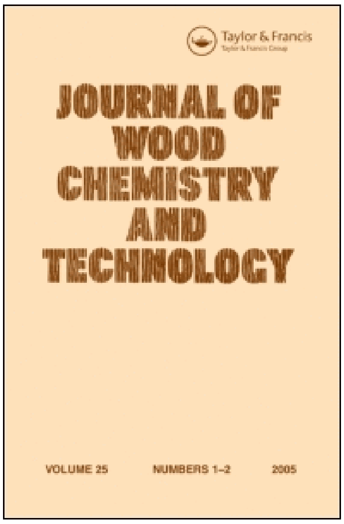

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INSOLUBLE LIGNIN MODELS (4): CONDENSATION REACTIONS OF A POLYMER-BOUND GUAIACYLPROPANOL MODEL

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ABSTRACT

The reactions of syringyl alcohol with itself and with either a soluble phenol, 3-methoxy-4-hydroxyphenylpropane (guaiacylpropane, **13**) or an insoluble polymer-bound phenol, guaiacylpropanol (**14**),[1] led to dimeric products. The low (11%), but significant yield of C5-Cα dimer **16** in the reaction of polymer-bound phenol with syringyl alcohol suggests that soluble lignin units are able to condense with insoluble lignin gels during the course of soda pulping. The yield of the C5-Cα dimer **15** in the soluble system was four times greater than that of the analogous heterogeneous dimer **16**. Reactions of the polymer model **14** were not mass transfer limited.

INTRODUCTION

Delignification and condensation reactions compete during alkaline pulping.[2] Condensation, which may occur both before and after lignin dissolution, can lead to alkali stable bonds between two lignin units and/or between lignin-carbohydrate units.[3, 4] Efforts to remove the residual condensation products by extended pulping result in excessive yield and pulp quality losses. More selective bleaching procedures are required to remove the remaining residual lignin.[5]

Lignin condensation during pulping has been an elusive reaction to characterize and quantify, owing to the complex nature of wood and interference from competing fragmentation reactions. Numerous model compound studies have been conducted in which the competing fragmentation reactions have been eliminated or controlled, thus revealing the mechanisms of condensation.[6-10] These studies have indicated that condensation reactions contribute to the formation of residual lignin.[10]

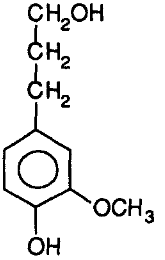
Inconclusive results have been obtained from the study of alkali lignins. Nitrobenzene oxidation and phenyl nucleus exchange methods have been used to detect increased formation of diphenylmethane structures during kraft pulping of Douglas-Fir.[11] Likewise, a ^{13}C-NMR study has indicated that the proportion of condensed units in the residual lignin from a kraft cook increased with time.[12] Kwoh, et al.,[13] who analyzed an isolated kraft lignin by ^{13}C-NMR, detected a signal associated with diphenylmethane (condensed) moieties; whereas Robert and coworkers,[14] who also employed ^{13}C-NMR techniques, did not observe any concrete evidence of lignin-lignin condensation.

The next logical step in the study of lignin condensation is to examine an insoluble lignin model, since a significant portion of pulping reactions are believed to occur when lignin is in the gel or solid phase.[14] A heterogeneous model, such as a monomeric lignin C-9 unit attached to an insoluble polystyrene network, should have the benefits of soluble systems, namely, definitive substrate structure and ease of product characterization and quantification. The polymer-supported models go one step beyond soluble models in that they implicate some of the physical phenomena encountered during the pulping of wood: solid-liquid interfaces and a porous insoluble polyionic substrate.

Insoluble lignin models will not, however, precisely model the heterogeneous lignin environment. For example, the insoluble model may lack the typical glass transition experienced by lignin during pulping.[15] Many different effects can be brought about by choice of the insoluble support; one must be aware of the system's limitations. The intent of this work was to determine the relative extent to which condensation occurs in a solid phase versus that in an analogous but completely soluble system. The results should further elucidate the likelihood that lignin condensation reactions contribute to the formation of residual lignin.

RESULTS AND DISCUSSION

Stability of the Polymer Model Under Alkaline Pulping Conditions



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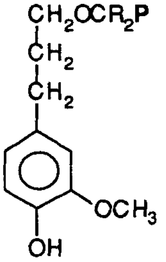


2, R=Ph (trityl)

3, R=H (benzyl, Bn)

Previous research in our laboratory has shown that the polymer-supported model **2**, obtained from bonding guaiacylpropanol (**1**) to a macroreticular polystyrene (**P**), was cleaved at the trityl ether linkage when subject to high temperature alkaline pulping conditions.[16] Con-

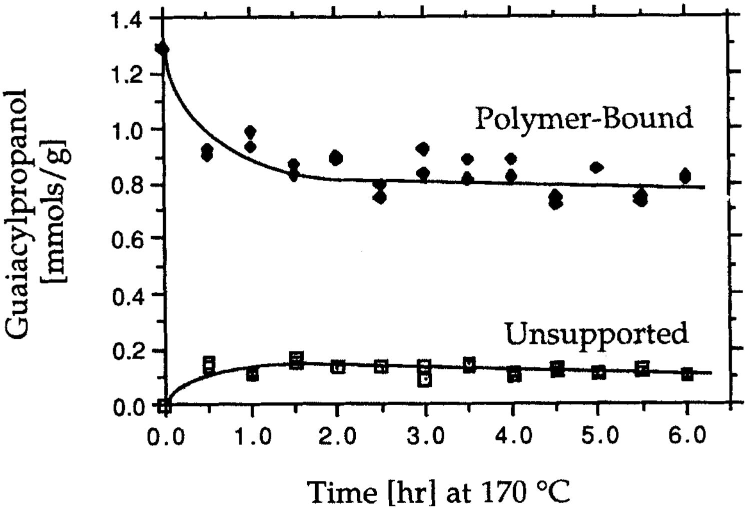


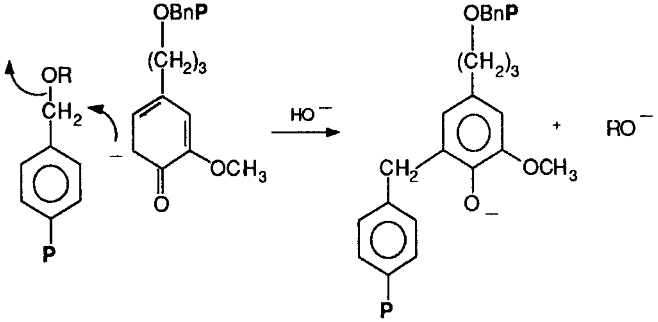
Figure 1. Stability of the heterogeneous benzyl ether linkage in 1M NaOH at 170 °C.

versely, a benzyl (Bn) ether linkage, which was used to attach a disaccharide to a polystyrene support, exhibited good stability under simulated pulping conditions.[17, 18] The corresponding benzyl ether-linked guaiacylpropanol model 3[1] would also be expected to demonstrate a high degree of stability under similar alkaline pulping conditions.

The stability of the benzyl ether linkage on the heterogeneous lignin model (3) was examined by cooking the resin in 1M NaOH for up to six hours at 170 °C. An iodotrimethylsilane (ITS) method[1] was used to determine the amount of guaiacylpropanol (1) remaining on the resin after it was washed and dried. The reaction liquor was also analyzed for guaiacylpropanol. Figure 1 shows the results of the high temperature alkaline treatments.

The low level (10%) of guaiacylpropanol found in solution remained relatively constant after 30 min at 170 °C. The resin, however, appeared to lose a significant amount of guaiacylpropanol during the first 90 min at temperature, after which the level of model remaining on the resin remained relatively stable. At the conclusion of the stability trial, the model loss was 40% based on the ITS analysis of the resin.

Several hypotheses may explain the loss of model from the resin. The first is depicted in Equation 1. Due to a high loading level, and thus close proximity, some ionized model may react with a neighboring benzylic carbon and displace a guaiacylpropanol unit or ethanol. Low levels of ethanol (ca. 0.03 mmol/g) were detected in the reaction liquor. Intrapolymeric reactions have been observed for other systems.[19] Crosslinked intrapolymeric units, as shown in Eq. 1, are difficult to detect by ^{13}C-NMR, thus eliminating this technique as a method to further confirm the interunit displacement hypothesis.[20]



R = model or CH_2CH_3

A second possibility is that a portion of the guaiacylpropanol is sorbed to the resin and not covalently bonded. Low levels of guaiacylpropanol (0.04 mmol/g) were observed in solution after the resin had been soaked in THF for 83 hr. A similar amount (0.03 mmol/g) was observed after 45 min in acetonitrile. At the higher temperatures used in the pulping trial, the morphology of the resin may change, freeing some internally absorbed guaiacylpropanol.

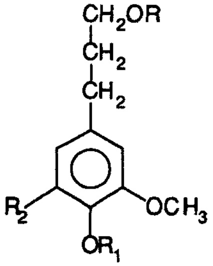
A change in resin morphology associated with high temperatures could also (a) release model into solution to relieve some internal stress and (b) collapse the resin in such a way that bound model is trapped in regions which, upon cooling, are inaccessible to the ITS reagent. In other words, the model was still attached to the polymer at roughly the same level as before heating, but the ITS loading technique fails to recognize the inaccessible guaiacylpropanol. This would explain the slight decline in polymer-bound model observed over the course of the extended soda cook.

The initial instability of the polymer-bound model necessitated that it be "conditioned" in alkali at 170 °C before undergoing any further reactions. A new loading value of 0.81 ± 0.04 mmol/g was determined for the conditioned model. This loading corresponds[1] to about 1 phenol unit per every 6 polystyrene aryl rings, or 17% phenolic rings. The FTIR spectrum and the elemental analysis (C, 80.71; H, 7.28; O, 11.64 %) of the conditioned model varied only slightly from that of the unconditioned material.[1]

A minor compound (**4**), amounting to less than 2% of the observed guaiacylpropanol, was identified by GC/MS in the acetylated ITS product solution of the conditioned resin. Compound **4**, which has an allyl group at the C5 position on the aromatic ring, is most likely derived from polymer-supported **5**. Compound **5** could result from a Claisen rearrangement[21] of the allyl group from the phenolic oxygen of structure **6** to C5 under high temperature alkaline conditions. The observation of **4** confirmed the results of a ^{13}C-NMR spectrum[1] which showed that the allyl groups were not completely removed during the polymer model synthesis. Any residual **5** structures on the polymer should be inactive toward condensation reactions since the otherwise reactive C5 position is blocked by an alkali-stable allyl group.

Diffusion in the Macroporous Network

The porous structure of the resin appeared to change during the synthetic preparation of the model[1] and is known to change upon thermal treatment.[22] Such changes were observed during the conditioning of the resin as described above. These porosity changes affect the local concentration of the model on the resin.



4, R=Ac, R_1=Ac, R_2=Allyl
5, R=BnP, R_1=H, R_2=Allyl
6, R=BnP, R_1=Allyl, R_2=H

Halász and coworkers report that the porous structure of the support will not be rate limiting if the pore size is greater than 2.5 times the random coil diameter of the infusing soluble species.[23, 24] The random coil diameter can be calculated from Eq. 2:[24]

$$d = 0.2457\,(Mw)^{0.5882} \qquad [2]$$

where d is the the random coil diameter in Å and Mw is the formula weight in grams. The random coil diameter for syringyl alcohol cal-

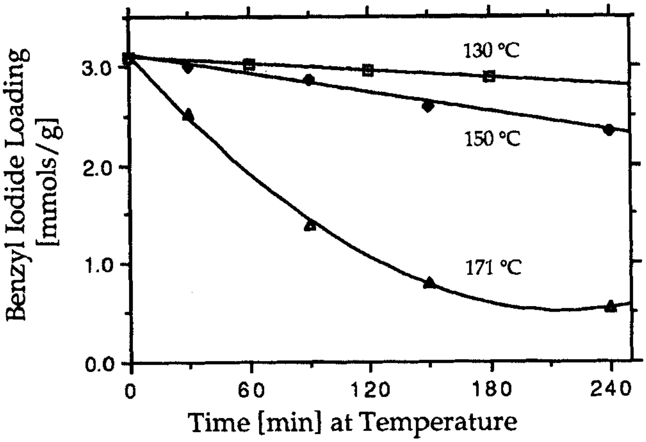


Figure 2. Polymer-bound benzyl iodide loading vs. time at the indicated temperatures.

culated from Eq. 2 is 5.28 Å, a value which is significantly smaller than the 1400 Å pore diameter of the unmodified resin support.

The activation energy for the hydrolysis of polymer-bound benzyl iodide (Eq. 3) was determined in order to confirm that diffusion of reactants into the functionalized resin would not be rate limiting under pulping conditions.

$$\mathrm{PBnI + NaOH \longrightarrow PBnOH + NaI} \qquad [3]$$

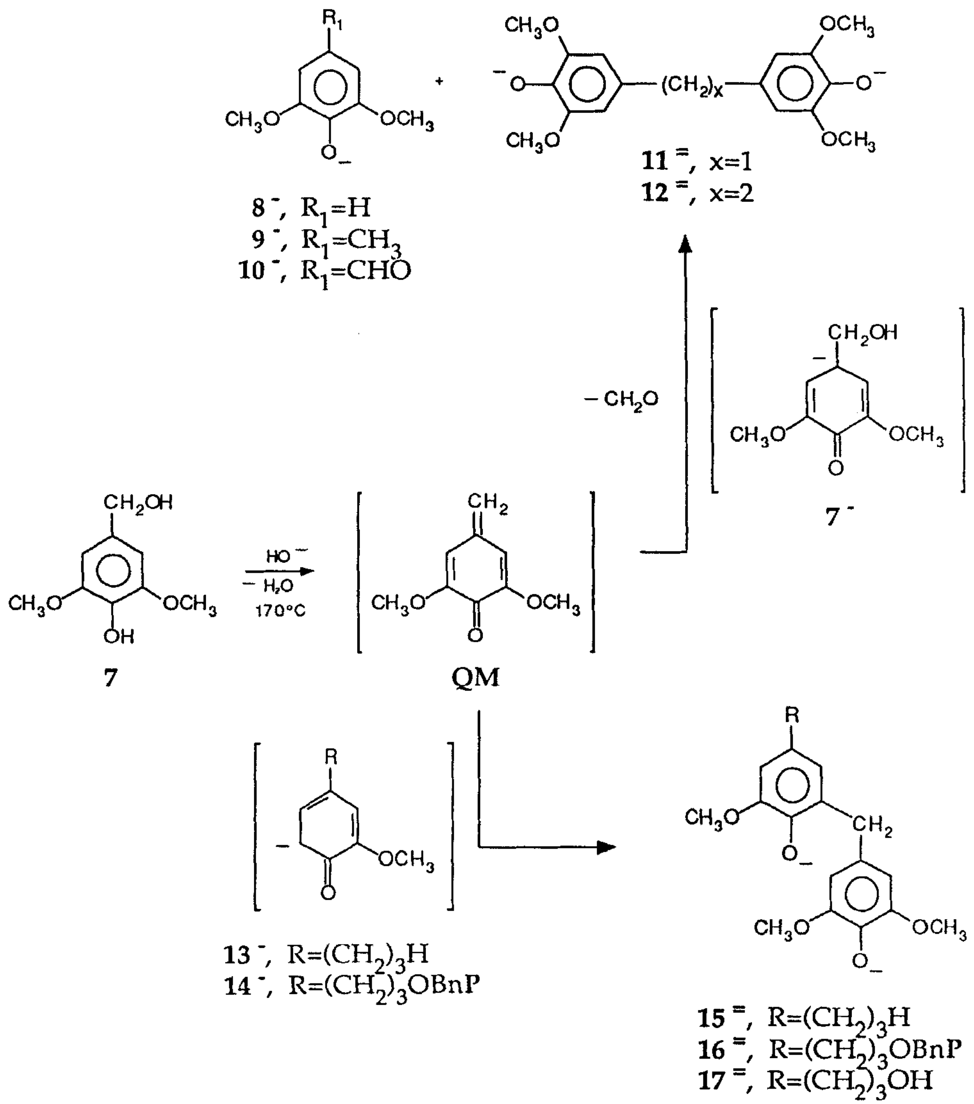
A semiquantitative kinetic analysis was conducted with polymer-bound benzyl iodide at 130, 150 and 171 °C in 1M sodium hydroxide (Fig. 2). The extent of reaction was determined by elemental analysis (single determinations for iodine). An activation energy of 25 kcal/mol was determined from a pseudo first order kinetic application of the Arrhenius equation; a correlation coefficient (R^2) of 0.973 was observed. Analysis of the product beads by FTIR gave a spectrum consistent with a polymer-bound benzyl alcohol.[25]

Activation energies for chemically controlled bulk phase delignification under soda pulping conditions range from 20.5 to 35.1 kcal/mol for various wood species.[26-28] The activation energies for the initial phase pulping of eucalyptus, where diffusion is the rate limiting step, range from 13.6 to 17.4 kcal/mol.[26] Therefore, the value found for the hydrolysis of polymer-bound benzyl iodide is consistent with chemical reaction control. Reaction rates in similar systems which employ Amberlite XE-305 as a support should also not be influenced by mass transport phenomena.

Condensation Reactions

The self-condensation of syringyl alcohol (7) under soda pulping conditions has been previously reported.[29] The major product, disyringylmethane (**11**), results from attack of a $C1^-$ anion of syringyl alcohol (7^-) on the a carbon of a syringyl quinone methide (QM), followed by loss of formaldehyde (Scheme 1). Trace amounts of a second dimer, bisyringyl (**12**), were also detected. Bisyringyl is presumably generated when two α-carbon radicals combine. Minor quantities of several non-condensation products, monomers **8** - **10**, were also identified. In the syringyl system, methoxyl groups at both the 3 and 5 aromatic ring positions prevent the formation of trimers and other higher order condensation products which are observed with the monomethoxy compound vanillyl alcohol.[30, 31]

For this study, we examined the reactions of syringyl alcohol with guaiacylpropane (**13**) and polymer-bound guaiacylpropanol (**14**). To directly compare the homogeneous (soluble system) and heterogen-


8⁻, R1=H
9⁻, R1=CH3
10⁻, R1=CHO
11⁼, x=1
12⁼, x=2
− CH2O
7⁻
HO⁻
− H2O
170°C
7
QM
13⁻, R=(CH2)3H
14⁻, R=(CH2)3OBnP
15⁼, R=(CH2)3H
16⁼, R=(CH2)3OBnP
17⁼, R=(CH2)3OH

Scheme 1

eous (supported system) reaction rates, the ratio of reactants in the two systems must be the same. However, the exact amount of polymer-bound guaiacylpropanol (**14**) accessible to the pulping liquor was not known. The quantity of **14** employed was based on the ITS loading value which represents a minimum level of supported model.[1] In both systems, a 25% excess of guaiacylpropane (**13** or **14**), vs. syringyl alcohol, was used. The solution phase reaction was conducted in the presence of inert polymer-bound benzyl ethoxide[1] in order to make the reaction environment and liquor work-up more analogous to that of the heterogeneous system.

In both the soluble and two-phased reactions, a new interunit condensation product, the C5-Cα dimer (**15** or **16**), was observed in addition to the standard syringyl-syringyl products (Scheme 1). The mechanism for the formation of C5-Cα dimer is similar to that of disyringylmethane (**11**), except that the nucleophile is the $C5^-$ anion of guaiacylpropane ($\mathbf{13}^-$ or $\mathbf{14}^-$). The level of C5-Cα dimer (**15**) formed in the soluble system was compared to the amount of dimer (**16**) produced in the analogous two-phased environment (Fig. 3).

The formation of soluble C5-Cα dimer (**15**), as shown in Fig. 3, was rapid and extensive. The final yield of dimer **15**, the major product, was 40% based on the initial level of syringyl alcohol. As expected, heterogeneous C5-Cα dimer (**16**) formation was slower and lower in yield (11%). A significant level of **16** was, however, observed early (10 min) in the cook. Only trace quantities (< 0.01 mmol/g) of a soluble C5-Cα dimer (**17**) were found in the heterogeneous reaction solution indicating that the resin preconditioning was successful.

In the homogeneous system, the final concentration of phenol-syringyl C5-Cα dimer **15** was greater, by a factor of 2.5, than the syringyl-

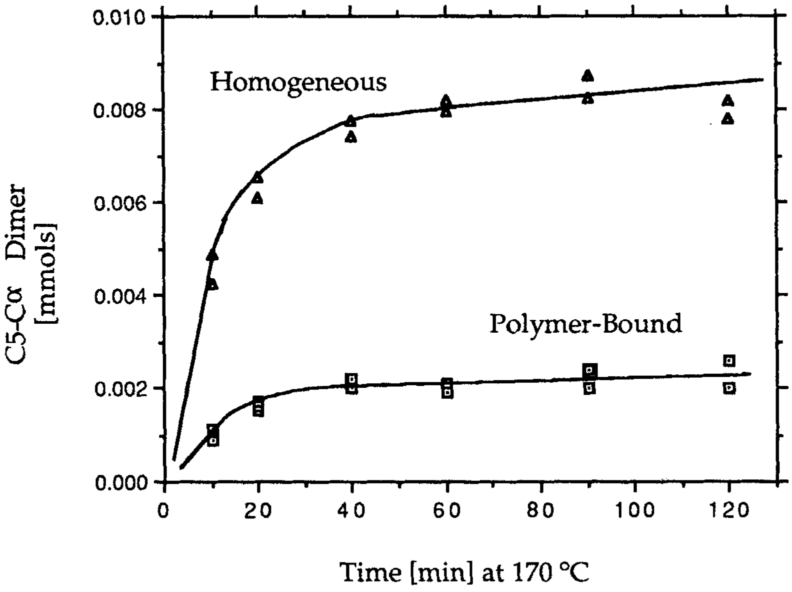


Figure 3. Concentration of the C5-Ca dimer vs. time at temperature.

syringyl C1-Cα dimer **11**. However, no conclusive evidence on the relative reactivities of the C5 and C1 nucleophiles could be ascertained from these data, since the C1⁻ anion and quinone methide concentrations were not known. A previous rate study incorporating a similar system has shown that the C1 position is more reactive than the C5.[32] The soluble reaction by-products, disyringylmethane (**11**), syringol (**8**), 4-methylsyringol (**9**), and syringaldehyde (**10**), did not follow a consistent pattern between the two systems. The latter three products were present at significantly higher levels at 170 °C than at 150 °C.[33] Bisyringyl (**12**) was not observed in either product mixture.

Quantitative kinetic expressions were not determined because (a) the amount of accessible polymer-bound guaiacylpropanol was not accurately known, (b) the local concentration between the soluble and insoluble systems may be quite different, (c) the formation of the minor products was inconsistent, and (d) an analytical GLC response factor, based on the value for the homogeneous dimer, would have to be assumed for the heterogeneous C5-Cα dimer.

Heterogeneous reaction rates have, in general, been found to be slower than in the analogous homogeneous reactions.[34-36] In systems without mass transfer limitations, the slower rates have been ascribed by Bernhard and Hammett[35] to the greater loss in internal degrees of freedom when forming the heterogeneous transition state. The explanation of Bernhard and Hammett should also apply to high temperature alkaline systems, although this was not experimentally verified.

CONCLUSIONS

The yield of insoluble condensation product **16** was approximately 25% of the level of corresponding C5-Cα dimer **15** observed in the analogous soluble system. The level of C5-Cα dimer **16** formed in the two-phased system exceeded expectations since the soluble codimerization species, syringyl alcohol (**7**), had several alternative "soluble" pathways for consumption (Scheme 1). The high local concentration of polymer-bound guaiacylpropanol (**14**) may have greatly increased the probability of condensation for those syringyl quinone methides that entered, or were formed in, the resin matrix. The lower, but significant level of heterogeneous condensation suggests that soluble lignin units are capable of condensing onto, and forming alkaline stable bonds with, the insoluble lignin gel during the course of an alkaline cook. The inhibition of such two-phased condensation reactions should lead to lower levels of residual lignin.

The polymer-supported benzyl ether bond, unlike the prototypic trityl ether linkage,[16] was found to be inherently stable under alkaline pulping conditions, although some resin morphology changes were observed. The Amberlite XE-305 network was shown, theoretically and by determination of an activation energy, not to impose mass transfer limitations under simulated soda pulping conditions.

The results of this study indicate that polymer-supported models can be used effectively to study pulping reactions in a controlled, two-phased environment. Several other applications of heterogeneous model systems, such as determining the effectiveness of pulping additives (HS^-, $AHQ^=$) on soluble vs. insoluble substrates, are currently envisioned. One could conceivably incorporate various effects on potential reaction systems by employing different supporting networks or by controlling other factors such as the degree of polymer functionalization. In this regard, heterogeneous models represent a vast resource which remains largely unexplored.

EXPERIMENTAL

A description of the specific instrumentation, the elemental analyses, the determination of model loading by the ITS method, and the reagents/solvents have been previously detailed.[1]

Syringyl alcohol (**7**), disyringylmethane (**11**), and bisyringyl (**12**), were prepared as described by Smith.[29] Syringol (**8**), 3,4,5-trimethoxytoluene (the methylated version of 4-methylsyringol, **9**), and syringaldehyde (**10**), were purchased.

A sample of guaiacylpropane (3-methoxy-4-hydroxyphenylpropane, **13**) was donated by Dr. P. Apfeld; it was prepared by the catalytic hydrogenation of eugenol.[37]

High temperature reactions, general method - The simulated pulping reactions were performed under nitrogen in small (4 mL) stainless steel pressure vessels (bombs). Once the bombs were placed in the constant temperature oil bath, a three-minute warm-up time was allowed before recording time zero. Likewise, a three-minute cool-down period was given between the time the bombs were removed from the oil bath and quenched with ice water. The bombs were slowly rotated end-over-end to facilitate mixing. All pulping-type reactions were conducted in 1M sodium hydroxide; the standard volume of solution per bomb was 3.5 mL. The 1M sodium hydroxide stock was freshly prepared before each trial from concentrated ultrapure sodium hydroxide (Alfa Products) and oxygen-free distilled water. The kinetic experiments were performed in duplicate unless otherwise noted; GLC analyses were also done in duplicate for each sample. The internal standard for all reactions was 4-ethoxyphenol in 1M sodium hydroxide.

Benzyl ether stability - Each bomb contained 25 mg of the heterogeneous model (**14**). Two separate trials at 169 and 171 °C were performed. Internal standard was added volumetrically to the cooled bombs after which the liquor was pipetted off the resin and added to a 50 mL flask. Alkaline rinses (1M NaOH, 3x2 mL) of the remaining resin were also added to the flask. The combined reaction liquor was then acidified with 2.50 mL of 5M acetic acid. Water was removed from the sample under reduced pressure at a maximum temperature of 40 °C. The residue was further dried by adding 5 mL of isopropyl alcohol which was then removed in vacuo. The product was acetylated with 0.75 mL of dry pyridine and 2.25 mL of acetic anhydride and isolated as previously described.[1] The reaction mixture was analyzed by GLC for guaiacylpropanol.

After the 4-ethoxyphenol had been added and mixed with the reaction liquor as described above, a 1 mL aliquot was removed from selected samples and analyzed for ethanol.[38] Each aliquot was added to 0.25 mL of 2M sulfuric acid after which methanol was added as an internal standard. The samples were analyzed on a 6 ft. x 2 mm ID Super Q column (program: isothermal at 135 °C; inj. temp. 200 °C; FID detect. temp. 300 °C; helium carrier gas (20 mL/min)).

The beads were isolated by filtration, rinsed initially with 1M NaOH as described above, and then washed successively with 5x2 mL of water, 50% aq. dioxane, 50% 1M acetic acid/dioxane, water, abs. ethanol, and anhydrous ether. The isolated resin was dried in a vacuum oven at 40 °C. The level of model remaining on the resin was determined by the ITS method.

The heterogeneous model (**14**) was conditioned (75 mg resin per bomb) in 1M sodium hydroxide at 169 °C for 90 min. Once cool, the reaction mixture was filtered and the collected resin washed with 5x100 mL of the above solvents and dried for several days in vacuo at 40 °C. The beads were characterized by FTIR and the ITS method. The ITS product solution from the conditioned resin revealed, in addition to the previously identified compounds,[1] the presence of **1-(4'-acetoxy-5'-allyl-3'-methoxyphenyl)-3-acetoxypropane (4)**: MS m/e (relative intensity) 306 (10, M^+), 264 (100), 210 (13), 204 (24), 177 (53), 163 (19), 150 (16), 137 (11), 131 (10), 115 (10), 91 (13), 44 (13), 43 (56), 40 (29).

Hydrolysis of polymer-bound benzyl iodide - The bombs were loaded with 100 mg (0.31 mmol) of polymer-bound benzyl iodide and 1M sodium hydroxide. Cooks were carried out according to the standard method at 130, 150 and 171 °C. The cooled, reacted resin was filtered and washed with 3x5 mL of water, methanol, and acetone. The beads were finally extracted in a Soxhlet apparatus for 4 hr with hexane and dried at 50 °C in a vacuum oven.

The pseudo first order kinetic equation took the following form: $\ln R = k't + \ln R_0$. The rate constant, k', was determined by plotting reaction time (sec) vs. the ln R, where R is the benzyl iodide loading. The activation energy (E) was calculated from the Arrhenius equation: $k' = Ae(-E/RT)$.

Condensation reactions - The bombs were prepared in the usual manner. The concentration of syringyl alcohol (**7**) was 0.0200 mmol per bomb for both the homo- and heterogeneous reactions; the concentration of guaiacylpropane (**13** or **14**) was 0.0250 mmol per bomb. The guaiacylpropane loading in the heterogeneous system was based on the ITS loading value of 0.81 mmol/g (30.9 mg resin per bomb). The homogeneous system contained inert polymer-bound benzyl ethoxide (32.0 mg/bomb) to eliminate any resin induced effects. In the heterogeneous case, an additional (single) cook was performed to confirm the results obtained from the initial (duplicate) experiment. The temperature of the homogeneous trial was 172 °C, the heterogeneous reactions were conducted at 170 °C.

The bombs were cooled in ice-water, opened, and an internal standard added volumetrically. The resin was isolated by filtration. The bombs and isolated resin were washed with 3x3 mL of 1M sodium hydroxide. The reaction liquor and washes were then combined and methylated. The methylation procedure consisted of adding 1 mL of dimethylsulfate to each solution and stirring for 40 min. The methylation was quenched by adding 4 mL (excess) of 40% aqueous dimethylamine and stirring for 15 min. Dichloromethane (4 mL) was then added and stirring continued for an additional 5 min. The contents of the reaction flask were added to a separatory funnel along with 3x4 mL water rinses. The layers were separated and the aqueous layer extracted twice more with 4 mL of dichloromethane. The organic layers were combined, dried over sodium sulfate, and concentrated under reduced pressure at room temperature. The solutions were quantitatively analyzed by GLC.

The resin from the heterogeneous reaction was isolated by filtration and washed as described for the stability test. The beads were then dried in vacuo at 40 °C before ITS analysis. A response factor for the GLC analysis of ITS cleaved C5-Cα dimer (acetylated **17**) was estimated from homogeneous dimer **15** which was acetylated according to the conditions described for the ITS method.[1] The average mass balance for the heterogeneous reaction was 83.4 ± 4.0%, based on syringyl alcohol. Based on polymer-bound guaiacylpropanol, the average mass balance was 93.2 ± 8.8%. Mass balance data for the solution phase reaction could not be obtained due to incomplete GLC resolution of guaiacylpropane (**13**) and 4-methylsyringol (**9**). The FTIR spectrum of the polymer-bound benzyl ethoxide after the homogeneous trial was similar to that of the unreacted material.

2,4'-Dihydroxy-5-propyl-3,3',5'-trimethoxydiphenylmethane (15) - Guaiacylpropane (**13**) (1.00 g, 6.02 mmol) and syringyl alcohol (**7**) (2.22 g, 12.05 mmol) were heated under a nitrogen atmosphere for 18 hr at 138 °C in 200 mL of 2M sodium hydroxide. The reaction vessel has been described elsewhere.[39] The cooled reaction mixture was acidified to pH 2 with 5M sulfuric acid and then extracted repeatedly with chloroform. The combined chloroform extracts were reduced in volume to give a brownish oil which was purified by column chromatography (silica gel 60, 30% hexane/chloroform (v/v) followed by a 15% solvent mixture). The fractions containing **15**, as determined by GLC, were combined and concentrated. The resulting yellowish oil was crystallized from toluenepet. ether to give 0.20 g (20% yield) of a white solid: mp, 74.5-76.2 °C, ^{1}H-NMR ($CDCl_3$) δ 0.90 (t, 3, J = 7.5 Hz, CH_3), 1.57 (sextet, 2, J = 7.3 Hz, β-CH_2), 2.47 (unresolved d of d, 2, $ArCH_2$), 3.82 (s, 6, OCH_3'), 3.85 (s, 3, OCH_3), 3.88 (s, 2, Ar_2CH_2), 5.37 (s, 1, OH, exchangeable in D_2O), 5.59 (s, 1, OH, exchangeable in D_2O), 6.49 (s, 2, $C_{2',6'}H$, and unresolved doublet, 1, C_4H), 6.57 (d, 1, J = 1.7 Hz, C_6H); ^{13}C-NMR ($CDCl_3$) ppm 13.8 (q, CH_3), 24.9 (t, β-CH_2), 35.6 (t, Ar_2CH_2), 37.7 (t, $ArCH_2$), 55.9 (q, OCH_3), 56.2 (q, OCH_3'), 105.6 (d, $C_{2',6'}$), 108.8 (d, C_4), 122.0 (d, C_6), 126.4 (s, C_1), 131.8 (s, $C_{4'}$), 132.8 (s, C_2), 133.5 (s, $C_{1'}$), 141.0 (s, C_5), 145.9 (s, C_3), 146.6 (s, $C_{3',5'}$); MS m/e (rel. int.) 332 (55, M^+), 257 (15), 179 (40), 178 (41), 154 (100), 149 (39), 139 (14), 115 (16), 91 (16), 77 (17).

Anal. calcd. for $C_{19}H_{24}O_5$ (%): C, 68.7; H, 7.3; O, 24.1. Found: C, 68.5; H, 7.3; O, 24.2.

2,4'-Dihydroxy-5-propan-3"-ol-3,3',5'-trimethoxydiphenylmethane (17) - A solution of 1.96 mmolar syringyl alcohol (7) in 1M sodium hydroxide (reagent grade) was prepared under nitrogen. The solution was then added (55 mL per bomb) to each of four 70 mL capacity titanium reaction vessels (bombs) containing 100 mg of the polymer-bound model (**14**). The bombs were rotated at 170 °C for 3 hr and then cooled. The reaction mixture was filtered and the collected beads washed with 4x50 mL of the solvents described for the stability test, and dried in a vacuum oven at 40 °C. The supported lignin model **14** was subjected to the condensation procedure a total of three times.

The ITS method, employing the following quantities, was used to cleave reacted and unreacted starting material from the resin: 340 mg of reacted resin, 15 mL of dry acetonitrile, 0.68 mL of ITS, 10 mL of anhydrous methyl alcohol, and 4.25 mL of pyridine. The liquor from the beads, along with 5x10 mL methanol rinses of the resin, were concentrated under pressure at a maximum of 40 °C. The residue was stirred in 10 mL of water and then extracted with 3x10 mL of dichloromethane. The organic extract was dried over sodium sulfate and then concentrated to a dark oil (0.101 g). The oil was purified by column chromatography, employing first 10:1, 8:1, and 6:1 dichloromethane-ethyl acetate mixtures, and finally a 5% methanol-dichloromethane solution. A second chromatography of select coeluted fractions, with a 3% methanol/dichloromethane solution as the eluent, gave only 8 mg of **17**, as a yellow solid: ^1H-NMR ($CDCl_3$) δ 1.83 (pentet, 3, J = 7.7 Hz, β-CH_2, also contains a D_2O exchangeable OH proton), 2.59 (t, 2, J = 6.4 Hz, $ArCH_2$), 3.65 (t, 2, J = 7.0 Hz, CH_2O), 3.84 (s, 6, OCH_3'), 3.87 (s, 3, OCH_3), 3.88 (s, 2, Ar_2CH_2), 5.37 (s, 1, ArOH, exchangeable in D_2O), 5.60 (s, 1, ArOH, exchangeable in D_2O), 6.49 (s, 2, $C_{2',6'}H$), 6.52 (d, 1, J = 1.6 Hz, C_4H), 6.59 (d, 1, J = 1.8 Hz, C_6H); ^{13}C-NMR ($CDCl_3$) ppm 31.9 (t, $ArCH_2$), 34.5 (t, β-CH_2), 35.6 (t, Ar_2CH_2), 56.0 (q, OCH_3), 56.5 (q, OCH_3'), 62.2 (t, CH_2OH), 105.7 (d, $C_{2',6'}$), 109.0 (d, C_4), 122.2 (d, C_6), 126.8 (s, C_1), 131.9 (s, $C_{4'}$), 132.9 (s, C_2), 141.4 (s, C_5), 146.3 (s, C_3), 146.9 (s, $C_{3',5'}$), a signal for $C_{1'}$ was not observed; MS m/e (rel. int.) 348 (72, M^+), 195 (25), 194 (11), 167 (18), 154 (100), 150 (60), 149 (15), 121(12). The NMR spectra of (**17**) were performed by Spectral Data Services.[40]

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