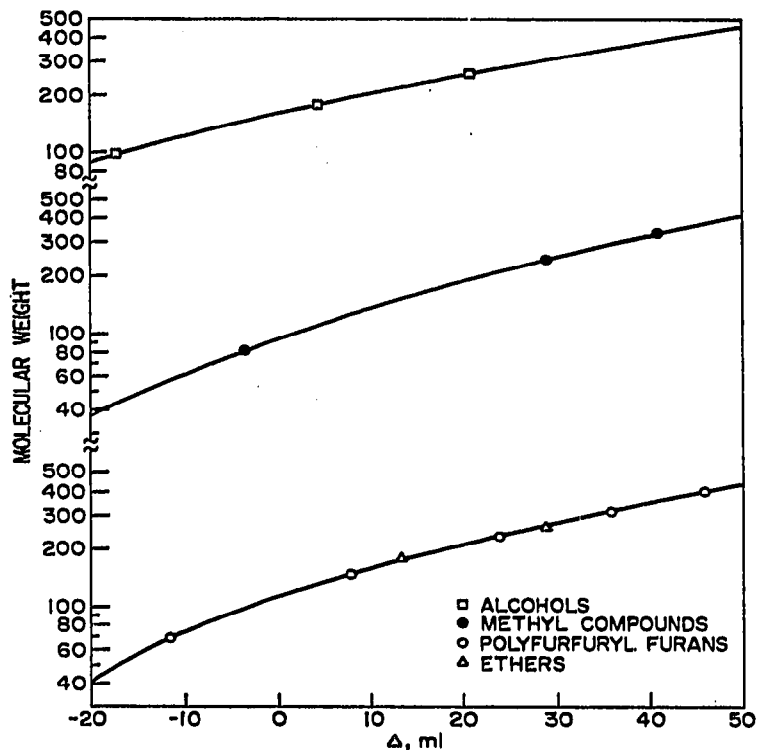


Fig. 1. Calibration curves for gel permeation chromatograph.

infrared spectrum of this fraction indicates that it contains higher molecular weight homologs of the identified components. The resin is completely soluble in tetrahydrofuran, and similar extrapolation of the GPC curves in this solvent also indicated a maximum separated molecular weight of 1,000. The positions of the maximum breaks in the calibration curves are not known; these extrapolations are based on data available at this time.

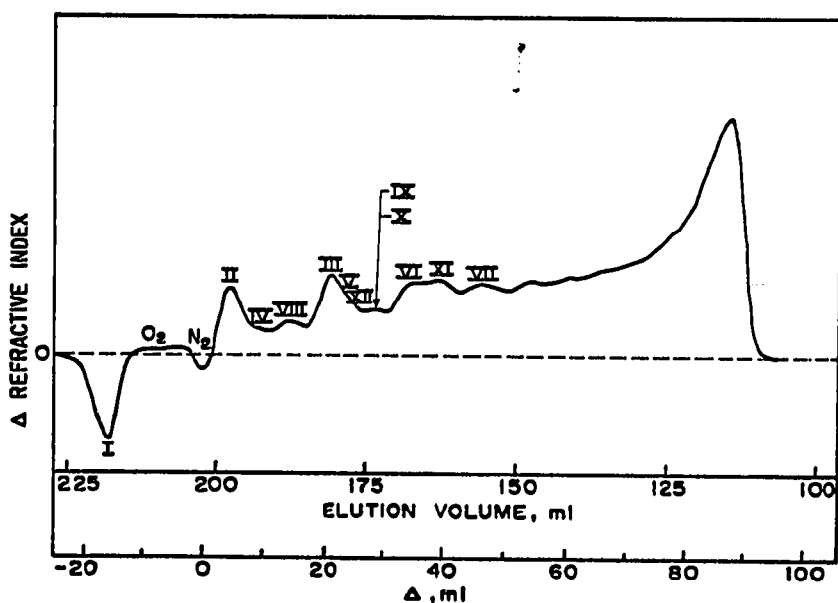


Fig. 2. Gel permeation chromatogram of Varcum 8251. For key see Table I.

WEWERKA has reported separation of materials up to 5,000 molecular weight by using polyglycols as calibration standards^{10,11}. Since a separate calibration curve is necessary for each type of compound in a given solvent, a curve should be drawn through only the points corresponding with the furfuryl alcohol compounds of WEWERKA's data¹⁰; then, a maximum separated molecular weight of 1,000 will be indicated at 80 ml (18 counts). That value is in agreement with the data reported herein.

The resins prepared in the laboratory contained more of the lower molecular weight components than are usually present in commercial resins. These components elute at 160–200 ml. Some of the experimental resin constituents show distinct peaks; however, for the most part, the absorptions overlap, and the resolution is poor. Fig. 3 shows chromatograms of the fractions of an experimental resin separated by distillation with a vigreux column. The chromatograms clearly show the composition of each distillation range.

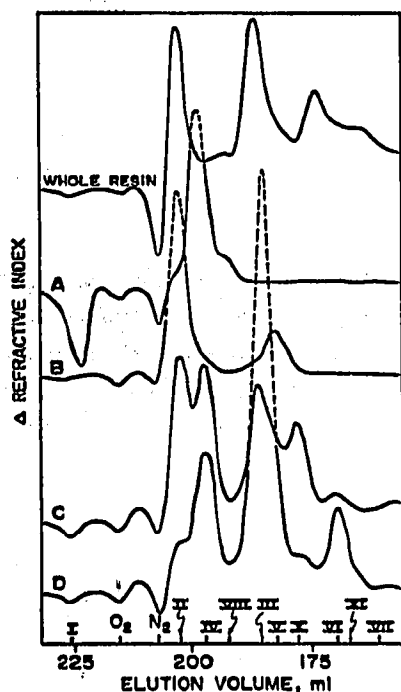


Fig. 3. Gel permeation chromatograms of furfuryl alcohol resin fractions. For key see Table I.

Quantitative data were obtained for six compounds in an effort to determine the amounts of these components in a given resin. Curves were obtained for a minimum of three concentrations of each compound. The calibrating compounds, which exhibited well-defined elution peaks, were chosen from those shown in Table I and included the alcohols (I, II, and III), difurylmethane (IV), 2,5-bis(5-furfuryl)furan (V), and difurfuryl ether (VIII). The calibration data are summarized in Fig. 4 as least squares plots of concentration *vs.* peak area ($100 \text{ cm}^2 = 0.8784 \text{ g}$).

One of the goals of the project was to develop some means of monitoring the composition of the resin without resorting to separation processes. As a quantitative tool, the GPC approach showed potential as a time-saving technique. A scan of the

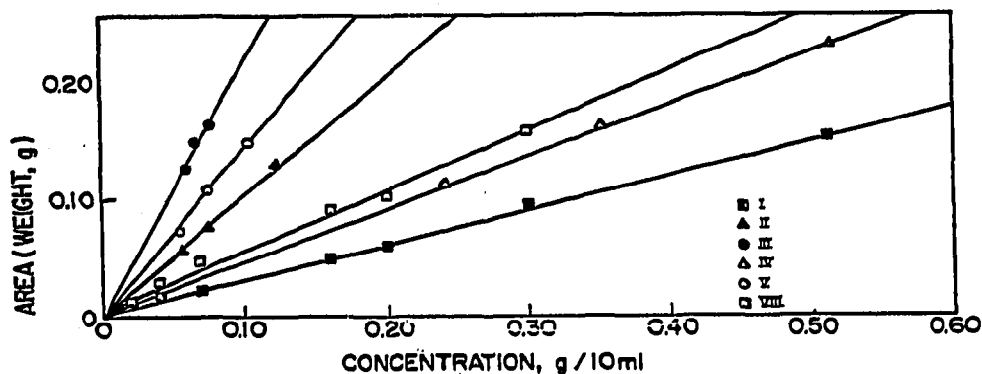


Fig. 4. Quantitative calibration curves for gel permeation chromatograph. For key see Table I.

whole resin shows several peaks which could be identified from the data obtained for the pure compounds; however, the chromatogram is very complex, and the overlapping of peaks, as well as the presence of both negative and positive peaks, precludes even a crude quantitative analysis of the resin. A composite of the GPC curves of the individual compounds is shown in Fig. 5B. A curve for a resin prepared in the laboratory is presented in Fig. 5A for comparison.

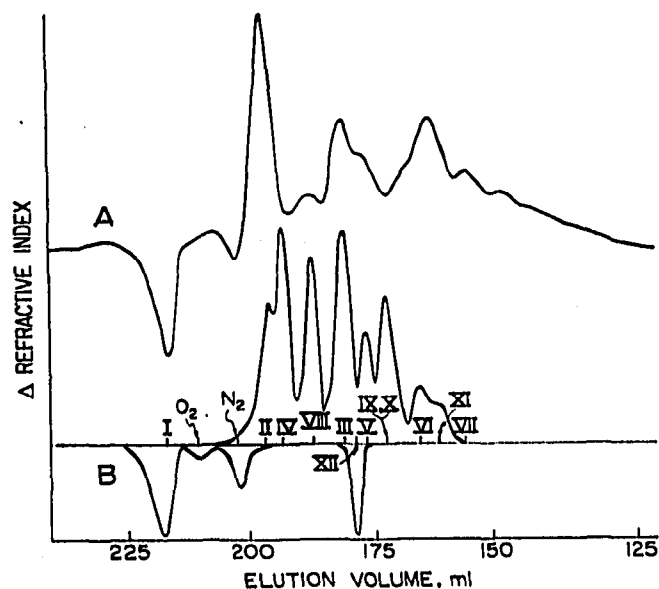


Fig. 5. Composite gel permeation chromatogram. For key see Table I.

Heat treatment of furfuryl compounds

The polymerization of furfuryl alcohol has been studied extensively, and researchers agree that the rate of resinification depends on reaction temperature and on pH; it is also influenced by oxygen and numerous other catalysts. The basic mode of polymerization is the intermolecular condensation of the hydroxymethyl group of one molecule and the α -hydrogen of another furan ring. Water is eliminated in the process:



Repeated condensation leads to a linear arrangement of furan rings connected with methylene links and terminated with a hydroxymethyl group. Several competing reactions occur which produce difurfuryl ether (dehydration reaction), difurylmethane (formaldehyde elimination), and levulinic acid.

Some investigators have pointed out that the polymerization mechanism is more complex than is indicated by this simple scheme, particularly when the curing is carried out in air¹³. Atmospheric oxygen attacks the furan ring, and the condensation route is different from that followed by the acid-catalyzed reaction. In practice, a combination of oxygen and acid catalysis is generally encountered.

To determine the origin of some of the new compounds isolated during this study, several resin components representing the major classes of compounds present in the resin were heat-treated, and the products were subjected to GPC analysis. Furfuryl alcohol polymerized readily in evacuated ampoules without a catalyst, but other alcoholic components are more stable and required the presence of air. Maleic anhydride catalyst (1.65 wt. %) was added to the remaining compounds.

Furfuryl alcohol (I) and the alcohol dimer (II) condensed to give products having chromatograms similar to that of Varcum. The contributions of the methyl compounds, (X) and (XI), were particularly evident in the products from compounds II and III. The chromatogram of products from difurylmethane (IV) was strikingly different. The latter exhibited well-defined major peaks of the ethers, (VIII) and (IX), and of the tetramer (VI). Heat treatment of the trimer (V) for 24 h produced only a single product peak which was identified as pentamer (VII). Difurfuryl ether (VIII), when heated for the same period, decomposed extensively and produced a tan solid which was highly insoluble. The infrared spectrum of the solid showed absorptions characteristic of carbonyl, hydroxyl, and ether groups.

The gel permeation chromatographic analyses clearly show some of the complexities of the polymerization. In addition to furfuryl alcohol and its homologs, other intermediate compounds can undergo rearrangement and condensation reactions. Difurylmethane is a source of ethers as well as higher unsubstituted homologs, whereas difurfuryl ether decomposes, producing a complex solid material. The methyl substituted polyfurfuryl compounds were not observed in the products from compounds other than furfuryl alcohol and the dimer alcohol.

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