MICROWAVE PROCESSING OF LIGNIN AND CELLULOSE

PART I - AN INVESTIGATION OF THE REACTIONS OF LIGNIN AND HYDROGEN USING A CONTINUOUS FLOW MICROWAVE DISCHARGE REACTOR

PART II - THE EFFECT OF MICROWAVE RADIATION ON BATCH PROCESSING OF CELLULOSE IN WATER

Thesis for the Degree of M. S.
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ABSTRACT

MICROWAVE PROCESSING OF LIGNIN AND CELLULOSE

By

Jack D. Junttila

Experiments have been performed investigating the application of microwave technology to chemical processing of waste products produced by the paper and pulp industries. The purpose of this study was to determine if use of microwaves as a catalyst could promote production of useful chemical products from the decomposition of paper waste byproducts, lignin and cellulose. Two separate microwave processing schemes were utilized for this investigation: (1) continuous flow microwave plasma processing and,(2) high pressure batch microwave processing.

Part I of this study describes experiments which used microwave radiation for generating a low pressure hydrogen plasma in a quartz tube flow reactor. The reactions of this plasma with lignin contained in Kraft Process Black Liquor were studied. The reaction product produced in largest quantity in this reactor was a solid char. Small amounts of methoxy-phenols were also produced. These reaction products obtained are similar to those produced in conventional pyrolysis reactions and indicates that high energy pyrolysis reactions dominate over radical reactions when lignin is injected into a hydrogen microwave plasma.

It was concluded from these experiments, that a single one step process of direct injection of lignin into a hydrogen plasma is not a viable method for producing useful chemicals from lignin. The most appropriate direction for further study of lignin processing should incorporate a two-stage process scheme which combines existing lignin technology with microwave technology.

Described in Part II of this study are experiments which involved use of a batch reactor for investigating the effect of microwave radiation on high pressure and high temperature reactions. A specially designed teflon-brass coaxial coupling was used to conduct the microwave radiation from the microwave source into the reactor interior. The effect of microwaves on the reactions of crude cellulose and water was investigated at 500 psig and 450^{o}F using this apparatus. Microwave catalysis appeared to have little effect on this reaction and did not promote production of useful products. The product produced in greatest quantity, regardless of catalyst used, was a black, water soluble, tar-like decomposition product with a yield of approximately 35 percent.

The results of this two part experimental study indicate that the techniques developed for the application of microwave radiation to chemical processing are feasible. These techniques have been successfully demonstrated for both low pressure plasma processes and for high temperature,high pressure batch processes. Interesting and unusual results may be obtained if the techniques and apparatus developed for this study are applied to other types of process feeds.

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Jack D. Junttila

A THESIS

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for the degree of

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To My Parents

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1. INTRODUCTION

Plants, primarily made up of cellulose and lignin, are a potential source of hydrocarbons. Each year large amounts of lignin and cellulose are produced as waste byproducts of the paper-making industry. For example, approximately 12.6 billion pounds of lignin are produced annually as byproduct waste, contained in Kraft Process Black Liquor. A significant quantity of cellulose is also produced as a waste byproduct. Presently, the primary use of these wastes is for fuel. However, as petroleum shortages increase and as prices rise, it may become economical to use cellulose and lignin from plants or from waste byproducts of paper production as sources of hydrocarbons for chemicals.

The alternatives of cellulose and lignin are not well developed technologically. Cellulose can be converted to various chemicals by biochemical methods or pyrolysis techniques. Hydrocarbons produced from cellulose would be mainly chain compounds. Lignin is a complex structure containing aromatic rings and is essentially non-biodegradable. Thus, pyrolysis and hydrocracking technology are expected to result in the production of both chain and aromatic types of compounds. Significant technological development is required in order to place lignin processing and cellulose processing in the category of viable alternatives for producing hydrocarbon feedstocks. However, it is expected that processes that are useful for converting coal to chemicals may also be useful for converting lignin to chemicals.

Experiments have been conducted at Michigan State University studying the use of microwaves for catalyzing the decomposition reactions of the paper waste byproducts, lignin and crude cellulose. Two process schemes were experimentally investigated and are described in this thesis: Part I) microwave plasma processing of lignin, and Part II) high pressure, microwave catalyzed, batch processing of cellulose and water. Both of these process schemes involve unique application of microwave technology to paper waste processing, but these techniques may be used for a variety of feeds.

The method used for the lignin processing experiments and described in Part I involved using microwaves for generating a low pressure hydrogen plasma in a quartz tube reactor, and then continuously injecting a liquid feed solution containing lignin into this plasma. Lignin used in these experiments was extracted from Kraft Process Black Liquor supplied by the Kimberly Clark Corporation. The apparatus used for the lignin experiments was similar to the apparatus used for studies performed earlier at Michigan State University investigating the reactions of H_2 and CO in a microwave plasma[1].

One goal of this study of lignin processing was to develop lignin-microwave plasma experimental techniques and to compare the results of lignin-microwave experiments to other methods, including pyrolysis. Another major objective of this study was to determine what chemicals may be produced by reacting lignin in a microwave plasma and to determine a feasible microwave plasma processing scheme.

Described in Part II are preliminary experiments which have been carried out to study the chemical reactions of cellulose waste in water and the effect of microwave radiation on this reaction. The feed used for these batch experiments was a cellulose containing "sludge", which is produced as a waste byproduct by the paper industry, and was supplied by Kimberly-Clark. Experiments were conducted at high pressure and temperatures (500 psig, 450^{o}F) and included use of acid and base chemical catalysts. The major objective of this study was to determine if microwave radiation could catalyze the reaction of cellulose and water to volatile low molecular weight organic products.

Parts I and II of this Thesis were prepared as manuscripts for publication purposes. Recommendations for future work are contained in a separate section following Part II.

PART I - AN INVESTIGATION OF THE REACTIONS OF LIGNIN AND HYDROGEN USING A CONTINUOUS FLOW MICROWAVE DISCHARGE REACTOR

Paper prepared for publication

By

Jack D. Junttila, Martin C. Hawley and Jes Asmussen, Jr.
Michigan State University
Departments of Chemical and Electrical Engineering

ABSTRACT

AN INVESTIGATION OF THE REACTIONS OF LIGNIN AND HYDROGEN USING A CONTINUOUS FLOW MICROWAVE DISCHARGE REACTOR

By

Jack D. Junttila, Martin C. Hawley and Jes Asmussen, Jr.
Departments of Chemical and Electrical Engineering
Michigan State University
East Lansing, Michigan

The reactions of lignin, contained in Kraft Process Black Liquor, and hydrogen in a continuous-flow microwave discharge reactor have been studied. The goal of this study was to determine what chemicals may be produced by reacting lignin in a microwave plasma and to suggest a feasible microwave plasma processing scheme.

The reaction products were primarily carbonaceous char and small amounts of guaiacol, 4-hydroxy-3-methoxytoluene, and other methoxyphenols. These reaction products are similar to those produced in conventional pyrolysis. This result indicates that high energy pyrolysis reactions dominate over radical reactions when lignin is injected into a hydrogen microwave plasma.

It was concluded that a simple one step process of direct injection of lignin into a hydrogen plasma is not a viable method for obtaining useful chemicals from lignin. The most appropriate direction for further study of lignin processing should incorporate a two-stage process scheme which combines existing lignin technology with microwave technology.

In the conventional hydrocracking of lignin, low value methoxy-phenols are produced and the yield of useful products is low, (less than 10%). The microwave processing of methoxy-phenols has the potential to increase the yield of useful products from lignin to over 50%. The economics of a scheme which combines hydrocracking and microwave processing of lignin were examined. These economics are highly speculative, but they indicate that there is incentive for further study.

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1. Introduction

Presently, the petrochemical industry obtains hydrocarbon feedstocks from petroleum and natural gas. Increasing worldwide demand for energy is depleting the known petroleum and natural gas reserves, and is causing petroleum and natural gas costs to rise rapidly. Thus, other sources of hydrocarbons, such as coal and plant life, must be considered for the long-term as alternatives for the production of hydrocarbon feedstocks.

Coal processing for the production of fuels and chemicals has been studied extensively for many years and is at a fairly advanced stage of development throughout the world.[1] Large coal gasification/methanation demonstration plants are under construction. Chemicals can be manufactured from the synthesis gas produced in the gasification process. Production of acetylene from coal has been studied for a number of years in the United States, but has not been yet commercialized.[2]

Plants, primarily made up of cellulose and lignin, are also a potential source of hydrocarbons. Each year large amounts of lignin and cellulose are produced as waste byproducts of the paper-making industry. For example, approximately 12.6 billion pounds of lignin are produced annually as byproduct waste, contained in Kraft Process Black Liquor. A significant quantity of cellulose is also produced as a waste byproduct. Presently, the primary use of these wastes is for fuel. However, as petroleum shortages increase and as prices rise, it may become economical to use cellulose and lignin from plants or from waste byproducts of paper production as sources of hydrocarbons for chemicals.

The alternatives of cellulose and lignin are not nearly as well developed technologically as coal processing. Cellulose can be converted to various chemicals by biochemical methods or pyrolysis techniques. Hydrocarbons produced from cellulose would be mainly chain compounds. Lignin is a complex structure containing aromatic rings and is essentially non-biodegradable. Thus, pyrolysis and hydrocracking technology are expected to result in the production of both chain and aromatic types of compounds. Significant technological development is required in order to place lignin processing and cellulose processing in the category of viable alternatives for producing hydrocarbon feedstocks. However, it is expected that processes that are useful for converting coal to chemicals may also be useful for converting lignin to chemicals.

Reactions of coal and benzene in plasmas have been investigated experimentally. Bond, Ladner, and McConnell[3] have investigated the reactions of powdered coal in a plasma jet. In their experiments, they obtained yields of 20% acetylene. The pyrolysis of coals in a microwave discharge has been studied by Fu and Blaustein.[4] Again, the hydrocarbon product produced in largest quantity was acetylene. A continuous-flow microwave discharge reactor was used to study the reactions of carbon monoxide and hydrogen to methane and acetylene.[5] This reaction is of importance for coal processing schemes being considered whereby coal is first gasified to carbon monoxide and hydrogen; these reactants can in turn be used to produce a variety of hydrocarbons. Brooks and Sambrook[6] obtained high yields of acetylene and butadiene in experiments in which they studied the reactions of benzene in a continuous-flow microwave discharge reactor. They reported that the reactions occurring in the microwave discharge are quite different from the reactions of benzene which take place in a lower frequency or d.c. reactor. Results of experiments of coal and benzene in microwave plasmas suggest that plasma technology be investigated for converting lignin to useful hydrocarbon products.

The source of lignin for the experimental studies reported in this paper was Kraft Process Black Liquor. Kraft Process Black Liquor is produced as a byproduct of the paper and pulp industries. It typically consists of 28% lignin, 14% Na_2SO_4, and the balance is fixed solids and other residue.

Experiments were conducted in which black liquor was continuously injected into a hydrogen plasma induced by a microwave discharge. The goal of this study was to develop lignin-microwave plasma experimental techniques and to compare the results of lignin-microwave experiments to other methods, including pyrolysis. There were two experimental objectives. First, it was necessary to determine if a microwave discharge reactor could be operated continuously when using a combination of liquid and gaseous feeds. It is relatively easy to operate a microwave discharge reactor continuously when using gas feeds, but it was not known how liquid feed would affect reactor operation. A second objective of this study was the determination of the product distribution when lignin and hydrogen react in the microwave discharge.

2. Experimental

A schematic flow diagram of the experimental apparatus used in this study is presented in Figure 1. The experimental reactor system consisted of a vertically mounted quartz reactor tube which passed through two cylindrical microwave cavities in series. The quartz tube was 4 feet long and had an outside diameter of 25 mm. This tube was cooled by an air stream directed into the cavity. A specially designed gas-liquid feed nozzle was used to mix and inject the lignin solution and hydrogen into the reactor. Feed rates of lignin solution and hydrogen were measured and controlled using flowmeters. Two cold traps in series were located at the reactor outlet. Product samples were collected in the first cold trap, which was cooled with ice water, and the second trap, which was cooled with liquid nitrogen. A vacuum pump connected to the second cold trap was used to evacuate the system and to control the experimental pressure between 10 and 60 mm Hg.

The microwave apparatus includes two microwave sources coupled to two variable-length cylindrical cavities by a system of waveguides. The two cavities can be operated to produce one long reaction zone or two separate reaction zones. The cavities are water cooled by externally soldered cooling coils. The two microwave sources operate at a frequency of 2.45 GHz and maximum power levels of 1500 and 600 watts. Only 50% of the input power is absorbed by the reactants. Heat produced by reflected power is removed by a water-cooled heat exchanger. Incident and reflected power levels are measured with power meters to determine absorbed power. The microwave system has been used for experiments with gaseous feeds and has been described in detail previously.[5,7]

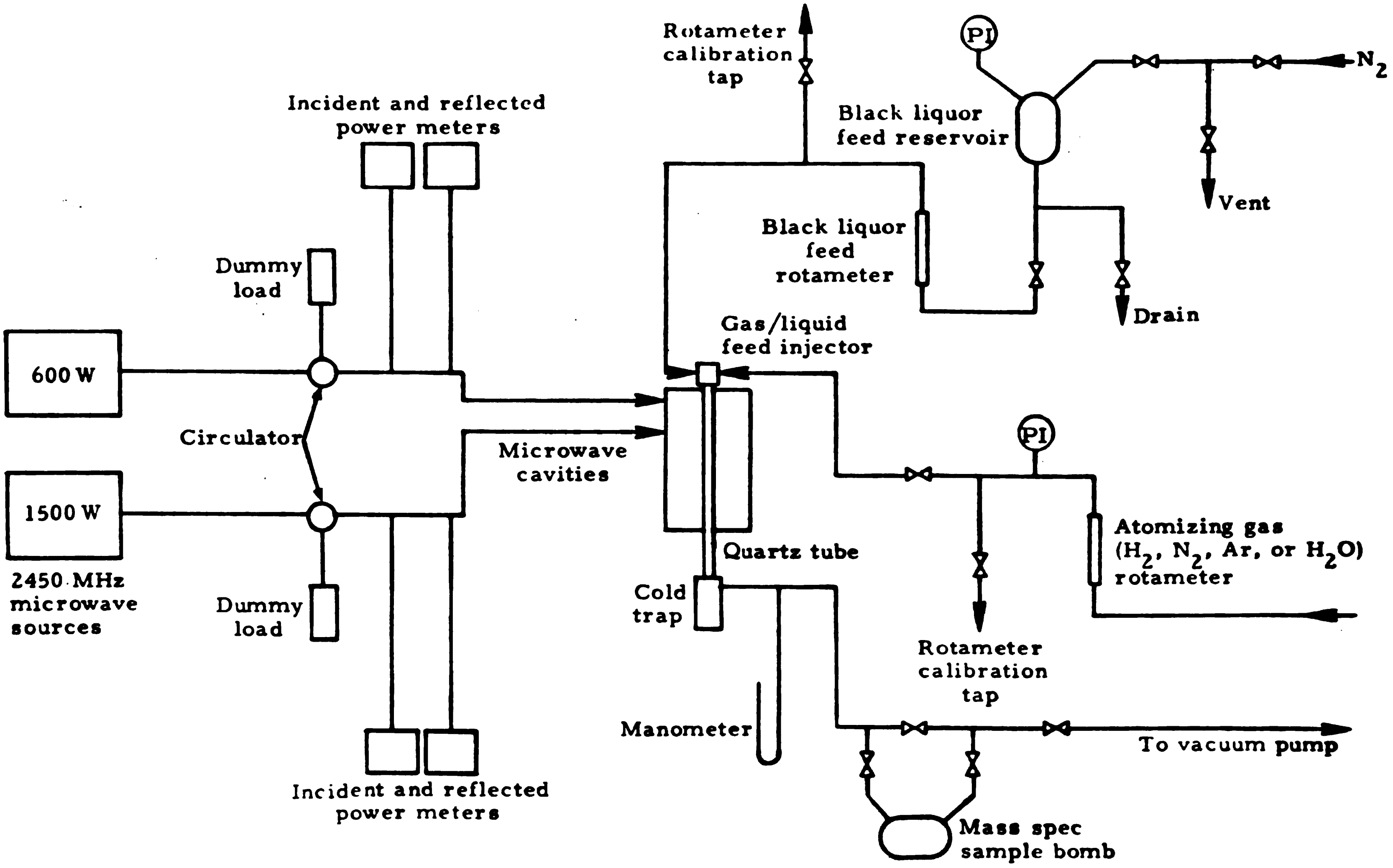

Figure 1. Microwave flow system.

The experimental procedure developed for investigation of the reactions of lignin in a microwave plasma basically consisted of: (1) generation of a hydrogen plasma at 1 mm Hg (2) increasing the pressure to 20 mm Hg or more while maintaining the plasma, (3) injection of the lignin solution mixed with hydrogen, (4) adjustment of vacuum pumping rate and inlet flow rates for pressure control, and (5) collection of products for chemical analysis.

The products which condensed in the ice water cold trap were analyzed using gas chromatography. A 10% Carbowax column was used for this purpose. Mass spectrometry was used to analyze the products which condensed in the liquid nitrogen trap. The solid products were not chemically analyzed, but were collected for estimating mass balances.

3. Results

The experimental conditions and results of the investigation of the reactions of black liquor and hydrogen in the microwave plasma reactor are summarized in Table 1.

Lignin in a black liquor solution was used as the feed for runs 1-3, whereas lignin in methanol was used for the remaining runs. It was discovered that using black liquor directly resulted in tube degradation due to deposition of sodium salts. Extracting the lignin from black liquor with methanol and utilizing this solution of lignin and methanol as the feed to the plasma eliminated the problem of reactor tube failure.

Several observations were made during runs when aqueous solutions of lignin in black liquor were fed to the reactor. As this liquid feed first entered the reaction zone, the color of the plasma changed from a reddish color to a yellowish color. A few seconds later, the quartz reactor tube would begin to glow red hot and the experiment would be halted to prevent tube failure. When the tube was examined after an experimental run, the inner surface of the reactor tube was found to be coated with a black soot. This soot could be easily washed off, but there were also areas where the tube itself had started to decompose and had become opaque and brittle. It was speculated that the presence of inorganic salts in the black liquor was largely responsible for the degradation of the reactor tube.

When methanol was utilized for extraction of lignin from black liquor, the problem of tube failure was eliminated. Approximately 67% by weight of the black liquor dissolved in the methanol. Apparently,

Table 1. Summary of Experimental Conditions and Results

Run	Black Liquor[a] wt. per cent concentration	Liquid flow rate cc/min	H_2 flow rate cc/sec	Absorbed power zone I (W)	Reactor pressure mm Hg	Solid Products	Results of GC analysis of liquid sample	Observations
1	10% in H_2O	5.1	21	400	15	Carbon deposits	GC not used when solvent is water	Tube degradation and overheating, short reaction times.
2	10% in H_2O	3.7	40	400	18			
3	10% in H_2O	2.0	36	580	27			
4	10% in meth.	8.0	21	400	33	Char produced representing 80% of feed	5 GC peaks before methanol peak, 2 peaks after.	Some sparking, slight tube overheating, reactor zone becomes filled with char.
5	10% in meth.	10.	15	500	23			
6	30% in meth.	3.0	22	440	20	Char produced, representing 75% of feed.	13 GC peaks after methanol peak, no phenol peak.	Reactor zone filled with char.
7	30% in meth.	12.0	40	250[b]	49			
8	40% in meth.	4.2	45	400	33	Char produced, representing about 75% of feed.	13 GC peaks after methanol peak, no phenol peak due to reaction, 2 peaks after phenol peak used for reference.	Reactor zone filled with char.
9	40% in meth.	4.8	45	480	29			

In reactor zoneII: incident power = 480W (constant) and absorbed power not measured.
Length of reactor zones: zone I = 7-13 cm., zone II = 13 cm.

[a] Composition of Black Liquor (dried): 28% lignin, 49% fixed solids, 14% Na_2SO_4, 9% other residue.

[b] Only plasma zone I was operated.

Slight amounts of methane were found in the liquid nitrogen cold trap in all experiments much of the black liquor salts (and some of the lignin) did not dissolve into the methanol because when this liquid feed was injected into the hydrogen plasma the problem of tube degradation did not occur. As before, when this liquid feed entered the reaction zone, the plasma would change color from red to yellow. As more feed reacted, a powdery black char would collect on the inner surface of the reactor tube. Occasionally, the char near the tube surface would emit sparks. This char was capable of absorbing large amounts of microwave power and the char in contact with the surface of the reactor tube would overheat the reactor tube. Despite the occasional problems with sparking, use of methanol as solvent allowed experiments to be carried out successfully.

Experiments were conducted with feeds of 10, 30, and 40% solutions of black liquor in methanol. The primary constituents of these black liquor solutions were lignin and fixed solids. In all of these experiments, the results were similar. The product produced in largest quantity was a solid char. Although difficult to measure, this char represented approximately 75% of the liquid feed.

The reaction products were collected in the ice water cold trap and in the liquid nitrogen trap, and analyzed for chemical composition. The reaction products collected in the ice water cold trap were analyzed using gas chromatography. Thirteen different species were contained in this sample. Eleven of these species were produced in very small quantities and show up in gas chromatograph analysis as GC peaks after a methanol peak and before a phenol peak. Larger quantities of two other species were found in the liquid product and a comparison of the chromatogram for the products of these microwave experiments was made with a chromatogram of products of conventional pyrolysis reported by Watanabe and Kitao[8]. This comparison indicated that guaiacol and 4-hydroxy-3-methoxytoluene were produced in the microwave reactor. No phenol was produced in the microwave discharge, although phenol was used as a reference peak CG runs.

The contents of the liquid nitrogen trap were analyzed by mass spectrometry and a small amount of methane was detected. A run was conducted with pure methanol feed, and the material collected in the liquid nitrogen trap was found to be methane. Therefore, methane formation was due, at least in part, to hydrogenation of methanol.

4. Discussion

Complex reactions occur in a hydrogen discharge and several reactive species are available for reaction: hydrogen atoms, ionic species, and electrons. Vastola, Walker and Wightman[9] studied the reactivity of these various species with carbon in a hydrogen discharge. They determined that hydrogen atoms were relatively nonreactive when they collided with a carbon surface. Hydrogen atoms recombine on the carbon surface instead of reacting with the solid phase carbon. They also theorized that reactions of carbon with hydrogen which do occur in the discharge were due to the action of high energy ionic species. The collisions of these energetic ionic species with the solid carbon produces gaseous carbon which can react with hydrogen.

Char formation is the major reaction which occurs when lignin is injected into a hydrogen plasma. It is suspected that reactions of hydrogen atoms with lignin are of little significance in the discharge. Collisions of hydrogen atoms with lignin probably result in recombination of hydrogen. It is likely that the large production rate of char in the discharge is due to the reactions of ionic species with lignin. The bombardment of lignin molecules by high energy ionic species probably strips the lignin of hydrogen and converts the lignin to char.

4.1 Alternative Methods of Processing Lignin

A spectrum of products, which have no commercial use presently were produced in experiments when lignin was fed directly into a microwave plasma reactor. Lignin processing to produce chemicals may become of commercial significance if either a) chemical routes are developed utilizing the various presently non-useful products, or b) alternative processes are used to convert lignin to present day usable products.

A microwave discharge reactor could be useful if the lignin was first processed using conventional methods. A study of existing lignin technology shows that lignin can be depolymerized without producing large amounts of char[10,11]. Controlled oxidation of lignin to vanillin and other products[10] is a process used commercially, and a high pressure hydrogenation process which converts lignin to a variety of phenols has been patented[11]. These processes successfully depolymerize the lignin but they produce such a wide variety of products so that it is impossible to fully utilize the lignin feed.

What is needed for economically successful processing of lignin, is some method of converting a wide variety of single ring aromatic compounds (mainly methoxy-phenols) to a select few useful products. Results of experiments reported by Brooks and Sambrook[6] suggest that use of a microwave discharge reactor may fulfill the above requirements. They studied the reactions of benzene in a microwave discharge reactor and obtained large conversions of benzene to acetylene and butadiene. If it is possible to sustain a microwave discharge when the reaction feed is a mixture of methoxy-phenols, useful products may be formed in the discharge, and use of microwave processing could be the critical component of an overall scheme for converting lignin to useful hydrocarbons.

4.2 Two Stage Lignin Processing

Approximately 200 million pounds per year of lignin are available from a typically-sized Kraft pulp mill. A two-stage processing scheme for converting 200 million pounds per year of lignin to useful products is illustrated in Figure 2. This scheme provides a basis for evaluating

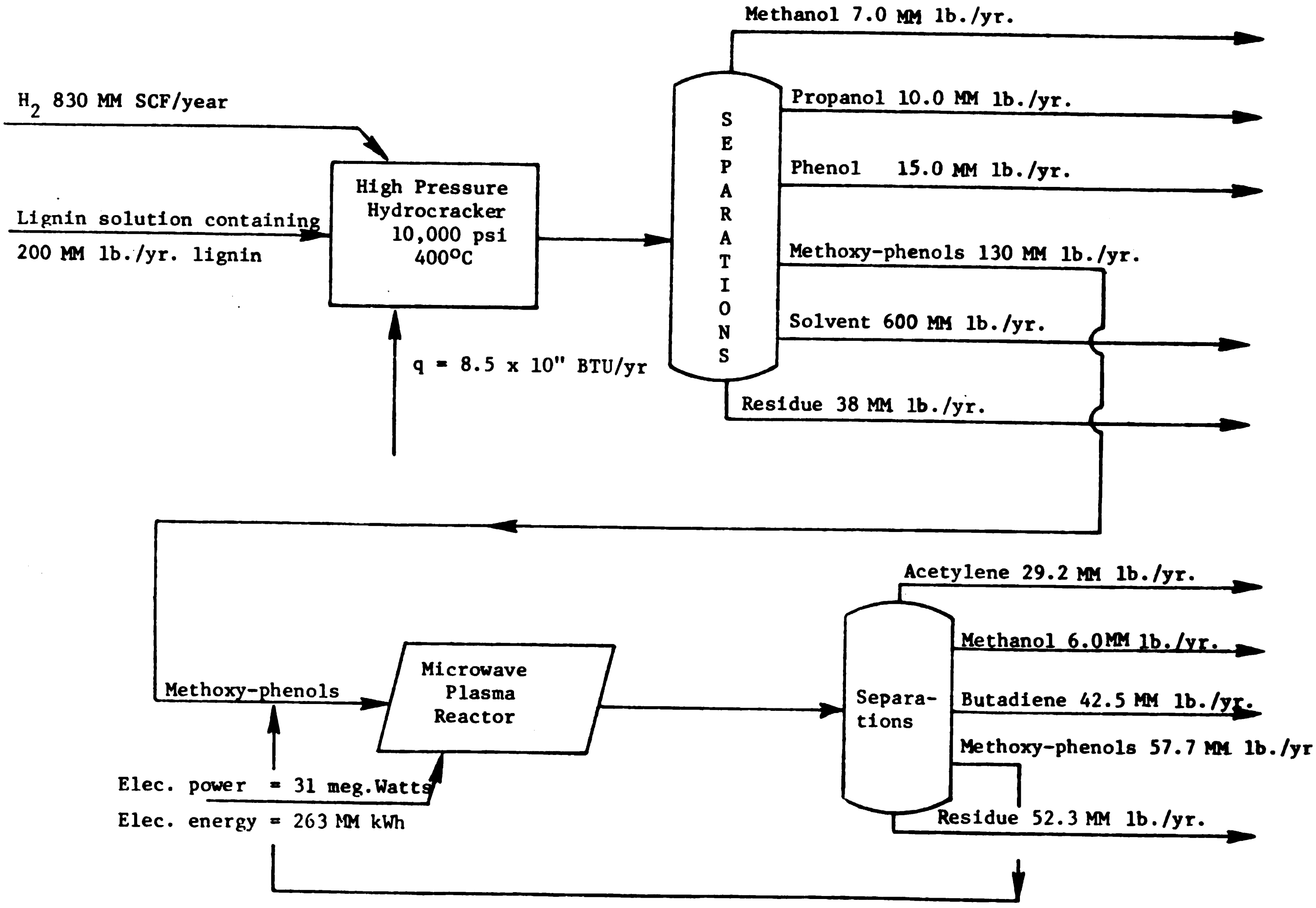

Figure 2. Two stage lignin processing.

the economic feasibility of including microwave plasma reactors as part of a two-stage lignin process. In the first stage, it is speculated that lignin could be hydrocracked to mainly low value methoxy-phenols using the process patented by Giesen[11,12]. Useful products which may also be produced in the hydrocracking stage include phenol, propanol, and methanol. The methoxy-phenols would be fed to the second stage, a microwave plasma reactor, where the low value methoxy-phenols can be possibly upgraded to useful products, such as acetylene and butadiene. It is suspected that a microwave plasma may be unique in its ability to convert low value monocyclic aromatics to useful products.

Several assumptions were required for this analysis because of a lack of directly related experimental information. However, the assumptions for yield, product distribution, and energy requirements for each of the stages represent extrapolation of results of experiments closely related to each process. Extrapolation of published results of lignin hydrocracking[8,11,12] provided the information needed for designing the hydrocracking step. Lignin was assumed to be converted to 65% (by weight) methoxy-phenols, 19% residue, 8% phenol, 5% propanol, and 3% methanol. The yields of useful products (acetylene and butadiene) produced in the second stage, were estimated by extrapolating the results of experiments with benzene in a microwave plasma performed by Brooks and Sambrook[6]. Thus, it was assumed that the molar conversion of the aromatic ring part of the feed to the microwave plasma system was 30% to butadiene, 20% to acetylene, 10% to residue, and the remaining feed did not react. It was also assumed that the side chain methoxy groups would be hydrogenated to methanol in the discharge with a molar conversion of less than 20%. The microwave energy requirement was estimated to be 690,000 J per gram mole of aromatic feed, and was based on the work on benzene by Brooks and Sambrook.

Results of an economic analysis based on these assumptions is contained in Table 2 which indicates that over $18 million for capital investment for a plant can be justified. These estimates were based on 1976 values for chemicals. The economics of this process are highly sensitive to yields of lignin to useful products and energy requirements.

Microwave plasma processing appears to be most useful as part of an overall process to upgrade low value products to valuable products. These products would be, in general, different than those obtained from conventional pyrolysis and/or hydrocracking. It is important in microwave processing schemes to maximize the microwave reaction efficiency. This would minimize the capital investment and energy cost for a microwave generation plant. Many assumptions were made for this test case, but the results of the economic analysis indicate that application of microwave technology to lignin processing may be significant.

Table 2

Economic Summary for Hydrocracking and Microwave Pyrolysis of Lignin

Lignin: 200 MM[1] lb./yr. Useful products: 110 MM lb./yr. Conversion: 55% Maximum Total Investment for 20% DCF: $18,100,000

Raw Materials	Unit	Quantity/ Year	Cost $/Unit	Cost $/year
Lignin	lb.	200 MM	.02	$4,000,000
Hydrogen Gas	MSCF	.830 MM	.800	700,000
Subtotal				4,700,000
Utilities				
Fuel	MM BTU	.851 MM	2.000	1,700,000
Electricity	M kWh	.263 MM	20.000	5,300,000
Steam	MM BTU	.226 MM	1.310	300,000
Cooling water	M gal.	-	.050	-
Subtotal				7,300,000
Fixed Costs				
Labor and Miscellaneous (20% of Investment)				3,600,000
Depreciation (10% of Investment)				1,800,000
Subtotal				5,400,000
Total Manufacturing Cost				
Revenue				
Methanol	lb.	13.0 MM	.07	900,000
Propanol	lb.	10.0 MM	.25	2,500,000
Phenol	lb.	15.0 MM	.28	4,200,000
Acetylene	lb.	29.2 MM	.18	5,300,000
Butadiene	lb.	42.5 MM	.20	8,500,000
Char and other	lb.	52.3 MM	.02	1,000,000
Subtotal				22,400,000
Before Tax Profit				5,000,000
Net Profit				2,500,000
Annual Cash Flow				4,300,000

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[1] MM = million

5. Conclusions

Experimental results show that lignin is degraded to char when lignin or black liquor is injected into a hydrogen plasma induced by a microwave discharge. The desired result of hydrogenation and depolymerization of lignin in the discharge does not occur. Actually, the collisions of high energy ionic species with lignin dehydrogenate the lignin and overwhelm any radical reactions which may occur. Therefore, use of a one-step process involving a microwave plasma reactor is not applicable for production of commercially useful chemical products from lignin. A two-step process utilizing conventional hydrocracking to depolymerize lignin, followed by microwave plasma cracking of methoxy-phenols (to convert these monocyclic aromatics to acetylene and butadiene, for example) may be a practical processing scheme.

The results of a preliminary economic analysis show that use of microwave plasma processing as part of a two-stage system for converting lignin to useful chemicals might be economically feasible. Based on the results of this study, it is possible to identify the most important problems related to lignin processing which should be investigated further. The reactions of methoxy-phenols in a microwave discharge need to be investigated experimentally in order to determine the nature and quantities of reaction products. It is expected, however, that acetylene and butadiene will be among the predominant products. Carrying out these additional experiments will provide the basic information needed to adequately design a system for processing the lignin and will permit a realistic evaluation of the process.

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PART II - THE EFFECT OF MICROWAVE RADIATION ON BATCH PROCESSING OF CELLULOSE IN WATER

Paper prepared for publication

By

Jack D. Junttila, Martin C. Hawley and Jes Asmussen, Jr.

Michigan State University

Departments of Chemical and Electrical Engineering

ABSTRACT

THE EFFECT OF MICROWAVE RADIATION ON BATCH PROCESSING OF CELLULOSE IN WATER

By

Jack Junttila, Martin C. Hawley and Jes Asmussen, Jr.
Departments of Chemical and Electrical Engineering
Michigan State University
East Lansing, Michigan 48824

A batch reactor system has been designed and constructed for investigating microwave radiation effects on gas or liquid phase reactions at high temperature and high pressure. Several batch experiments were conducted in this specially constructed reactor with cellulose in water. A fifteen percent solution of crude cellulose waste in water was placed in a high-pressure reactor vessel and heated to 450°F and a pressure of 500 psig. In some experiments microwave radiation was injected into the reactor interior to study the effects of microwave catalysis. Samples of both liquid and gas products were obtained for analysis. Reaction products were analyzed using mass spectrometry of gas products and distillation of liquid products.

The objectives of this study were to determine if microwave radiation would catalyze the hydrolysis reactions of cellulose and to determine the yield of reaction products for various experimental

conditions. Of particular interest was the yield of volatile, low-molecular weight organic products, and the effect of microwaves on their production.

Several reaction products were identified in the experimental gas sample. Products present in large quantities were CO_2 and CO. Also present in small quantities were methane, formic acid, and acetaldehyde.

The liquid product samples consisted of two main reaction products. The major product found in the liquid sample was a water soluble, black sticky tar. This tar probably consisted of glucose and glucose decomposition products. Formic acid in small quantities was also identified.

Based on the results of this study, it was concluded that microwave radiation has no positive effect on the hydroloysis reactions of cellulose. The decomposition of cellulose seems to occur via the same reaction mechanism, cellulose → glucose → decomposition products, with or without use of microwaves.

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LIST OF FIGURES

1. INTRODUCTION

Recent investigations in our laboratory of microwave plasma catalysis for chemical reactions have suggested the use of microwave processing of cellulose for the production of chemicals. Details of experiments on microwave processing of cellulose are reported in this paper.

The use of cellulose and cellulose wastes as chemical, food, and energy resources has been widely studied.[1] Many processes have been considered for converting cellulose to useful products: thermal pyrolysis, enzymatic hydrolysis, fermentation, high pressure water processing, and many others.[1,2,3] Chemical, enzymatic, microbial, and macrobial catalysts and their effects on cellulose processing have also been investigated.[2] Products which have been produced in cellulose decomposition processes include glucose, char, tar, levoglucosan, carbon black, organic acids, alcohols, aldehydes and ketones. Synthesis gas (CO and H_2) can be produced by partial oxidation of cellulose; this synthesis gas can in turn be used to produce a variety of chemical products[1]. Although a substantial amount of research has been performed investigating the problem of cellulose processing, most schemes for converting cellulose or cellulose waste to useful products are not yet economically feasible.

The paper and pulp industries produce large quantities of solid waste containing cellulose. Currently, the primary use of this waste product is for fuel. However, as petroleum shortages increase and prices rise, it may become economical to use cellulose from plants or from waste byproducts of paper production as sources of hydrocarbons for chemicals.

The Kimberly-Clark Corporation has supported exploratory experiments at Michigan State University to study the processing of cellulose waste for the production of chemicals. This report summarizes the exploratory experiments which have been carried out to study the chemical reactions of cellulose waste in water and the effect of microwave radiation on these reactions. The feed used for these batch experiments was a cellulose containing "sludge", which is produced as a waste byproduct by the paper industry, and was supplied by Kimberly-Clark. Experiments were conducted at high pressure and temperatures (500 psig, 450°F) and included use of acid and base chemical catalysts. The major objective of this study was to determine if microwave radiation could catalyze the reaction of cellulose and water to volatile low molecular weight organic products.

2. EXPERIMENTAL

A batch system as shown in Figure 1 was used for the experimental studies. The pressure vessel used had a 1-inch thick cylindrical shell. Removable flat circular plates 2 inches thick were used for the head and bottom of the vessel and were bolted down for high pressure operation. The vessel head was tapped to allow attachment of the sampling valve, pressure gauge, and the microwave coaxial coupling. The microwave coupling consisted of a variable length brass microwave probe inserted in a conical piece of Teflon. This allowed introduction of microwave radiation to the reactants in the interior of the vessel while at the same time permitting high pressure operation. The shell of the vessel was tapped to permit insertion of a thermocouple lead for temperature measurement. The heavy pressure vessel (approximately 200 pounds) was supported on a stack of cement blocks and direct fired heating was used for supplying the large amount of heat needed to bring the vessel and the reactants up to operating temperature. Fiberglass insulation was wrapped around the vessel to decrease heat losses during experimental runs.

A microwave source operating at a frequency of 2.45 GHz and a power level of 1,500 Watts generated the microwave radiation used in most experiments. The radiation generated at the microwave source passed through a series of wave guides which transmitted the radiation to the coaxial coupling connected to the vessel head of the reactor. The microwave radiation could then pass through the coupling into the reactor interior. Incident and reflected microwave power levels were measured with power meters. The microwave system has been used for

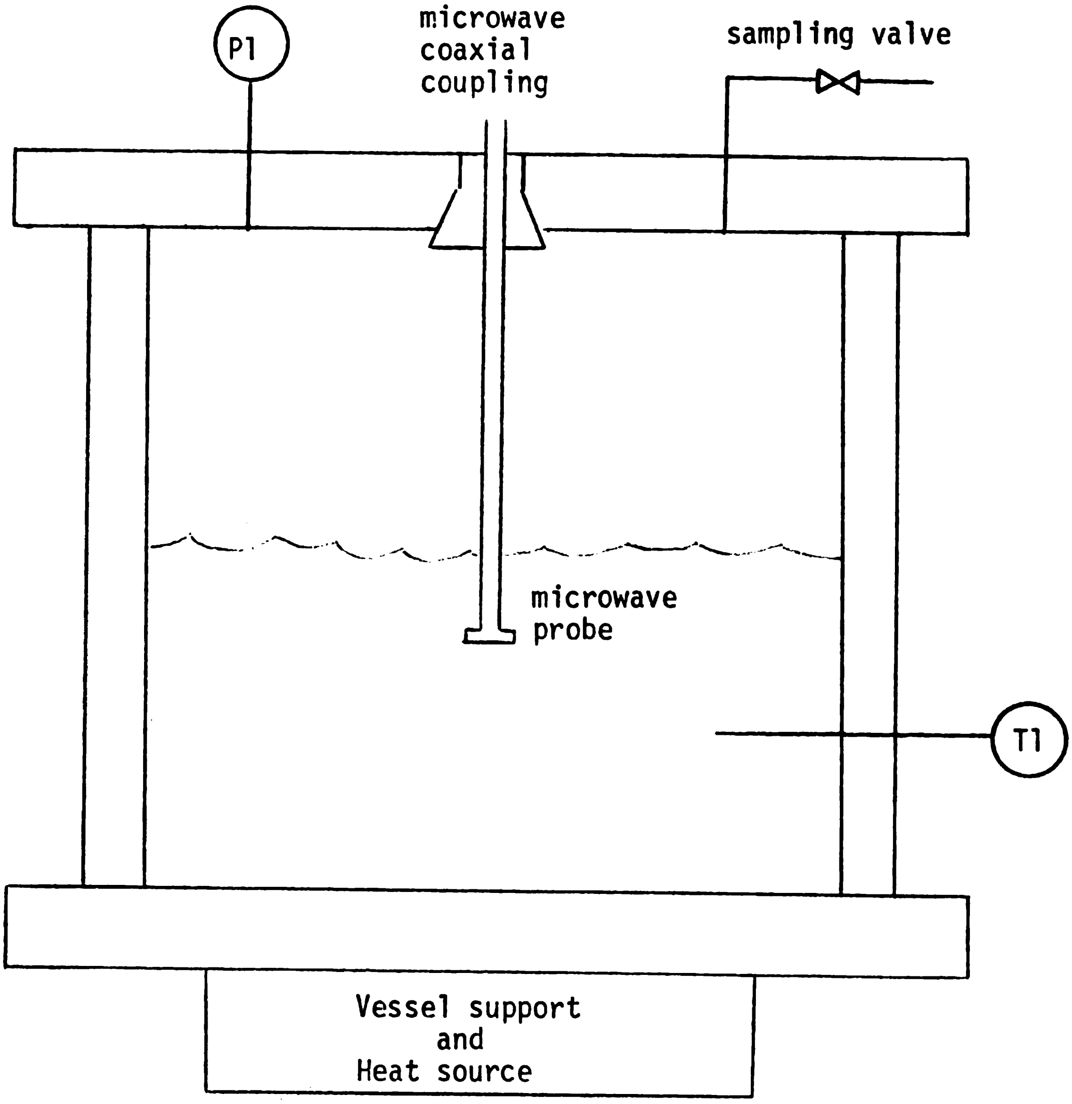

Figure 1. High Pressure Microwave Batch Reactor System.

microwave plasma experiments and has been described in detail previously.[4]

The experimental procedure basically consisted of: (1) charging the reactor with the cellulose-water mixture, (2) heating the reactants until the pressure reached 500 psig, (3) recording temperature, pressure, and microwave power absorption data during the heat-up and cool-down stages, and (4) collecting product samples for chemical analysis. Approximately 3,000 grams of reactant slurry were used for each run. Experiments were conducted with various cellulose and catalyst concentrations (see Table 1). Two types of cellulose waste were supplied and used in making the reactant slurry. The Type-1 cellulose waste was brown in color, dry, and very difficult to crush or crumble because of its fibrous nature. The Type-2 of cellulose waste sludge was grey, moist, did not need to be ground up because it had a fairly fine consistency, and had an offensive odor. The Type-1 waste was used in the initial experiments while Type-2 was used in later experiments. The type of cellulose waste used appeared to have little effect on the experimental results.

Air was purged from the vessel interior during the heat-up period by opening the gas-sampling valve for a short period of time after the pressure in the vessel reached 10 psig. The heat-up period for an average run lasted approximately 3 hours. At the same time, microwave radiation would be injected into the reactor vessel (except for runs 2 and 4).

When the pressure in the vessel reached 500 psig, the heat supply was shut off and the vessel was allowed to cool. The

TABLE 1

Summary of Experimental Program

Run	Catalysts	Weight % Cellulose in Aqueous Feed	Average Absorbed Power
1	Microwave	1% Type-1	180 Watts
2	None	10% Type-1	-
3	Microwave	20% Type-2	230 Watts
4	None	15% Type-2	-
5	Microwave	15% Type-1	350 Watts
6	Microwave, .3% Na_2CO_2	15% Type-2	440 Watts
7	Microwave, .4% HCl	15% Type-2	490 Watts
8	Microwave, .8% HCl	15% Type-2	330 Watts
9	Microwave, .6% HCl	20% Type-2	570 Watts*
10	Microwave, 1% NaOH	20% Type-2	840 Watts*

*These experiments used a long-length microwave probe such that tip of probe was immersed in the reactant solution.

In all experiments, reactor contents were heated from room temperature and pressure to final conditions of about 450°F, 500 psig. The time required for heating was about 2 hours and for cooling was about 5 hours.

Reaction products, runs 2-10

1. Gas products: CO_2, CO, formic acid, methane, acetaldehyde.
2. Liquid products: water soluble, black sticky char, representing 30-40% of the cellulose feed; formic acid.
3. Solid products: few grams of flat, black crystals which floated on water surface; unreacted cellulose waste.

temperature of the reactants was usually about 450^{o}F at a pressure of 500 psig. After the pressure decreased below 300 psig, a gas sample was collected by connecting an evacuated sample tube to the gas-sampling valve and opening the valve. Filter paper was used to screen out some of the water droplets in the vapor entering the sample tube in order to facilitate mass spectrometric analysis of the gas sample. Liquid and solid products were collected when the system cooled to room temperature. The liquid product solution would be filtered and then distilled in an effort to determine if volatile organic liquid products were produced.

3. RESULTS

A summary of experimental conditions and results is presented in Table 1. The results of all experimental runs were similar, regardless of which catalyst was used. Product distributions and yields were essentially the same for all runs.

In experiments involving injection of microwave radiation, it was observed that absorption of microwave energy was greatest at the beginning of the run, at low pressures and temperatures. For example, in run 9, absorbed power varied from 980 Watts at the beginning of a run to 690 Watts at the end of a run. The injection of microwaves into the interior of the pressure vessel produced no noticeable increase in temperature of the reactor contents, and was due to the large heat capacity of the heavy pressure vessel. Experiments were peformed with the microwave probe both above the surface of the water and with the probe partially submerged in the water. With the probe projecting into the reactants, there was more efficient absorption of microwave energy. However, this arrangement had no effect on the product yield or product distribution.

The product gas samples were analyzed using mass spectrometry. Results of these analyses were essentially the same for all cases, and typical spectrograms are shown in Figures 2 and 3. The mass spec peaks were identified using information from the Atlas of Mass Spectral Data[5], shown in Table 2. Use of acid, base, or microwave radiation catalysis had no effect on the distribution of products found in the gas sample. Product species present in largest quantity in the gas sample were CO_2 and CO. Species which were present in

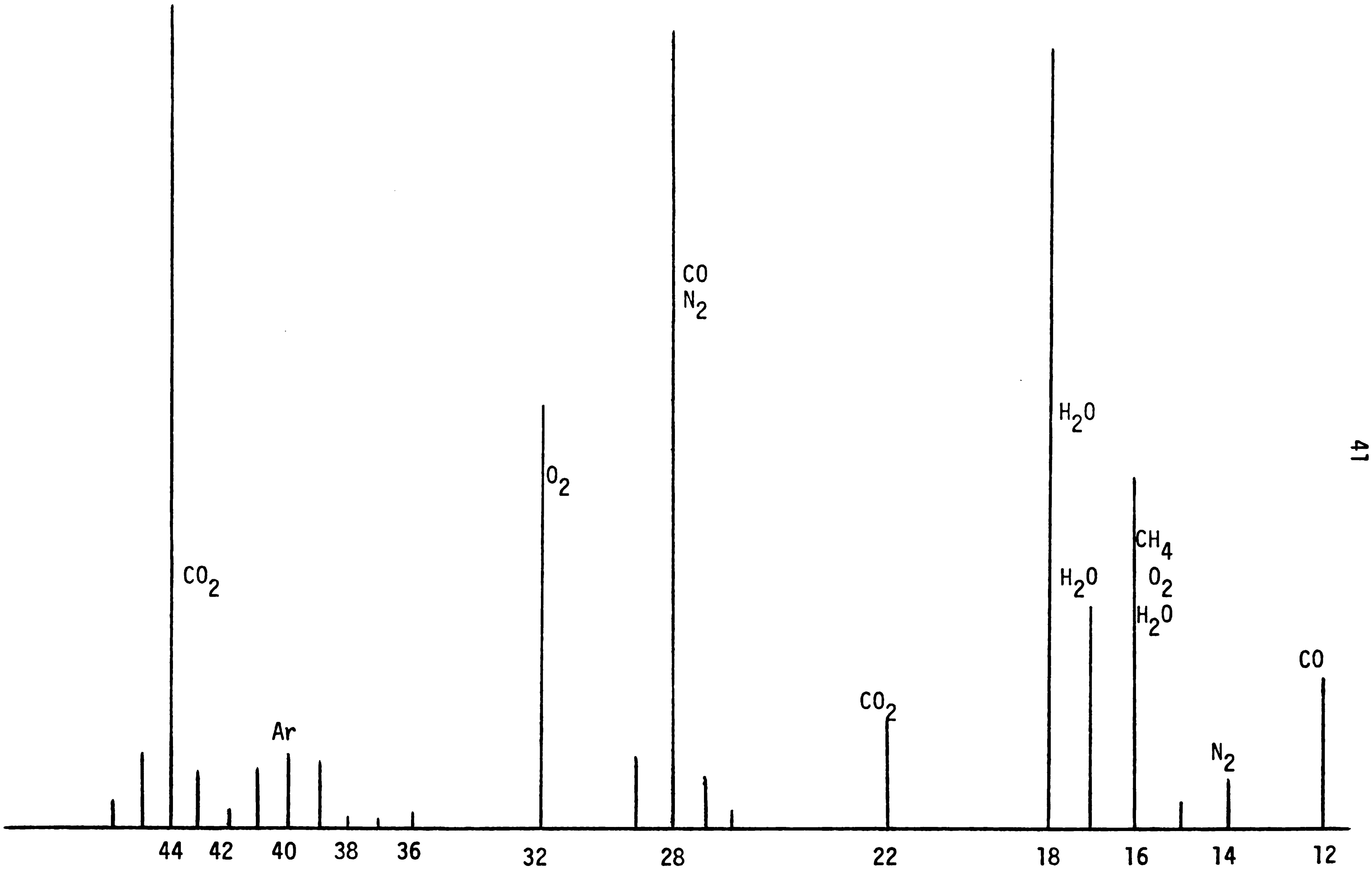

Figure 2. Mass spectrogram of gas sample, run 4-no catalysis.

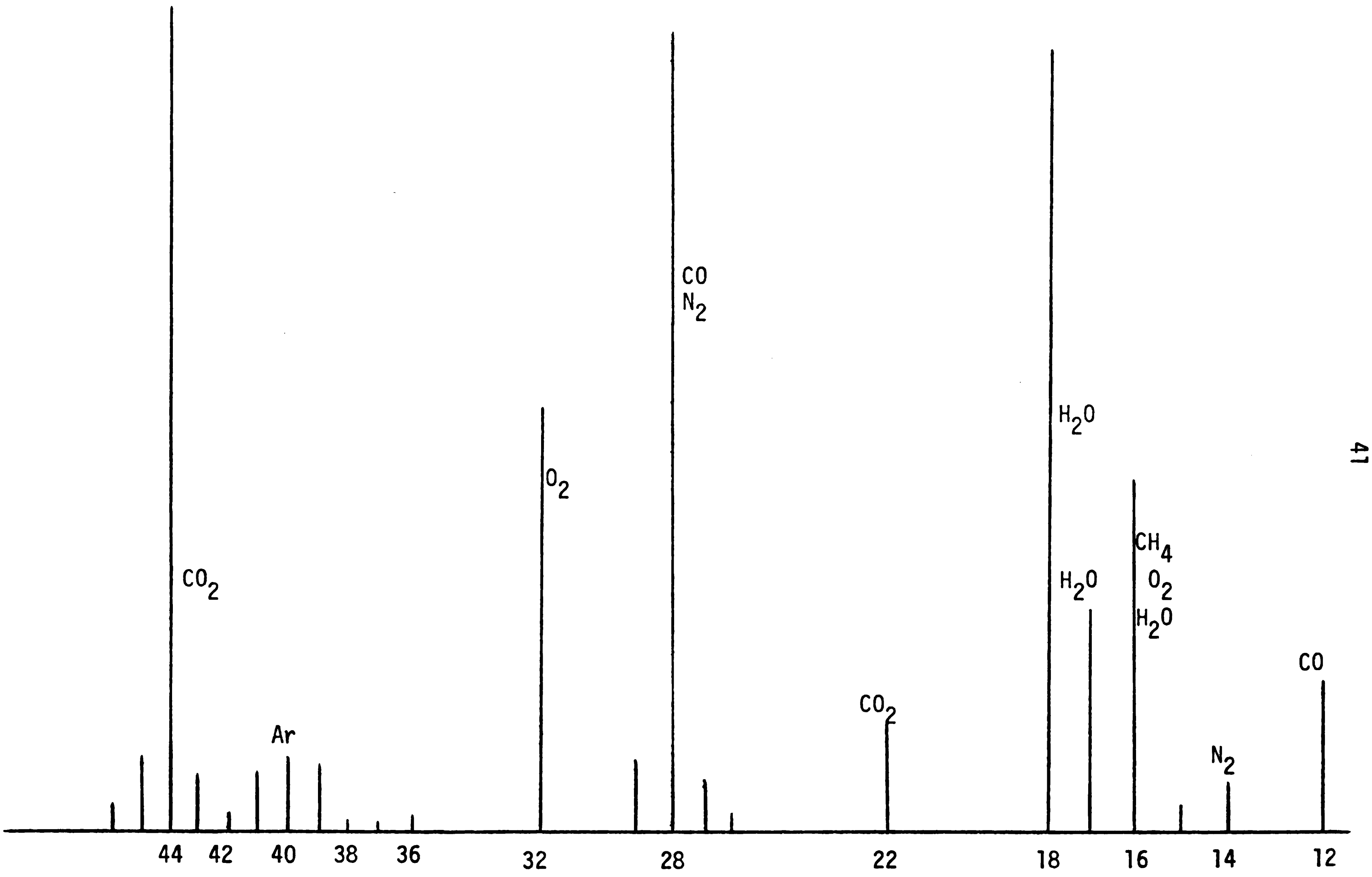

Figure 2. Mass spectrogram of gas sample, run 4-no catalysis.

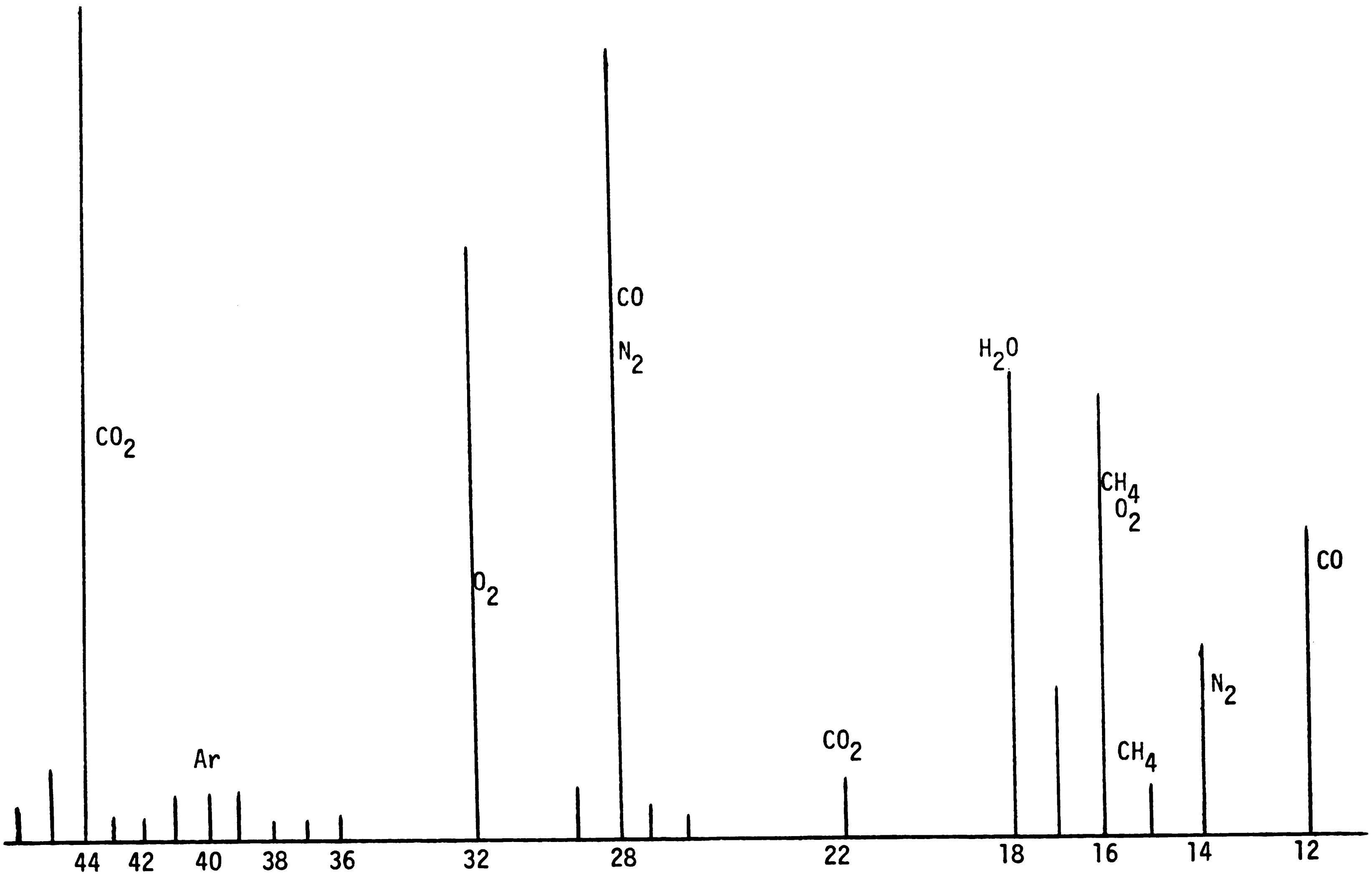

Figure 3. Mass spectrogram of gas sample, run 10 - microwave and NaOH catalysis.

TABLE 2

Identification of Mass Spectroscopic Peaks

Chemical Species	Mass Spec Peaks (descending order)*
CO_2	44, 28, 16, 22, 45
CO	28, 12, 16, 29, 14
O_2	32, 16
N_2	28, 14, 29, 14
H_2O	18, 17, 16, 19, 20
Ar	40, 20, 36, 38
CH_4	16, 15, 14, 13, 17, 12
Formic acid	29, 46, 45, 28, 17
Acetaldehyde	29, 44, 43, 42, 26
Propane	29, 28, 27, 44, 43
Propene	41, 42, 39, 27, 40
Dimethyl ether	45, 29, 15, 46, 14
HCl	36, 38, 35, 37, 76
Methanol	31, 32, 29, 28, 18
Ethanol	31, 45, 29, 27, 43

*Information from Atlas of Mass Spectral Data[3].

small quantities were methane, formic acid, acetalydehyde, and possibly propene. Unexpectedly, there was no indication of methanol or ethanol in the gas sample. The presence of O_2 and N_2 in the gas sample, as shown in the mass spectrograms, probably was due to some leakage of air into the gas sample tube.

The reactant pressure-temperature relationship for run 10 is shown in Figure 4. Also shown in this figure is a comparison of the reactor pressure to the vapor pressure of water. The largest difference between the vapor pressure of water and the reactor pressure occurred at a temperature of 450°F. This difference in pressure was about 70 psi and indicates that a significant amount of gaseous product (mainly CO_2) was being produced.

After an experimental run when the vessel cover was first removed, several preliminary observations could be made. First, the reactor contents had a pronounced smoky odor. Usually there was a very thin layer of flat black crystalline material floating on the water surface. The liquid product was black in color and had a viscosity that was slightly greater than water. This black product solution was produced whether acid, base or no catalyst was used. It was easily observable that the cellulose had undergone significant reaction. For example, with the Type-1 cellulose, which was very difficult to grind up, it was discovered that after reaction it was easily pulverized. The Type-2 cellulose seems to change color with reaction, as it was grey before reacting and brown after.

Distillation was used for characterization of the aqueous liquid product. It was expected that if there were significant quanti-

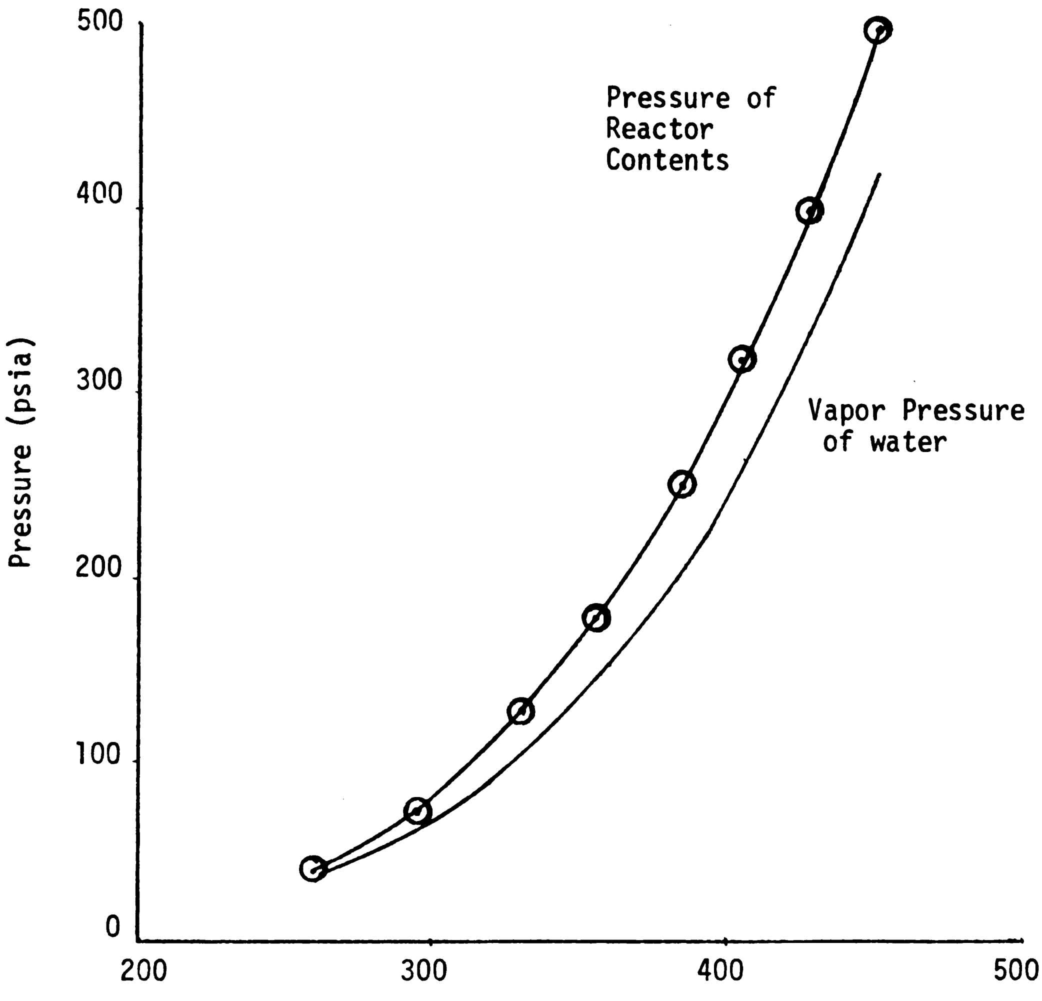

Figure 4. Reactor pressure as a function of temperature.

ties of any volatile organic product, it would be possible to separate and identify these products using a batch still. Distillation of the filtered liquid product indicated that all vapor which boils off from the liquid product boils at about 100°C at 1 atmosphere pressure. However, the first overhead cut had a heavy odor and was definitely not pure water. This behavior was due to the presence of formic acid, which also boils at 100°C. There was no indication of the presence of significant quantities of any other volatile organic products in the liquid sample.

After all volatile products were evaporated off during distillation, what remained was a sticky, black, sweet-smelling tar. This water soluble material was the product produced in largest quantity; approximately 30 to 40% of the cellulose waste feed was converted to this tar. It is suspected that this tar consisted of glucose, levoglucosan, and other carbohydrates. Glucose and glucose decomposition products were reported to be obtained from high temperature cellulose hydrolysis reactions[6]. Levoglucosan was reported as being the tar produced in cellulose pyrolysis experiments[2]. The presence of sugars in the tar was also indicated by the rapid growth of mold on the air-exposed surface of the liquid product. Attempts were made to analyze the product tar using mass spectrometry[2], but because of the presence of large amounts of associated water, use of mass spectrometry was impossible.

4. DISCUSSION

Exploratory experiments were conducted on the decomposition of cellulose in water at high temperatures (480 to 660^{o}F) by Appell, Wender, and Miller at the Bureau of Mines[6]. Their operating procedure consisted of: (a) charging the reactor with a cellulose slurry and reactant gas, either H_2 or CO, (b) heating to operating temperature, (c) maintaining this temperature for two hours, and (d) then quenching the reactor. They obtained a yield of about 40% char.

Saeman[5] investigated the reaction mechanism for the hydrolysis of cellulose in acid mediums at temperatures ranging from 447 to 463^{o}K. He determined that the decomposition of cellulose proceeded via two steps: cellulose → glucose → decomposition products. The reaction: cellulose → decomposition products was found to be of little importance.

Amin, Reid, and Modell[3] investigated the decomposition of glucose in an aqueous phase. They discovered that at temperatures below the critical point of water, gluclose decomposed to a sticky black char, liquid products, and very little gas. When they compared the composition of the char they obtained to the char produced in the experiments performed by Appell (et al), they found that the two chars were similar. They concluded that cellulose and glucose decompose to similar products, and that the Saeman mechanism for cellulose decomposition appeared to be correct. The most interesting result of their study occurred when they injected glucose into water at its critical point; no solid char was produced and gas production greatly increased.

The results obtained in this experimental study of the reactions of cellulose waste with water were quite similar to the results obtained by others[3,5,6]. The reaction product produced in largest quantity was a black, sticky, water soluble tar. The reaction mechanism hypothesized by Saeman and Amin (et al) for the decomposition of cellulose also seems to correctly describe the decomposition of cellulose waste in water. The cellulose waste first depolymerizes to glucose, then the glucose decomposes to char or tar, and formic acid.

Use of microwave radiation had no positive effect on the reactions investigated. It was determined that microwave radiation did not promote production of volatile organic products from cellulose. The product species and the product yields were the same for all runs, regardless of the type of catalysis used--acid, base, or microwave radiation.

However, it may be possible that if the microwave power levels were greatly increased, low molecular weight organic products would be formed. Microwave radiation is probably greatly absorbed by the large amounts of water present and converted to heat before the radiation can interact with the cellulose. Thus, an activation of the cellulose by microwave radiation would be greatly reduced in the presence of liquid water. Interesting results may possibly be obtained if cellulose were injected into high pressure water vapor irradiated with microwaves, especially if the water were at its critical point, as in the experiments by Amin[3] (et al).

5. CONCLUSIONS

Microwave radiation appears to have no catalytic effect on the liquid phase reactions of cellulose with water. Glucose and glucose chars are the reaction products produced in greatest quantity when cellulose and water react at conditions below the critical point of water. The high production rates of these low-value products probably rules out the use of high-pressure water-cellulose reactions for the production of chemicals from cellulose.

This study has demonstrated that it is possible to investigate the effects of microwave radiation on high temperature and high pressure reactions. Although use of microwaves was ineffective for cellulose-water reactions, the effect of microwave radiation on other high-pressure and temperature chemical reactions may be of interest.

ACKNOWLEDGEMENT

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RECOMMENDATIONS FOR FUTURE STUDY

Several general areas of research related to microwave processing were suggested during the course of this study. These general topics are outlined below along with recommendations for improving experimental procedures:

1. Studies should be made to determine the nature of products obtained when lignin is processed in a high pressure hydrocracker. The aromatic methoxy-phenols produced by the hydrocracker may possibly be upgraded to useful products with use of a microwave plasma.

2. Experiments should be performed investigating the possibility of generating a methoxy-phenol (e.g. guaiacol) microwave plasma. Although a carrier gas (H_2 or He) may be necessary for these experiments, it would be preferable if no carrier gas were used. In past experiments with benzene feeds in a microwave plasma, the most useful results occurred when no carrier gas was used[2].

3. The decomposition reactions of cellulose in water should be studied at conditions at the critical point of water. Interesting results were obtained by Amin[3] (et al) when they studied the decomposition of glucose in water at the critical point. It is important in these experiments that the cellulose or glucose be injected into the water after the water has been heated to its critical point.

4. The apparatus for two microwave process schemes has been demonstrated to be experimentally viable: microwave plasma pro-

cessing and microwave radiation catalysis of high pressure and temperature reactions. Although these schemes are probably not useful for paper waste processing, they may be useful for other applications. A microwave plasma could be useful for processing vinyl chloride or sulfur oxides, and microwaves may have a catalytic effect on high pressure vapor phase reactions.

5. The experimental procedures and apparatus could be improved for future experiments. There are better methods[4] for removing lignin from Kraft Process Black Liquor than the methods that were used for this study. A better vacuum system is needed for the experimental plasma system, especially when studying a methoxy-phenol plasma. Problems were encountered during preliminary experiments with benzene and vinyl chloride because of incomplete air removal by the vacuum pumps. Finally, improvements should be made in the reactor feed system for experiments in which it is necessary to vaporize a liquid feed. This may require use of a small boiler type heat exchanger and a source of steam, but this would greatly facilitate vaporized feed experiments.

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