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Pyrolysis Mechanisms

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Thomas A. Milne
Michael N. Soltys

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Solar Energy Research Institute

A Division of Midwest Research Institute

1617 Cole Boulevard
Golden, Colorado 80401

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PYROLYSIS MECHANISMS

QUARTERLY REPORT
APRIL - JUNE 1981

THOMAS A. MILNE
MICHAEL N. SOLTYS

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PREFACE

This report is the second in a series of quarterly progress reports prepared under Task no. 1217 (formerly Task no. 3356.10) for Battelle Pacific Northwest Laboratories. Donald Stevens is the technical monitor under Memorandum Purchase Order B-96245-A-Q, Contract no. EG-77-C-01-4042.

Thomas A. Milne, Chief
Thermochemical and Electrochemical
Research Branch

Michael N. Soltys
Associate Scientist
Thermochemical and Electrochemical
Research Branch

Approved for

SOLAR ENERGY RESEARCH INSTITUTE

Thomas A. Milne, Chief
Thermochemical and Electrochemical
Research Branch

Clayton S. Smith, Manager
Solar Fuels and Chemicals Research Division

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ABSTRACT

The data acquisition system for fast pyrolysis studies is summarized and discussed, based on preliminary applications to fast scans and peak switching of the quadrupole mass spectrometer. The free-jet expansion phenomena of internal-state cooling and clustering are discussed in terms of their relevance to pyrolysis product sampling interpretation. Primary pyrolysis spectra are shown for cotton, wood, and steam-exploded extracted lignin. Both pulsed and steady-state pyrolysis were used to observe the secondary cracking of cotton, wood, levoglucosan, glycerol, and methanol in steam-argon at a nominal 900°C. The general plan of future studies is presented.

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SECTION 1.0

INTRODUCTION: APPROACH AND STUDY PHASES

In this task we are approaching the detailed, molecular study of the mechanisms of fast pyrolysis through the use of direct, high pressure molecular-beam, mass spectrometric sampling techniques. Laboratory heating arrangements are being structured to permit both steady-state and pulsed heating profiles with real-time observation of both primary and secondary pyrolysis products with millisecond time resolution. The apparatus and its performance are described in a progress report (Milne et al. 1980) and a SERI technical report (Soltys and Milne 1981). Preliminary results and system performance with hydrocarbons and cotton are detailed in the previous report in this series (Milne and Soltys 1981).

With this report we begin to report substantive details on fast pyrolysis behavior at the molecular level. With the capabilities developed to date and the observations reported below, the experimental program appears to resolve itself into three well-defined phases. During phase I, essentially completed with this report, we have tested several heating arrangements, determined the fast-data acquisition capabilities and sensitivity of our present apparatus, and obtained qualitative information on both the complexity of primary and secondary pyrolysis products and the time scale for secondary cracking of the cellulose and wood in steam-argon at about 900°C. The results indicate that our approach has good promise to obtain unique data on the molecular processes of pyrolysis that will complement data obtained by other workers using other approaches.

In phase II, which will occupy much of the next quarter, emphasis will be on determining the molecular precursors of the observed mass spectral peaks for wood, cellulose, lignin, and hemicelluloses and on estimating the relative proportions of primary and secondary products.

In phase III, which will occupy most of the FY 1982 period, quantitative experiments will be carried out on wood and its constituents under a variety of temperature, heating, and environmental conditions, with the results interpreted kinetically and mechanistically. Techniques to be employed in this third phase will include MS/MS for mass spectral interpretation and resistance-heated grid experiments for achieving forced, high heating rates.

The following sections describe results bearing on the heating and sampling technique and their application to several model compounds and biomass samples.

SECTION 2.0

NEW DATA ACQUISITION CAPABILITY

During this quarter we have extensively employed the normal data acquisition modes of our equipment for both rapid scans and peak switching. In addition, we have significantly increased our capability with the routine use of the Nicolet multichannel analyzer (MCA).

The block diagram presenting the system interconnection logic is shown in Fig. 2-1. The signal from the quadrupole is always taken from the electron multiplier in sampling experiments. The Faraday plate is only used to measure multiplier gain.

The principal branching for the quadrupole signal occurs at the fast electrometer. Primary system sensitivity is set here in steps of 100 by selection of an appropriate feedback resistor in the preamplifier. This is, of course, aside from the gain in the electron multiplier. The "AC" scope and computer outputs exit the fast electrometer without additional amplification, but the "DC" signal (total beam plus background signal) is amplified for direct presentation to the strip-chart or XY recorders. This signal can be processed by the HP log amplifier for over five decades of dynamic range within the limits of either recorder. "AC" information (the phase-locked component of the total beam plus background signal) is detected and amplified by the lock-in amplifier and then plotted on paper, in either linear or logarithmic form.

Digitally processed analog information is available from the Nicolet 1174 multichannel analyzer, which also makes possible rapid data acquisition and spectrum arithmetic for readout onto strip chart, scope, or magnetic tape or an on-line computer for additional processing and storage.

The chart depicted in Table 2-1 shows our present data acquisition capabilities. The major limitations in real-time are the recorder speed and the lock-in response time. However, the multichannel analyzer is able to overcome these speed limitations when operated in certain modes (Greene 1977).

"DC" in this work refers to the measurement of the collector current from a beam plus background. There is no discrimination between species in the beam and those populating the residual gas in the system due to scattering of the beam and outgassing of vacuum components. The DC mode is of limited utility, as many of the components detected from these spurious sources are common to those in the beam and constitute an important set of interferences.

The column headed "AC" describes the data acquisition rates with the molecular beam periodically interrupted by the chopper wheel. This is done in order to distinguish the beam from the background gas in the system, which, having no coherent velocity, cannot be so interrupted. In this mode the detection is tuned to the frequency of interruption by the lock-in which can distinguish small coherent signals on great amounts of physical and electronic noise. To gain this advantage, some slight sacrifice must be made. First, only one half of the molecular beam reaches the collector since the chopper square-wave

Figure 2-1. System Interconnection Block Diagram

Table 2-1. Data Acquisition Rates in Various Modes

		"AC"	"DC"
Chart	Peak switch	0.3 s/mass	0.3 s/mass
	Scan	0.6 s/amu	0.6 s/amu
Scope	Peak switch ^a	0.010 s/mass	0.010 s/mass
	Scan	0.01 s/amu	0.0002 s/amu
MCA	Peak switch ^a	0.010 s/mass	0.010 s/mass
	Scan	0.01 s/amu	0.0002 s/amu

^aLimited by some "ion phenomenon" in the quadrupole.

modulates it, and second, the step response time of the lock-in is short but not infinitesimal. The signal discrimination accruing to this technique overwhelms the first consideration by orders of magnitude, but the step response time is real and limiting.

In the "chart" row, the AC and DC characteristic responses are limited by pen slewing speed and are the same while the "scope" row shows clearly the effect of the lock-in on response time. Here the DC characteristic of the fast electrometer shows a step response time of 0.02 that of the lock-in (at a gain of 10^4 on the electrometer and 1 kHz chopping frequency).

The multichannel analyzer has the advantage of rapid signal acquisition with digital storage and leisurely readout of the memory for presentation, and its real-time capability is limited by what precedes it. In the AC mode, this limitation is still the lock-in, but in DC, improvement by a factor of about 50 can be reasonably expected in response speed per pass. Data presented in later sections will illustrate actual data acquisition under the fast AC modes.

SECTION 3.0

RELEVANT FREE-JET EXPANSION SAMPLING PHENOMENA

The use of direct, free-jet molecular-beam sampling offers the ultimate in quenching ability for extractive sampling. The extreme cooling of the adiabatically sampled gas has interesting consequences, both beneficial and potentially adverse.

3.1 TEMPERATURE DEPENDENCE OF FRAGMENTATION PATTERNS

The benefit of direct, line-of-sight sampling of hot vapors into a mass spectrometer ion source is that one achieves rapid quenching and minimizes secondary reactions either within the vapor or upon collision with system walls. However, with direct insertion probes or other line-of-sight systems (Wells et al. 1981) operating in a low pressure environment, the mass spectrometer "sees" thermally hot molecules. In the case of the high temperature, fast pyrolysis of complex organic molecules, the mass spectrometric fragmentation pattern can be quite temperature dependent. An example is the well-studied n-butane molecule (Milne et al. 1972), whose parent and fragment ions are strongly temperature dependent in the 10°-1000°C range. In the absence of calibrations of mass spectral patterns as a function of temperature (a difficult accomplishment in the temperature range where pyrolysis is rapid), the line-of-sight mass spectra may be difficult to interpret.

In free-jet expansions, the gases are cooled extensively, yet on a time-scale such that even fast reactions such as condensation may often be prevented. One thus has the potential advantage of molecular-beam, line-of-sight sampling that preserves the species in their high-temperature proportions, but with the sampled molecules being vibrationally and rotationally cooled before the mass spectral ionization occurs. It appears from data we have obtained in the steam cracking of hydrocarbons and methanol, that our present sampling through a 0.508-mm orifice essentially cools the solute molecules from ~900°C to an effective internal temperature near room temperature. The high dilution of the steam with argon, in our present flame-generation systems gives a low average λ value (the ratio of specific heats) for the free-jet expansion, leading to extreme cooling. In Fig. 3-1 are plotted experimental ion ratios for propane and n-butane sampled from various regimes of a hot steam-argon column. For comparison, literature values for the temperature dependence of fragmentations of these molecules are plotted (Osberghaus and Taubert 1955; Cassuto 1961). Note that in each case, within the scatter of the data, and at both 16- and 70-eV ionizing electron energy, the principal parent/fragment ion ratios from flame-sampled species are constant and equal to the room temperature values, while the literature values (determined under effusive sampling conditions) are from 3- to 50-fold lower. This fortuitous circumstance with our present large sampling orifice will greatly simplify data analysis in pyrolysis studies where chemical decomposition can be hard to distinguish from temperature-dependent fragmentation effects.

Figure 3-1. Variation of Major Hydrocarbon Parent/Fragment Ratios with Temperature

3.2 CLUSTERING PHENOMENA

It is a well-known phenomenon in free-jet expansion that supersaturations can readily be achieved that cause even the rare gases to partially condense, or cluster. Such clusters are of interest in the study of intermolecular forces and the field of Van der Waals clusters is attracting much attention. In the case of sampling, clustering is to be avoided. In high temperature systems, such as those involved in our pyrolysis studies, major constituents such as steam and argon are too hot to cluster, while solute pyrolysis species are usually too dilute to form even dimers at elevated temperatures. In calibrating room temperature gas mixtures, however, misleading results can be obtained in terms of both the appearance of cluster ions and the alteration of presumed monomer ion ratios through contributions of cluster fragments. As an example, the $58^+/43^+$ ratio for n-butane is about 2.0 when about 0.1% n-butane in the unignited H_2-O_2-Ar mixture is sampled. With the gases ignited, the n-butane ratio in the hot steam-argon is about 0.2 while the value from pure n-butane at a few torr of pressure is also about 0.2. The interpretation is that the n-butane, sampled in one-atmosphere cold H_2-O_2-Ar clusters, and that cluster fragments contribute more to 58^+ than to 43^+ (Milne et al. 1972).

In the course of sampling a number of pure gases for calibration purposes the ion ratios shown in Table 3-1 were obtained. Particularly noteworthy is the extensive clustering in acetylene and the highly pressure-dependent parent-plus-one peak in acetic acid vapor. Clustering is very temperature and expansion-pressure dependent and these parameters can be used to diagnose suspected cases of cluster interference.

Table 3-1. Examples of Clustering in Free-Jet Expansion of Cold Gases and Gas Mixtures Through a 0.508-mm-Diameter Orifice

Gas	Pressure	Electron Energy	Ion Intensity ^a	%
Ethane	About 0.1% unignited H ₂ -O ₂ - Ar flame gases at 1 atm	16 eV	30 ⁺	100
			42 ⁺	75
			60 ⁺	87
			72 ⁺	17
			90 ⁺	12
Ethylene	About 0.1% unignited H ₂ -O ₂ - Ar flame gases at 1 atm	16 eV	28 ⁺	100
			56 ⁺	189
			84 ⁺	32
Acetylene	About 0.1% unignited H ₂ -O ₂ - Ar flame gases at 1 atm	16 eV	26 ⁺	100
			52 ⁺	50
			78 ⁺	57
			104 ⁺	1.4
			130	1.0
			156	0.68
			182	0.34
	About 0.1% unignited H ₂ -O ₂ - Ar flame gases at 1 atm	70 eV	26 ⁺	100
			52 ⁺	23
			78 ⁺	31
			104 ⁺	3.1
Methanol	~8.5 torr	70 eV	31 ⁺	123
			32 ⁺	100
			64 ⁺	<0.27
			65 ⁺	3.2
	~8 torr	16 eV	31 ⁺	58
			32 ⁺	100
			64 ⁺	0.21
			65 ⁺	2.1
Ethanol	~15 torr	70 eV	45 ⁺	105
			46 ⁺	100
			92 ⁺	<0.26
			93 ⁺	2.6
			19 ⁺	26.3
	~8 torr	16 eV	45 ⁺	110
			46 ⁺	100
			92 ⁺	<0.048
			93 ⁺	0.29
			19 ⁺	1.4
Acetic Acid	16 torr	70 eV	60 ⁺	100
			61 ⁺	100
			120 ⁺	<0.1
	1 torr	70 eV	60 ⁺	100
			61 ⁺	2.0
	7 torr	16 eV	60 ⁺	100
			61 ⁺	49
	1 torr	16 eV	60	100
			61 ⁺	8.3

^aNormalized to the monomer.

SECTION 4.0

MASS SPECTRA OF PRIMARY PRODUCTS FROM COTTON, WOOD, AND LIGNIN

In the course of the many exploratory pyrolysis experiments, in both the pulsed and steady-state modes, reported below, certain distinctive features were recurrent. Though we have not yet attempted to fully interpret our mass spectra or compare them in detail with reported pyrolysis spectra of others, we present here "typical" spectra. The cotton thread spectrum (16 eV) is shown in Fig. 4-1. This was obtained under steady-state conditions by drawing the thread slowly through the flame-generated hot steam-argon column (see previous progress report) and sampling just a few millimeters above the thread surface. Figures 4-2 and 4-3 show spectra of pulse-heated toothpicks at both 16 and 70 eV. The spectra were synthesized from scans taken during the peak of the pyrolysis wave. Finally, in Fig. 4-4 is shown the one successful pyrolysis of powdered lignin (from the Iotech steam explosion process) coated on a wire and placed in the hot steam-argon column. The lignin scan did not extend beyond mass 125 in this first look. A detailed discussion of the spectra and their relation to previously reported spectra is deferred until the next report, pending more careful and complete experiments to elucidate the precursors of the ions shown.

Noteworthy, however, are the similarity in the spectra of wood and cellulose, the dissimilarity of the lignin spectra, and the prominence of masses 31, 32, 60, and 73 for both cotton and wood. Tentative identifications are: 31⁺ and 32⁺ - methanol; 60⁺ and 73⁺ - levoglucosan; 126⁺ - 5-hydroxymethyl-2-furfural. The lignin spectrum shows clear evidence of aromatics.

Figure 4-1. Typical Mass Spectrum of Cotton Thread (16 eV)

Figure 4-2. Typical Mass Spectrum of Wood Splint (16 eV)

Figure 4-3. Typical Mass Spectrum of Wood Splint (70 eV)

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Figure 4-4. Mass Spectrum of Steam-Exploded Lignin (16 eV)

SECTION 5.0

PYROLYSIS PRODUCTS AND SECONDARY CRACKING IN STEAM-ARGON

The H_2 - O_2 -Ar flat-flame burner system described in the previous progress report has been used for extensive qualitative tests of the secondary cracking of primary pyrolysis products from biomass and of pure product compounds. The burner system provides a wall-less column of steam-argon that is reasonably isothermal over 30 to 40 mm at uncorrected thermocouple temperatures of about 900°C. The hot gas velocity is such that a millimeter in distance along the axis corresponds to a millisecond of time. The H_2/O_2 ratio is tuned to lower the O_2 level below detectability. Biomass samples can be injected on the axis, entering just above the reaction zone, or samples can be suspended at a chosen distance in the steam-argon column. The sampling orifice is moved relative to the pyrolyzing surface to observe the effect of variable residence time in the steam/argon. For steady-state heating, the sample is either continuously injected through the axial tube or continuously drawn through the burnt gases. For pulsed heating, the sample is placed in the unburnt flame gases. The flame is ignited and in a few milliseconds the sample is engulfed in the hot gases and allowed to pyrolyze to char (until most of the volatiles are emitted). In the following presentation, both methods are used, together with either repetitive scans or peak switching for time-resolved data acquisition.

5.1 COTTON THREAD: STEADY-STATE AND PULSED HEATING

The richest spectra obtained so far have been from cotton thread (0.45-mm diam., approximately 0.14-mg/mm length) drawn continuously through the flame as shown in Fig. 13 of the previous quarterly. Two limited scans were shown also in that report. We have extended these measurements, scanning to beyond mass 144, the heaviest ion seen in searches up to 200 amu. Figure 5-1 shows the systematic cracking of primary pyrolysis products as a function of residence time in the steam. Large changes occur from 4 to 12 ms, with the appearance of acetylene and olefins as well as a small amount of benzene. It is instructive to plot the intensities of various ions (normalized to a constant Σ of organic peaks to give a first-order correction for diffusive spreading) as a function of residence time in the steam. Such plots are shown in Figs. 5-2 to 5-5 in families of decreasers (reactants), peakers (intermediates) and increasers (products). Such plots, when properly quantified should provide valuable clues as to the precursors of given ions as well as the mechanism of decomposition.

The experimental results just described involve an average mass spectrum of the early-to-late stages of a continuously pyrolyzing cotton thread. Such information corresponds to the total-collection gas analyses reported in a number of pyrolysis studies. Another, and more definitive, way to characterize the pyrolysis is to observe the time evolution of species through a heating pulse. This can be done by using fast repetitive scans or by selective ion monitoring through peak switching.

Figure 5-1. Progressive Secondary Pyrolysis of Cotton in Steam at 900°C

Figure 5-2. Variation with Distance in Hot Steam of Selected Ions from the Mass Spectrum of Cotton (Species That Decrease)

Figure 5-3. Variation with Distance in Hot Steam of Selected Ions from the Mass Spectrum of Cotton (Minor Species That Decrease)

Figure 5-4. Variation with Distance in Hot Steam of Selected Ions from the Mass Spectrum of Cotton (Species That Go Through a Maximum)

Figure 5-5. Variation with Distance in Hot Steam of Selected Ions from the Mass Spectrum of Cotton (Species That Increase)

An example of the evolution of selected peaks during the pulsed heating of a 10-mm-long piece of cotton thread, suspended about 20 mm above the burner with the sampling orifice just 2 mm away to monitor primary products, is shown in Fig. 5-6. The 18^+ and 40^+ peaks are from H_2O and Ar. Their intensities dip at the peak of the pyrolysis wave, in response to factors of lowered gas temperature and dilution with pyrolysis products because they affect the supersonic beam expansion. The 28^+ and 60^+ peaks rise and fall together; the 32^+ peak appears to be slightly delayed. The entire pyrolysis wave occurs in about 1 s, with the rise to peak evolution requiring about 0.4 s. Heating rates could thus be of the order of $1000^\circ C/s$.

In connection with the heating of cotton thread fed continuously through the hot gas column, we had occasion to use a zinc-coated iron wire of 0.406-mm diam. to carry through the thread as it charred. As a blank test, we scanned over the zinc atom isotopes with just the bare wire being pulled through the steam-argon. Detection of zinc ions from vapor species containing zinc gave the expected isotope ratios. Whether the ions came from atomic zinc vapor or from a gaseous hydroxide, the ability to preserve such highly condensible species is a significant test of the capabilities of our sampling method.

5.2 PULSED HEATING: WOOD SPLINTS

A large number of experiments were carried out with short (20-mm long) wood splints, either attached to the ends of cotton swabs (2.4-mm diam.) or to flat toothpicks (typically 1.14×1.14 mm in cross section). These were performed in connection with optimizing data acquisition parameters in the pulsed heating mode, as well as to observe the characteristic species from wood under moderately rapid heating (pyrolysis lasting about 8 to 10 times longer than that of the cotton thread). Raw data from a typical toothpick heating, with sampling occurring 5 mm above the wood surface, is shown in Fig. 5-7. In this case, the mass spectrometer was programmed to dwell for 0.2 s on each of six peaks in the repeating sequence 28^+ , 30^+ , 32^+ , 40^+ , 43^+ , 60^+ , 28^+ The output of the phase-sensitive detector presented the AC data to the memory of the multichannel analyzer for storage and later readout. The endothermic pyrolysis wave is reflected in the dip in the largest peak, 40^+ from argon. The other peaks rise and then fall over a time period of about 10 s. A fast way to reduce such data, which can be gathered more rapidly than they can be analyzed, is to simply trace over the peaks to produce curves as shown in Fig. 5-8. Such traces are quite reproducible in width, with time shifts to adjust for the synchronization of the lighting of the flame and the starting of the multichannel analyzer sweep. Reproducible features from many such runs are the early peaking of 43^+ ; the later peaking of 32^+ (shown not to be O_2 by its unaltered appearance in a large excess of H_2); the broad, slightly double-humped 28^+ peak ($xCO^+ + yC_2H_4^+$, with x and y not yet determined); and the intermediate peaking of 60^+ and 30^+ . A series of such pulsed heatings, monitoring the major peaks in groups of six or less depending on the time resolution needed, with sampling at varying distances from the pyrolysis surface, would give a rather detailed picture of the primary and secondary pyrolysis processes for a given physical dimension of the biomass and a given steam-argon temperature.

Figure 5-6. Time Dependence of Selected Ions in the Mass Spectrum of Cotton During Pulsed Heating

Figure 5-7. Raw Ion-Peak Data from Peak Switching During Pulsed Heating of a Wood Splint

Relative Intensity

Figure 5-8. Time Dependence of Selected Ion Peaks During Pulsed Heating of Wood Splints

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Similar data can be taken from fast, repetitive scans over regions of the spectrum. With the present time response limitations of our phase-locked amplifier (chopping frequency = 1 kHz) a scan of about 100 amu in 1 s is possible. Figure 5-9 shows a series of 1-s scans over the mass range 25-95, during the pulsed heating of a toothpick (as above). In the case shown, the full pyrolysis wave was not completed before the memory of the 4096 channel multichannel analyzer was filled. Plots of the time evolution of given peaks show the trends indicated in Fig. 5-8.

As indicated in the previous quarterly report, these techniques can be readily extended to the study of the effects of both catalysts and hydrogen on fast pyrolysis. The fire extinguishment and slow-gasification literature abounds in considerations of the effects of inorganic salts on both flaming and glowing combustion and on pyrolysis and gasification (Broido 1976; Shafizadeh 1968; Robertus et al. 1981). At the suggestion of L. Mudge during a recent visit to our laboratory, we treated several toothpicks with an aqueous potassium salt solution. After air drying for a few days, the toothpicks (containing an unassayed amount of potassium) were pyrolyzed in steam under conditions identical to those in Fig. 5-9. Qualitative changes were noted in both the relative proportions and time of evolution of prominent species, with the most pronounced effect being the reduction in the time for the total pyrolysis wave from about 10 s to about 4 s.

Such qualitative observations promise a rich field for future study of the effects of catalysts on both primary and secondary pyrolysis processes. The effects of H_2 can likewise be studied by simply burning a very rich H_2 - O_2 -Ar mixture on the present burner.

5.3 LIGNIN AND HEMICELLULOSES: PULSED HEATING

Attempts to pyrolyze lignin suspended in the hot steam-argon column have been largely unsuccessful. The lignin (steam-exploded, ethanol-extracted, low-molecular-weight lignin from the Iotech process) froths up and appears quite refractory in the 900°C gases. Volatiles emission is not copious and detection of primary pyrolysis products is difficult. It is hoped that coating on screens, either flame- or resistance-heated, will yield better results.

The partial spectrum shown in Fig. 4-4 reveals how unique the lignin products are vis-a-vis wood or cellulose.

Hemicelluloses have not yet been examined, but they will be surveyed in the next quarter.

5.4 LEVOGLUCOSAN AND GLYCEROL: PULSED HEATING

In order to check on the suspected parentage of the prominent 60^+ and 73^+ peaks from cellulose and wood, samples of pure levoglucosan (obtained from Senn Chemicals, Switzerland) were coated on bare Litz wire and pulse-vaporized in hot steam-argon. The two major peaks were 60^+ and 73^+ , with important peaks at 70^+ , 57^+ , and 42^+ . When the primary products transited through the

Figure 5-9. Repetitive Mass Spectral Scans During the Pulsed Heating of Wood Splints

hot gas column for 23 ms before being sampled, all peaks above 44^+ disappeared and were replaced by major peaks at 26, 28, 30, 42, 43, and 44.

A similar experiment with glycerol coated on Litz wire gave the expected glycerol peaks for primary pyrolysis product, but at 23 ms in the nominal 900°C steam-argon it showed complete conversion to 28^+ , 26^+ , 42^+ , 43^+ and 32^+ peaks. Our observations should complement the carefully analyzed flow reactor studies by Antal et al. (1981).

5.5 METHANOL: STEADY-STATE PYROLYSIS

The reader should be cautioned against attributing undue quantitative significance to the relative proportions of species indicated by the ion intensity ratios shown in Figs. 4-1 to 4-4, pending calibration of known compounds under the free-jet expansion, mass spectrometer conditions being used. Nevertheless, the prominent peaks at 31 and 32 (at both 16- and 70-eV ionizing electron energy) are intriguing. The logical parent is methanol, since O_2 is unlikely under the slightly H_2 -rich conditions of our burnt-gas reactor. Pure methanol vapor was injected into the central tube of the burner by bubbling He through the liquid. Concentrations were probably 0.1% or less in the total hot gases. The spectrum of this methanol as it emerged into the steam agreed with cold, low pressure, pure methanol. At 70 eV the 31^+ peak was slightly greater than 32^+ , while at 16 eV the reverse was true. A similar reversal is seen in the spectra of pyrolyzing wood.

The destruction of methanol in the 900°C steam-argon was observed as a function of residence time from a few milliseconds to 43 ms. The results were normalized and plotted in the same manner as reported for ethane and n-butane earlier and are shown in Fig. 5-10. The methanol (the $32^+/31^+$ ratio remains constant throughout the pyrolysis) is almost completely consumed in 43 ms under these conditions. Products at 28^+ and 44^+ are probably the expected CO and CO_2 . The 30^+ peak could be ethane formed from CH_3 radical recombinations, which is subsequently cracked to acetylene (26^+), but sensitivity calibrations and literature study are needed to validate the plausibility of this interpretation. Formaldehyde is another likely parent for 30^+ . Speculation of this sort is premature, but the compositional features so readily shown by our real-time, direct sampling technique do indicate the possibilities for mechanistic studies.

Figure 5-10. Steam-Cracking of Gaseous Methanol

SECTION 6.0

WORK FOR THE NEXT QUARTER

The qualitative results to date indicate that the chosen techniques can reveal important details of both the primary and secondary pyrolysis processes. The next step in the program will be to try to identify the parents of as many of the significant peaks (e.g., the top 10 contributors) in the spectra of wood, cellulose, hemicellulose, and lignin as possible. This will be done by use of known compound mass spectra, isotope ratios, cataloging of important pyrolysis products in the studies of others and inference from the behavior of the peaks with time and residence in steam. Later it is hoped to add MS/MS techniques, which appear particularly suitable in a molecular beam, direct inlet sampling situation where no prior separation of species is possible (as in GC-MS).

A second task, just starting this quarter, is to construct a resistance-heated wire grid that can be interfaced with the free-jet sampling system. Such a system, with its forced heating of powders by direct contact, will permit higher heating rates and will tie our time-resolved results to the important work being done on the fast pyrolysis of biomass and its components by Hajaligol et al. (1981). Such a device will allow observation of pyrolysis into a vacuum or cold surrounding gas, a process that we could not successfully implement with the pyroprobe (Milne and Soltys 1981).

The next quarter's work will emphasize these two thrusts, before proceeding to systematic quantitative kinetics.

SECTION 7.0

FUTURE DIRECTIONS

In FY 1982 we propose to continue the primary and secondary pyrolysis studies taking the care in temperature measurement, sensitivity calibrations, and modeling of the spreading pyrolysis plume necessary to enable quantitative interpretation.

As a second thrust, MS/MS techniques and ion counting will be added to permit better spectra deconvolution and faster data acquisition.

As a third thrust, depending on capital equipment acquisition, two additional methods of achieving fast heat transfer will be explored (in addition to convective heating by the hot flame gases and contact heating by the electrically heating wire mesh). One is the use of the large fluxes available from CW lasers. Such work would be relevant to direct solar-augmented fast pyrolysis. If there are any unique chemical decomposition effects attendant with direct photon irradiation, our sampling techniques should have a good chance of revealing them. The second method is the sliding contact, ablative heating and pyrolysis demonstrated by Diebold (1981) in his hot wire experiments and which he is trying to implement at the engineering scale. We will try to sample directly the tars and oils seen to evolve at the hot wire/wood interface.

SECTION 8.0

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