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Research into the Pyrolysis of Pure Cellulose, Lignin, and Birch Wood Flour in the China Lake Entrained- Flow Reactor

James Diebold



SERI

Solar Energy Research Institute

A Division of Midwest Research Institute

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RESEARCH INTO THE PYROLYSIS OF
PURE CELLULOSE, LIGNIN, AND
BIRCH WOOD FLOUR IN THE CHINA
LAKE ENTRAINED-FLOW REACTOR

JAMES DIEBOLD

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PREPARED UNDER TASK NO. 3356.30

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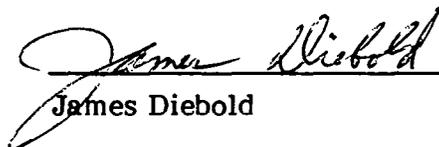
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PREFACE

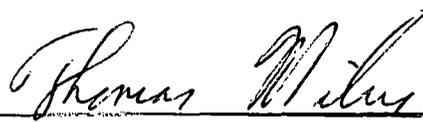
This report documents the fast pyrolysis of relatively pure feedstocks in the China Lake entrained bed reactor. The project proved that most of the hydrocarbon yields previously reported with a processed municipal solid waste feedstock could have come from the lignocellulosic fraction. This experimentation concluded the pyrolysis effort at the Naval Weapons Center, although the key personnel associated with the project are continuing the pyrolysis studies at SERI. This effort was supported by SERI through Contract No. EG-77-C-01-4042 with the Naval Weapons Center.

The skillful operation of the scanning electron microscope to produce the high-resolution photographs was performed by Rowland McNeil of the Naval Weapons Center, China Lake, Calif. Nathan Sippel, also of the Naval Weapons Center, discovered the magnetic properties of the char while conducting the heat-of-combustion tests.


James Diebold

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SUMMARY

This experimental program used the China Lake entrained-flow pyrolysis reactor to briefly investigate the pyrolysis of pure cellulose, pure lignin, and birch wood flour. The study determined that the cellulose and wood flour do pyrolyze to produce primarily gaseous products containing significant amounts of ethylene and other useful hydrocarbons. During attempts to pyrolyze powdered lignin, the material melted and bubbled to block the reactor entrance. The pure cellulose and wood flour produced C_2+ yields of 12% to 14% by weight, which were less than yields from an organic feedstock derived from processed municipal trash. The char yields were 0.1% by weight from cellulose and 1.5% from birch wood flour—one to two orders of magnitude less than were produced from the trash-derived feedstock. In scanning electron microscope photographs, most of the wood flour char had a sintered and agglomerated appearance, although some particles retained the gross cell characteristics of the wood flour. The appearance of the char particles indicated that the material had once been molten and possibly vapor before it formed spheroidal particles about $1\mu m$ diameter which agglomerated to form larger char particles. The ability to completely melt or vaporize lignocellulosic materials under conditions of high heating rates has now been demonstrated in a continuous flow reactor and promises new techniques for fast pyrolysis. This char was unexpectedly attracted by a magnet, presumably because of iron contamination from the pyrolysis reactor tube wall. The production of water-insoluble tars was negligible compared to the tars produced from trash-derived feedstock. The production of water-soluble organic materials was fairly low and qualitatively appeared to vary inversely with temperature.

This study was of a preliminary nature and additional studies are necessary to optimize ethylene production from these feedstocks.

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SECTION 1.0

INTRODUCTION

In recent years it has become increasingly evident that during pyrolysis, cellulosic and lignocellulosic materials are acted upon by several competing reactions simultaneously. The slow, low-temperature pyrolysis reaction in which a dehydration mechanism predominates has long been utilized to produce char. Intermediate temperatures of 300° to 500°C favor a depolymerization of the long cellulose molecule to form tarlike fragments, of which levoglucosan is an example. Higher temperatures favor the formation of smaller fragments, which have been referred to as "combustible volatiles" [1]. These volatiles can consist of significant quantities of water-soluble, oxygenated compounds as well as ethylene, propylene, methane, carbon oxides, and hydrogen. At the elevated temperatures needed for gasification, all of the pyrolysis reactions proceed quite rapidly. If a particle of pyrolyzing material is relatively large and the heat transfer fairly slow, the transient temperature gradient (dT/dx) in the particle will be such that the material will pyrolyze deep inside the particle before it reaches the temperatures necessary for the desired gasification reaction to predominate. For this reason, smaller particles which have characteristically higher heating rates with steeper temperature gradients are desired for gasification to the chemically interesting pyrolysis products. To take advantage of the small particle size, high rates of heat transfer are desirable such as those obtained by conduction and radiation in the fairly high temperature range of 600° to 900°C. Since the particles outgas very rapidly, it is doubtful that convection plays a very important role in rapid-pyrolysis heat transfer. When the particles collide with each other or the pyrolysis reactor wall, intermittent conduction produces the very high heat transfer rates observed in fluidized beds. Radiation from the reactor walls to the particles is optimized in dilute concentrations, in which the individual particles are exposed to radiation from the walls in nearly every direction with a minimum of interference from other particles. From these considerations, for the study of rapid, high-temperature gasification, a reactor employing a turbulent gaseous flow with entrained particles has many advantages. The high linear velocity of the entrained pyrolysis stream makes possible very short residence times for the gaseous products, allowing the pyrolysis reaction to be quenched to recover the chemically interesting, nonequilibrium pyrolysis products such as ethylene, propylene, and butylene.

An entrained-flow pyrolysis reactor was developed at the Naval Weapons Center (NWC) for the pyrolysis of powdered municipal solid waste (MSW) during a program sponsored by the U.S. Environmental Protection Agency (EPA). This bench-scale system produced very promising yields (14% to 24% by weight) of hydrocarbons such as ethylene and propylene when refuse-derived fuel (ECO II Fuel by Combustion Equipment Assoc.) was the feedstock. Pyrolysis of pure feedstocks such as lignin, cellulose, or sawdust was not pursued in the EPA program since the major goal was to demonstrate that the pyrolysis gases made from trash could be purified using existing petrochemical technology. The purified gases (olefins) were used to make high-octane gasoline without catalysis [2].

The goal of the program described in this report was to investigate pyrolysis using pure feedstocks to learn more about the pyrolysis mechanisms and to determine whether the process could be applied to lignocellulosic biomass in general. More specifically, the program was to determine if olefins were produced from cellulose and lignin or from mostly hydrocarbon materials (such as plastics, fats, or waste oils) in the municipal solid waste. By using a uniform feedstock such as cellulose rather than heterogeneous powdered trash, at least one variable of unknown extent was eliminated. A powdered

sawdust feedstock was also pyrolyzed for comparison with the cellulose and lignin feedstocks to determine the feasibility of interpolating pyrolysis results for biomass materials containing both cellulose and lignin.

SECTION 2.0

EXPERIMENTATION

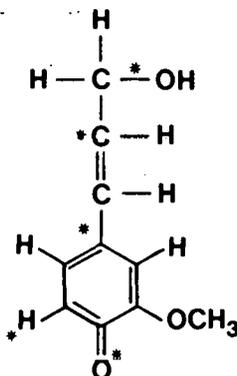
2.1 FEEDSTOCKS

2.1.1 Cellulose

Cellulose was purchased from the FMC Corporation, Philadelphia, Pa., where it has the trade name Avicel PH-102. It is a white, crystalline, free-flowing powder having a nominal particle size of 100 μm ($\geq 45\%$ retained on a 200-mesh screen). The powdered cellulose is prepared from fibrous cellulose by acid hydrolysis, which dissolves away amorphous cellulose, leaving the crystalline material. The resultant material is claimed to have an ash content of 0.1% and less than 10 ppm heavy metals. The material was sampled and analyzed for ash, moisture, carbon, hydrogen, oxygen, and gross heat of combustion. The results of the analyses of the feedstocks are shown in Table 2-1. The material has a nominal empirical formula of $(\text{C}_6\text{H}_{10}\text{O}_5)_x$.

2.1.2 Lignin

Indulin AT, which is derived from a basic, sugar-free alkali lignin (pine kraft lignin), was purchased from Westvaco, North Charleston, S.C. It is a very fine brown powder, appearing to be much finer than the cellulose powder. It has a flash point of 176°C and a sintering temperature of 188°C. Lignin is often thought of as the glue that holds the cellulose fibers together in plants. It is a very complex molecule which has a repeating group called a coniferyl radical:



This radical has five possible chemically active sites for crosslinking, as indicated by the asterisks. The radical randomly polymerizes to form a very complex, three-dimensional, crosslinked network. Depending on the plant species, some of the lignin monomers may have no methoxy groups (coumaryl) or two methoxy groups (sinapyl). Lignin has some chemical similarity to phenolic plastics (Bakelite) and can be used as an extender in Bakelite plastics. Lignin was of interest to the program because it has the thermally

Table 2-1. ANALYSES OF FEEDSTOCKS

Material	Wt % Moisture As Received	Feedstock Composition (wt % dry basis)						Dry Major Empirical Formula	HHV (kJ - dry gram) ^a	LHV
		C	H	O	S	N	Ash			
Cellulose (2911)	3.59	43.44	6.39	50.11	0.001	0.02	0.03	C ₆ H _{10.6} O _{5.20}	17.23	15.82
Cellulose (2907)	3.19	43.20	6.20	50.57	0.001	0.02	0.01	C ₆ H _{10.3} O _{5.3}	17.32	15.96
Lignin (Indulin AT)	3.54	61.57	5.78	26.78	2.22	1.49	2.16	C ₆ H _{3.76} O _{1.96}	26.26	24.99
Birch Flour (-80 mesh)	3.87	48.75	6.36	44.40	0.02	0.08	0.40	C ₆ H _{9.40} O _{4.11}	19.38	17.97
Birch Flour (-325 mesh)	7.62	48.56	6.38	44.26	0.08	0.13	0.60	C ₆ H _{9.45} O _{4.10}	19.84	18.44
Pine Flour (-80 mesh)	5.09	50.49	6.45	42.64	0.03	0.05	0.34	C ₆ H _{9.20} O _{3.80}	20.46	19.04
ECO II (T-51)	0.91	49.64	6.45	32.38	1.04	0.22	9.73	C ₆ H _{9.28} O _{2.93}	22.19	20.79

^a1 kJ/g = 430 Btu/lb.

stable aromatic ring structure and a low oxygen content, which give it more of a hydrocarbon composition than cellulose [3]. Idealized lignin has an empirical formula of $C_9H_{11}O_3$; or, on a six-carbon basis for easy comparison with cellulose, lignin is $C_6H_{7.3}O_2$. The sample of lignin analyzed had unexpectedly high sulfur (2.2%) and nitrogen (1.5%) contents.

2.1.3 Raw Biomass

Very fine sawdust (wood flour) is used in the plastics industry as a filler to reduce the amount of expensive plastic in the product. Various types and sizes of wood flour are commercially available and the following were purchased for this program: minus-80-mesh pine flour, minus-80-mesh birch flour, and minus-325-mesh birch flour. Microscopic examination of the minus-80-mesh birch flour revealed it to be primarily very fine fibers with some small chunks.

2.1.4 Discussion of Feedstock Analyses

To deduce from the analyses of pure cellulose and lignin the potentials of various biomass feedstocks for olefin production, the lignin and cellulose contents of the biomass materials need to be known. The data from Table 2-1 were used to estimate the lignin content by three different methods: the oxygen balance, the carbon balance, and the higher heating value. These values are shown in Table 2-2 and graphically presented in Fig. 2-1. The higher heating value (HHV) is plotted in Fig. 2-1 as a function of lignin content, assuming a linear relationship. Literature values for extracted lignin content are also presented in the figure, as well as the results of the carbon and oxygen balances. There does appear to be a trend of increasing heating value with increased

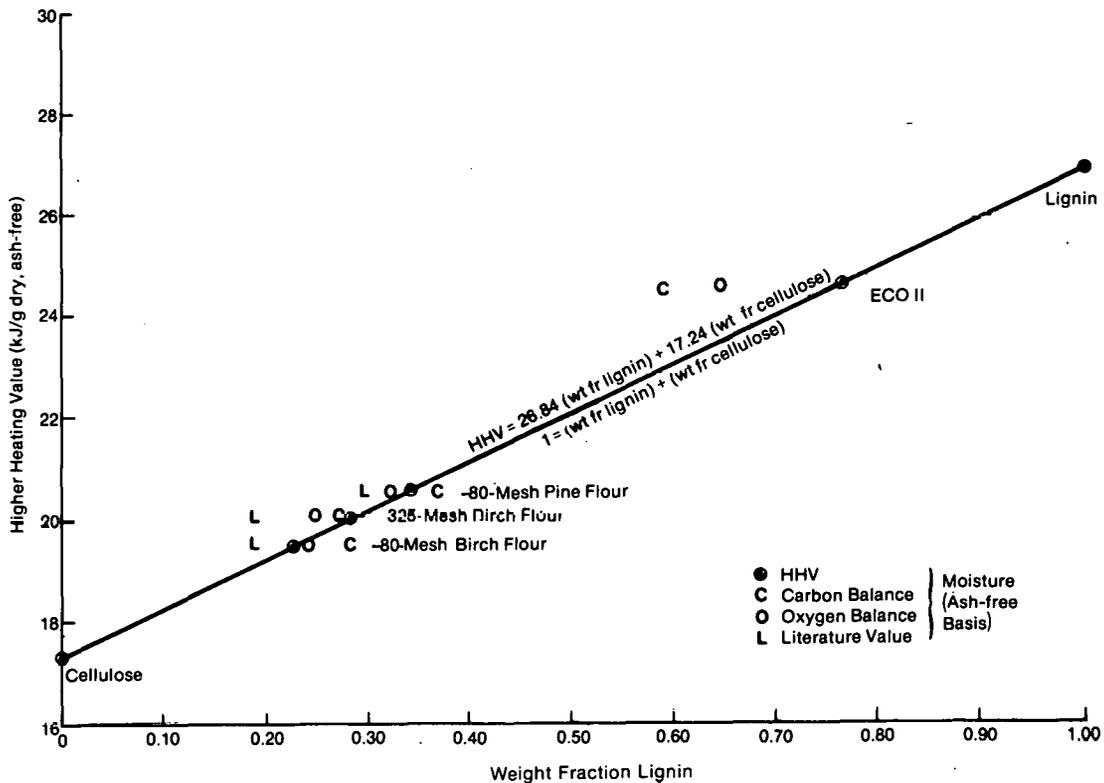


Figure 2-1. Heating Value vs. Lignin Content

Table 2-2. CALCULATED LIGNIN CONTENT OF FEEDSTOCKS

Material	Empirical Formula	Wt % Lignin				% Error in Lignin Content ^d		
		By HHV	By C Balance	By O Balance	By Literature	By HHV	By C Balance	By O Balance
Cellulose	$C_6H_{10.5}O_{5.2}$	0	0	0	0 ^a	0	0	0
Birch Flour -80 mesh	$C_6H_{9.33}O_{4.10}$	23	28	24	21 ^b	10	33	14
Birch Flour -325 mesh	$C_6H_{9.39}O_{4.11}$	28	28	25	21 ^b	33	33	19
Pine Flour -80 mesh	$C_6H_{9.13}O_{3.80}$	34	37	32	29 ^b	17	28	10
ECO II (lot T-51)	$C_6H_{9.28}O_{2.94}$	76	59	64	—	—	—	—
Lignin	$C_6H_{6.71}O_{1.96}$	100	100	100	99 ^c	0	0	0

^aFrom the Avicel PH Microcrystalline Cellulose Bulletin PH-6, FMC, 2000 Market St., Philadelphia, PA 19103.

^bFrom "Bioconversion of Plant Biomass to Ethanol," by Brooks et al. (Ref. 4).

^cFrom the Indulin AT data sheet, Westvaco, Bcx 5207, North Charleston, NC 29406.

^dRelative to values quoted in the literature.

lignin content. All of the parameters used to estimate the lignin content resulted in values that were 10% to 33% higher than values reported in the literature. The carbon balance method gave the highest average error (31%). Estimating the lignin content by heating value had an average error of 20% (10% to 33%). The lowest average error was encountered using the oxygen balance (14%).

The estimates of lignin content for ECO II are included for comparison and show that this material has a higher heating value than would be predicted from its carbon or oxygen balances, assuming it to be a simple mixture of lignin and cellulose. ECO II is degraded during processing by a combination of acid hydrolysis and low-temperature pyrolysis.

All three of the biomass feedstocks evaluated appear to have a higher inferred lignin content than reported in the literature [4]. The lignin content of biomass is highly dependent upon the extraction technique used. The "lignin" used in this study was most likely modified chemically during the kraft process. Perhaps the lignin content varies considerably within each species. For example, a very fast growing tree with broad growth rings probably contains less lignin (more cellulose) than a slow growing tree with narrow growth rings. Also, pine wastes having a high pitch content would be expected to have a higher heating value tending more toward that of hydrocarbon liquids than that of lignin. In conclusion, it appears that the lignin content can be estimated from the heating value, the carbon content, or the oxygen content. However, until more data is generated, these methods are imprecise.

2.2 EQUIPMENT

The pyrolysis equipment used was that which evolved during the trash-to-gasoline program and is extensively described in Ref. 2. The feed is metered by a 2.5-cm-diameter screw feeder. At the end of the screw feeder, a jet of carrier gas blows the feed off the screw and pneumatically conveys the feed to the steam ejector. The steam ejector uses superheated steam at about 275 to 500 kPa (40 to 75 psig) and 600° to 750° C (1100° to 1400° F). The solid feed particles, carrier gas, and superheated steam then immediately enter the 6.1-m long, helical pyrolysis tube. This tube has an inside diameter of 1.6 cm and a helical diameter of 41 cm. The pyrolysis tube is located inside a gas-fired kiln. After a short residence time (estimated to be a fraction of a second), the solids pyrolyze and leave the heated reactor zone at 700° to 800° C. After the pyrolysis stream has traveled about 60 cm outside of the kiln, it has cooled to about 350° C and enters a 7.6-cm-diameter cyclone to remove the char. The relatively char-free pyrolysis stream then passes to the "quench drum," where water is sprayed into the stream to cool it and to condense the steam and tars. Any entrained char in the gases at this point is also removed. The noncondensable gases leave the quench drum to be scrubbed with ice water. The cooled gases pass through another 7.6-cm cyclone to remove entrained tar and mist. The gases then travel about 2 m to an orifice meter, where the pressure drop is monitored and used in conjunction with the gas composition to determine gas flow rates.

The pyrolysis gas is sampled downstream of the demisting cyclone. A dedicated Carle gas chromatograph (Carle 111-H, spec 1-511) is used to analyze the pyrolysis gases including hydrogen, carbon oxides, and the hydrocarbons methane through pentane. Pentanes and larger hydrocarbons are backflushed. The chromatograph uses an isothermal system with multiple columns and mechanically timed valve sequencing [2].

This pyrolysis system was developed during the preceding EPA program so that it would fairly reliably produce pyrolysis gases for purification and polymerization to gasoline. This evolution did not necessarily result in a system optimized for pyrolysis research, as discussed in Sec. 2.3.

2.3 PYROLYSIS

2.3.1 Cellulose

The first material pyrolyzed in the test series was the microcrystalline cellulose, lot 2911. As shown in Table 2-3, the average pyrolysis temperature of the first run was 744°C. The temperature gradually drifted up from 724° to 771°C during the 61-minute run. The steam temperature, as measured by a thermocouple clamped to the outside of the steam line, was between 527° and 582°C. Distilled water was used to make the steam in this and the other pyrolysis runs, although the system is capable of recycling the quench water through the boiler. The cellulose powder was very free flowing. Before the screw feeder was turned on, it was connected to the steam ejector with a transparent plastic tube. The cellulose was then seen to begin to flood the feeder due to minor oscillations in the steam ejector inlet pressure. These pressure fluctuations peak to peak were equivalent to only about 1 kPa (4 in. of water column) but were sufficient to cause the cellulose and carrier gas to move intermittently into the reactor. Due to this cyclic flow, the pressure at the orifice meter fluctuated, although much of the oscillation was damped by the gas volume of the gas cleanup section. The intermittent feeding caused most of the feed to pass through the reactor in a more concentrated manner than would be calculated using the average values of carrier gas and solids flow rates. In this first run, a composite gas sample was taken during the run and compared to a sample taken early in the run; differences in composition were fairly minor. Thereafter, samples were taken at discrete times. The gross pyrolysis gas compositions (including carrier gas) are shown in Table 2-3 with the reactor conditions at the times the samples were taken. Table 2-4 gives the calculated yields.

The residence time was calculated using the following simplifying assumptions: the particles are gasified to the final products at the reactor entrance, the gases are ideal, the particles have a negligible volume, and the exit temperature is attained at the reactor entrance. The real residence time is probably slightly longer than that calculated; however, because the steam volume is fairly large, the impact of the inaccuracy of the assumptions on the calculated value is probably low. Many of the pyrolysis runs attempted did not produce data useful for quantitative yield calculations. The quench water from the first run was filtered to determine the amount of char and tar collected. These amounts were negligible.

A 200-ml sample of the scrubbing water from the secondary, iced reservoir from the first run was distilled through a 25-cm column of 3-mm (1/8-in.) glass helices. Of particular interest were the volatile, water-soluble organic compounds (including thermally stable organic acids, aldehydes, and esters). These compounds are too volatile to accumulate in the first quench water. Only 1.3 ml of condensate were recovered prior to the elution of water from the column. These low-molecular-weight compounds had a pale yellow color and a very pungent odor. The odor abated somewhat upon aging in a closed container. Although it had been planned to analyze these liquids, the necessary gas chromatograph/mass spectrometer equipment was down for repair for the duration of the program. The amount of water-soluble volatiles formed was estimated to be 1% by weight

Table 2-3. GROSS COMPOSITION OF PYROLYSIS GAS

(Includes CO₂ carrier gas)

Run	Feedstock	Pyrolysis Temp. (°C)	Steam Temp. (°C)	Relative Steam Rate	Relative Dry Pyrolysis Gas Flow Rate	Vol %												
						H ₂	CH ₄	CO	CO ₂	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	C ₄ H ₈	C ₅ ⁺	N ₂	O ₂
S-1	Cellulose	744	549	6.2	0.7	16.8	7.1	54.8	11.2	0.8	5.5	0.5	0.9	tr	0.3	1.3	0.6	0.1
S-2	Cellulose	793	488	9	0.5	20.3	5.2	47.9	18.4	0.4	5.1	0.5	0.5	tr	0.1	0.2	1.1	0.3
S-2	Cellulose	821	921	6	0.4	20.9	4.7	43.0	24.5	0.2	5.0	0.3	0.2	0	0.1	0.3	0.8	0.1
S-3	Cellulose	693	NA	10	0.25	13.6	2.5	50.9	23.2	0.6	4.3	0.5	0.9	tr	0.3	1.2	1.6	0.3
S-3	Cellulose	788	NA	10	0.5	20.2	6.0	50.2	14.5	0.5	5.7	0.6	0.6	tr	0.2	0.3	0.8	0.2
S-4	Cellulose	757	743	4	0.3	19.1	6.5	43.8	19.6	0.4	5.2	0.4	0.2	tr	0.1	0.2	3.6	0.8
S-8	-80 Birch	766	648	5	0.2	22.2	9.0	33.3	22.5	0.3	4.5	0.3	0.3	tr	0.2	0.1	6.0	1.2
S-9	-80 Birch	732	538	10	0.2	17.3	9.5	39.7	20.4	0.6	4.8	0.7	0.8	tr	0.5	0.3	4.6	0.7
S-10	-80 Birch	704	268	9.5	0.2	16.3	7.0	34.0	8.8 ^a	0.5	3.9	0.6	0.7	tr	0.4	0.5	26.9 ^a	0.3

^aRun S-10 used N₂ for carrier gas.

Table 2-4. CALCULATED PYROLYSIS YIELDS

Run	Feed	Feed Rate (kg/h)	CO ₂ Flow Rate (m ³ /kg)	kg steam per kg feed	Avg. Pyrolysis Temp. (°C)	Pyrolysis Temp. When Sampled (°C)	Avg. g feed per m ³ gases	Calc. Avg. Residence Time (s)	kg Products/100 kg Dry Feed											
									H ₂	CO	CH ₄	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₄ H ₈	C ₅ ⁺	CO ₂	Char	
S-1	Avicell PH 102	5.63	0.09	0.7	744	744	142	0.114	1.3	58.2	4.3	0.8	5.9	0.6	1.4	0.6	4.6	1.7 ^a	0.001	
S-4	Avicell PH 102	2.26	0.22	1.2	732	754	84	0.167	2.5	79.2	6.7	0.8	9.3	0.8	0.6	0.2	1.2	14.5 ^a	—	
S-8	Birch	1.68	0.29	1.9	739	765	65	0.169	3.0	63.4	9.8	0.7	8.6	0.5	0.9	0.6	0.8	12.1 ^a	0.028	
S-9	Birch	2.11	0.24	2.5	739	732	58	0.121	1.9	59.0	8.1	0.9	7.1	1.1	1.8	1.5	1.7	3.5 ^a	0.016	
S-10	Birch	1.52	0.45 ^b	4.1	416	704	37	0.108	1.8	53.1	6.2	0.7	6.2	1.0	1.7	1.1	2.6	21.7	0.015	

^aThese values for CO₂ formation are lower limits and are subject to error due to variable losses of carrier gas back through the hopper.

^bNitrogen carrier gas.

of the feedstock. After the water in the sample boiled out of the distillation flask, the temperature rose very rapidly to above 260°C before the heating mantle was removed. The material left in the bottom of the flask turned from a liquid to a solid during this runaway heating period. The volume of residue was estimated to be about 3 to 5 ml, which corresponds to about 3% to 5% by weight conversion of the feed to higher-molecular-weight organics. Additional high-molecular-weight, water-soluble products were in the primary quench water, but no attempt was made to distill them. This distillation test established that most of the water-soluble organics found in the quench and scrubbing water have a fairly low volatility and probably a relatively high molecular weight.

The second attempted run was intended to have a much lower feed rate. However, the steam ejector pressure oscillations of about 1/2 Hz pumped the free-flowing cellulose out of the feeder at a rate independent of the screw speed. The run time was spent trying different physical configurations of the feed transfer tube, including different lengths, and creating antinodal chambers with tube clamps. The latter method appeared promising.

The next pyrolysis run, labeled S-2, also had problems with feed rate oscillations. These caused considerable downtime since the feed rate oscillations were conducive to plugging of the feed system. Greater stability was finally achieved by reducing the steam flow by half. The quench and scrubbing water from this high-temperature run appeared to be relatively low in organic content, which may have been due to the high average pyrolysis temperature (805°C).

It was thought that part of the problem with the steam system could be due to momentary blockage of the 1.6-mm (1/16-in.) diameter ejector nozzle by condensed steam. A 0.6-cm (1/4-in.) diameter sheathed thermocouple was inserted into the steam line immediately upstream of the steam ejector. The kiln was extended to include the steam line and the ejector system. Steel and aluminum cooling fins were press-fitted onto the steam ejector feed tube. The fins were intended to thermally protect the transparent plastic feed tube connecting the screw feeder to the steam ejector.

After some experimentation it was concluded that the steam ejector was unstable during the warm-up period. The kiln was further modified, so that flue gases would be drawn up past the steam ejector for faster warm-up and hotter operation. This did reduce the warm-up time. A check valve was added to the boiler water line to protect the pressure gauge and the glass rotameter. This check valve also dampened out the steam pressure fluctuations.

There were still some steam flow fluctuations even after the steam seemingly was sufficiently hot to avoid condensation during expansion. It was then hypothesized that possibly the boiler tubes were scaling and that the scale was flaking off during the temperature cycling of shutdown and start-up. The flow of scale particles through the nozzle would cause pressure fluctuations. Although the boiler tubes visually appeared clean, a small centrifugal scale trap was installed just upstream of the steam ejector.

Pyrolysis run S-4 was the next successful run. In addition to the above modifications, the pyrolysis system pressure was raised about 2.5 kPa (10 in. of water column), which eliminated the partial vacuum in the feed line. This run was relatively successful.

Pyrolysis run S-5 was to have been similar to S-4, but with a much higher steam flow rate. Unfortunately, the system was still unstable at the higher steam rates, and

pressure fluctuations at the steam ejector caused the feed system to flood and plug. One pyrolysis gas sample was taken during run S-5 but due to the poor run, no yield data were obtained. Run S-6 had a very low feed flow rate and several shutdowns to clear the feed system; no gas analysis or char yield data were taken.

Although the data on cellulose pyrolysis in the NWC reactor were only preliminary, time and funding constraints necessitated proceeding to the evaluation of the other feedstocks.

2.3.2 Lignin

Run S-7 was the first attempt to pyrolyze lignin powder in the NWC system. The powdered lignin flowed very smoothly through the screw feeder when the feeder was not attached to the steam ejector. However, when the lignin was fed into the hot steam ejector, the lignin sintered, bubbled, and then blocked the entrance to the reactor as it hardened. Increasing the carrier gas flow and decreasing the feed rate did not solve the problem. A small quantity of lignin did pass through the reactor and was collected in the char cyclone. This partially pyrolyzed lignin had sintered and agglomerated into relatively large, irregular composite pieces of spheroidal subparticles. The subparticles were visible to the naked eye and were an order of magnitude greater in size than the feed. No gas samples were taken because the run never successfully started (the pyrolysis-gas-flare flame never became fully established). To better understand the problem, a sample of lignin powder was placed on a paint can lid and indirectly heated with a propane torch. The lignin in contact with the red-hot lid melted and then formed a single bubble as pyrolysis near the lid occurred. The bubble very rapidly solidified (due to either a charring or polymerization reaction) to form a hard brittle material. The feeding of lignin appears to require a different system than has been developed for feedstocks that do not melt before pyrolysis. Further lignin experiments were postponed until after the wood flour experiments.

After the wood flour runs (discussed in Section 2.3.3), run S-11 was made with lignin and was the last pyrolysis attempt in the program. Indulin AT lignin is partially soluble in water and was found to form a pumpable slurry with 33% by weight lignin in water. This slurry had to be stirred to stay in suspension but had a thin appearance (like thick chocolate milk). The steam ejector was removed, and the pyrolysis system was modified so that the lignin slurry could be injected directly into the pyrolysis reactor. The water in the slurry was to flash to steam, which would have resulted in a fairly acceptable ratio of steam to feed. The slurry was pumped by a small centrifugal pump. The pyrolysis run was started by pumping distilled water into the reactor. After the system had run for several minutes on distilled water, the valves were turned to begin the introduction of the slurry. Almost immediately, the system was plugged by the sintered and charred lignin. Upon removal of the slurry injector, red-hot glowing bubbles of lignin could be seen blocking the entrance to the reactor. Air was used to oxidize the charred lignin out of the pyrolysis tube. At this time, the experimental portion of the program had to be terminated. No successful pyrolysis runs were obtained with lignin powder.

2.3.3 Birch Wood Flour

The minus-80-mesh birch wood flour was selected for pyrolysis. Preliminary attempts to feed this wood flour revealed that it would not feed well and that it appeared to be damp. The flour was spread out to a depth of about 2 to 4 cm in large drying trays and

placed in a large walk-in oven at 77°C (170°F). After about 24 hours, the flour had lost 3% of its original weight. After 2.5 more days in the oven at 77°C, no further weight loss was observed. The final moisture content in the dried flour was about 1% by weight after 89 hours in the oven.

Pyrolysis run S-8 was the first to use the birch wood flour. The drying of the flour helped its flow properties considerably, but the feed rate was still a bit erratic due to the steam ejector operation. The average pyrolysis temperature was 766°C. At the end of the run, the steam orifice appeared to be partially plugged (probably by scale). Some of the recovered char had a flaky appearance and may have included char left in the reactor tubing from the lignin experiment (S-7).

The next pyrolysis was run at a lower temperature, 732°C, to try to avoid losing the olefin products to secondary pyrolysis reactions. The temperature in the kiln near the pyrolysis tubes was measured to be about 850°C during run S-9 (as compared to about 910°C for run S-8). The difference thus appeared to be 140°C between the kiln and the pyrolysis gas exit temperatures. A small amount of acetone-soluble tars were noticed in the quench drum and had a greaselike appearance at room temperature. These tars were present after run S-8 in only trace amounts. The lower pyrolysis temperature of S-9 may account for the small increase in the presence of tar due to incomplete pyrolysis of the lignocellulosic material.

The last successful pyrolysis run, S-10, used nitrogen rather than carbon dioxide as the carrier gas to allow more accurate determination of the amount of carbon dioxide formed during pyrolysis. Problems were encountered with plugging at the feed entrance of the steam ejector, caused by steam condensing inside the feed tube. A smaller-diameter feed tube was slipped inside the original feed tube, so that steam could condense on the outside of the tube to heat it to the saturated steam temperature. This kept the inside of the feed tube dry and the feed more free flowing.

The amount of char recovered from S-10 was 1.5% and was similar to that recovered from S-9 but only about half that recovered from S-8. This further indicated that the higher char content of S-8 could have been due to residual char from the attempted lignin run S-7, which probably left the walls of the reactor coated with a film of lignin char. The lignin char would tend to flake off during the cool-down and heat-up phases of reactor operation due to probable different rates of thermal expansion of the stainless steel and the char. The char from run S-10 was found to have a heat of combustion of 18.0 kJ/g (7750 Btu/lb) and an ash content of 39%. From these figures, the heat of combustion is calculated to be 29.5 kJ/g (12,700 Btu/lb) on an ash-free basis. The ash was in the form of fused metallic beads. The char and the ash were unexpectedly found to be magnetic, although the feedstock was not.

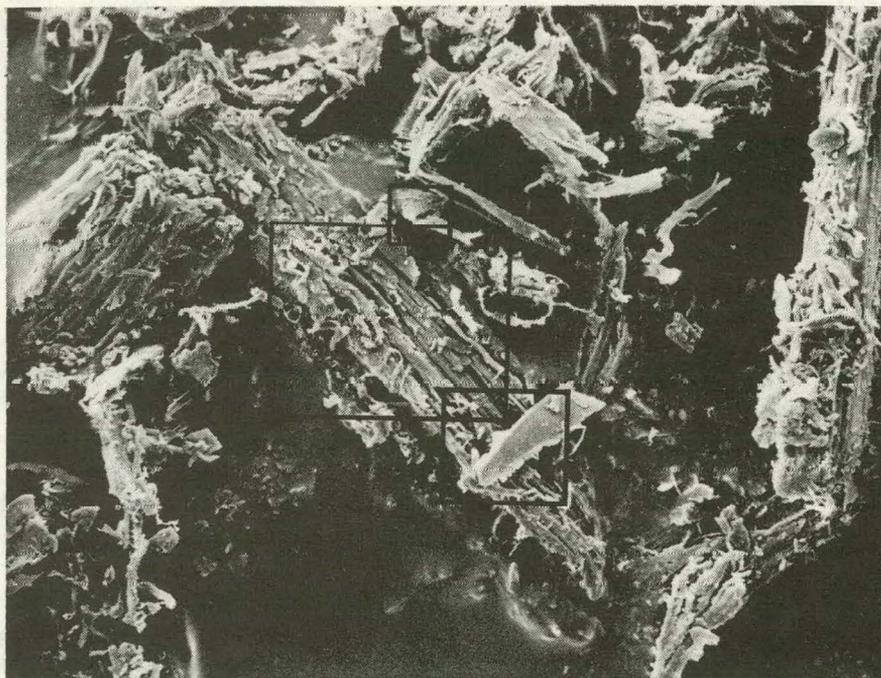
Samples of the minus-80 birch wood flour and the char from run S-10 were examined in an optical microscope at a magnification of 400X. The wood flour appeared as short fibers. The char had no resemblance to the feedstock except for a few elongated pieces which were apparently material that had not been completely pyrolyzed. Most of the char was sintered, agglomerated, spheroidal globules which once must have been molten or at least tacky. Due to the refraction of visible light at this magnification, it was decided that an electron microscope was needed to better determine the structure of the recovered char particles.

A field emission scanning electron microscope (SEM) made by Coates and Welter (model 102-A), located at the Naval Weapons Center, was used for this study. Samples of the

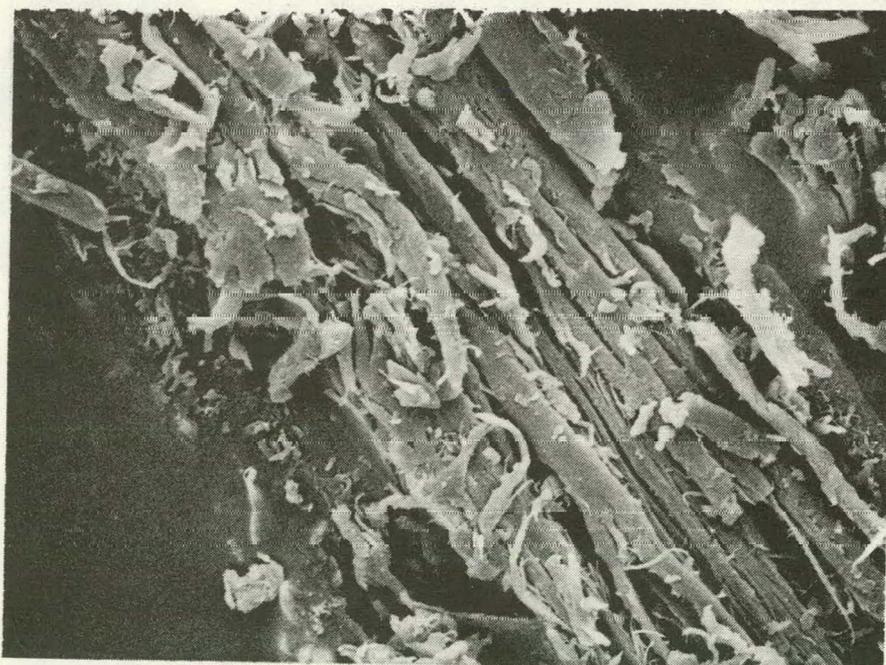
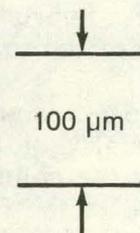
minus-80-mesh birch wood flour and char from run S-10 were examined first in the uncoated condition. Preliminary results showed that the flour was fibrous and the char was primarily agglomerated. To obtain better-quality images and resolution, the samples were subsequently coated with a thin film of vapor-deposited gold-paladium alloy. This coating improved the quality of the images but did not appear to change the physical shape of the samples.

Figure 2-2 is an SEM study of minus-80-mesh birch wood flour. The fibrous nature of the material is quite prominent. Very few particles have a surface cut across the grain that shows the cellular structure. As can be seen in Fig. 2-3, the char typically has no resemblance to the feedstock and is characterized by porous agglomerations of spheroidal particles having diameters in the range of 1 to 2 μm . Also some char particles appear to have small platelets imbedded in the agglomerated larger particles. Some small platelets (~ 5 to 15 μm) and a 7- μm sphere can be seen in Fig. 2-4. An estimated 1% to 10% of the char retained a structure similar to the original feedstock except that only the cell walls remained, as seen in Fig. 2-5. Figure 2-6 appears to be a partially pyrolyzed chip of wood flour with some of the inner portions of the cells missing. The cell walls still have some fine structure and there are some 1- μm spheres on the char.

In summary, most of the char particles had the appearance of having been formed primarily from small particles that agglomerated while in the molten or semimolten state. A fairly small percentage of particles retained the general shape and structure of the feedstock. Small platelets were also visible which may have been formed by the breakup of these particles. Most of the char particles did not resemble the material normally considered to be charcoal (before compaction).



(a) 177X



(b) 659X

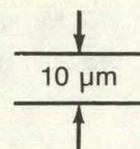
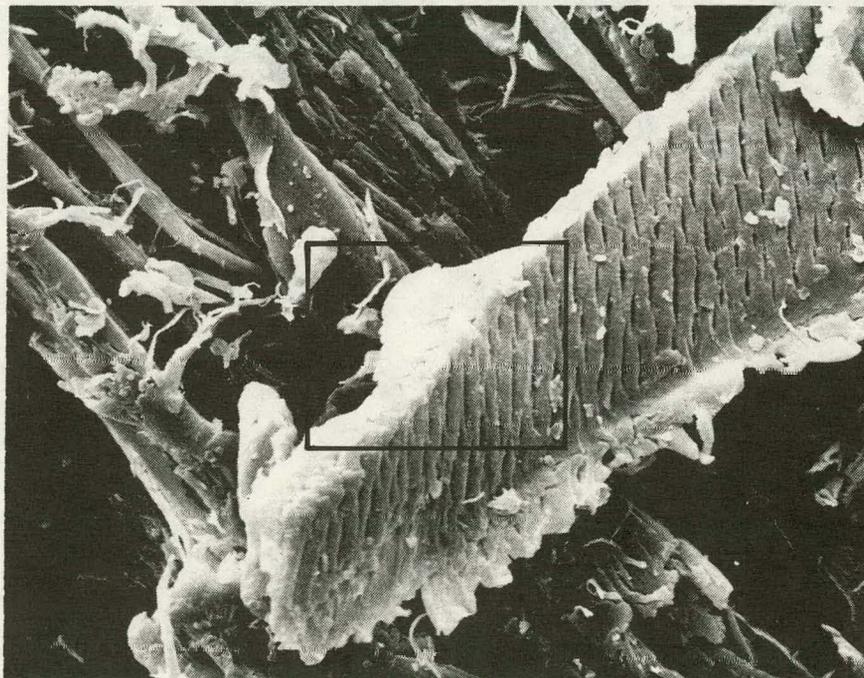
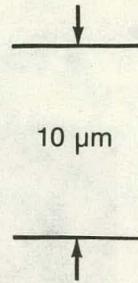


Figure 2-2. SEM Photographs of Minus-80-Mesh Birch Wood Flour



(c) 2470X



(d) 1368X

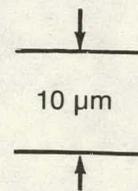
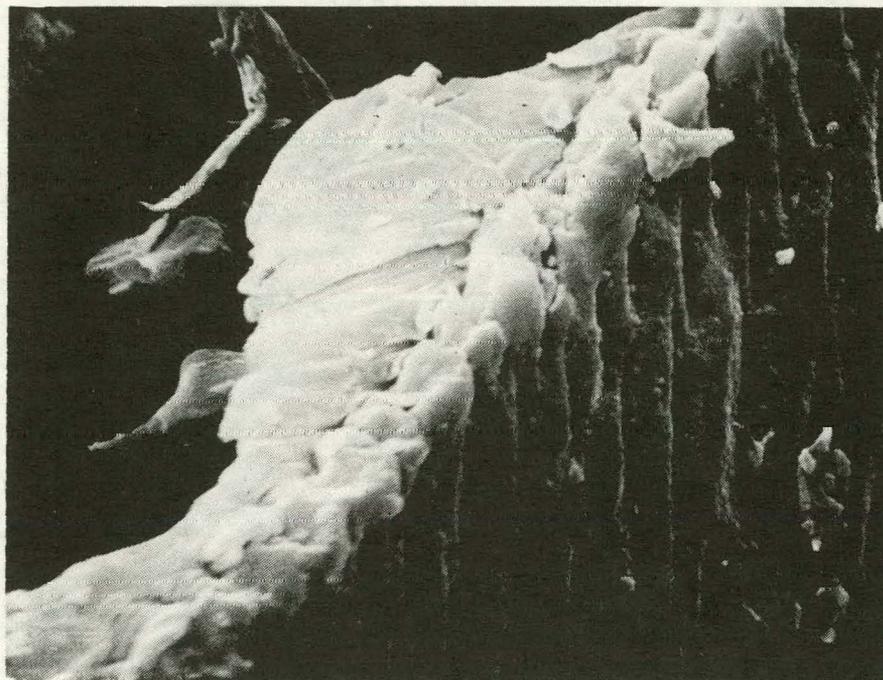


Figure 2-2 (Cont.)



(e) 4210X

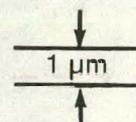
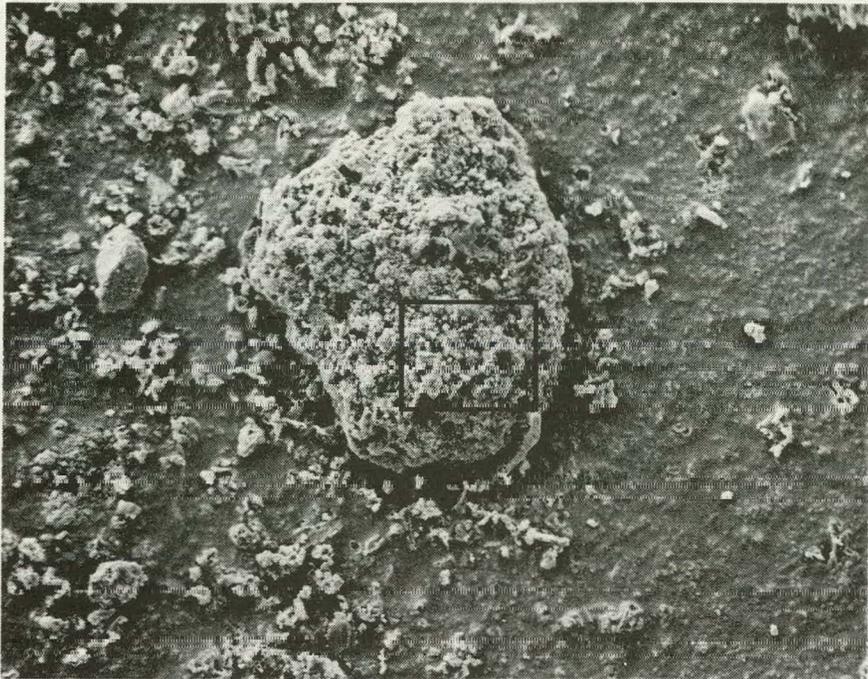
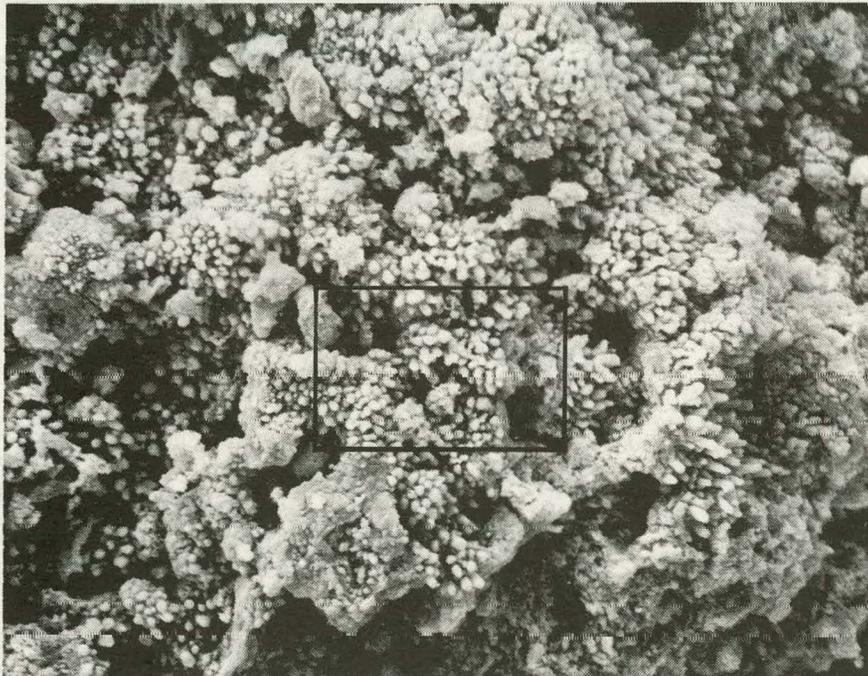
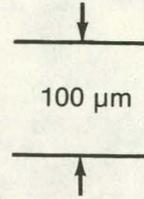


Figure 2-2 (Cont.)



(a) 147X



(b) 853X

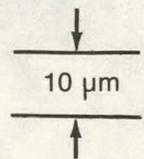


Figure 2-3. SEM Photographs of Birch Wood Flour Char Showing Agglomeration



(c) 2500X

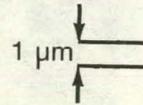
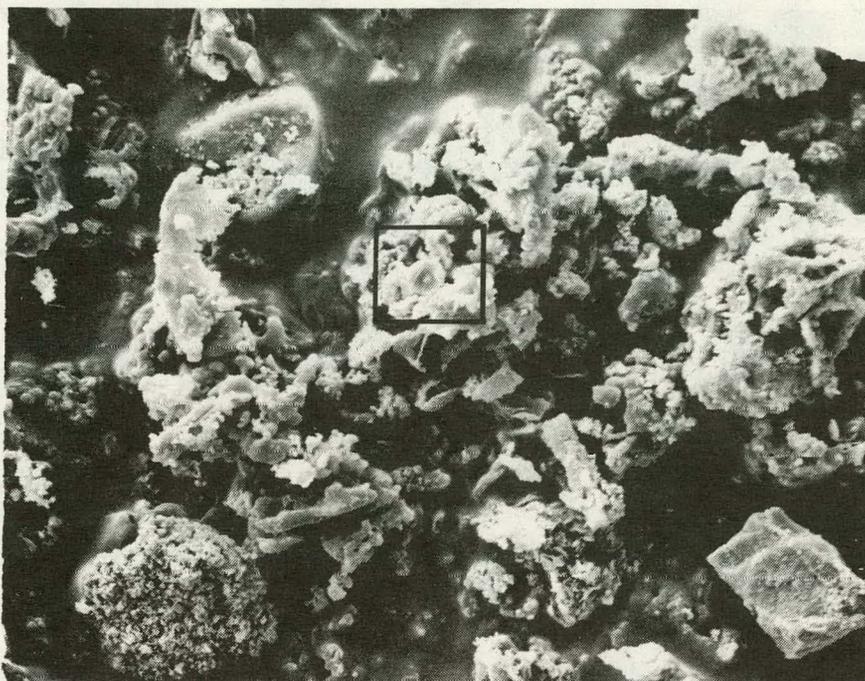
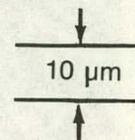


Figure 2-3 (Cont.)



(a) 746X



(b) 5920X

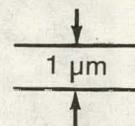
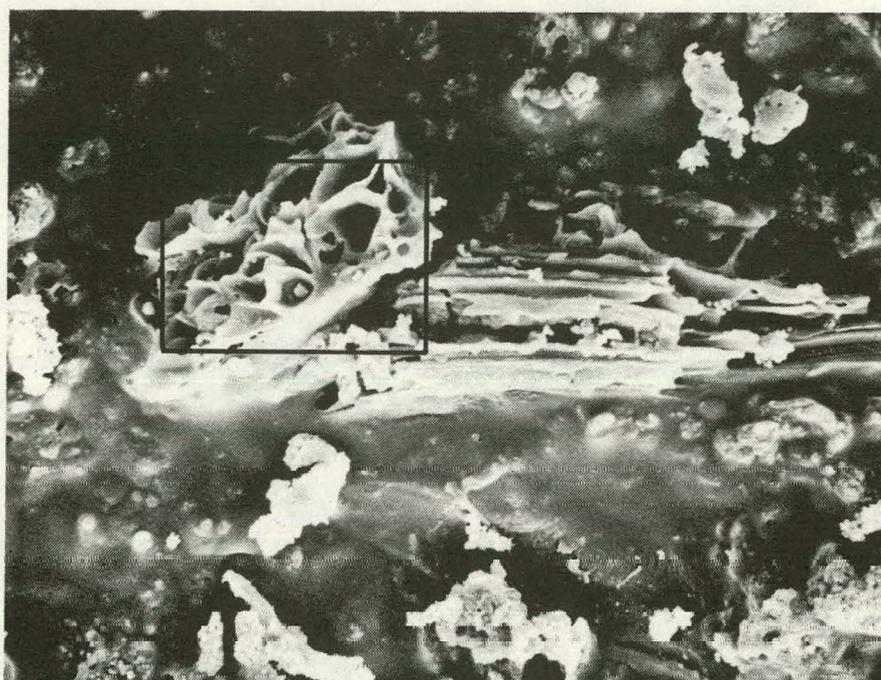
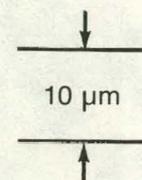


Figure 2-4. SEM Photographs of Birch Wood Flour Char Showing Platelike Particles



(a) 1223X



(b) 2280X

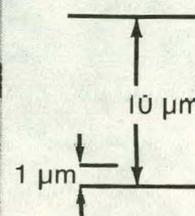
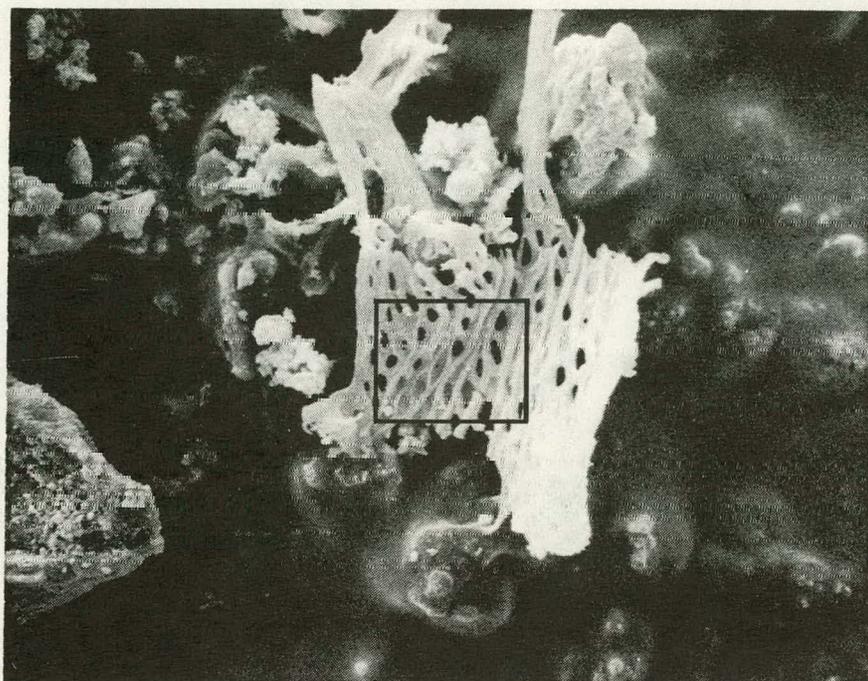
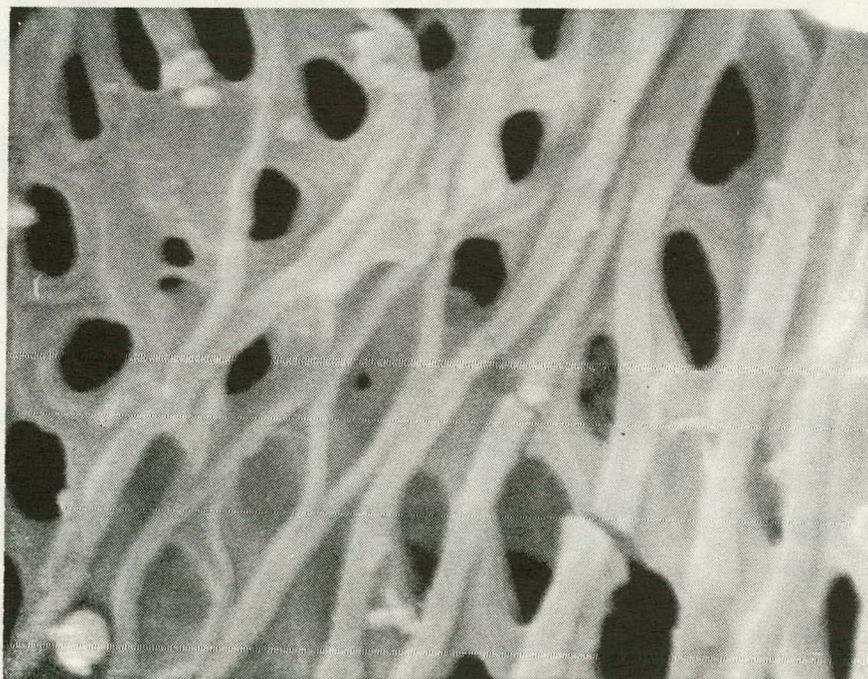
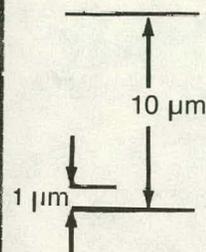


Figure 2-5. SEM Photographs of Thick Birch Wood Flour Char That Retained Much of the Original Cell Structure



(a) 1550X



(b) 8100X

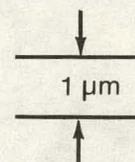


Figure 2-6. SEM Photographs of Thin Birch Wood Flour Char That Retained Much of the Original Cell Structure

SERI 

SECTION 3.0

DISCUSSION OF PYROLYSIS RESULTS

3.1 CHAR

3.1.1 Cellulose

The pyrolysis of cellulose in the China Lake tubular reactor produced virtually no solid residue or char. A considerable portion of the 0.1% by weight of cellulose feedstock recovered as char in the cyclone was probably scale from the reactor. The complete (99.9%) gasification of the cellulose is consistent with rapid pyrolysis results in the literature: very intensive thermal radiation onto blackened cellulose is reported to produce about 1% char [5], and cellulose samples sandwiched between two electrically heated wire screens produced no char at heating rates between 400° and 10,000° C/s [6].

3.1.2 Birch Wood Flour

Considerably more char formed from the birch wood flour (~1.5%) than from the cellulose. It is interesting to note that the ratio of original ash content to char formed was 0.3 for both cellulose and the wood flour. Perhaps a char-forming reaction is catalyzed by the ash particles or the ash particles act as condensation nuclei for the very large tar molecules. By either of these two mechanisms, the char would be expected to form agglomerates composed of small spheroidal particles.

The scanning electron microscope (SEM) study of the birch wood char revealed that most of it had the appearance of agglomerated spheroidal particles, although a few char particles retained the original cell structure. These latter particles may have been incompletely pyrolyzed material or material that pyrolyzed in the slow, traditional manner, forming a char that retained its initial structure. Described in the literature are SEM studies of char produced in very slow acting charcoal kilns. The gross cellular wall structure of the wood survived, but the fine structure of the cell wall disappeared, giving a fused appearance to the wall. Wood cells are composed of cellulosic fibers surrounded primarily by lignin, which glues the fibers together [3]. In SEM photographs of the slowly formed char, the cellulosic center of the cell appears to have volatilized, leaving the more lignitic wall structure behind. The yield of char from hickory after several hours was reported to be 24% by weight at a final temperature of 800° C. The amount of lignin in the hickory feedstock was 25% [7,8]. The char yield reported for oak containing more lignin (32%) was higher: 28% by weight at 800° C. It may well be that in very slow pyrolysis the cellulose preferentially volatilizes, leaving the more thermally stable lignin behind in the cell walls. The lignin would sinter during this process and chemically react to form a thermally resistant, highly cross-linked structure. During pyrolysis occurring several orders of magnitude more rapidly than pyrolysis in a charcoal kiln, the volatilized cellulose would be leaving at such high gas velocities that the sintering lignin could be blown off the cell wall before it solidified and be entrained in the pyrolysis gas flow as tiny spheres. The lignin particles would tend to agglomerate to form larger particles which would offer some thermal protection to enhance survival probability during the short residence time in the entrained pyrolysis reactor. Apparently only a small fraction (~5%) of the lignin in the birch wood actually survived to become char.

The birch wood char was unexpectedly found to be attracted to a magnet, although the feedstock itself was not. A few char particles were not attracted to the magnet, which may have been the few particles that had a charred wood appearance. Most likely, the agglomerated type of char particles had enough iron scale in them to make the whole agglomerate respond to the magnet. Possible sources of the iron are the steam boiler tube (316 SS), the pyrolysis reactor tube (304 SS), and the char cyclone (304 SS). These stainless steels are nonmagnetic, but apparently the scale from inside the tubes is magnetic. The scaling of the stainless steel reactor system may be avoided by using protective coatings such as aluminum, which forms an aluminum oxide (carborundum) protective surface. On the other hand, advantage could be taken of the magnetic properties of the char to separate the char from the pyrolysis gas stream by the use of electromagnetic fields, if the loss of iron could be tolerated. However, the minute yield of very fine char from biomass feedstocks may make unnecessary the removal of the char prior to the quench step. The fine, suspended char in the quench water could easily be pumped as a slurry to be recycled through the boiler to the pyrolysis reactor to be gasified.

3.2 TAR

The amount of tar formed during these pyrolysis runs was very small compared to previous experiences with trash-derived ECO II Fuel [2]. The pyrolysis of the wood flour produced a small amount of tar (a few grams each run), which collected in the quench reservoirs. In contrast, the pyrolysis of cellulose produced negligible amounts of tar and the gas cleanup system was remarkably tar-free and required no breakdown of the system between runs to clean the connecting tubes.

3.3 GASES

3.3.1 Cellulose

The pyrolysis gases produced from cellulose during this program had a very noticeably higher carbon monoxide content than observed previously with ECO II [2]. Two factors explain this phenomenon: the higher oxygen-to-carbon ratio of the cellulose feedstock and the near absence of free carbon or char in the pyrolysis product stream. Pyrolysis at these temperatures favors the formation of carbon monoxide rather than carbon dioxide. Consequently, the oxygen in the feedstock appears in the pyrolysis gases as carbon monoxide. The gasification of what otherwise would have been char also appears to form carbon monoxide rather than hydrocarbons.

The pyrolysis gases from several runs with cellulose had relatively similar compositions. As the pyrolysis temperature exceeded 750°C, however, the amounts of propylene and butylenes rapidly decreased while the amount of ethylene increased. During the same temperature increase, the molar ratio of hydrogen to carbon monoxide increased from 0.27 at 693°C to 0.49 at 821°C. Since none of the cellulose runs produced significant amounts of char, the increase in hydrogen could come from the polymerization of the propylenes and butylenes to form aromatics, from the reaction of carbon monoxide and water to form hydrogen and carbon dioxide (CO shift), or from the more complete pyrolysis of the cellulose. A calculation of the amount of hydrogen made available by the aromatization of the higher hydrocarbons indicated that the observed generation of hydrogen was an order of magnitude larger. It appears that the CO shift reaction may be favored at the higher temperatures in this situation because the hydrogen content of the

gases is well below that predicted from chemical equilibria considerations. Although the CO shift reaction is slightly exothermic, it produces two moles of noncondensable gases for every mole of carbon monoxide consumed. This would place an extra burden on the gas purification system requirements if the pyrolysis gases were to be used for their olefinic values. It is also possible that part of the shift in the hydrogen-to-carbon ratio seen at the higher temperatures is due to the pyrolysis of the water-soluble compounds that survive the lower-temperature pyrolysis conditions. These water-soluble compounds may pyrolyze to different product ratios.

This program showed the production of olefins and higher hydrocarbons from pure cellulose to be possible, although the yields were not as high as those obtained previously from ECO II [2]. As noted in Table 2-1 and Fig. 2-1, the empirical formula of ECO II shows it to be relatively deficient in oxygen when compared to cellulose. In fact, ECO II has the carbon and oxygen content, as well as heat of combustion, that would be predicted for a material containing a large amount of lignin (60% to 75% by weight).

The yield data generated in this study indicate that conversion of cellulose to the desirable C_2+ hydrocarbons was in the range of 13% to 14% by weight. However, because the system was not operating smoothly, it was difficult to accurately read the differential pressure gauge monitoring the orifice flow meter. This uncertainty, in turn, made the volume and mass of gases produced limiting factors in the precision of the calculations. It seems safe to say that the demonstrated C_2+ yields from cellulose were in the 10% to 15% by weight range. These yields are lower than had been expected and may have resulted from the oscillatory nature of the feeding system, which caused the feed to pass through the reactor in concentrated slugs. Data from the previous experiments with ECO II feedstock indicated that the relative dilution in the reactor was an important parameter, with C_2+ yields increasing with more dilute conditions. The feeding system oscillations caused most of the feedstock to be pyrolyzed in a relatively concentrated atmosphere and to not have the advantage of the average low concentration present in the reactor. Thus, even though the average concentrations of feed per cubic meter of pyrolysis gas stream were in the fairly dilute range considered favorable for olefin production, a large proportion of the feedstock did not pass through the reactor in these dilute concentrations. This would tend to lower the olefin yields below those probably attainable at more uniformly dilute conditions.

3.3.2 Birch Wood Flour

The pyrolysis gases produced from the birch wood flour had a lower carbon monoxide content than those obtained from cellulose pyrolysis, which correlates with the relative oxygen contents of the two feedstocks. The same trend of an increasing hydrogen-to-carbon-monoxide ratio with an increase in pyrolysis temperature was observed as discussed previously for the cellulose pyrolysis.

The yields of pyrolysis gases were made difficult to estimate by the continued oscillations in the feed system. The values for the C_2+ fractions were between 12% and 14% by weight and appear to be in the same range as cellulose. The 25% to 35% by weight lignin in the birch flour did not appear to increase the yield of the C_2+ material.

The propylene and butylene contents of the pyrolysis gases seemed to be much more sensitive to exit pyrolysis temperatures above 735°C than was observed previously with ECO II feedstock. This increased sensitivity indicates that the time-average temperature of the pyrolysis gases increased during their residence in the reactor. The pyrolysis

helical coil became noticeably shorter in height as a result of high-temperature creep of the stainless steel. Thus, the coil was almost entirely in the bottom, hotter portion of the kiln where the flue gas temperatures were well over 100° C higher and the heat transfer from the combusting gases was more efficient due to the higher turbulence induced by the kiln design and by the radiation from the hotter kiln walls near the bottom.

3.4 POSSIBLE PYROLYSIS MECHANISM

Although only limited experiments with wood have been carried out, new speculations on the pyrolysis mechanism are in order. Many attempts to model pyrolysis are based on the apparent pyrolysis mechanism at work during relatively slow combustion; e.g., as occurs in a fireplace. In the typical slow-pyrolysis model, it is generally assumed that a char layer exists having a significant thickness through which the pyrolysis gases and vapors pass. Heat transfer from the particle surface would occur by conduction through the thick char layer in the slow pyrolysis model to reach the unpyrolyzed substrata. In the pyrolysis experiments conducted in this program, a very small amount of char was produced, which implies that the formation of char is not necessarily part of the overall gasification pyrolysis reaction mechanism. Furthermore, the sample of birch char examined with SEM appeared to be primarily composed of agglomerated spheroidal particles which did not appear to have been derived by the same char-forming mechanism observed in slow pyrolysis. If char formation is not part of the initial pyrolysis mechanism, then the feed particle surface would make the transition from a relatively chemically unchanged condensed phase (liquid or solid) to a vapor phase. The vapor phase would rapidly offgas, leaving a relatively virgin strata to wait for the next quantum of energy input. In the turbulently-entrained-flow reactor, the particles are in intermittent sliding and impact contact with the red-hot reactor walls and each other. Crude preliminary calculations show that about half of the heat transfer to the particle can come from thermal radiation and the other half from conduction, assuming the particle surface is at a low temperature and in contact with the wall. In the helically shaped tubular reactor, the larger particles tend to be centrifuged to the major diameter of the helix, which increases the probable frequency at which the pyrolyzing particles impact the wall. As a particle impacts the wall, it receives a significant amount of heat by conduction. This heat input raises the temperature of the particle surface in contact with the wall to that necessary for pyrolysis. If the reactor wall is hot enough, the temperature of the particle surface could be in the range required for rapid gasification to proceed while the center of the particle is still at the initial feed temperature. A very steep temperature gradient would exist within the particle. Depending upon the pyrolysis reaction rate of the material, the surface of the particle could be pyrolyzing while the center of the particle is still quite cool. This would be an ablative type of pyrolysis mechanism and any intermediate char that might be formed would be frangible and quickly removed by the sliding contact on the reactor wall and/or by impact with the wall or with other particles. The asymmetric pyrolysis of the particle would cause it to offgas, similar to a miniature rocket motor, and might create enough thrust to overcome the "g" field and be propelled off the wall surface, thus increasing the turbulence of the reactor.

This ablative pyrolysis mechanism has a very interesting implication. If the pyrolysis to gaseous products takes place only in the heated surface strata, with a very steep temperature gradient present, then the initial size of the particle is fairly unimportant and relatively large particles could be used as feedstock. The problem then would be to provide a continuous high heat transfer and a sufficiently long time for the larger particles to completely pyrolyze, while providing the pyrolysis gases with short residence times to preserve the reactive olefins. This could be done by separating the unpyrolyzed feed

particles from the gas stream by centrifugal means (i.e., in a cyclone), so that the unreacted material could be recycled directly through the pyrolysis reactor. The cyclone could be situated so that the unreacted material would flow directly into the entrance of the pyrolysis reactor. This physical flow of material is attained in attrition mills used for rapid drying of heat-sensitive materials and for the fine grinding of solids.

The typical attrition mill has an elongated toroidal shape and uses a motive gas stream, e.g., pressurized steam or hot gases, through an ejector that entrains the metered solid feed into the mill. The entrained solids enter near the bottom of the toroid and pass over several supersonic nozzles that introduce a high degree of turbulence to the flow and reduce particle impingement on the wall. The high turbulence causes the particles to collide with each other, creating a grinding action. The larger particles are centrifuged to the major diameter of the toroid where they impact the wear plate. The replaceable wear plate can be composed of a very abrasion-resistant material, such as carborundum or tungsten carbide. Near the top of the toroid is a cyclone separator through which only the gas and very fine entrained particles escape. The larger particles continue around the major diameter of the toroid where they again encounter the very highly turbulent attrition zone caused by the supersonic motive gas nozzles. The overall velocity inside the mill appears to be very high, so that even if the average molecule of gas were to travel the "race track" route for several laps, gaseous residence times could be less than a second. If sufficient heat could be passed into the attrition mill by the use of superheated steam and/or by indirect heating through the walls, a very compact pyrolysis reactor having a high throughput might be developed which would be able to pyrolyze fairly large feed particles to the desired gaseous products rich in olefins. To achieve the needed heat transfer, tubular heat exchangers may be necessary in the lower-velocity region of the toroid (downstream of the centrifugal separator). The placement of the nozzle should probably be changed to encourage, rather than inhibit, contact of the particles with the wall. This type of pyrolysis reactor could use large feedstock particles, e.g., 1-cm chips, and would make unnecessary the energy-consuming fine-grinding operation prior to pyrolysis.

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SECTION 4.0

CONCLUSIONS

The pyrolysis of pure cellulose and minus-80-mesh birch wood flour in a low-residence-time, entrained-flow tubular reactor yielded primarily gaseous products, with virtually no char formation. There were some condensable by-products which were almost entirely water soluble. The gases contained significant amounts of olefinic hydrocarbons such as ethylene. Although the yields of the olefinic hydrocarbons were not as high as previous yields from trash-derived organics, this study demonstrated that cellulose and biomass can be used to produce ethylene and other olefins in better yields than attained in slow-acting conventional gasifiers. Very little of the char from birch wood pyrolysis had a charcoal appearance in scanning electron microscope photographs; instead, it had a sintered or agglomerated appearance. This implies that the char was formed by a different mechanism than forms charcoal, a mechanism involving a liquification step. The results of the attempts to feed lignin powder into the reactor—a sintering, bubbling, and charring of the material at the reactor entrance—suggest that the agglomerated birch char particles may have been agglomerated birch lignin char particles; in fact, the heat of combustion of the char was close to that of lignin on an ash-free basis.

A feed system for continuous pyrolysis research should be more reproducible and resistant to mass flow fluctuations than the China Lake pyrolysis system as it was evolved to make pyrolysis gases for the previous gas purification system check out and demonstration. This study consisted of only a preliminary screening of the pyrolysis of pure cellulose, wood flour, and pure lignin. The pyrolysis of these materials needs to be further characterized.

The prediction of pyrolysis products based upon the percentages of the cellulose and lignin contents of the feedstock was not demonstrated in this program due to insufficient data. Only two of the three feedstocks generated quantitative yield data and the olefin yields were not greatly different between the pure cellulose and the birch wood flour. Because of the problems encountered with feeding pure lignin into the reactor, the use of biomass feedstocks having widely varying lignin contents should be considered. For example, the experiments with corncob flour (5% lignin) [9], birch flour (21% lignin) [4], and oak flour (32% lignin) [8] would produce data over the range of lignin naturally occurring in biomass.

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SECTION 5.0

RECOMMENDATIONS

Additional pyrolysis studies should be made, but with a modified pyrolysis system. In particular, it would be very advantageous to use an electronically controlled, mass-flow system to meter the feed to the pyrolysis reactor at a constant, preset rate. The China Lake feed system had only a feed-screw speed adjustment and the mass flow rate varied considerably depending upon the manner in which the feed filled the screw. With a solids feeder controlled by mass flow rate, instantaneous rather than average yield data could be generated during a run. Much more gasification data could be generated per run because the entrained pyrolysis system attains equilibrium relatively quickly after process variable changes. This type of feed system is commercially available.

Immediately downstream of the feeder, a mechanical delumper is recommended to dampen small feed rate fluctuations and to produce a homogeneous mixture of feed in the fluidizing gas stream. Provisions should be made to preheat the feed to slightly above the condensation temperature of steam at the pressure expected in the feed hopper (probably with indirect steam heating), so that steam can be used as all of the carrier gas. Preheating the feed would prevent problems with steam condensation. The use of low-pressure steam heat would prevent overheating the feedstock. The pressure above the feed in the hopper should be equalized with the outlet of the metering screw to minimize feeding problems.

The pyrolysis reactor should be scaled-up to a tube having a diameter of 4 to 5 cm to simulate a full-scale pyrolysis tube. In scale-up, a multitude of these tubes would be placed in parallel flow. The feasibility of the division of a pilot plant's feed into a multitude of equal flows to pass through the individual tubes needs to be investigated (e.g., by consulting pneumatic flow experts). Cold flow demonstration of the flow splitting might be contracted out to a university or to a company specializing in pneumatic conveying.

The recommended tubular reactor for pyrolysis research should have the capability of temperature control over the length of the reactor tube. The superheated steam used for the steam ejector and for dilution should be generated independently of the pyrolysis reactor. Pressure measurements down the length of the tube would be useful qualitative indicators of gas flow rate (extent of pyrolysis reactions). The pyrolysis reactor would thus consist of several separate heated sections through which the pyrolysis tube would pass. Measurement of the heat flux into each section would help elucidate the reactions. Temperature measurements of the oven, the tube wall, and the pyrolysis stream would be needed, with the option to use any one of them to control the heat input to the system. A pyrolysis reactor heated by gas or electricity would be feasible, but a gas-heated system would be chosen for pilot plant scale-up. This reactor would probably be straight rather than helical.

In addition to the tubular reactor research, the concept of recycling solid particles in an attrition-mill-like reactor for pyrolysis of large particles should be explored and, if promising, pursued experimentally.

The use of the scanning electron microscope to examine char from several different pyrolysis methods may contribute greatly to a more detailed understanding of pyrolysis mechanisms. It may be possible to videotape a pyrolyzing organic particle in a vacuum using SEM techniques, which could establish if a liquid phase is present on the pyrolyzing surface and if particulates are ejected from the surface.

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SECTION 6.0

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