

Chemical Modelling in the Manipulation of Lignin Pyrolysis Pathways

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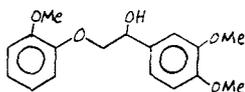
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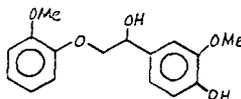
1. Introduction

Lignin is an abundant renewable resource of chemical structure apparently amenable to pyrolytic depolymerization to phenolics. However, the utility of recovered products is low, as only 10-15 wt.% of lignin mass is typically recovered as single-ring phenolics and the major products are gases, char and other high-molecular weight materials.

Chemical modelling provides insight into the intrinsic chemical pathways that superimpose to make observable lignin pyrolysis complex. This use of model compound information can also implicate both the favorable and deleterious reaction pathways that may be susceptible to acceleration or circumvention through catalysis or solvolysis. Along these lines, the three classes of experiments reported herein are of : i) lignin pyrolysis; and thusly derived modification strategies of ii) catalytic dehydrogenation of lignin prior to pyrolysis and iii) solvolytic depolymerization of lignin in supercritical water (SCW). We focus on the reactions of the β -ethers that help link lignin into a polymer, of which the glycols veratrylglycol- β -guaiacyl ether (VGE, structure I) and guaiacylglycol- β -guaiacyl ether (GGE, structure II) are simple models.



I



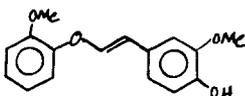
II

Thermolyses of pine wood, kraft lignin and a milled wood lignin in SCW also permit scrutiny of the relevance of model results to the reactions of real systems.

2. Experimental

Table I summarizes the experiments in terms of the reactants, catalysts and solvents, as well as the associated reaction conditions of temperature, pressure and reactants' concentrations. The reactants VGE and GGE were synthesized as described fully elsewhere (1). The reactor was a 316 stainless steel batch tubing bomb whose construction and use has been described fully elsewhere (2). Product analysis was accomplished by GC and GC-MS, which enabled the calculation of a mass balance index, defined here as the sum of the masses of the product spectra components divided by the initial mass

GGE. The major products of GGE pyrolysis at 250°C were guaiacol and acetovanillone; lesser amounts of cis and trans 1-(3-methoxy-4-hydroxyphenyl)-2-(2-methoxyphenoxy) ethylene (vinyl ether VI) and vinyl-guaiacol.



VI

The temporal variations of the molar yields of the major products and the mass balance are shown in Figure 2. The disappearance rate of GGE far exceeded that of VGE. The mass balance approached an approximate value of 0.4, as was observed for VGE pyrolysis. The initial slopes of guaiacol and acetovanillone formation were both positive, suggesting these to be primary products, although that for guaiacol far exceeded that for acetovanillone. The acetovanillone yield passed through a maximum at approximately 30 min whereas guaiacol appeared to be stable with time. Finally, both forms of the vinyl ether VI appeared to be primary products, whereas vinyl-guaiacol appeared to be the product of a secondary reaction.

3.1.2. Reaction Pathways

The foregoing suggests that VGE pyrolysis comprised the pathways illustrated in Figure 3. Two primary pathways were operative, the major of which being dehydration to the vinyl ethers and the minor being direct fragmentation to guaiacol and, likely, an enol intermediate capable of rapid tautomerization to 3,4-DMA. Each of the primary products was susceptible to secondary reactions. The detection of the dimer of the vinyl ether as well as the progressive nonclosure of observable products' material balance are both indicative of vinyl ether polymerization to species too heavy to elute during GC analyses. Paring of the vinyl ether or its presumed oligomers was also clearly operative. It is noteworthy that the ultimate material balance of 0.4 is closely equal to the weight fraction of the guaiacol moiety in VGE.

Whereas GGE pyrolysis pathways were analogous to those for VGE, the selectivity to each was markedly different: α - β dehydration of GGE was much less significant than its cleavage to guaiacol and acetovanillone. The large yields of guaiacol, far in excess of the acetovanillone yields, indicate secondary guaiacol formation by the cleavage of the guaiacyl group from the vinyl ether VI or any of its subsequent polymers. Of interest is the presence of vinyl-guaiacol, which could be a product of the homolytic cleavage of vinyl ether VI. Its analogue, vinyl-veratrole, was absent from VGE pyrolysis. Acetovanillone was subject to secondary degradation.

3.1.3. Motivation of Catalytic and Solvolytic Modification Strategies

The pyrolysis results detailed above show that a significant β -ether reaction pathway was its undesirable dehydration to a vinyl ether that subsequently underwent yield-reducing polymerization reactions. The ultimate recovery of single-ring products from these substrates could thus be enhanced by reducing the reaction selectivity to the dehydration pathway. Catalytic dehydrogenation of the aliphatic hydroxyls of VGE and GGE to carbonyls would not only prevent the dehydration, and thus circumvent its associated ill effects, but also allow better utilization of the two substrate hydrogen atoms that would otherwise be rejected with the water. For example, shuttling of this hydrogen would allow for the stabilization of free-radicals formed during the subsequent pyrolysis of a dehydrogenated and deoxygenated residue.

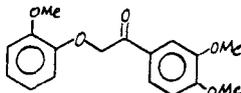
The selectivity of the β -ether reactions may be modified by SCW as well. For example, Lawson and Klein (2) showed that the reaction of guaiacol in SCW was a superposition of parallel pyrolysis and hydrolysis pathways, the selectivity to the latter increasing with increasing water density. The hydrolysis of guaiacol to catechol and methanol was in material balance and the water apparently suppressed a secondary char-forming reaction of catechol. Also, Townsend and Klein (3) showed that the hydrolysis by SCW of DBE to benzyl alcohol competed with the slower pyrolysis of DBE toluene and benzaldehyde. It thus seems reasonable that hydrolysis of the β -ethers by pathways formally similar to those observed for DBE hydrolysis could compete with the formation of the vinyl ethers and circumvent its polymerization. In short, the reactions of guaiacol and DBE in SCW suggest that a suitable modification of the β -ether reaction might be achieved in SCW.

In what follows directly we describe the results of the experiments relevant to both of these strategies

3.2. Modification Strategy-Related Results

3.2.1. Catalytic Dehydrogenation of VGE and GGE

Catalytic dehydrogenation of VGE over $\text{Ni/SiO}_2\text{-Al}_2\text{O}_3$ at 250°C yielded guaiacol, 3,4-DMA, 1-*veratryl*-2-(2-methoxy-phenoxy)-ethanone-1 (the dehydrogenated form of VGE, structure VII), and trace amounts of vinyl ether. The rate of VGE conversion



VII

was roughly threefold higher in the presence of the catalyst than when VGE was pyrolyzed neat.

Figure 4 illustrates the temporal variations of product molar yields for reaction at 250°C . The initial

The variation of methanol yield with water density is illustrated in Figure 7. The addition of external water caused a greater than five-fold increase in the mass yield of methanol over that obtained from neat pyrolysis. The insignificant difference between the yields of methanol observed from pyrolysis at the two highest water densities suggests that both of these pyrolyses were at essentially infinite dilution in water.

For both temperatures examined, the sum of the yields of guaiacol, methyl-guaiacol, catechol and methyl-catechol were only slightly sensitive to water density. However, the yields of these phenolics increased monotonically with time during neat thermolysis. In contrast, the yield of guaiacols traversed relative maxima while the yields of catechols increased or were asymptotically stable during reaction in water. Also, the decay of guaiacols was fastest at the highest reduced water density of 1.6 and their maxima in yield occurred at 10 min, compared to 20 min at the intermediate reduced water of 0.8. In general, the total yields of the four major phenolics increased with temperature with the influence of the water being slightly greater but still small at the higher temperature.

Thus the reaction of kraft lignin in SCW included pyrolysis and solvolysis reaction pathways. The hydrolysis of the aromatic methoxyl groups increased methanol yields and shifted the phenolic product spectrum from guaiacols toward catechols. Interestingly, since the mass yield of methanol of 5-6 wt% was higher than the sum of the mass yields of all of the various phenolics, most of the methanol likely resulted from hydrolysis of the methoxyl groups present in the structural skeleton of lignin. These methoxyl groups would be lost to the char fraction under neat pyrolysis conditions.

Milled-wood Lignin. Pyrolysis of milled-wood lignin neat and in the presence of supercritical water at 383°C yielded methanol, guaiacol, methyl-guaiacol, catechol and methyl-catechol as major products.

The temporal variations of the single-ring products are shown in Figure 8. The positive initial slopes of guaiacol and methyl-guaiacol indicate primary formation of these products. The zero initial slope of catechol and methyl-catechol suggest secondary product formation. The guaiacols traversed maxima at approximately 10 min for reaction both neat and in SCW. The sum of the four major phenolic products increased twofold in the presence of SCW. This is markedly different from the kraft lignin results where no net increase of the phenolics was noted.

Figure 9 shows the temporal variations of the methanol yields parametrically with reduced water density. The initial slopes of the methanol yields indicate primary product formation for all cases. The yields of methanol increased approximately fourfold with the addition of external water. The intermediate density produced virtually the same methanol results as the highest density. This is similar to the kraft lignin results.

Loblolly Pine Wood. Neat pyrolysis of loblolly pine wood at 383°C yielded methanol and guaiacol

slopes of both guaiacol and 3,4-DMA are near zero and thus suggestive of secondary product formation. The 1-veratryl-2-(2-methoxy-phenoxy)-ethanone-1 had a small but positive initial slope and was likely a primary product. All products attained maxima at approximately twenty minutes. The maximum yield of single-ring products (guaiacol and 3,4-DMA) was approximately 0.43, which compares with the 0.06 yield obtained from neat thermolysis at 250°C for 30 minutes. Particularly notable in this enhanced product recovery was the large yield of 3,4-DMA which represents the veratryl portion of the VGE molecule. The initial rate of formation of 3,4-DMA approximately equaled that for guaiacol but the ultimate yields of 3,4-DMA were in excess due to the secondary degradation of guaiacol. This portion of VGE recovered as 3,4-DMA was normally lost to the vinyl polymerization during neat pyrolysis.

Thus catalysis by $\text{Ni/SiO}_2\text{-Al}_2\text{O}_3$ not only effected the desired dehydrogenation but also appeared to crack the resulting keto-ether with hydrogen addition. The net reaction of VGE to guaiacol and 3,4-DMA was thus in hydrogen balance and a selective rearrangement of the hydrogen already present in the substrate.

The catalysis of GGE over $\text{Ni/SiO}_2\text{-Al}_2\text{O}_3$ yielded the same major products as did its pyrolysis: guaiacol, acetovanillone, vinyl-guaiacol and cis and trans forms of vinyl ether VI. However, the rate of GGE reaction was significantly higher than observed during its pyrolysis, as its conversion was essentially 1.0 after a reaction time of only 10 min. This rate also exceeded the rate of VGE catalysis.

The temporal variations of the product molar yields and mass balance are depicted in Figure 5. The mass balance quickly dropped to 0.2. The only product observed in a significant yield was guaiacol, and its initial rate of formation was higher than for GGE pyrolysis. Guaiacol was also subject to a moderate secondary reaction. The rate of formation of vinyl ether VI was approximately equal to that for neat pyrolysis indicating little or no inhibition of the dehydration pathway by the catalyst. A keto-ether analogous to VII, and hence any evidence of a dehydrogenation pathway, was not observed. The presence of the catalyst thus seemed both to enhance the deleterious dehydration and polymerization pathways as well as to promote charring of guaiacol.

3.2.2. Solvolysis in Supercritical Water

Kraft Lignin. The major products of kraft lignin pyrolysis both neat and in water were methanol, guaiacol, methyl-guaiacol, catechol and methyl-catechol. Smaller amounts of phenol and cresols were also detected.

Temporal variations of these major products for reaction at 383°C are shown in Figure 6. The positive initial slopes associated with guaiacol and methyl-guaiacol shown in Figure 6 indicate that these were primary products. Slopes for catechol and methyl-catechol of essentially zero indicate that these were secondary products. The small positive initial slope for methanol suggests that it formed by a primary pathway, although it was likely both a primary and a secondary product.

while reaction in the presence of supercritical water at the same temperature yielded methanol, guaiacol, methyl-guaiacol, catechol and methyl-catechol as major products.

The temporal variations of the single-ring products are shown in Figure 10. The initial slope associated with guaiacol yield from neat pyrolysis was too small to be determined conclusively. However, for reaction in SCW, the initial rate of formation of both guaiacol and methyl-guaiacol was positive and these thus appear to have been primary products. Catechol and methyl-catechol were evidently secondary products. The overall yield of single-ring phenolics increased three-fold with the addition of external water.

The temporal variations of the yield of methanol is shown in Figure 11 for two reduced water densities. The initial slopes indicate primary product formation in both cases. The yield of methanol was virtually unaffected by the addition of water, which is consistent with the isolated lignin experiments. During pyrolysis, the carbohydrate fraction of the wood should lead to significant yields of water capable of hydrolyzing the methoxyl groups present in the lignin. Since the milled-wood lignin results demonstrated the attainment of an asymptotic yield as the external water loading increased, the addition of external water to the wood would prove an insignificant increment to the water originating from the carbohydrate pyrolysis.

4. References

1. Landucci, L. L.; Geddes, S. A.; Kirk, T. K. *Holzforschung* 1981, **35**, 1, 67.
2. Lawson J. R.; Klein, M. T. *Ind. Eng. Chem., Fundam.* 1985, accepted.
3. Townsend, S. H., and Klein, M. T. *Fuel* 1985, accepted.

Table I - Summary of Reactants and Reaction Conditions

Reactant	Loading (mg)*	Catalyst	Solvent	Temperature	Pressure (psia)
VGE	15	--	--	250°C	26
VGE	15	--	--	315°C	29
VGE	15	--	--	335°C	30
VGE	15	--	--	380°C	32
GGE	15	--	--	250°C	26
VGE	15	Ni/SiO ₂ -Al ₂ O ₃	--	250°C	26
GGE	15	Ni/SiO ₂ -Al ₂ O ₃	--	250°C	26
Kraft Lignin	15	--	--	383°C	32
Kraft Lignin	15	--	H ₂ O	383°C	4260
Kraft Lignin	15	--	H ₂ O	383°C	3466
Kraft Lignin	15	--	--	408°C	34
Kraft Lignin	15	--	H ₂ O	408°C	5750
Milled-Wood Lignin	10	--	--	383°C	32
Milled-Wood Lignin	10	--	H ₂ O	383°C	4260
Milled-Wood Lignin	10	--	H ₂ O	383°C	2467
Pine Wood	35	--	--	383°C	32
Pine Wood	35	--	H ₂ O	383°C	4260

*Reactor Volume was 0.589 cm³

VGE PYROLYSIS 315°C

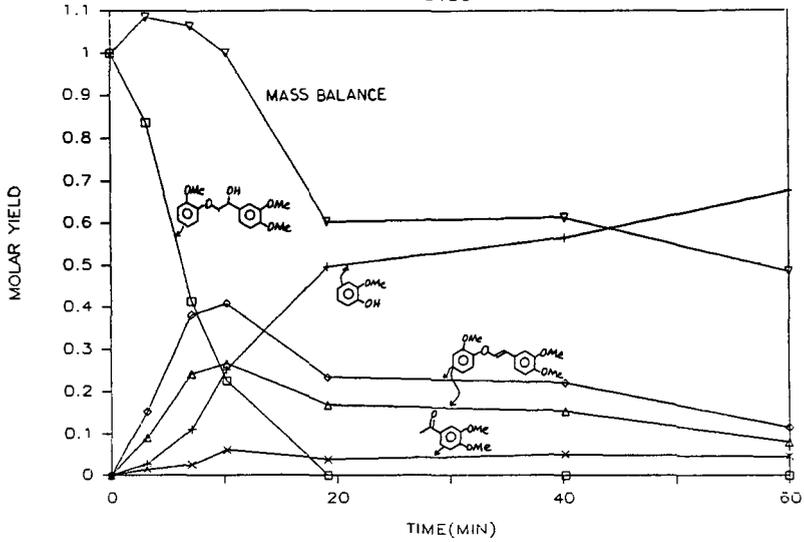


Figure 1. Temporal variations of the yields of the major VGE pyrolysis products at 315°C.

GGE PYROLYSIS 250°C

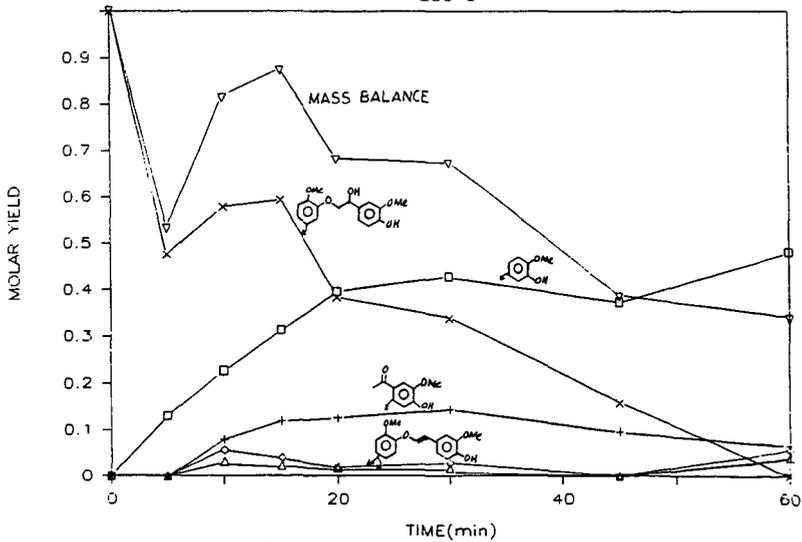


Figure 2. Temporal variations of the yields of the major GGE pyrolysis products at 250°C.

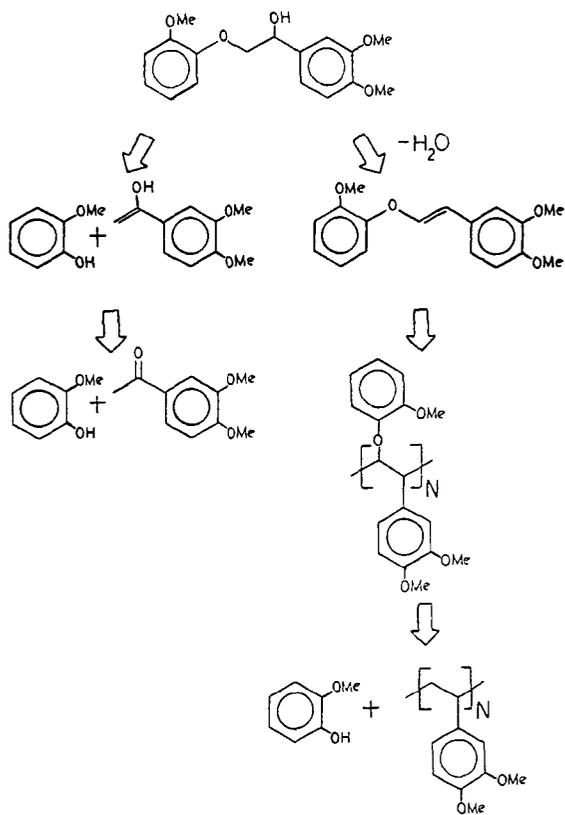


Figure 3. VGE pyrolysis pathways.

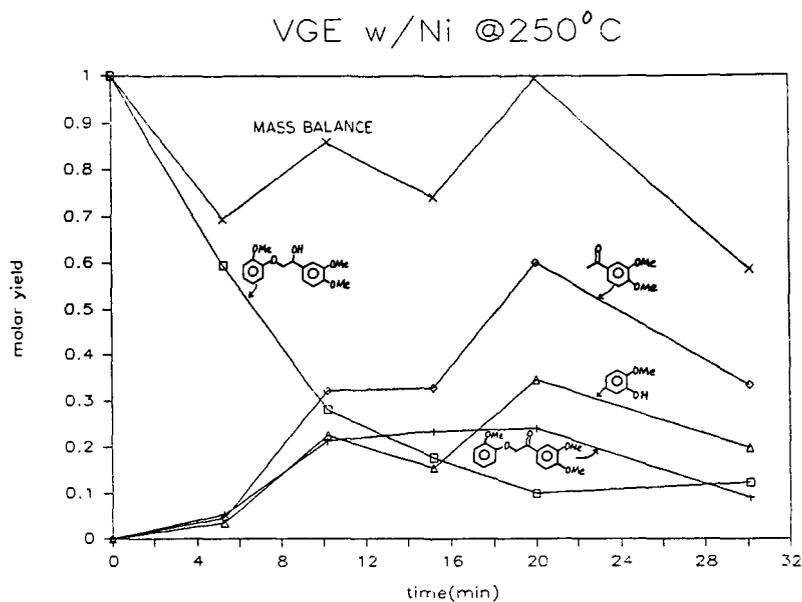


Figure 4. Temporal variations of the yields of the major VGE catalysis products at 250°C.

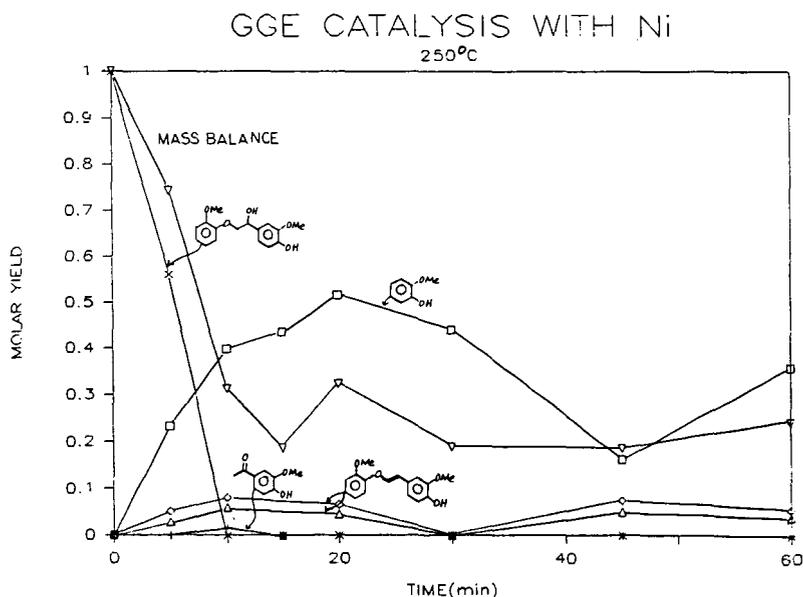


Figure 5. Temporal variations of the yields of the major GGE catalysis products at 250°C.

a) KRAFT LIGNIN PYROLYSIS 383°C
NEAT

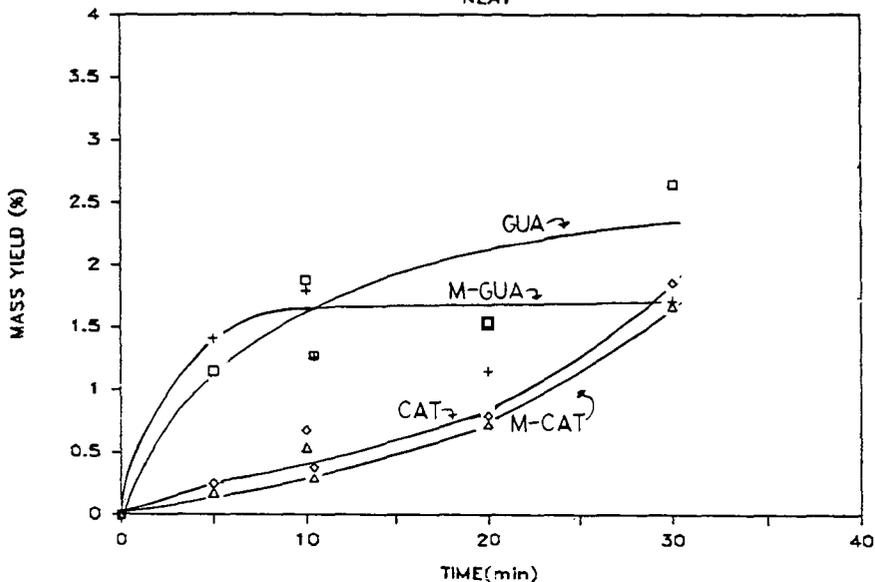
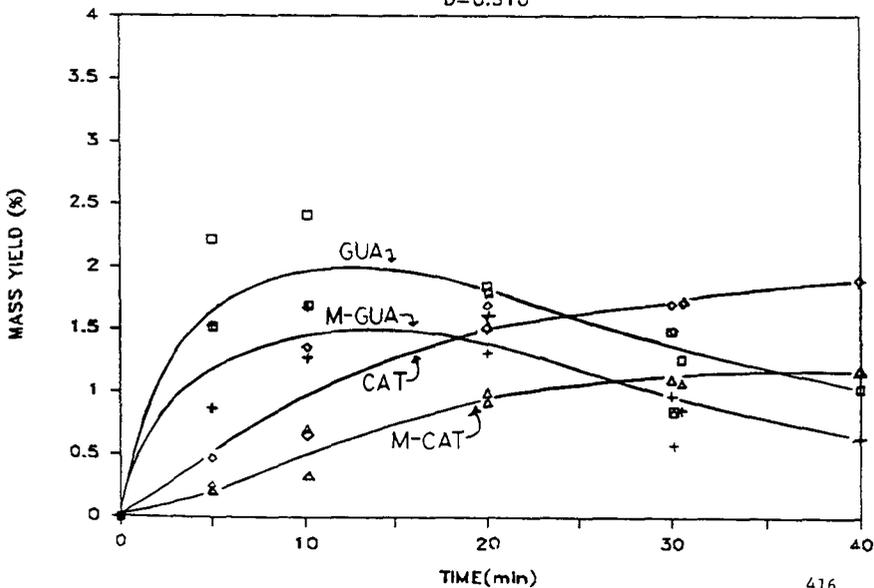


Figure 6. Temporal variations of the yields of the major single-ring products of kraft lignin pyrolysis a) neat b) with water.

b) KRAFT LIGNIN PYROLYSIS 383°C
D=0.510



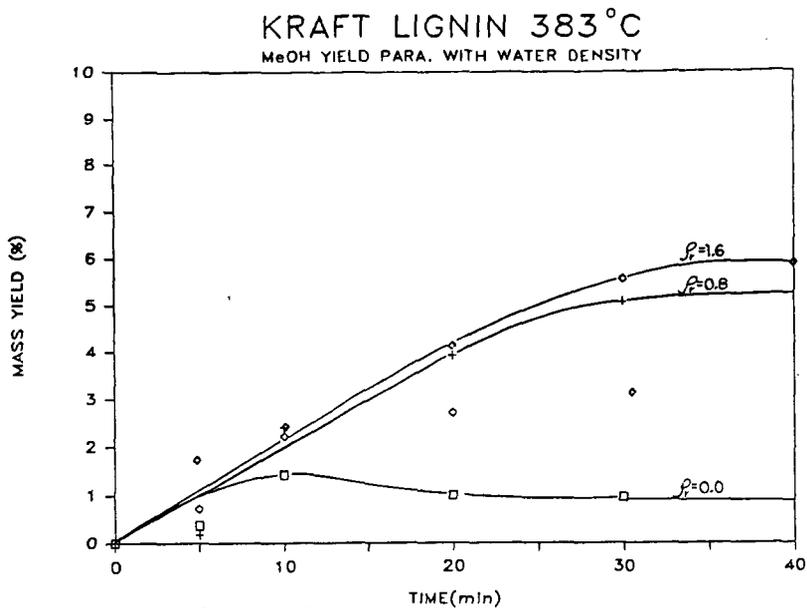


Figure 7. Temporal variation of methanol yield parametric with reduced water density for kraft lignin.

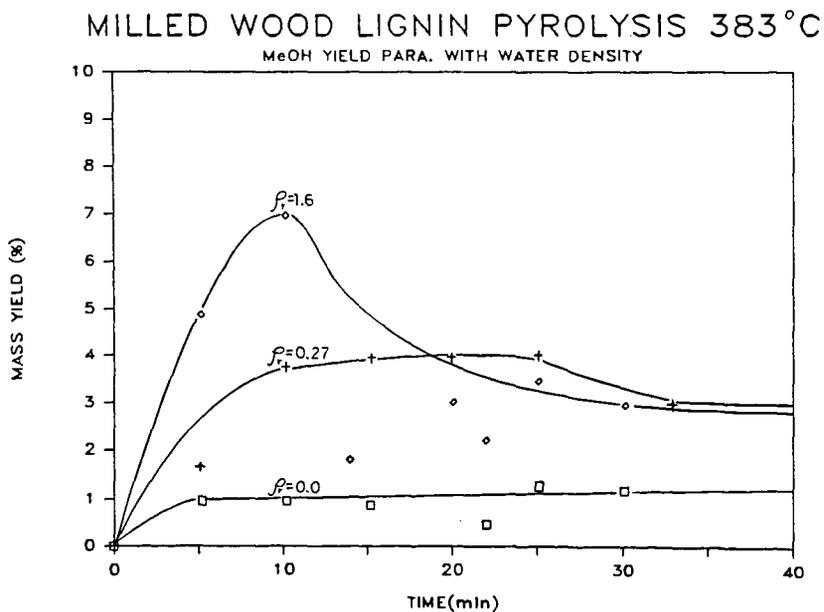


Figure 9. Temporal variation of methanol yield parametric with reduced water density for milled-wood lignin.

a) MILLED WOOD LIGNIN PYROLYSIS 383°C
NEAT

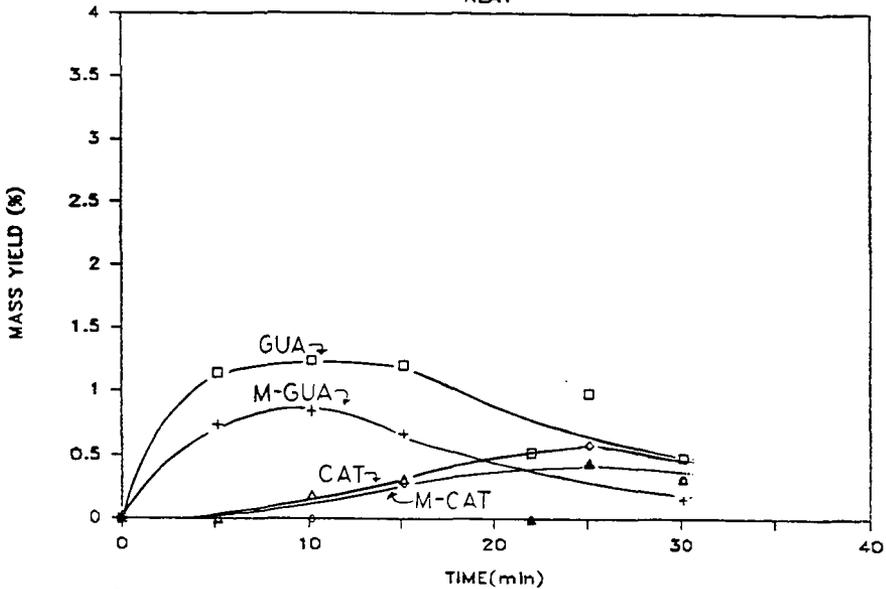
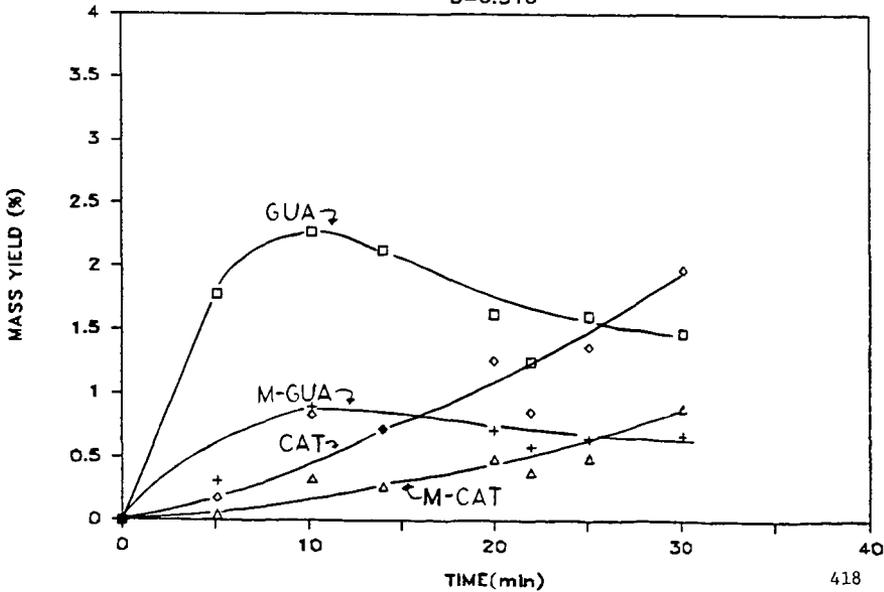


Figure 8. Temporal variations of the yields of major single-ring products of milled-wood lignin pyrolysis a) neat b) with water.

b) MILLED WOOD LIGNIN PYROLYSIS 383°C
D=0.510



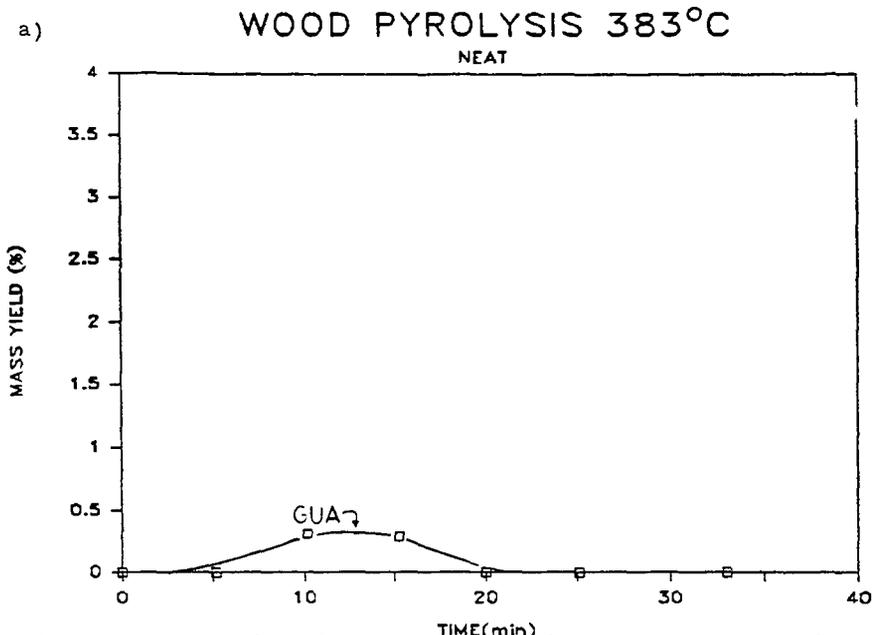
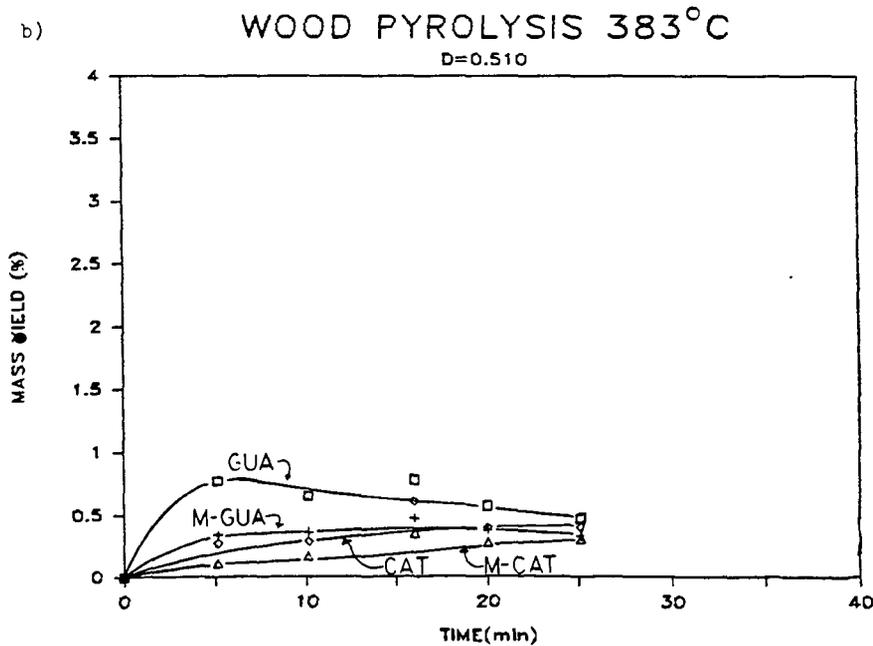


Figure 10. Temporal variations of the yields of the major single-ring products of pine wood pyrolysis a) neat b) with water.



WOOD PYROLYSIS 383°C

MeOH YIELD PARA. WITH WATER DENSITY

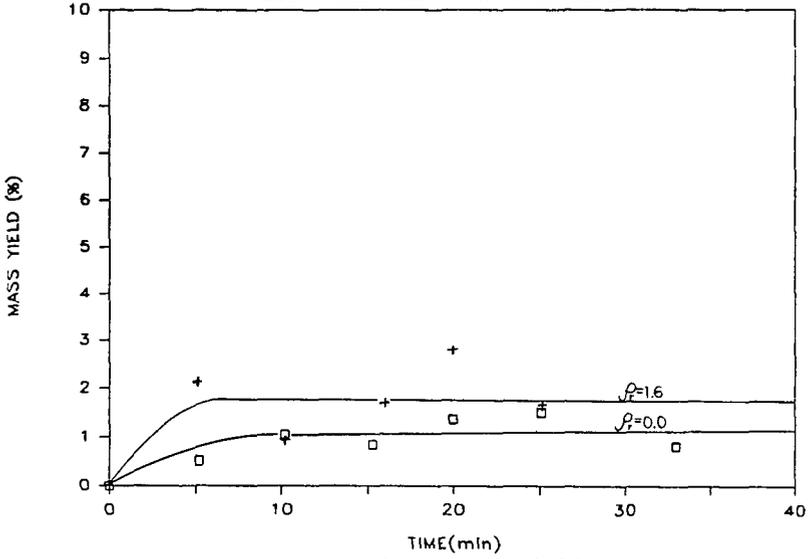


Figure 11. Temporal variation of methanol yield parametric with reduced water density for loblolly pine wood.