Chemical Modeling in the Deduction of Process Concepts: A Proposed Novel Process for Lignin Liquefaction

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The topic of hydrogen consumption during lignin liquefaction is used herein as a vehicle with which to illustrate the application of chemical modeling in the deduction of conceptual process flow sheets. Chemical modeling is the use of model compound information, such as reaction pathways, kinetics, and mechanisms, in the analysis of real reaction systems. Experiments with the model compound α-[(o-methoxyphenoxy)methyl]veratryl alcohol (VGE: Brezny et al., 1983), a structural mimic of prevalent ß-ether moieties within lignin, allowed resolution of a major dehydration reaction and a minor fragmentation reaction as the primary pathway of its thermolysis. These new experimental results, coupled with reaction pathway analyses, suggest that optimal utilization of the hydrogen contained in not only lignin, but also any donor solvent present, would result from following a processing scheme where dehydrogenation, not hydrogenation, is the first step. The general usefulness of chemical modeling is emphasized over the details of the specific vehicle strategy.

Mathematical modeling permits chemical engineers to analyze reaction systems whose fundamentals might otherwise be obscured in their complexities. For example, the design of a fixed-bed catalytic reactor can be complicated because of the intrusion of heat and mass transport limitations on both the laboratory procurement of a reaction rate expression and the actual commercial operation. However, these intrusions are accounted for almost routinely because of the classical analyses of Thiele (1939), for example, wherein the combination of physical insights and mathematical modeling permits the extraction and utilization of intrinsic kinetics parameters. A chemical analogue to mathematical modeling might also find use.

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The present communication uses lignin liquefaction as a specific vehicle example to develop a chemical modeling approach to the analysis of complex reaction systems.

The production of chemicals and fuel from alternative resources like lignins, cellulose, coal, oil shale, tar sands, and heavy oils is of considerable interest. These resources are carbon-rich relative to typically desired liquefaction products, e.g., distillates, gasoline, or phenolics, and the utilization of hydrogen during the liquefaction of these materials is an important processing variable.

Lignin depolymerization requires hydrogen transfer from a donor or within lignin because most of the bonds that link its phenolic moieties into a polymer are hydrogen-deficient, i.e., require the formal uptake of two hydrogen atoms for fragmentation to stable-end products. This capping of reactive centers is therefore useful and necessary and, as the sole mode of hydrogen transfer, would represent an optimal utilization of hydrogen during lignin depolymerization. However, the formation of hydrogen-rich products like methane and water during lignin pyrolysis and liquefaction is well-known (Iatridis and Gavalas, 1979; Chan and Krieger, 1981; Allan and Matilla, 1971; Jegers and Klein, 1985). This increases liquefaction hydrogen consumption and, hence, processing costs. The formation of hydrogen-rich products must be attended by the formation of carbon-rich products (relative to lignin) during neat thermolysis. Process strategies aimed at minimizing the formation of these products during the liquefaction of lignin would thus be useful.

This motivates the present use of chemical modeling toward the deduction of such strategies or conceptual process flow sheets. Specifically, the details presented here suggest that an optimal utilization of the hydrogen contained in lignin or a donor solvent would result from following a processing scheme that involves an initial dehydrogenation and not hydrogenation of the lignin, which is hydrogen-poor relative to useful low molecular weight phenolics. In what follows, the generalities of chemical modeling are briefly described first. The remaining discussion is divided into two parts. In the first, chemical modeling is applied through a brief analysis of lignin, a description of experimental methods, the delineation of new pyrolysis results, and the deduction of the novel processing concept. In the second part, the limitations and utility of both the deduced process and chemical modeling in general are considered.

Background

The origins of the chemical modeling approach are elsewhere (Virk, 1979; Klein and Virk, 1983). It is motivated from a need for the fundamental information that is disguised in but nevertheless controls complex reacting systems. Reactions of well-characterized low molecular weight model compounds to comparatively simple product spectra allow resolution of fundamental pathways, kinetics, and mechanisms, but these are of the model system and are thus of indirect relevance to the real system. Clearly the mapping of these resolved reaction fundamentals from the model to the real domain can be equivocal; this is the challenge of chemical modeling.

In summary, scrutiny of the chemical structure of the real system allows the selection of model compounds that mimic the structural features of its important chemical moieties. A first set of experiments is then designed to elucidate model compound reaction pathways, kinetics, and mechanisms. The critical step of the approach is where the model compound reaction pathways, kinetics, and mechanisms are used to infer the reactions of the macromolecule. This combination of model compound

results with any appropriate theoretical analysis, e.g., substituent effects not discerned in the model compound experiments, permits the prediction of both the primary reactions of lignin and its reaction intermediates. Additional experimentation and modeling probe the fate of reaction intermediates.

These predictions are truly a priori in the sense that only model compound reaction pathways and kinetics are used to infer the temporal variations of the yields of the products obtained from the reaction of the real system. This compensates for the questionable practical relevance of model system results and allows the development of process concepts that might otherwise have been lost to the complexity of the feedstocks.

Application of the Approach: Hydrogen Utilization in Lignin Liquefaction

Lignin Structure and Model Compounds. Lignin is a phenolic copolymer of coumaryl, coniferyl, and sinapyl alcohol monomers. Lignin aromatic units are linked into a macromolecule by β-ether, α-ether, phenyl ether, diphenylmethane, biphenyl, phenylcoumaran, and pinoresinol bonds (Adler, 1977; Freudenberg and Neish, 1968; Harkin, 1967; Glasser and Glasser, 1974), of which the β-ether bonds are most prevalent. α-[(o-Methoxyphenoxy)methyl]veratryl alcohol (VGE, structure in Figure 3) mimics key structural aspects of lignin β-ethers and was thus selected as a model compound to probe lignin thermolysis.
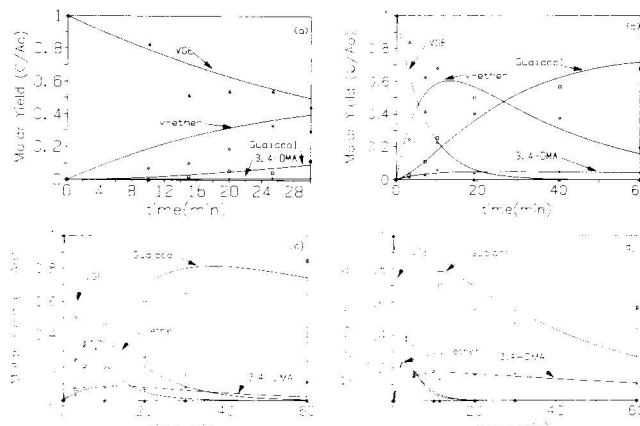
Experimental Section. The synthesis of VGE was similar to the method of Landucci et al. (1981). Commercial argon or nitrogen gas was used to purge the reactors of oxygen. Methylguaiacol (MG), which was used as a standard in the later determination of the product yields, was obtained from Pfaltz & Bauer in reagent grade and used as received.

The 316 stainless steel batch reactor used consisted of a ¼-in. Swagelok port connector and two end caps and had an internal volume of approximately 0.6 cm³. A typical reaction procedure was as follows. The reactor was loaded with 10–16 mg of the substrate VGE, flushed with inert gas, and sealed. It was then placed in a metal basket that was in turn lowered into a heated sand bath. The heat-up time was approximately 2–3 min (Jegers and Klein, 1985). After the reactor had been in the sand bath for the desired time, it was then quenched in a cool air sand bath. A measured amount (—5–6 mg) of the external standard, methylguaiacol, was added to the reactor prior to product extraction with acetone and methylene chloride in approximately equal amounts. The product solution was then analyzed by GC and GC/MS.

Products were identified with electron impact mass spectra obtained on a Finnigan 4510 mass spectrometer (Finnigan MAT Corp., San Jose, CA) operating at 70 eV. Pyrolysis products were separated over a 50 m × 0.25 mm i.d. borosilicate glass WCOT capillary column, with a stationary phase of SE-54, in a Hewlett-Packard 5880A gas chromatograph equipped with a flame ionization detector and electronic integrator. Product yields were determined by relating the area of each product to the area of the methylguaiacol. Product response factors were determined by the analysis of solutions of measured amounts of available standards. The response factors of some of separately unavailable higher molecular weight products were estimated to be equal to those for compounds of similar molecular weight and structure. The foregoing quantitation of reaction products permitted estimation of material balance closure, here defined as the sum of the weights of the components in the product spectrum, in-

Table I. Experimental Conditions for VGE Pyrolysis

| temp, °C	holding time, min	observable prod normalized mass, g/g of VGE_0
250	10.1	0.89
	15.0	0.63
	20.0	0.75
	25.3	0.88
	30.1	0.78
315	3.2	1.09
	7.1	1.06
	10.2	1.00
	19.2	0.60
	40.2	0.61
	60.0	0.48
335	3.0	0.79
	5.1	0.80
	10.2	0.41
	20.0	0.54
	30.0	0.45
	60.0	0.45
380	5.1	0.55
	10.1	0.39
	11.5	0.43
	20.1	0.41
	30.0	0.40
	60.0	0.39

Figure 1. (a) Temporal variations of the yields of major VGE pyrolysis products at 250 °C. (b) 315 °C, (c) 335 °C, and (d) 380 °C.

cluding the unreacted substrate, divided by the initial weight of the substrate loaded to the reactor.

Results. Table I summarizes the VGE pyrolysis conditions. VGE was pyrolyzed neat at temperatures ranging from 250 to 380 °C. The initial VGE concentration was approximately 2.7×10^{-3} mol/cm³. The mass balance, described above, is also listed in Table I and showed progressive nonclosure with increasing pyrolysis temperature and time in an asymptotic approach to 0.4.

The four major products were guaiacol, 3,4-dimethoxyacetophenone (3,4-DMA), and cis and trans forms of a vinyl ether formed through $\alpha-\beta$ dehydration of VGE. Less prevalent products included o-cresol, veratrole, 3,4-dihydroxyacetophenone (3,4-DHA), (o-methoxyphen0xy)-acetaldehyde, β-hydroxy-3,4-dimethoxyacetophenone, and a dimer of the vinyl ether that had a molecular weight of 572.

The temporal variations of the major products' molar yields are shown in Figure 1, parts a, b, c, and d depicting the pyrolysis at 250, 315, 335, and 380 "C, respectively. The positive initial slope of the vinyl ether (in both cis and trans forms) is suggestive of primary product formation. Guaiacol appeared with a smaller but nonzero initial slope and was likely a minor primary product; the large ultimate
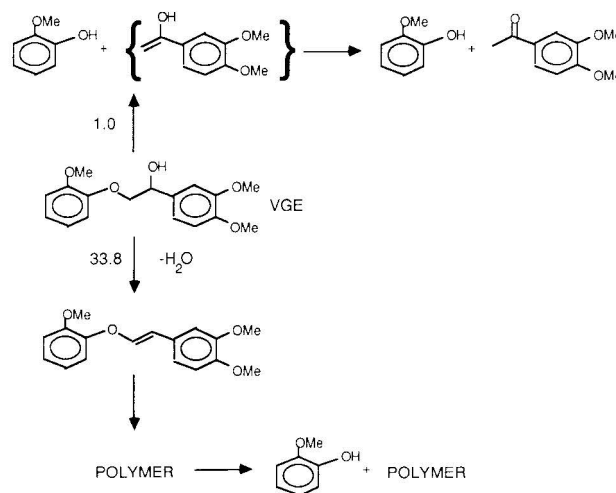
Figure 2. VGE pyrolysis pathways.
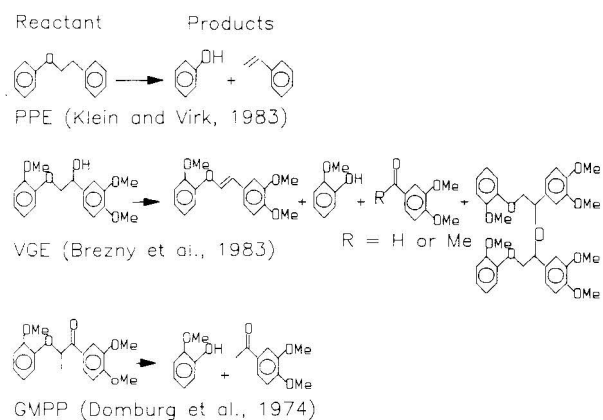
Figure 3. Summary of previous pyrolyses of VGE and related compounds.

yields of guaiacol indicate that it is also a significant secondary product. Similarly, 3,4-DMA appeared with a small positive initial slope that suggests primary product formation; it is difficult to compare quantitatively the initial rate of 3,4-DMA formation with the small and uncertain primary rate of guaiacol formation.

The variation of the product spectrum with pyrolysis temperature is informative. The only observable products at 250 °C were the two forms of the vinyl ether, which were asymptotically stable with time, and trace amounts of guaiacol. At the two intermediate temperatures the vinyl ethers appeared with initial slopes far greater than that for guaiacol and attained maxima in yields before undergoing secondary decomposition. Pyrolysis was so facile at 380 °C that the initial slopes of both vinyl ethers and guaiacol could not be determined with precision. Guaiacol yields traversed a maximum at this temperature, and its secondary decomposition was to catechol, phenol, and o-cresol products. It is also interesting to note that the yield of guaiacol was always in excess of the yield of 3,4-DMA and its likely secondary reaction products acetovanillone and 3,4-DHA.

The foregoing suggests that VGE pyrolysis comprised the pathways illustrated in Figure 2. Two primary pathways are 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 analysis. Paring of the vinyl ether or its presumed oligomers was also clearly operative.

Discussion of Experimental Results

Results of previous pyrolyses of VGE or closely related compounds are summarized in Figure 3. A very simple model of the carbon–oxygen skeleton of VGE, phenethyl phenyl ether (PPE), yields the primary pyrolysis products phenol and styrene in initially equimolar proportions, with styrene yields subsequently decreasing due to secondary reactions (Klein and Virk, 1983). Formal application of this pathway to the VGE skeletal atoms would suggest the formation of guaiacol and an enol, the latter capable of tautomerization to 3,4-DMA. Thus, the minor of the primary VGE pyrolysis pathways is akin to primary PPE pyrolysis. The secondary decomposition of styrene is analogous to the vinyl ether polymerization observed here.

β-Ethers more closely related to VGE have been studied by Brezny et al. (1983) and Domburg (1974). Brezny et al. (1983) conducted low-temperature, nonisothermal thermolyses of VGE on a heated glass plate. Major products observed were like those noted above and included guaiacol, 3,4-DMA, and the vinyl ethers. These workers also reported the formation of an α-O-α ether to occur by the intermolecular dehydration of two VGE molecules. No other high molecular weight products were reported.

Domburg's (1974) pyrolyses of β-ethers with three-carbon side chains like those found in lignins revealed substantial dehydration of the aliphatic hydroxyls at temperatures as low as 200 °C. These workers also observed very low yields of single-ring products, which accords with the present work and also suggests that 0-ether cleavage was not a major primary reaction. In fact, most of the guaiacol yield was attributed to fragmentation of two unknown dimeric compounds, which were found in considerable yield. The present results suggest that these unknown compounds were either vinyl ethers or their oligomers.

Domburg (1974) also studied the dehydrogenated β-ether l-(3,4-dimethoxy-l-phenyl)-2-(o-methoxyphenoxy)-1-propanone (GMPP), shown in Figure 3. GMPP has functionality similar to the keto ether that would result from the dehydrogenation of VGE. GMPP was more thermally stable than the a-hydroxylated β-ethers, but its higher severity fragmentation led to higher yields of single-ring products than were observed in the present pyrolyses. The major GMPP pyrolysis products were guaiacol and acetovanillone, the latter of which is analogous to the 3,4-DMA produced from VGE pyrolysis.

Deduction of Process Concept. The VGE pyrolysis network of Figure 2 suggests that lignin pyrolysis contains at least two undesirable pathways. First, the dehydration of a-hydroxyls represents the rejection of hydrogen from a carbon-rich resource in the formation of a low-value product (H_2O). Second, the polymerization of the vinyl ether dehydration coproducts is an undesirable sink of potentially recoverable single-ring aromatic products. Prevention of the dehydration would thus appear useful.

Dehydrogenative pretreatment of aliphatic hydroxyl groups prior to pyrolysis could prevent pyrolytic dehydration and its deleterious consequences. Carbonyls like those that would be concomitantly formed are well-known to decarbonylate upon pyrolysis (Brower, 1977; Klein and Virk, 1981; Ingold and Lossing, 1953), and a scheme involving dehydrogenation prior to pyrolysis might thus ultimately yield 1 mol each of H_2 and CO for every mole of H_2O prevented. Here it is cogent to recall that Domburg

(1974) found higher yields of single-ring products from the pyrolysis of the carbonyl-containing GMPP than from its hydroxylated form.

It is intriguing that the initial direction of hydrogen transfer suggested above is contrary to both conventional coal liquefaction strategies and the guidance of overall stoichiometry: the suggestion is to dehydrogenate a hydrogen-poor resource. The foregoing analysis shows that it is the high oxygen content of lignin, and the propensity of this oxygen to be rejected as water during pyrolysis, that makes this strategy reasonable. Oxygen rejection as water is costly, since it implies rejection of the lignin's hydrogen and establishes a vinyl ether which can later polymerize. In contrast, pyrolysis after prior dehydrogenation would permit the oxygen to be rejected as CO, which, in addition to allowing hydrogen to remain in the lignin, also leaves the residue less carbon-rich. With this oxygen rejection accomplished, traditional coal liquefaction strategies would be proper; the hydrogen accumulated during the initial dehydrogenation step could be reintroduced into the liquefaction to assist depolymerization by capping reactive centers.

It is also interesting to examine the fate of the hydrogen atoms of any donor solvent present during liquefaction of the lignin by traditional methods. Since a donor solvent like tetralin reduces carbonyls to hydroxyls (Brower, 1977; Kamiya et al., 1979), which are in turn susceptible to dehydration (Kamiya et al., 1979), it is reasonable to suspect that carbonyls, either initially present in the lignin or resulting from pyrolysis reactions, could likewise be reduced and lead to the formation of additional water. Consider, for example, the implied consequences of the pyrolysis of lignin in fully deuterated tetralin-d_{12}: if the formation of H_2O from dehydration of β-ethers containing lignin's hydrogen is undesirable, it would be even more unfortunate to form D_2O through the subsequent reduction and dehydration of carbonyls.

Summary and Conclusions

Chemical modeling has permitted the deduction of a novel process strategy that is contrary to conventional, stoichiometrically motivated hydroprocessing approaches. This use of model compound reaction information allowed reasonable, testable speculation into the fundamentals that control the reactions of real systems but are obscured in its complexity. This is the significant result, with the dehydrogenation of lignin prior to its pyrolysis being but one specific example.

Important conclusions are as follows:

1. The analysis of VGE pyrolysis allowed a pathway for the evolution of pyrolytic water from lignin to be discerned. A concurrent polymerization pathway is likely responsible for the high yields of adducts and low yields of single-ring products obtained from lignin pyrolysis.

2. A specific process strategy involving dehydrogenation of lignin prior to its pyrolysis was developed. Implementation of this strategy should prevent water formation and enhance the recoverability of single-ring products.

3. A more general chemical modeling approach to the delineation of important reaction pathways of complex chemical substrates was developed and demonstrated. It is reasonable to suspect that the approach might permit the development of process strategies that would otherwise be unapparent because of the complexity of actual reacting systems.

Registry No. VGE, 17078-88-5; lignin, 9005-53-2.

Literature Cited

Adler, E. *Wood Sci. Technol.* **1977,** *11,* 169.

Allan, G. G.; Matilla, T. In Lignins: *Occurrences, Formation, Structure and Reactions*; Sarkanen, K. V., Ludwig, C. H., Eds.; Wiley-Interscience: New York, 1971.

Brezny, R.; Mihalov, V.; Kovacik, V. *Holzforschung* **1983,** *37,* 199.

Brower. K. R. Fuel **1977,** *56,* 245.

Chan, R. W.; Kreiger, B. B. *J. Appl. Polym. Sci.* **1981.** *26,* 1.

Domburg, G. E. In Thermochemical Analysis, Proceedings of the 4th International Conference on Thermal Analysis, Budapest; Wiley: New York, 1974; Vol. 2, p 211.

Freudenberg, K.; Neish, A. C. *Constitution and Biosynthesis;* Springer-Verlag: New York, 1968.

Glasser, W. G.; Glasser, H. R. *Macromolecules* **1974,** *7,* 17.

Harkin, J. M. In *Oxidative Coupling of Phenols;* Taylor, W. I., Battersby, A. I., Eds.; Marcel-Dekker: New York, 1967.

Iatridis, B.; Gavalas, G. R. *Ind. Eng. Chem. Prod.* Res. *Dev.* **1979,** *18,* 127.

Ingold, K. V.; Lossing, F. P. *Can. J. Chem.* **1953,** *31,* 30.

Jegers, H. E.; Klein, M. T. *Ind. Eng. Chem. Process Des. Dev.* **1985,** *24,* 173.

Kamiya, Y.; Yao, T.; Oikawa, S. *Prepr. Pap. Am. Chem. Soc., Div. of Fuel Chem.* **1979,** *24*(2), 116.

Klein, M. T.; Virk. P. S. Energy Lab Report No. MIT-EL-81-005, 1981; M.I.T., Cambridge, MA.

Klein, M. T.; Virk, P. S. *Ind. Eng. Chem. Fundam.* **1983,** *22,* 35.

Landucci, L. L.; Geddes, S. A.; Kirk, T. K. Holzforschung 1981, *35*(1), 67.

Thiele, E. W. *Ind. Eng. Chem.* **1939,** *31,* 916.

Virk. P. S. Fuel 1979, 58, 149.