Kinetics of Dielectric-Loss Microwave Degradation of Polymers: Lignin

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Synopsis

The rate of product formation as well as detailed product composition were measured in the rapid pyrolysis of a 1.3-cm cylindrical pellet of lignin, a major component of biomass. Volume heating by dielectric-loss microwave heating resulted in rapid weight loss with an apparent rate coefficient of 1–5 min^{-1}. Char yield was surprisingly low (33%) owing to the rapid heating rate and high temperature of the pellet. Total gas yield was 38%, of which 12% were simple hydrocarbons and H$_2$ (both weight percent, of original lignin). Product composition showed extensive secondary reaction at high temperatures evidenced by the significant yields of C$_2$H$_2$, H$_2$, and condensed aromatics as well as the typical lignin cracking products such as phenols. Poor coupling of microwave energy to lignin required large power settings in order to initiate reaction. Once initiated, the reaction rate was difficult to control because of the exothermic nature of the reactions. Additives of a suitable composition to increase coupling may be a possible solution to this problem and may result in more favorable economics.

INTRODUCTION

Lignin is a complex polymer as demonstrated by the representative structure in Figure 1.[1,2] It is part of the organic residue remaining in solution when wood is pulped chemically to remove the valuable cellulose fiber. Lignin structure and composition vary, of course, depending on the process used to separate lignin from its parent wood.[1,3] Because of its aromatic structure, it has been compared to coal with respect to its degradation products. It is currently used as a fuel in the forest products industry and has a heating value of roughly 2.7 × 10^4 kJ/dry kg (11,479 BTU/dry lb, Douglas fir lignin[4]).

Integrated utilization plans for biomass including thermal conversion processes emphasize the existing structure of the forest products industry and recognize the high value of cellulose as a fiber. In this context, biomass conversion processes focusing on residues, hemicelluloses, and/or lignin as feedstocks are of interest. The literature contains several critical reviews of the production of chemicals and fuel from lignin and biomass.[5–10] Processes that convert lignin to primarily gases or to liquid products, preferably containing large fractions of simple phenols, have received renewed attention. Recent work reports that phenols can be prepared by hydrocracking lignin in a hydrogen-donating solvent to give yields of phenols near 10%[11] and as high as 42%.[12,13] The economics, however, are not currently favorable for commercialization. The liquid-phase degradation processes are slow and generally require high pressures and the removal of solvent or separation steps. Pyrolysis, on the other hand, requires no other reactants and is quite rapid. Thus, there is renewed interest in examining the gas and liquid (tar) yields from lignin pyrolysis. The effect of heating rate
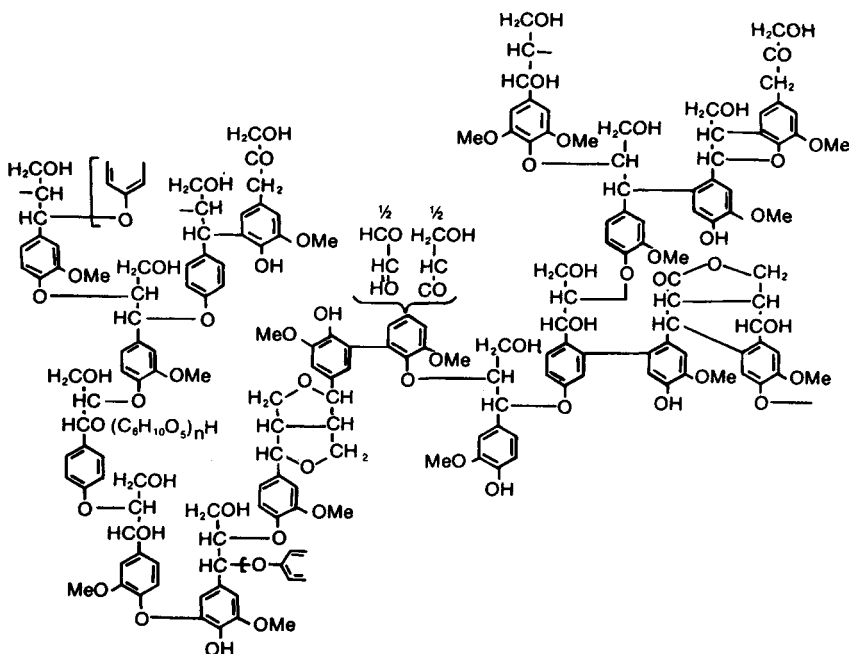
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Fig. 1. Representative structure of coniferous lignin.[1]

and particle size on reaction product composition, in particular, must be examined. Unconventional processes are also being studied,[14] one of which is described in this article.

This article reports product yields from lignin microwave pyrolysis. In dielectric-loss microwave pyrolysis, extremely rapid volume heating of large particles is accomplished. The optimization of microwave applicators and microwave-induced chemical reactions is beyond the scope of this paper. The intent is rather to provide data showing the effect of unusual heat transfer (volume heating) on reaction product distribution in a complex kinetic and mass transfer context. The results here will emphasize detailed product analysis and the extent to which pyrolysis rates can be enhanced in large particles. Data from pyrolysis of cellulose and other substrates are reported elsewhere.[15,16] Models of the heat transfer and chemical reaction mechanisms are discussed in two other studies.[16,17]

PREVIOUS STUDIES

Chemical Aspects

Although cellulose degradation has been discussed extensively in the literature,[2,18–27] lignin has received less attention. The pyrolysis studies on lignin have been reviewed by Goldstein,[5,6] Allan and Matilla,[28] Goheen,[7–9] Wenzl,[29] and Pearl.[30] Recently, Iatridis and Gavalas[31] performed a small-sample lignin pyrolysis with an electrically heated screen. This apparatus has been described in detail by Anthony et al.[32] and Lewellen et al.[21] It is specifically designed to

pyrolyze materials while minimizing heat and mass transport limitations (i.e., to allow rapid escape of volatiles from the isothermal solid), to provide a wide range of constant heating rates by intimate contact of the small particle sample with a heated screen, and to determine initial products before secondary reactions can occur. Because of the increasing use of this method for obtaining intrinsic thermal degradation chemical kinetics for complex polymers,[33] this method will be compared to microwave pyrolysis throughout this article, and the heating mode will be referred to as "grid heating."

One of the motivations for pyrolyzing the *components* of wood (cellulose, lignin, and hemicelluloses) is that it has been suggested that the major components of biomass degrade in separate pathways delayed in temperature.[2,34] This has not been demonstrated. However, when one examines the thermal behavior of each polymer as indicated by weight loss as a function of slowly increasing temperature in Figure 2,[35] it is evident that the lignin undergoes degradation over a wider temperature range than cellulose. These data imply that lignin exhibits a wider distribution of bond strengths and larger number of reactive volatiles. It seems that no single intermediate dominates the pyrolysis pathways of lignin as levoglucosan appears to dominate the pyrolysis of cellulose.[19,34] The weaker ester linkages and aliphatic hydroxyl bonds of the cellulose undergo degradation at lower temperatures than the aromatic bonds of lignin. Soltes[10] has proposed a mechanism for wood pyrolysis that includes a pathway for interaction of the primary volatiles identified by Franklin for cellulose and by Iatrides and Gavalas for lignin. According to Figure 2, lignin volatiles can react with cellulose reaction products after a temperature of roughly 300°C is attained. This effect is enhanced if the pyrolysis occurs at high pressures or high heating rates, or the volatiles are confined inside a large pellet. Large wood particles are typically used to avoid expensive milling, and densified biomass pellets are being considered as a possible fuel, yet particle size strongly influences pyrolysis rate. Thus, to increase understanding and for prediction of products from large-particle biomass pyrolysis, separate examination of the component devolatilization must be made.
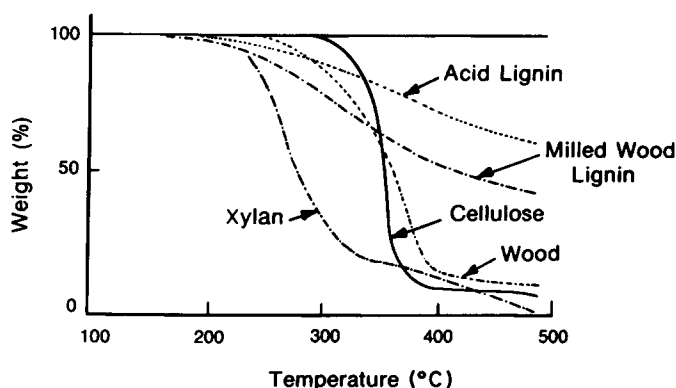

Fig. 2. Examples of thermogravimetric analysis of cottonwood and its components. From Shafizadeh and McGinnis.[35]

Transport Process Aspects

In large-particle pyrolysis, the role that heating rate and temperature play in the description of thermochemical conversion of biomass to useful fuels and chemicals is not yet established. The inability to unify the kinetic parameters appearing in the literature into a coherent pyrolysis mechanism for biomass can sometimes be attributed to experimental conditions that do not give full consideration to the rate of volatiles and energy transfer in the particle itself. Few experimental studies have systematically investigated the process variables such as particle size, heat transfer rates, and ultimate temperatures with a view to studying their interactions and effects on the competitive reaction rates which may alter the product distribution obtained in pyrolysis of complex solid materials. Often the sample size that would enable evaluation of mass and heat transfer rates is not reported. The slow heat transfer rate and the slow rate of volatiles escaping from a large wood particle are analyzed as part of the intrinsic chemical kinetics when in fact the product distribution and rate are altered due to physical, not chemical considerations.

Roberts[36-39] has thoughtfully reviewed the wood pyrolysis data appearing before 1971. He attempts to account for heat generation or heating requirements during pyrolysis and comments on the consistency of the kinetics data. Kansa et al.[40] model the effect of the internal structure of wood, and Gavalas and Wilks[41] address the effect of pore structure in coal on the course of pyrolysis and the rate of heat transfer. Kanury,[22] Lee et al.,[42] and Fan et al.[43] have proposed more complex chemical reaction models coupled to heat and mass transfer descriptions to account for conductivity, porosity, and heat capacity changes in wood pyrolysis. Russel et al.[44] point out that when coal is pyrolyzed, there are large differences in time scales for heat transfer and volatiles escape, relative to chemical reaction. Estimation of these times for wood pyrolysis indicates that heat transfer is two orders of magnitude slower than reaction for temperatures above 400°C in rapid wood pyrolysis. None of the above models adequately predicts weight loss in pyrolysis of large particles and cannot predict tar or detailed product yields.

Heat transfer under microwave heating conditions is somewhat unusual and treated separately below.

Microwave Heating Aspects

An unusual alternative to conventional furnace heating is the rapid heat transfer achieved in larger wood particles using spatially uniform or volume heating. This can be accomplished by microwave energy deposition in the dielectric-loss heating mode even though dry woody materials do not couple well with microwave energy.[45] The practical considerations in microwave heating are discussed in several articles.[46-47]

Microwave heating is used for bonding,[48] drying,[49] and food processing. Industrial applications of microwaves are discussed by several authors.[50-52] A successful example is the curing and reclamation of used rubber.[53,54] The Japanese have used microwave heating to kill insects in straw matting when the use of insecticides would be harmful.[52] Additional information, especially with regard to low-power microwave interactions with biologic materials for com-

mercial cooking, appears in Snyder,[55] and biochemical applications appear in Chen and Lin[56] and D'Andrea et al.[57]   In a recent theoretical study of microwave freeze-drying,[49,58] a detailed model of spatial and temporal temperature distributions in an anisotropic sample (raw, frozen beef) is developed.   Ohlsson and Risman[59] verified types of temperature distributions using thermography. Bhattracharyya and Pei[60] discuss the advantages of microwave heating over gas–solid heat transfer.   This study differs in several ways from the previous studies since more intense microwave fields and higher temperatures are required to pyrolyze lignin, and chemical reaction, not phase transformation (water evaporation), is the objective.

The application of microwave heating to induce unusual chemical reactions is in its early stages.[61]   Some of the few studies that have been conducted are reviewed in Allan et al.[15]   Of particular interest are process alternatives using microwave-induced chemical reactions that narrow the product distribution and selectively fragment the polymers or alter the high-molecular-weight tar fraction.

EXPERIMENTAL

Apparatus

The experiments were conducted in a quartz reactor placed through the broad face of an S-band (7 X 3.2 cm) waveguide as shown in Figure 3.   The variable (0–2.5 kW) microwave power generation unit (Gerling–Moore), load for impedance matching, forward and reflected power monitors, and an E–H field tuner are also shown.   This reactor/applicator geometry is not optimized for maximum power absorption but rather facilitates the gas and particle handling.
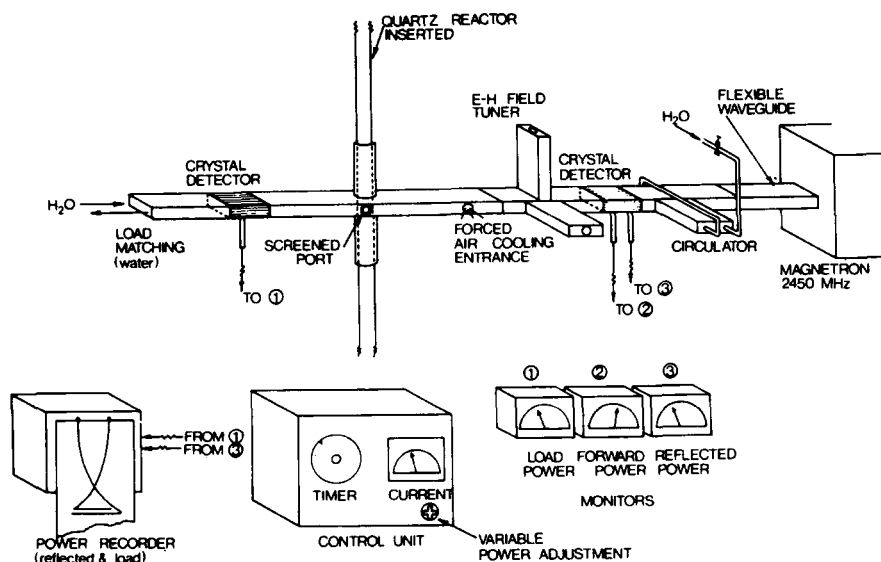

Fig. 3. Schematic diagram of the microwave power system.

A 1.3-cm pellet of lignin is supported by a hollow quartz rod in the center of the reactor, as shown in Figure 4.   The microwave energy is absorbed by the pellet and reaction proceeds in batch fashion.   A helium stream (about 2.2 l/min at
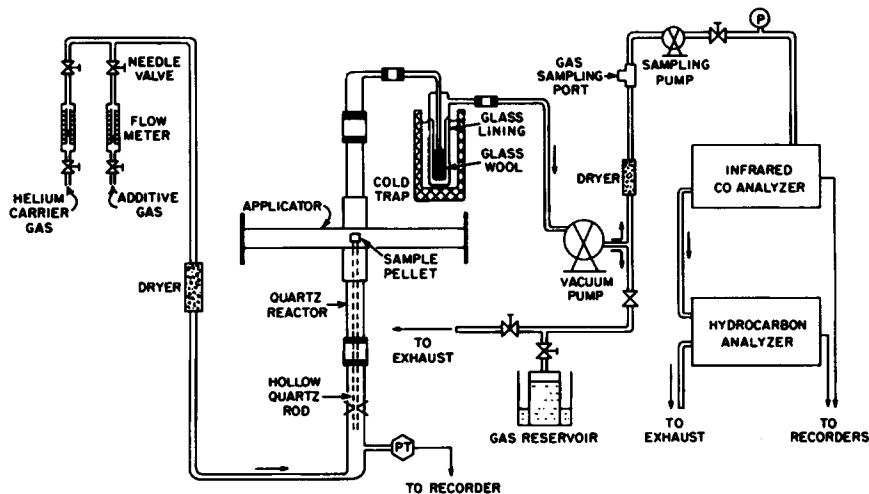

Fig. 4. Schematic diagram of the apparatus and the gas flow system.
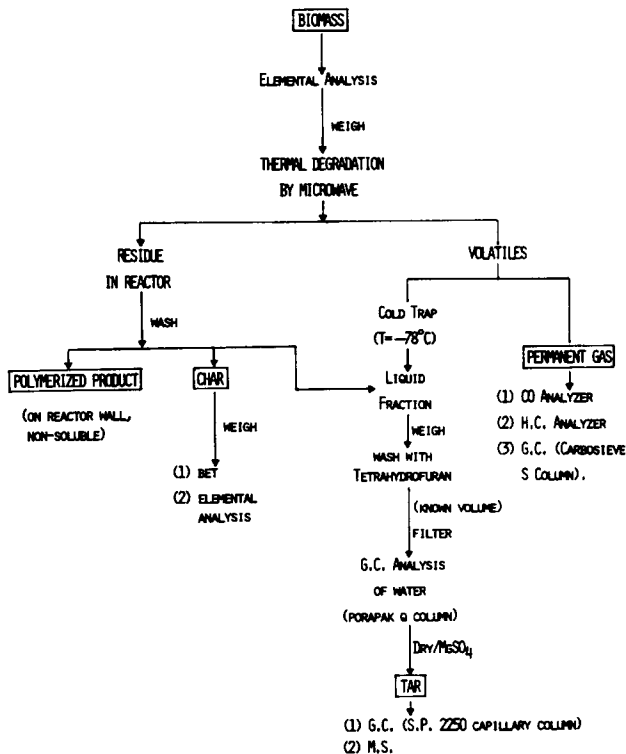

Fig. 5. Analysis scheme for products.

1 atm, 25°C) sweeps the volatiles from the reaction zone to the analysis zone, which is summarized in Figure 5. Permanent gases, water, condensible volatiles (tar), the residue (char) make up the gross product distribution. The cold trap (Dry Ice/acetone, −78°C) condenses the volatiles which are analyzed by gas chromatography (GC) and mass spectrometry (MS). A liquid nitrogen cold trap was used and made no difference in the results. The permanent gases are continuously analyzed by nondispersive infrared measurement of CO (Beckman model 864) and flame ionization detection of total hydrocarbons (Beckman model 400). These instruments are similar to those used for automobile emission analysis and are very sensitive to low concentrations. Thus, the accuracy of the gas composition is high. Periodic gas-chromatographic analysis was accomplished using a gas sampling port indicated in Figure 4.

Surface temperature measurements were made during reaction using an optical pyrometer (E^2 Thermodot) viewing through the port indicated in Figure 4. An emissivity for lignin was determined to be 0.91.[17] As discussed elsewhere,[15,62,63] temperature measurements using conventional thermocouples cannot be satisfactorily accomplished in the microwave field unless the field is turned off.[49] At the high temperature of this study, the error is unacceptable.

Procedure

Lignin (pinewood Kraft lignin, Westvaco Corp., Indulin AT; organo-solv lignin) is dried, pelletized to a 1.35 × 1.3-cm pellet with a density of 0.83 g/cm³, and placed in the reactor. The system is purged with helium, and the microwave power increases rapidly to 1.5 kW forward power. Pressure, power, and CO and HC concentrations are continuously recorded, and typical results are shown in Figures 6 and 7 (corrected for mixing effects—dispersion). Typical reactor pressures are 0.6–1.5 atm and are continuously measured by a pressure transducer (Viatran). The resulting distribution of gas-phase residence times ranges from 0.1 to 2.0 sec. For most experiments the absorbed power was insensitive to the *E–H* tuner setting so that the reflected power was minimized at the beginning of the experiment only.

Gas samples were taken at 15-sec intervals for the first minute of the experiment (and less frequently thereafter) and analyzed by GC with a ⅛-in. stainless
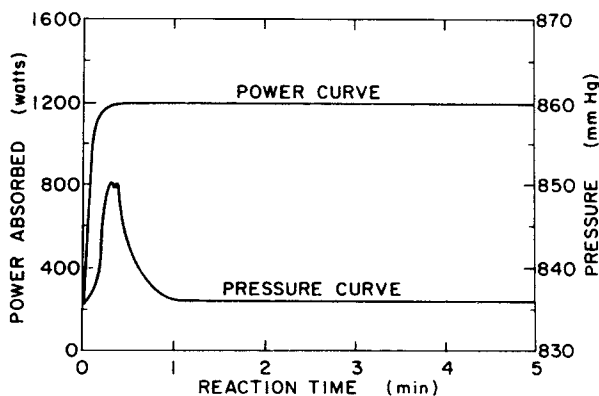

Fig. 6. Changes in pressure and absorbed power during the course of the experiment (dielectric loss mode of heating). Forward power = 1.5 kW, initial pressure = 1.1 atm.
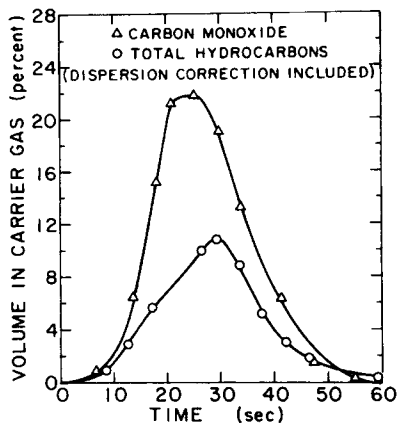
Fig. 7. Instantaneous concentration of carbon monoxide and total hydrocarbons measured by the analyzers during the course of the experiment. Same conditions as previous figures.

steel 3-ft column packed with carbo-sieve S (100/120 mesh, Supelco). The quantitative analysis of oxygen was not possible. Quantitative analysis of other components was accomplished by using authentic samples and calibrating peak height versus added sample size. Total gas yields were obtained by integrating the results obtained from samples at the indicated intervals. A cold trap packed with glass wool was improved to collect entrained liquid products until the mass balances indicated at least 95% recovery. Since the accuracy for measuring the amount of residue, water, and gases was good, the amount of tar calculated by a mass balance had high accuracy. Therefore, the calculated value is reported in the tables together with the experimentally collected tar fraction shown in parenthesis for comparison. Tar yields, as opposed to the quantitative gas and char yields, were complicated by accounting for the polymeric film deposited on the reactor surface. The polymeric material on the wall was included as part of the tar fraction. Much of this polymeric material was insoluble in ether, acetone, and tetrahydrofuran and generally represented 1–3% of the original substrate.

Liquid samples were washed with a known volume of tetrahydrofuran, filtered, and analyzed by GC for phenols with a 1.5-ft Porapak Q column. Trace amounts of methanol, ethanol, isopropanol, propanol, and acetic acid were observed, but quantitative analysis was not possible with the chosen column. After water analysis was made, the sample was dried and a silylating agent was added to allow analysis at moderate temperatures.[64] This analysis employed a 30-m glass capillary column with 50/50 methylphenyl silicon (SP-2250, Supelco). Mass spectra (Hitachi Perkin–Elmer RMS-4/Perkin–Elmer 990 with an OV-17 Scott column) confirmed the major peaks and quantitative measurements were accomplished through the addition of an internal standard, p-bromophenol. The usual caveats apply since determination of tar components is qualitative at best.

RESULTS

Product Distribution

For a 5-min total reaction time at 1.5 kW forward microwave power,* the weight percent yields of reaction products are presented in Table I as averages of three runs. For comparison, in Table I the lignin pyrolysis results of Iatridis and Gavalas using a grid heating apparatus (small lignin particles at 650°C for a reaction time of 2 min) are presented. The char and tar yields from microwave pyrolysis are nearly the same as those from grid heating. Char yields are typically near 50% when the lignin is heated slowly (400–450°C for 7.5 hr[28,65]). The char in this study was not heated to drive off condensed tars; but owing to the nature of microwave volume heating and the high internal pellet temperature, it is unlikely that volatile tars remain with the residue. A greater fraction of permanent

TABLE I
Product Distribution in Lignin Pyrolysis (Microwave, Dielectric Loss Mode)

Fraction	Yield, wt % lignin			
	Microwave pyrolysis	Grid (750°) heating[31]	Fletcher and Harris[65]	Allan and Matilla[28]
Residue (char)	33.5	34.8	53–65	~55
Volatiles (tar)	19.6	16.1	~9	15–22
	(12.8)[a]			
Phenol	0.282	0.19	yes	yes
o-Cresol	0.029		yes	yes
m-Cresol	0.038	0.41	yes	yes
p-Cresol	0.048		yes	yes
m-Ethylcresol	0.021		yes	yes
p-Ethylcresol	0.013		yes	yes
Guaiacol	0.069	2.62	yes	yes
Napthalene	0.824			
Methylnapthalene	0.114			
Methyldiphenyl	0.314			
Fluorene	0.091			
Anthracene	0.143			
Catechols			yes	
Organic acids	NQ[b]		yes	
Acetaldehyde	ANP[c]	trace		
Low MW alcohols	<4.0	3.76		
Acetone	NQ[b]			
C_1–C_4	11.2	6.65		
Water	8.6			
Gases	38.3	23.02		12
H_2	0.8			
CO	21.9	9.2		6.4
CO_2	5.1	7.2		2.06
CH_4	4.4	4.83		2.85
C_2H_2	4.9			
C_2H_4	1.8	0.33		
C_2H_6	0.1	0.35		0.68

[a] Recovered from cold trap.
[b] Not quantitative.
[c] Analysis not performed.

* The incident power is 130 W/cm² when expressed as power per unit waveguide cross-sectional area.

gases is produced by microwave pyrolysis. The amount of water appears to be greater although the gas-chromatographic column used by Iatrides and Gavalas precludes measurement of water in the condensible volatile fraction. It is difficult to make extensive comparisons since the detailed product distributions in the grid heating study do not account for 100% of the lignin.

The analyses described in Figure 5 indicate that tar from microwave heating contains methanol, ethanol, isopropanol, propanol, and acetic acid as well as the components in Table I such as guaiacols and cresols. The latter are typical lignin degradation products according to Allan and Matilla.[28] The gas-chromatographic column chosen for phenol separation, however, was not capable of analyzing for the low-molecular-weight alcohols and acids; therefore, we cannot report quantitative yields of these substances. An estimated 4 wt % (20% of the tar fraction) is contributed by these components, consistent with the approximately 4% found in the grid heating study. The phenolic compounds in the tar resulting from microwave pyrolysis represent 0.5% of the original lignin, whereas they represent 3.22% in the grid heating pyrolysis. Condensed aromatics with combined yields of 1.5% appear to be present only in microwave pyrolysis products but may not have been analyzed for in other studies. Adding the condensed aromatic fraction (1.5%) to the phenolic fraction represents a total aromatic-containing fraction in the microwave pyrolysis tar of only 2.% of the weight of the original lignin.

The gas composition in microwave pyrolysis differs from that of other pyrolysis studies because of significant quantities of H_2 and C_2H_2 (Table I). This is in contrast to a high methane yield in conventional lignin pyrolysis.

Figure 8 presents the pellet surface temperature measured by the optical pyrometer as a function of time. Since the pyrometer views only $1/120$ of the pellet surface area, it is a qualitative indication of temperature only. The measured peak *surface* temperature (650–750°C) is roughly the same as the maximum *isothermal* final temperature using grid heating (achieved after only 2 sec[31]). If one assumes the pellet is volume-heated and rapid exothermic reactions of lignin occur above 450°C,[38] then a simplified maximum internal temperature calculation (using the surface temperature) yields an estimated center temperature as much as 400–1000°C higher than the surface temperature.[16] These temperatures are generally found at combustion-level heat fluxes. The heating of lignin was nearly uncontrolled and quite rapid above the forward power setting of 1.5 kW. Experiments at lower power did not provide sufficient energy cou-
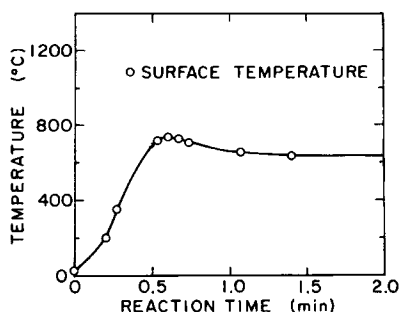

Fig. 8. Temperature of the lignin pellet surface as function of time in the dielectric loss mode of heating. Same conditions as previous figures.

pling for the reaction to occur. The experimental variables governing energy coupling are discussed elsewhere.[45–47,66]

Reaction products were determined as a function of shorter batch reaction times, and Figure 9 presents the gross product distribution. The faster rate of weight loss from the small sample used in the grid heating study is superimposed on the graph. The effective reaction period is about 1 min, after which only small changes take place. Judging from the pressure evolution presented in Figure 6 and the peak evolution of CO and total hydrocarbons (HC) presented in Figure 7, most reactions have been completed after 1 min. Although tar composition as a function of increasing batch reaction time would be informative, the sample size is very small and precludes quantitative measurement.

Kinetics Results

The weight loss data were initially analyzed as an apparent isothermal, first-order reaction; the results are shown in Figure 10 as the logarithm of the fraction of total volatiles remaining at a given time. In this study, V^* is taken as the cumulative volatiles evolution at infinite time. Other authors have described their data using a quantity for ultimate volatiles (V^*) that is a function of temperature.[67] This model is not suited to our purposes. At least two reaction rates are evident from the change in slope of the data. The smaller slope early in the reaction is evidence for an induction stage. As shown by the temperature in Figure 8, the isothermal assumption may be valid in the second stage where the major devolatilization occurs. The value of the apparent first-order rate coefficient in the second stage appears in Table II.

An approximate analysis using a nonisothermal rate expression employs the standard equation for volatiles release as follows:

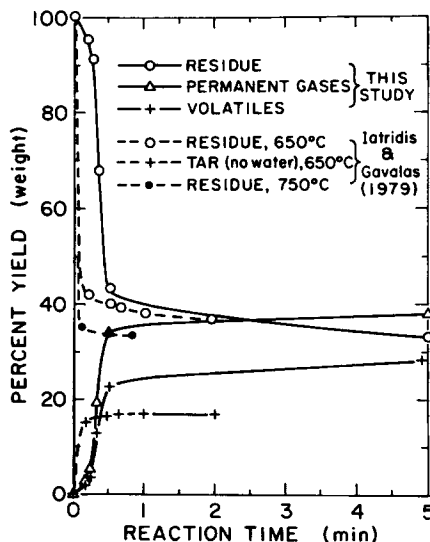$$\frac{dV}{dt} = k_0 \exp\left(-\frac{E_A}{RT}\right)(V^* - V) = -\frac{dW}{dt} \tag{1}$$

Fig. 9. Yield of gross pyrolysis products from lignin as function of time for dielectric loss heating compared to grid heating at two temperatures.
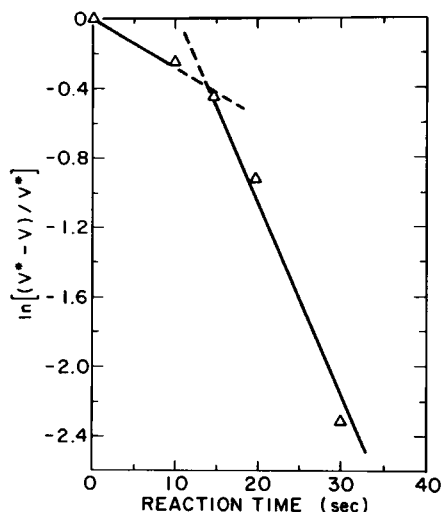
Fig. 10. Natural logarithm of the fraction of volatiles remaining in the lignin as function of batch reaction time.

where $(V^* - V)$ are the volatiles remaining in the solid, k_0 and E_A are the frequency factor and activation energy of the Arrhenius model for the rate coefficient, respectively, and dW/dt is the rate of weight loss. Rearrangement and transformation to logarithms yields

$$\ln\left(\frac{1}{V^* - V}\frac{dW}{dt}\right) = \ln k_0 - \frac{E_A}{RT} \qquad (2)$$

where the dW/dt term is obtained from the weight loss rate and measured surface temperatures are used. Comparison of the apparent first-order rate constant obtained in this study to those obtained in other studies of lignin pyrolysis is summarized in Table II and Figure 11.

DISCUSSION

Microwave radiation rapidly heats materials with high dielectric loss factors such as water. The heating rate depends on the molecular structure, dielectric properties and thermal properties of the substance. The dielectric loss factor

TABLE II
Comparison of Apparent Kinetic Parameters for Pyrolysis of Lignin (Single First-Order Reaction Model)

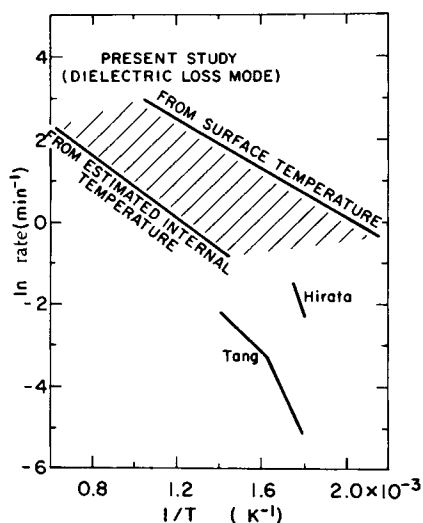|	Temperature, °C	k_0, min^{-1}	E, kcal/mole
Present study	160–680	4.7×10^2	6.0
	410–1890	9.0×10^1	7.3
Tang[68]	280–344	9.9×10^5	21.0
	344–435	5.6×10^0	9.0
Hirata[83]	280–300	4.3×10^{12}	34.8
Beall[84]	260–375	—	8.6–18.1
Ramiah[85]	245–330	—	13.0

Fig. 11. Arrhenius plot of apparent first-order rate as a function of reciprocal temperature from the pyrolysis in lignin in different investigations. Rate in eq. (2) described apparent rate of weight loss or devolatilization.

describes the lag molecules exhibit in orienting with an applied electric field, and it varies substantially for a single material over the microwave region of the electromagnetic spectrum.

It is desirable to selectively break bonds of a polymer such as lignin and thus narrow the pyrolysis product distribution. However, as discussed in the literature,[45–47,66] the rate of molecular polarization and relaxation in the polymeric material of interest are often such that the electromagnetic energy is rapidly converted into heat (dielectric loss) rather than localized to cause bond cleavage. Uniform thermal or volume heating occurs because the penetration depth through lignin of microwaves at this frequency is much greater than the pellet size. In this study, photographs taken of split pellet cross sections after very short reaction times show radially uniform black char coloration. Similar pellets rapidly but externally heated react in a shell-progressive manner with a sharp front between the black char and light-colored lignin.[17] Goodyear[54] has patented a process in which large fragments of tire rubber are rapidly and uniformly "devulcanized" by breaking the sulfur-containing bonds selectively using microwave irradiation. The success of this process, perhaps, is a result of the bond energy of the sulfur-containing bonds being substantially lower than that of the other bonds in the material, and volatiles are not produced. (Volatiles production reduces the sample density thereby reducing the microwave energy coupling.) For a polymer such as lignin whose bond energies are high and more uniformly distributed in energy, the selective bond breaking at frequencies available for commercial scale-up is not feasible.

Even though in this application microwave pyrolysis heats the material thermally rather than coupling to a set of particular bonds, it is not the same as conventional pyrolysis since the entire volume is heated at once. The heat of reaction for lignin has not been definitively determined and appears to depend on temperature.[37] However, the data from Tang[68] reworked by Roberts appear to be the most reliable and suggest an exothermic heat of reaction for lignin of

800 J/g.   Since the entire volume reacts, in poor heat conductors such as lignin the heat of reaction is less quickly dissipated, even by volatiles outflow, and higher internal temperatures result.   Owing to the convective cooling at the external pellet surface by the helium sweep gas, the surface and gases surrounding the pellet are cooler than the pellet interior.   This was evidenced by photographs showing a very thin unreacted surface layer and black char throughout the partially pyrolyzed pellets.   Ohlsson and Risman[59] demonstrate with thermographs and Schwartz et al.[53] discuss the occurrence of center heating and hot spots. Thus, microwave heating reverses the temperature gradients in an otherwise thermal process.   As a result, the interior of the large particle experiences high heating rates and temperatures.   This situation is not easily investigated with conventional modes of heat transfer.

Figure 12, taken from Wen and Tone,[69] qualitatively describes the effects of heating rate, residence time, and ultimate temperature on product distributions when coal is pyrolyzed.   From this figure it can be seen that very rapid (flash) pyrolysis simultaneously produces the most gas and least char.   However, at slower heating rates (even to high ultimate temperatures) in the figure, the total volatiles yield is less and more char is produced.   This is qualitatively the result when large particles are pyrolyzed; few studies, however, have investigated particle size effects on product distribution.   The dependence of gas yield on heating rate and residence time or temperature is complicated when large particles are pyrolyzed, since particle size affects local values of all three variables for the same external experimental conditions.

In light of the above comments, it is of interest to examine the heating rates in other lignin pyrolyses to see if wood or lignin pyrolysis follows the same trends put forth in Figure 12 for coal and to determine if the heating rate effect is con-
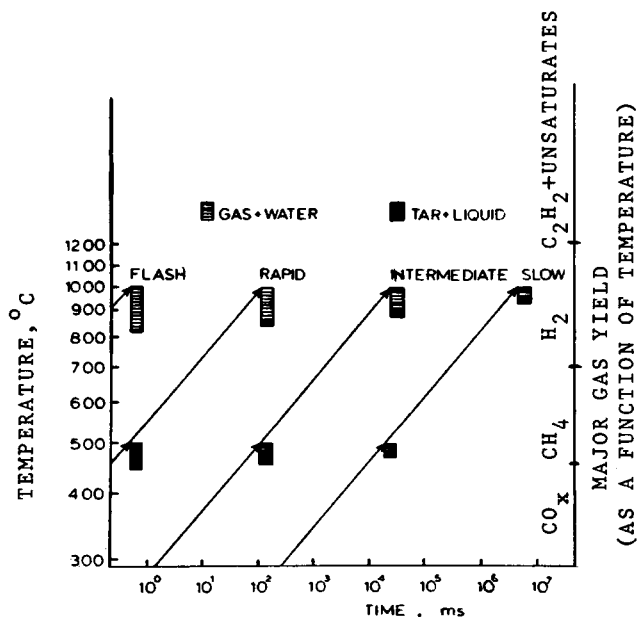

Fig. 12. Relative yields and product distributions of pyrolysis in inert atmosphere as functions of temperature, time, and heating rate.   Char yield is *difference* between the size of the histogram for flash pyrolysis (approximate) and any other histogram.   From Wen and Tone.[69]

sistent with the discussion in Soltes[10] of the physical and chemical effects in biomass degradation. Comparison of the reported heating rate of 325°C/sec in the grid heating study to an estimated maximum heating rate in this study of 40°C/sec (based on the measured surface temperature) to 100°C/sec (based on the estimated internal temperature) causes the ranked order to be grid heating rate > microwave heating rate > a representative slow heating rate.[65] The resultant char yields from lignin (34 ~33% < 50%) are found to be roughly consistent with Figure 12 according to this ranking. The higher temperature and batch nature of this study may have also decreased the char yield by causing some high molecular weight material to gasify at long reaction times. Since the diluent gas is inert, char gasification is not expected to occur, except from lignin volatiles, and cannot account for the rather low char yield. In order to achieve adequate coupling with the microwave radiation, this study used dense, large pellets. The intrapellet residence time could not be determined but is expected to be longer than in other experiments owing to the low porosity of the pellet which causes a reduced rate of volatiles outflow. The high internal pressure caused by rapid lignin fragmentation at high temperatures would be expected to favor polymerization or char-forming secondary reactions and result in a higher char yield than the grid-heating study. Since the char yield is surprisingly similar to that of grid heating, it appears the volume heating and high internal temperatures cause a greater pressure force inside the pellet which expels reactive volatiles from it quickly enough to prevent extensive secondary char-forming reactions from occurring.

The tar yields are also roughly consistent with Figure 12, considering the estimated ultimate temperatures as well as the heating rates in each study. Gavalas and Wilks[41] have mathematically described the influence of pore size on residence time of the reactive volatiles as they leave a coal matrix. It would appear that although their model and experimental data on tar yield are at variance, the intuitive picture is correct; that is, increased pellet size and reduced pore size cause a longer residence time in which reactive tar species (primary products) can react in second order reactions to produce char. It would appear from Table I that char and tar formation can be lowered in large pellets if the heat transfer rate limitation can be overcome. A stoichiometric analysis of lignin suggests that char yields substantially below 30% should be attainable and therefore that char-forming reactions occur to an appreciable extent in both the grid heating and microwave heating studies.

Allan and Matilla[28] suggest that the demethanation reactions of the methoxy group in lignin are the source of the roughly 4% methane (by weight of original lignin) found to be representative of the pyrolysis studies they reviewed. No obvious explanation exists for the 4% methane yield for all studies in Table I, since the experimental conditions varied widely. In the high-temperature pyrolysis of wood flour, Sanchez and Simmons[70] were able to correlate gas composition at temperatures above 500°C with equilibrium predictions. Methane yield was reasonably well correlated in this manner. In this study, equilibrium calculations[71] as a function of temperature were made. Little agreement between equilibrium composition and experimental concentration levels appeared until the C/H/O ratios of the gas phase products (exclusive of char, tar, and water) were used. The results of these equilibrium calculations appear in Figure 13 with the horizontal lines representing the experimentally determined compo-
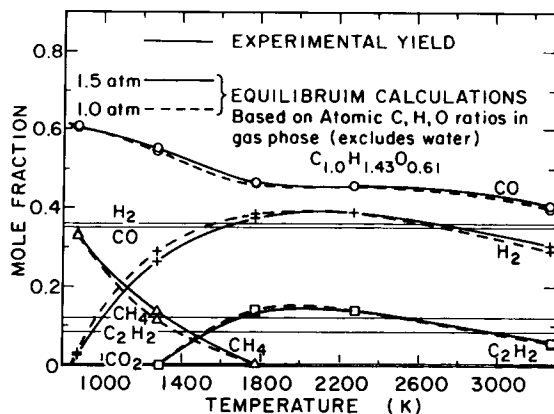
Fig. 13. Comparison of calculated equilibrium mole fraction (heavy lines) to experimentally measured mole fraction (light lines) of chemical species in the gas phase. Temperature dependence applies only to calculated mole fractions. Species identification is to the left in the figure for experimental values and to the right for calculated values. Atom ratios exclude char and water.

sition of the lignin pyrolysis products (no temperature is implied by the experimental data). Judging from the intersections of the experimental concentration levels and calculated compositions, methane, hydrogen, and acetylene concentrations in the proportions observed here are found at equilibrium temperatures between 1300 and 1700 K. It appears that the experimental concentration levels of H_2 and C_2H_2 are consistent with a high internal pellet temperature determining the chemical composition of the gases obtained from microwave pyrolysis. Figure 12 also suggests that temperatures above 1200°C promote the formation of C_2H_2. The experimental CO concentration is lower and the CO_2 concentration is higher than those found at equilibrium.

Within the gas and tar fractions from lignin microwave pyrolysis, the chemical composition indicates a high fraction of secondary reaction products. Sakai and co-workers[72,73] have studied gas-phase cracking of olefins and found secondary reaction products to include polycyclic aromatics when the reaction occurs at high temperatures. This is expected, since the discussion in Benson[74] of polymerization and stabilization of hydrocarbon fragments indicates the rate coefficients for polymerization to be 10 to 100 times faster than stabilization at 750°C. Surface reactions can increase the extent of secondary reactions. Berthelot long ago noted that acetylene trimerizes over hot glass to form benzene. Numerous studies have been conducted by Albright et al.[75,76] and others to determine the role surfaces play in char (coke) and high molecular weight hydrocarbon formation during the pyrolysis of simple organics such as propane[77,78] and methane.[79,80] The possibility has been suggested by Roberts[36] and Kanury[22] that hot char surfaces and inorganic ash catalyze the cracking reactions of outflowing volatiles in wood pyrolysis and perhaps promote the reactions that lead to the formation of condensed aromatics such as naphthalene which are not original polymer fragments. Condensed aromatics are found in wood combustion[81] and in the combustion of benzene, despite the fact both these fuels contain only single ring aromatic compounds.

In light of the previous paragraph, it is apparent that the residence time of volatiles (distributed between 0.1 and 2 sec) in the gas phase downstream of the

pellet is long enough for substantial thermal pyrolysis and cracking.[75-80] It is worth noting that the initial internal surface area [about $(4-8) \times 10^4$ cm^2, measured by BET] of the pellet is much greater and at a higher temperature than the relatively cool reactor surface (quartz) with a smaller (about 200 cm^2) surface area. It is reasonable to conclude that the increased temperature and greater area would enhance the rate of char surface reactions over reactor surface reactions and be the determining factor in producing the polycyclic aromatics in the tar and secondary reaction products in the gas phase. A purely speculative explanation for the presence of significant yields of phenols (lignin fragments) is that these primary reactive volatiles (as evidenced by the grid heating study) originated in the outer layers of the pellet and therefore spent less time transversing the hot char matrix. This hypothesis is consistent with the lower gas phase temperature found in microwave heating[15] and thus the lowered rate of gas phase secondary reactions outside the pellet. This also lends support to the argument stated earlier that although the gas-phase residence time and temperatures are sufficient for reaction to form condensed aromatics and cracking products, the product distribution is largely determined by surface-catalyzed reactions at the local temperature during the residence time of the volatiles inside the pellet. Current experiments with varying particle sizes are in progress but are complicated since the temperature distribution inside the pellet is changed by particle size. However, effects of solid-phase residence time will be determined from these experiments.

The kinetics data presented in Figures 10 and 11 are illustrative only. The heat transfer rate is not limited by the rate of conduction as in many externally heated large pellet pyrolyses, but the rate may be determined by other factors since the apparent activation energy in Table II is rather low. Microwave power absorption is partially determined by the dielectric loss factor which appears in the following equation:

$$P = \pi f \epsilon_0 \epsilon'' \frac{E^2}{\epsilon'^2 + \epsilon''^2} \tag{3}$$

where P is the absorbed power (W/cm^3); f, the frequency (sec^{-1}); ϵ_0, the dielectric constant in vacuum; ϵ', the real part of the dielectric constant (describes absorption); ϵ'', the complex part, dielectric loss factor (describes loss or heating); and E, the electric field strength.

Table III contains several dielectric constants of materials related to lignin.[47] Lignin probably has a low dielectric loss factor, but the overall energy coupling will also depend on density[82] and temperature in a complex way.[53] In this study, the density and field strength were large enough to compensate for the poor coupling to lignin.

TABLE III
Selected Dielectric Loss Constants[a]

Substance	Temperature, °C	Frequency, Hz	ϵ''
Mahogany	55	10^6	0.033
Paper	25	10^6	0.113
Balsa	26	10^6	0.016
Douglas beech	25	10^6	0.05
(H$_2$O)			(33.00)

[a] From Püschner.[47]

An induction period or a period of low reaction and low absorption is seen in Figure 10 evidenced by the lower slope early in the reaction. One factor that may determine the length of this induction stage is the increasing-with-temperature dependence of the dielectric loss factor which causes increased power absorption and increased heating rate. Or, alternatively, the induction period can be a result of the external cooling rate initially being greater than all heating, and then being slowly overtaken by exothermic heat release from reaction. Approximate calculations and curve shapes of the heat release rate from the reaction and the convective cooling rate (volatiles and helium) were compared to experimental temperature, pressure, and absorbed power curves. Little insight was gained. The accuracy of the data was not sufficient to determine whether the length of the induction period could be most effectively altered by a change in dielectric properties or by a change in thermal properties. Improvement of energy absorption would allow lower power to be used, which would improve the economics and alleviate thermal runaway for exothermic reactions. Experiments using additives to improve dielectric loss properties have been performed by Schwartz et al.,[53] and our work on these aspects is reported elsewhere.[16]

CONCLUSIONS

The primary conclusions from this study are that microwave heating can somewhat overcome heat transfer rate limitations and indeed speed the pyrolysis of large fragments of materials. Therefore, it offers certain processing advantages. However, for materials with low dielectric loss factors, the requisite power to initiate reactions is so high that currently, unless specific product distributions can be selected by the use of microwave power (i.e., rubber reclamation), the scheme is not economically attractive. Little flexibility is available in choosing the frequency since only certain bands are available for high-power commercial units. However, additives of appropriate composition and dielectric properties can alter the economics and have been successfully employed by Schwartz et al.[53]

The volume nature of the heating can cause rapid and great extents of reaction for large particles in which the reactions are exothermic. This is in contrast to the rather mild, but rapid, pyrolysis of cellulose reported in a previous article.[15] The less severe pyrolysis is attributed to the endothermic nature of the cellulose degradation reactions and energy coupling at lower power levels.

The commercial feasibility of microwave-induced reactions remains to be demonstrated. Current experiments focus on the role of particle density, size, and the extent to which additives can effect a change in dielectric loss factor that would reduce the energy requirements. The use of microwave heating in the laboratory, however, to explore the role of heat transfer is valid.[60]

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