US Army Corps
of Engineers®
Engineer Research and
Development Center

Pyrolytic Decomposition Studies of AA2, A Double-Base Propellant

Donald M. Cropek, Patricia A. Kemme,
and Jean M. Day

October 2001

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

Public reporting burder for this collection of information is estibated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burder to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY) 01-10-2001	2. REPORT TYPE Final	3. DATES COVERED (FROM - TO) xx-xx-2000 to xx-xx-2001

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Pyrolytic Decomposition Studies of AA2, A Double-Base Propellent Unclassified	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)	5d. PROJECT NUMBER
Cropek, Donald M. ; Kemme, Patricia A. ; Day, Jean M. ;	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Army Engineer Research and Development Center Construction Engineering Research Laboratory PO Box 9005 Champaign, IL61826-9005	8. PERFORMING ORGANIZATION REPORT NUMBER ERDC TR-01-66

9. SPONSORING/MONITORING AGENCY NAME AND ADDRESS ,	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
APUBLIC RELEASE
,

13. SUPPLEMENTARY NOTES

14. ABSTRACT
Pyrolysis is the thermal decomposition of a substance into a variety of by-products, usually in the absence of oxygen.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 46	19. NAME OF RESPONSIBLE PERSON Cropek, Donald M. Donald.M.Cropek@erdc.usace.army.mil
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER International Area Code Area Code Telephone Number DSN

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39.18

Foreword

This study was conducted for Headquarters, U.S. Army Corps of Engineers under Project 4A162720D048, "Industrial Operations Pollution Control Technology"; Work Unit EP-UC5, "Studies of Pyrolytic Behavior of Energetic Materials." The technical monitor was Richard L. Eichholtz, SFIM-AEC-TS.

The work was performed by the Environmental Processes Branch (CN-E) of the Installations Division (CN), Construction Engineering Research Laboratory (CERL). The CERL principal investigator was Dr. Donald M. Cropek. This research was supported in part by an appointment to the Research Participation Program at CERL administered by the Oak Ridge Institute for Science and Education through an interagency agreement between U.S. Department of Education and CERL. The technical editor was Linda L. Wheatley, Information Technology Laboratory — Champaign. Dr. Ilker Adiguzel is Chief, CN-E, Dr. John T. Bandy is Chief, CN; and Gary W. Schanche, CVT, is the associated Technical Director. The Acting Director of CERL is Dr. Alan W. Moore.

CERL is an element of the U.S. Army Engineer Research and Development Center (ERDC), U.S. Army Corps of Engineers. The Commander and Executive Director of ERDC is COL John W. Morris III, EN, and the Director of ERDC is Dr. James R. Houston.

Contents

List of Figures and Tables

1 Introduction

Background

The armaments industry generates approximately 1,600 tons/year of hazardous waste containing explosives and propellants as a result of munitions production (Stratta 1993). Controlled, high temperature incineration is identified as a Best Available Technology for the disposal of hazardous organic wastes (Taylor and Dellinger 1988; Smith, Vandell, and Hixson 1994), and several military installations have opted to use hazardous waste incinerators to dispose of much of this EM and waste (Subsinsky 1993). AA2 is an EM currently being incinerated during demilitarization operations at one Army installation.

EMs have high potential reactivity or ignitability, which makes them ideally suited for incineration (controlled combustion at high temperature in the presence of excess oxygen). Incineration, however, has its own reputation as a pollution source. Despite trial burns that guarantee at least 99.99 percent destruction and removal efficiency (DRE) of the input feed (NRC 1983; Koshland and Thomson 1992), incineration has low public acceptance. This is in large part due to the inevitable by-products generated by incineration. The two broad classifications of by-product emissions from incineration are principal organic hazardous constituents (POHC), which are compounds initially present in the waste that are not broken down, and products of incomplete combustion (PIC), which are any degradation by-product from POHC other than the most thermodynamically stable end product (Dellinger, Taylor, and Tirey 1991). A bench-scale method capable of predicting incineration effluent composition (i.e., POHC and PIC generated from a hazardous waste) is highly desirable. This method could test and optimize operational parameters off-line, identify the level of effluent control required to capture and eliminate recalcitrant POHC and PIC, and assess the potential of incineration for new waste streams (Dellinger et al. 1986).

A modern incinerator is designed to operate at temperatures greater than 1,800 °F (972 °C), a residence time for waste greater than 2 seconds and at least 50 percent excess air (Dellinger, Taylor, and Tirey 1991). Under these conditions, DREs exceed 99.9999 percent for even the most thermally stable compounds. Due to fluctuations in input feed and gas supply, inadequate mixing, decreased residence times due to short circuits, and localized temperature quenching, this level of DRE is not

obtained, POHC are not completely destroyed, and PIC are formed. With respect to these conditions, the following parameters are important to PIC formation: oxygen concentration, reaction temperature, composition of the waste, degree of atomization of the waste, mixing of waste with oxygen, quenching of the combustion reaction, residence time, and halogen atoms present (Young and Voorhees 1992). Of these, oxygen concentration likely plays the primary role in PIC formation.

Numerous studies on high temperature degradation of organic compounds have recognized that, as compared to oxygen rich atmospheres or stoichiometric ratios of required oxygen to waste, oxygen deficient conditions produce the most complex mixtures of PIC at the highest concentrations (Taylor and Dellinger 1988; Young and Voorhees 1992, and references therein; Taylor, Dellinger, and Tirey 1991; Fisher and Koshland 1992; Graham, Hall, and Dellinger 1986). Most bench-scale, laboratory experiments have studied waste containing chlorinated compounds (Taylor and Dellinger 1988; Young and Voorhees 1992; Taylor, Dellinger, and Tirey 1991; Fisher and Koshland 1992; Graham, Hall, and Dellinger 1986; Young and Voorhees 1991; Taylor et al. 1994, and references therein; Lee, Cicek, and Senkan 1993; Vitovec et al. 1996; Tirey et al. 1990; Young and Voorhees 1992; Duvall, Rubey, and Mescher 1980) due to the potential creation of products far more toxic and recalcitrant than the input feed. As a general rule, results from these experiments illustrate that, when compared to oxygen rich conditions, PIC generated under oxygen deficient conditions are more numerous, the molecular weight and the distribution increase, and the maximum yields and temperature stability of the by-products increase.

This reasoning has been extended to incineration. Work by Dellinger et al. on thermal degradation of municipal type waste in atmospheres of varying oxygen content shows that by-products generated under very low or no oxygen content conditions best match the PIC generated during incineration of these same wastes (Dellinger, Taylor, and Tirey 1991; Dellinger et al. 1986; Tirey et al. 1991; Taylor, Dellinger, and Lee 1990). It is postulated that under conditions of excess oxygen, POHC are completely oxidized to innocuous light permanent gases. In areas of low oxygen content, known as "pyrolytic pockets" (Tirey et al.) PIC are created. These areas are associated with poor micromixing of oxygen, fuel, and waste (Taylor, Dellinger, and Tirey 1991; Fisher and Koshland 1992; Vitovec et al. 1996; Taylor, Dellinger, and Lee 1990; Sidhu et al. 2001; Tanada et al. 1994). Replication of these pyrolytic pockets in the laboratory would generate the same PIC as incineration of the waste under worst-case conditions (Tirey et al. 1990). It has also been shown that DREs of POHC in oxygen deficient environments correlate well with full-scale emission data (Taylor and Dellinger 1988). These researchers conclude that laboratory pyrolysis can provide valuable qualitative modeling of the incineration of municipal waste (Dellinger et al. 1986; Graham, Hall, and Dellinger 1986; Tirey et al. 1991; Taylor, Dellinger, and Lee 1990).

Pyrolysis is the thermal decomposition of a substance into a variety of by-products, usually in the absence of oxygen. Pyrolytic reactions typically take place between 500 and 800 °C without the addition of any other assisting chemical (Moldoveanu 1998). Although pyrolysis experiments may be performed on samples in any physical state, the resultant by-products are generally gaseous with possibly a solid residue due to the high temperatures involved. The coupling of a pyrolytic reaction accessory with the appropriate analytical instrumentation provides identification of the gaseous by-products as well as chemical information regarding the decomposition mechanism. Study of these pyrolytic by-products yields valuable information on the identity of the initial substance or on its behavior in high temperature environments.

The group of by-products from pyrolysis of a material is known as the pyrolysate. Since the pyrolysate is mostly gaseous in nature, combining pyrolysis with a gas analyzing method best characterizes the pyrolysate composition. Information on the pyrolysate can frequently be the best technique for study of substances that are not amenable to direct introduction into an analytical device. Soils, polymers, paints, microorganisms, powders, and other large complex samples can be pyrolyzed to obtain a gaseous pyrolysate that is a unique fingerprint to the original material (Wampler 1995).

One of the most useful techniques to unite with pyrolysis is gas chromatography/ mass spectrometry (GC/MS) thus resulting in the technique abbreviated PY/GC/MS. The powerful GC/MS analytical device is capable of separating and identifying the gaseous components of a mixture. It is ideal for analysis of the pyrolysate, which can be replete with components from light permanent gases to compounds that are larger than the initial components.

Data from analysis of the pyrolysate can be used in several ways. Identification of the starting material is one powerful application. For instance, PY/GC/MS data on a polymer material can rapidly characterize the polymer even though these large macromolecules cannot be directly analyzed or detected by GC/MS (Wampler 1995). As a second example, these experiments can not only establish the presence of microorganisms in a sample but can also give taxonomy information (Moldoveanu 1998). Pyrolytic examination of forensic or environmental samples yields evidence for sample matching or sample origin. Other broad categories and applications of pyrolysis for sample characterization are given in Moldoveanu (1998) and Wampler (1995).

Pyrolytic data can further be used to characterize a material's behavior under high temperature conditions. Gaseous by-products from conditions such as fires or explosions can be produced from pyrolytic zones within these hot spots. Characteriza-

tion and study of the behavior of energetic materials (EMs) during high temperature decomposition with pyrolysis is a fertile field with primary relevance to the propellant industry. Understanding of the thermal decomposition of EMs provides predictions on new explosive molecules, predictions on sensitivity, and stability information for long-term storage (Brill and James 1993). Example references on pyrolysis of energetic compounds include studies on nitroaromatic compounds (Brill and James 1993a and 1993b; Maksimov 1971), RDX (Botcher and Wight 1993), HMX (Kubota and Sakamoto 1989; Behrens 1990), and ammonium perchlorate composites (Oyumi, Mitarai, and Bazaki 1993).

Objective

The objective was to study the pyrolytic by-products of the double-base propellant AA2. This research studied the independent pyrolytic behavior of each individual component of AA2 to illustrate that the sum of the individual behavior is equivalent to the behavior of the total AA2. The data will show the power of pyrolysis to predict which components will act as POHC and which generate individual PIC during incineration. Finally, pyrolytic experiments were studied to determine the beneficial effects of eliminating particular organic compounds from a double-base propellant formulation that create the largest variety of unwanted PIC.

Approach

Samples of original AA2 from the Army installation were collected for analysis. In addition, chemical standards were obtained for the major components of AA2. All samples and standards were subjected to pyrolysis and the by-products were analyzed by GC/MS.

Scope

This work details pyrolytic studies on AA2 and its major organic constituents. Future work will compare this data to by-product data collected during the incineration of AA2. Good matching between pyrolytic data and incineration data can support the use of laboratory pyrolysis to predict incineration behavior of energetic or explosive compounds.

Mode of Technology Transfer

The information derived from this study can be incorporated into guidance for environmental representatives at military installations for decisions regarding demilitarization of EMs and pollution control when using incineration. In addition, these data will be included in a peer-reviewed journal article illustrating the utility of bench-scale pyrolysis for rapid prediction of incineration emissions.

This report will be made accessible through the World Wide Web (WWW) at http://www.cecer.army.mil.

2 Experimental Parameters

Energetic Materials

AA2 was obtained from the hazardous waste incinerator input feed at Radford Army Ammunition Plant (RAAP). The composition of the double base propellant AA2 includes the following ingredients in order of decreasing percent: nitrocellulose (NC), nitroglycerin (NG), an organometallic salt, triacetin, di-n-propyladipate, 2-nitrodiphenylamine (NDPA), and candelilla wax. The energetic components, NC and NG, comprise nearly 90 percent of AA2. The remaining components function as stabilizers, plasticizers, and burn rate modifiers. All compounds were obtained for individual pyrolytic investigation. Picatinny Arsenal, NJ provided 13.4 percent-nitrated NC. Nitroglycerin in acetone/ether solvent was both synthesized at this laboratory and purchased from Radian Corporation (Austin, TX) as a 1.0-mg/mL solution in acetonitrile. Triacetin (J.T. Baker, Phillipsburg, NJ), di-n-propyladipate (Fisher, Pittsburgh, PA), and NDPA and candelilla wax (Aldrich, Milwaukee, WI) were also obtained. All chemicals and materials were used as received without further purification. Figure 1 shows the chemical structures of these components are shown in Figure 1. Candelilla wax is not shown, as it is a complex mixture of hydrocarbons, alcohols, sterols, and resins.

Equipment

A small pyrolysis chamber was installed on the injection port of a GC/MS. In this arrangement, the helium carrier gas flows through the chamber during pyrolysis and transports all gaseous by-products directly into the injection port of the GC. Two different instrument configurations were used in this study due to the expected characteristics of the pyrolysate. These configurations are described in the next two paragraphs.
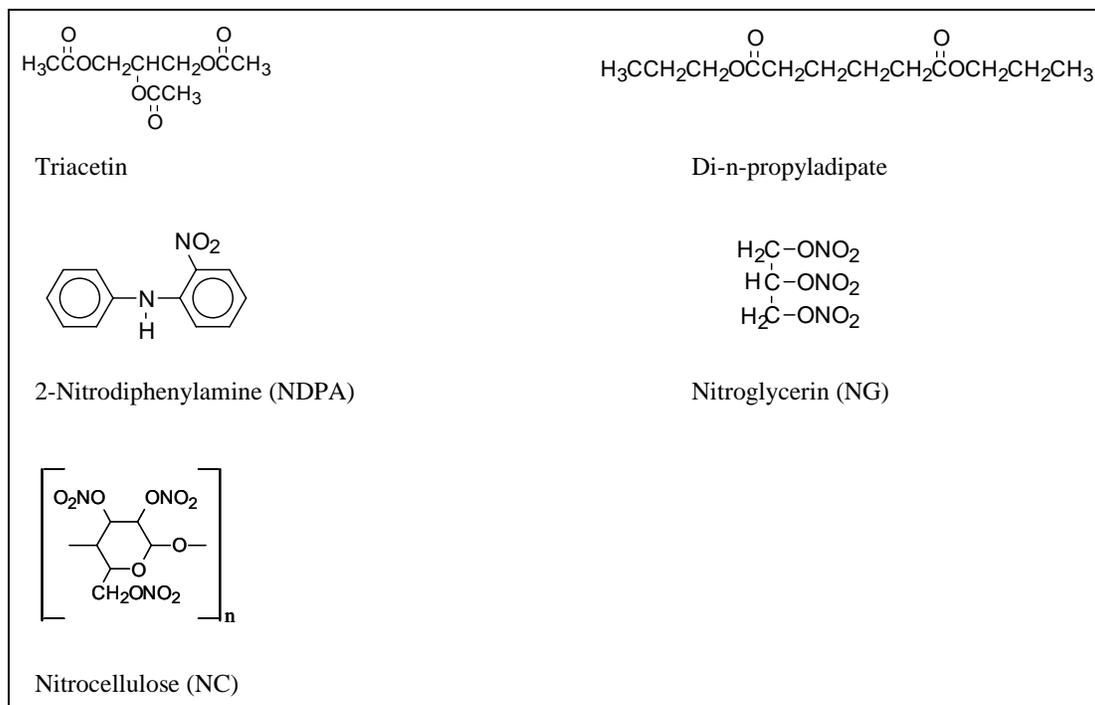
Figure 1. Chemical structures of AA2 components.

Configuration A

This configuration was used to analyze the light molecular weight (LMW) gases in the pyrolysate. A Pyroprobe 2000 (CDS, Oxford, PA) was interfaced directly onto an HP 5890 GC/5970 MS (Agilent Technologies, Palo Alto, CA). A PoraPLOT Q column (ChromPack, Raritan, NJ), 50 m x 0.32 mm i.d. x 10 μm film thickness, was used for separation of the low molecular weight species. The GC oven program began at 40 °C for 13 min, ramped to 200 °C at 10 °C/min, and stayed at 200 °C for 60 min. The injector port was held at 200 °C, the detector port was held at 280 °C, and all experiments were performed in the splitless mode. The mass detector was programmed to scan from 10 to 400 amu.

Configuration B

Heavy molecular weight (HMW) gases in the pyrolysate were analyzed in this configuration. The same pyroprobe unit and GC/MS as mentioned earlier were used but now an Agilent Technologies HP-5MS column, 25 m x 0.20 mm i.d. x 0.33 μm film thickness, is required for adequate separation. The GC oven program began at 40 °C for 2 min, ramped to 250 °C at 10 °C/min, and stayed at 250 °C for 7 min. The injector port was held at 250 °C, the detector port was held at 280 °C, and all experiments were performed in the splitless mode. The mass detector was programmed to scan from 10 to 450 amu.

Pyrolysis

A complete pyrolytic investigation for a sample consisted of two separate experiments, one using Configuration A and one using Configuration B. A quartz tube (CDS, Oxford, PA) was loaded with a plug of quartz wool to keep the sample in the hot zone of the probe during pyrolysis. This tube was cleaned three times at 1200 °C for 20 s. A sample mass between 2 and 6 mg was loaded onto the wool. The prepared tube was placed inside a platinum wire coil on the probe and the probe was inserted into the pyrolysis chamber. A 20-min wait period allowed entrant air to pass through the system. The pyrolysis chamber was then heated from 40 to 150 °C at 20 °C/min and was held at this elevated temperature throughout the run time. The probe was fired after the pyrolysis chamber reached 150 °C, heating the sample from ambient to 900 °C at a rate of 20 °C/ms and holding at 900 °C for 100 s.

The timing among the interface box, the pyrolysis probe, and the GC oven program are shown in Figures 2 and 3 for the two configurations. The probe fires after the interface box has reached its final temperature of 150 °C. In some cases, the run time was extended due to the observation of late eluting peaks. In Configuration A (Figure 2), the oven temperature begins ramping only after the probe is fired. Some of the LMW species rapidly elute from the PoraPLOT Q column even at ambient (40 °C) temperatures. This oven temperature profile allows these compounds to experience longer elution times and better separation. A long run time is needed because the PoraPLOT Q column strongly, if not irreversibly, retains many of the HMW species. A blank run with no loaded sample was repeated after each sample until no residual peaks were observed. Experiments were also performed without firing the probe and no evolution of LMW by-products due solely to the 150 °C interface box temperature was noted. In Configuration B (Figure 3), the oven temperature begins ramping before the probe is fired. An oven temperature of approximately 90 °C is reached during pyrolysis. The HMW species have reasonable retention on the HP5 MS column even at higher temperatures and initial heating of the oven serves to shorten the total analysis time. There is also no generation of HMW by-products due solely to the 150 °C interface box temperature.

Identification of the pyrolysate peaks was accomplished by comparing mass spectral data to library standards. No attempt was made to acquire standards of these identified peaks for duplication of elution times and mass spectra due to the difficulty in replicating pyrolysis conditions via injection and the sheer number of pyrolysate peaks.
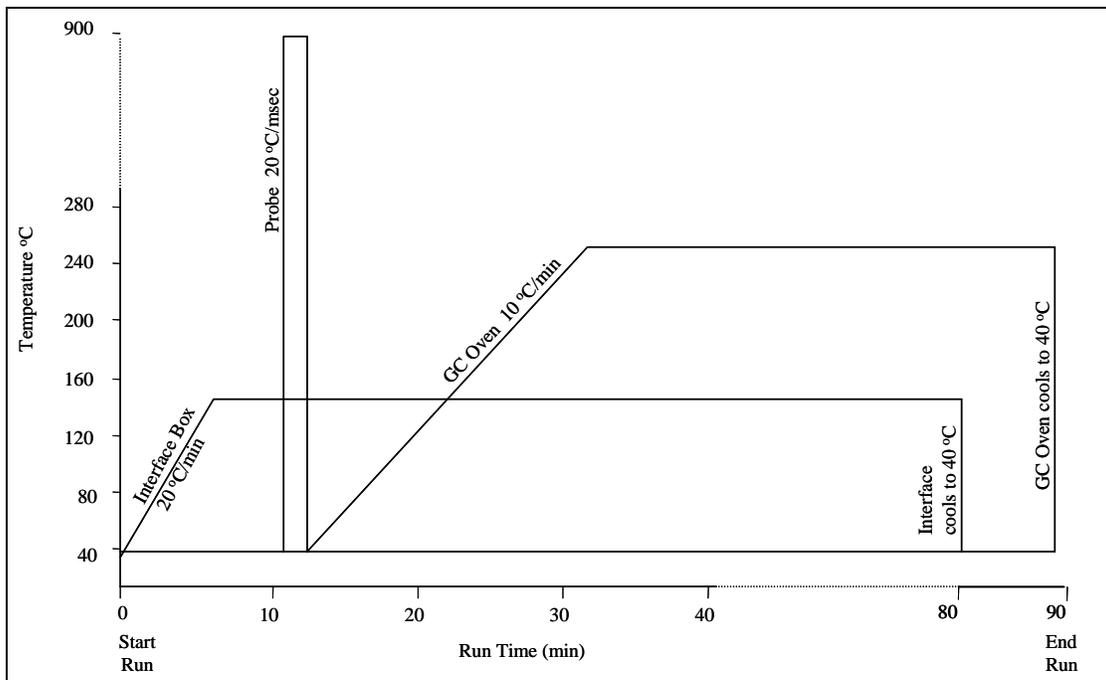
Figure 2. Timing profiles for the interface box, the pyrolysis probe, and the GC oven for Configuration A.
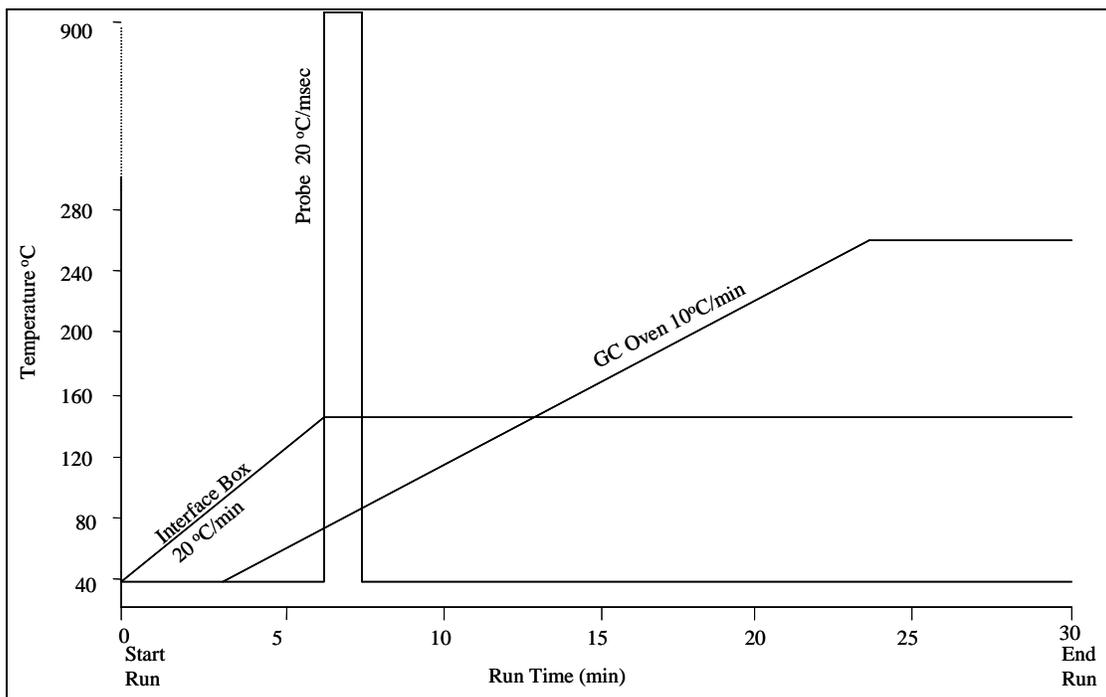
Figure 3. Timing profiles for the interface box, the pyrolysis probe and the GC oven for Configuration B.

The resultant peaks in the LMW pyrolysates were analyzed by the Autointegrate function of the HP ChemStation software. Only in cases where the baseline for a peak was clearly skewed was manual integration performed. Peak areas are reported as a percent of the total peak area. The total peak area does not add to 100 percent since no attempt was made to disregard or eliminate unidentified peaks or to completely correct grossly broadened peaks. The percent area values in the tables listed in the next sections can provide comparative information on the by-products in each pyrolysate.

The peaks in the HMW tables later in this chapter were analyzed differently. Due to the difficulty in measuring a peak area for the broad HMW peaks in each pyrolysate, these data were analyzed by manual integration of each major or identified peak. The total percent areas in these tables are therefore always 100 percent. Again, the peak areas are primarily for comparative information.

3 Results and Discussion

Light Molecular Weight Pyrolysis Results

AA2

Figure 4 shows the pyrogram of AA2 using Configuration A. The inset expands the time scale to show a number of the smaller peaks. Table 1 identifies the numbered peaks by compound name, molecular formula, molecular weight, and peak area as a percent of the total area. AA2 comprises a considerable amount of EM. As expected for these types of materials, exposure to high temperatures generates a great deal of light gases. Carbon monoxide, nitric oxide, carbon dioxide, and water make up almost 70 percent of the peak area. Formaldehyde, acetylene, acetic acid, propene, ethylene oxide, and 2-propenal make up the next 20 percent of the LMW species. All other by-products are small in comparison. Furan stands out as the by-product of highest notoriety. This experiment was repeated for an aqueous slurry of AA2 both as received from RAAP and dried at room temperature. The pyrogram was identical for both samples except for elevated levels of water in the slurry pyrogram. After demonstrating this negligible effect of water, only dried samples were pyrolyzed for better control of the sample mass placed in the pyrolysis tube.
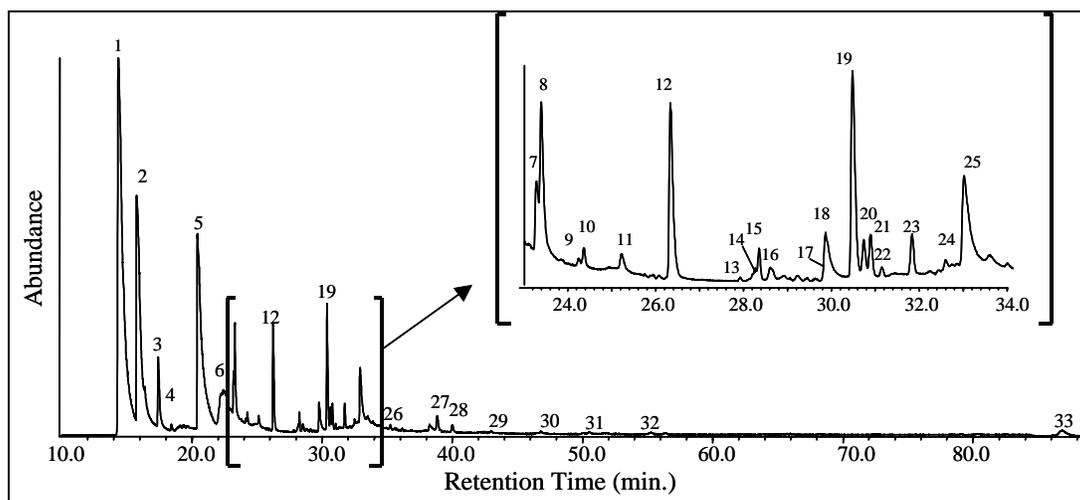
Figure 4. LMW pyrogram of AA2 using Configuration A (Filename: AA2b.d).

Table 1. Identification of numbered peaks in Figure 4 (LMW by-products from AA2 pyrolysis).

Peak #	Compound	Formula	MW	% Area
1	carbon monoxide, nitric oxide	CO, NO	28, 30	34.3
2	carbon dioxide	CO_2	44	18.7
3	acetylene	C_2H_2	26	2.9
4	ethane	C_2H_6	30	0.2
5	water	H_2O	18	16.1
6	formaldehyde	CH_2O	30	5.8
7	hydrogen cyanide	HCN	27	0.9
8	propene	C_3H_6	42	3.1
9	1,2-propadiene	C_3H_4	40	0.1
10	1-propyne	C_3H_4	40	0.3
11	methanol	CH_4O	32	0.2
12	ethylene oxide	C_2H_4O	44	2.2
13	methyl formate	$C_2H_4O_2$	60	0.03
14	1-buten-3-yne	C_4H_4	52	0.02
15	1,3-butadiene	C_4H_6	54	0.4
16	formamide	CH_3NO	45	0.2
17	acetonitrile	C_2H_3N	41	0.1
18	formic acid	CH_2O_2	46	1.1
19	2-propenal	C_3H_4O	56	2.7
20	furan	C_4H_4O	68	0.5
21	propanal	C_3H_6O	58	0.6
22	acetone	C_3H_6O	58	0.2
23	2-propenenitrile	C_3H_3N	53	0.7
24	formic acid, 2-propenyl ester	$C_4H_6O_2$	86	0.1
25	acetic acid	$C_2H_4O_2$	60	3.1
26	3-buten-2-one	C_4H_6O	70	0.3
27	methyl formate	$C_2H_4O_2$	60	0.6
28	benzene	C_6H_6	78	0.3
29	acetic acid, 2-propenyl ester	$C_5H_8O_2$	100	0.05
30	pyridine	C_5H_5N	79	0.06
31	cyclopentanone	C_5H_8O	84	0.07
32	2-furancarboxaldehyde	$C_5H_4O_2$	96	0.1
33	phenol	C_6H_6O	94	0.8
			Total Area	96.8

Nitrocellulose

A dry sample of highly nitrated NC was pyrolyzed and its pyrogram is shown in Figure 5. The inset expands a region of close eluting peaks. Table 2 identifies the numbered peaks. NC is an EM that produces primarily carbon monoxide, nitric oxide, methane, carbon dioxide, and water (75 percent of the total area). The second group of compounds includes ethane, acetylene, formaldehyde, propene, ethylene

oxide, acetonitrile, and 2-propenal (17 percent). Furan is produced in small amounts. Peak 26 is unidentified.
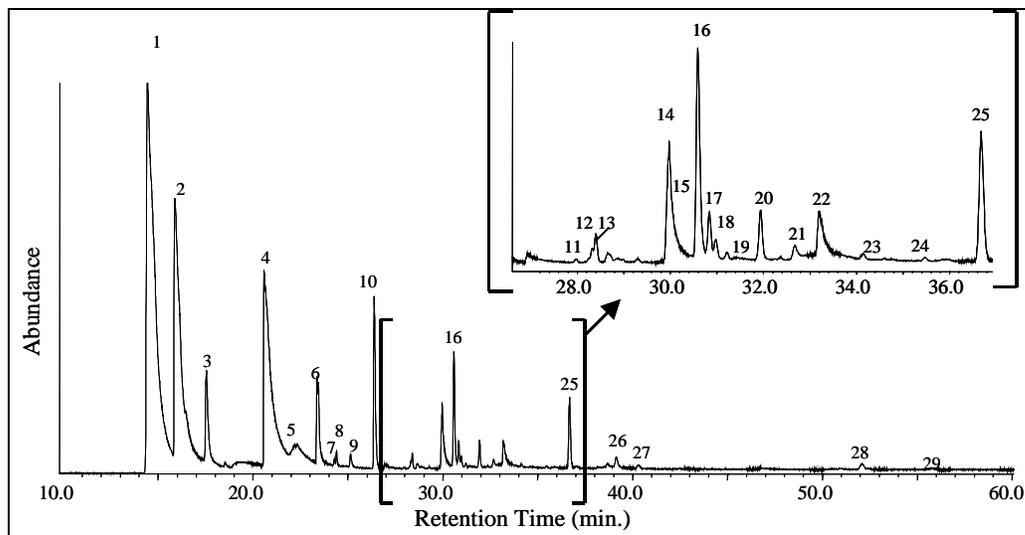
Figure 5. LMW pyrogram of NC using Configuration A (Filename: NCF.d).

Table 2. Identification of numbered peaks in Figure 5 (LMW by-products from NC pyrolysis).

Peak #	Compound	Formula	MW	% Area
1	carbon monoxide, nitric oxide, methane	CO, NO, CH_4	28, 30, 16	37.4
2	carbon dioxide, nitrous oxide	CO_2, N_2O	44,	21.4
3	ethene, acetylene	C_2H_4, C_2H_2	28, 26	3.7
4	water	H_2O	18,	16.3
5	formaldehyde	CH_2O	30	3.2
6	hydrogen cyanide, propene	HCN, C_3H_6	27, 42	3.0
7, 8	1,2-propadiene	C_3H_4	40	0.3
9	methanol	CH_4O	32	0.3
10	ethylene oxide	C_2H_4O	44	3.2
11	methyl formate	$C_2H_4O_2$	60	0.01
12	1-buten-3-yne	C_4H_4	52	0.02
13	1,3-butadiene	C_4H_6	54	0.3
14	acetonitrile	C_2H_3N	41	2.0
15	formic acid	CH_2O_2	46	1.0
16	2-propenal	C_3H_4O	56	2.1
17	furan	C_4H_4O	68	0.7
18	propanal	C_3H_6O	58	0.1
19	acetone	C_3H_6O	58	0.1
20	2-propenenitrile	C_3H_3N	53	0.5
21	2-propen-1-ol	C_3H_6O	58	0.3
22	acetic acid	$C_2H_4O_2$	60	1.2
23	propanenitrile	C_3H_5N	55	0.08
24	3-buten-2-one	C_4H_6O	70	0.04
25	ethyl acetate	$C_4H_8O_2$	88	1.4

Peak #	Compound	Formula	MW	% Area
26	60, 42, 31, 29 amu	-	-	0.5
27	benzene	C_6H_6	78	0.2
28	toluene	C_7H_8	92	0.3
29	2-furancarboxaldehyde	$C_5H_4O_2$	96	0.1
			Total Area	99.75

Nitroglycerin

A syringe was used to inject several aliquots of the NG/acetone/ether solution directly onto the quartz wool in the tube. The solvent was evaporated before pyrolysis by heating at 50 °C for several minutes. Figure 6 shows the pyrogram for NG using Configuration A, and Table 3 lists the identified peaks. NG is also an energetic compound and heat sensitive. Carbon monoxide, nitric oxide, carbon dioxide, nitrous oxide, and water make up nearly 80 percent of the total peak area. Formaldehyde and ethylenediamine contribute another 10 percent of the total peak area. Furan is not observed. It is interesting to note that this small three-carbon compound (NG) can recombine under high temperature conditions to create six-carbon aromatic structures such as benzene and toluene. Two acetone peaks are observed. One is likely due to incomplete elimination of the solvent and the second may be a pyrolytic by-product.
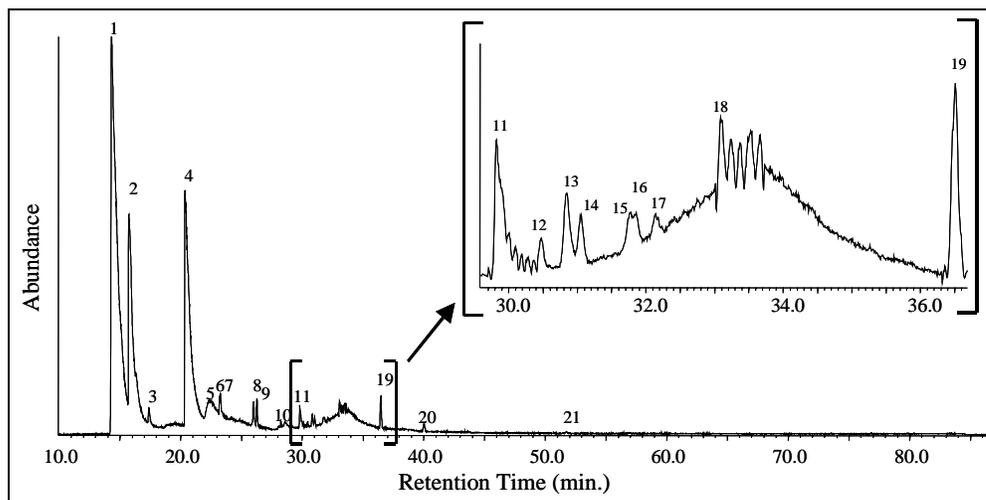

Figure 6. LMW pyrogram of NG using Configuration A (Filename: NG1B.d).

Table 3. Identification of numbered peaks in Figure 6 (LMW by-products from NG pyrolysis).

Peak #	Compound	Formula	MW	% Area
1	carbon monoxide, nitric oxide	CO, NO	28, 30	49.6
2	carbon dioxide, nitrous oxide	CO_2, N_2O	44	13.8
3	acetylene, ethene	C_2H_2, C_2H_4	26, 28	0.4
4	water	H_2O	18	22.5
5	formaldehyde	CH_2O	30	9.4
6	hydrogen cyanide	HCN	27	0.2
7	propene	C_3H_6	42	0.3
8	ethylene oxide	C_2H_4O	44	0.5
9	ethylene oxide	C_2H_4O	44	0.4
10	1,3-butadiene	C_4H_6	54	0.1
11	formic acid	CH_2O_2	46	0.6
12	2-propenal	C_3H_4O	56	0.1
13	acetone	C_3H_6O	58	0.3
14	acetone	C_3H_6O	58	0.2
15	2-propenenitrile	C_3H_3N	53	0.1
16	formic acid, ethyl ester	$C_3H_6O_2$	74	0.1
17	nitromethane	CH_3NO_2	61	0.1
18	ethylenediamine	$C_2H_8N_2$	60	0.4
19	ethyl acetate	$C_4H_8O_2$	88	0.7
20	benzene	C_6H_6	78	0.2
21	toluene	C_7H_8	92	0.1
			Total Area	100.0

Triacetin

Figure 7 is the pyrogram for triacetin using Configuration A, and Table 4 lists the identity of the numbered peaks. Since triacetin is not an energetic molecule, the pyrogram is not dominated by light permanent gases as occurred in the three previous samples. Instead, acetic acid is the major by-product, followed by 2-propenal. Although 2-butenal and 3-buten-2-one, which co-elute with the broad acetic acid peak, are grouped with the acetic acid peak area in the % Area column, they are not major peaks. The second tier of by-products includes the light gases, water, propene, 1,3-butadiene, acetone, and the acetic acid, 2-propenyl ester. For the first time, the pyrolyzed compound is also observed in the pyrogram. Triacetin is observed as a plateau eluting at the end of the analysis. It is not classified as a pyrolytic by-product and is not included in the % Area analysis in Table 4. Apparently, triacetin has a large degree of thermal stability and volatilizes at the pyrolysis temperature. Triacetin was exceedingly difficult to remove from the GC column used in Configuration A, with continual carryover and repeated presence in blank runs following this experiment.
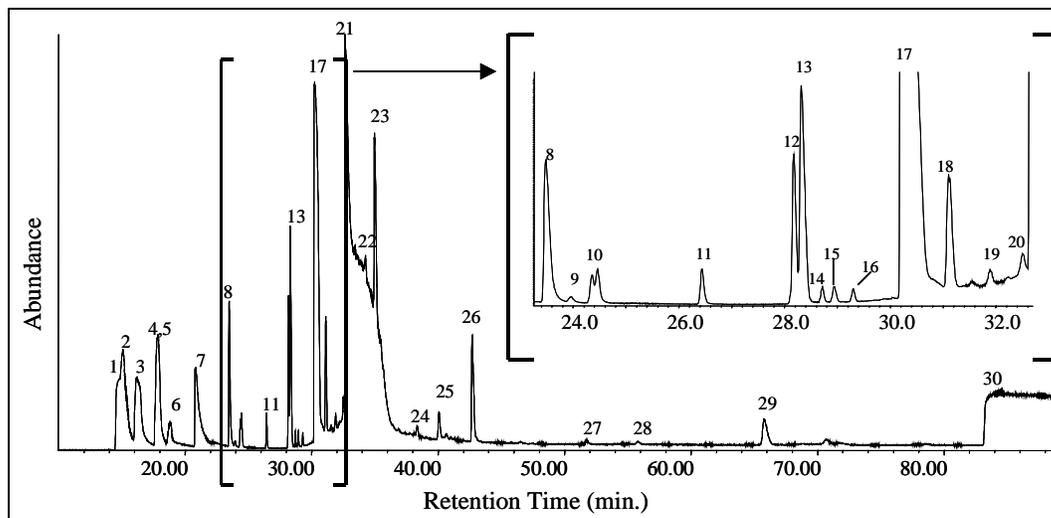
Figure 7. LMW pyrogram of triacetin using Configuration A (Filename: TRI830.d).

Table 4. Identification of numbered peaks in Figure 7 (LMW by-products from triacetin pyrolysis).

Peak #	Compound	Formula	MW	% Area
1	carbon monoxide	CO	28	6.4
2	methane	CH_4	16	
3	carbon dioxide	CO_2	44	3.8
4	ethene	C_2H_4	28	3.9
5	acetylene	C_2H_2	26	
6	ethane	C_2H_6	30	1.3
7	water	H_2O	18	3.1
8	propene	C_3H_6	42	1.6
9	propane	C_3H_8	44	0.1
10	1,2-propadiene	C_3H_4	40	0.5
11	ethylene oxide	C_2H_4O	44	0.2
12	1-butene	C_4H_8	56	1.0
13	1,3-butadiene	C_4H_6	54	2.0
14	1-butyne	C_4H_6	54	0.1
15	1-butyne	C_4H_6	54	0.1
16	1,2-butadiene	C_4H_6	54	0.1
17	2-propenal	C_3H_4O	56	11.7
18	acetone	C_3H_6O	58	1.5
19	1,3-pentadiene	C_5H_8	68	0.12
20	1,1-dimethylcyclopropane	C_5H_{10}	70	0.13
21	acetic acid	$C_2H_4O_2$	60	
22	2-butenal	C_4H_6O	70	49.9
23	3-buten-2-one	C_4H_6O	70	
24	2-butenal	C_4H_6O	70	0.2
25	benzene	C_6H_6	78	0.4
26	acetic acid, 2-propenyl ester	$C_5H_8O_2$	100	1.7
27	toluene	C_7H_8	92	0.1
28	2-cyclopenten-1-one	C_5H_6O	82	0.1
29	1-(acetyloxy)-2-propanone	$C_5H_8O_3$	116	0.9
30	triacetin	$C_9H_{14}O_6$	218	-
			Total Area	90.95

Di-n-propyladipate

This compound is another oxygenated species similar in structure to triacetin. Its pyrogram is shown in Figure 8. Table 5 lists all major by-products. Cyclopentanone and propene are the two dominant by-products. Light gases and 1-propanol are secondary species.
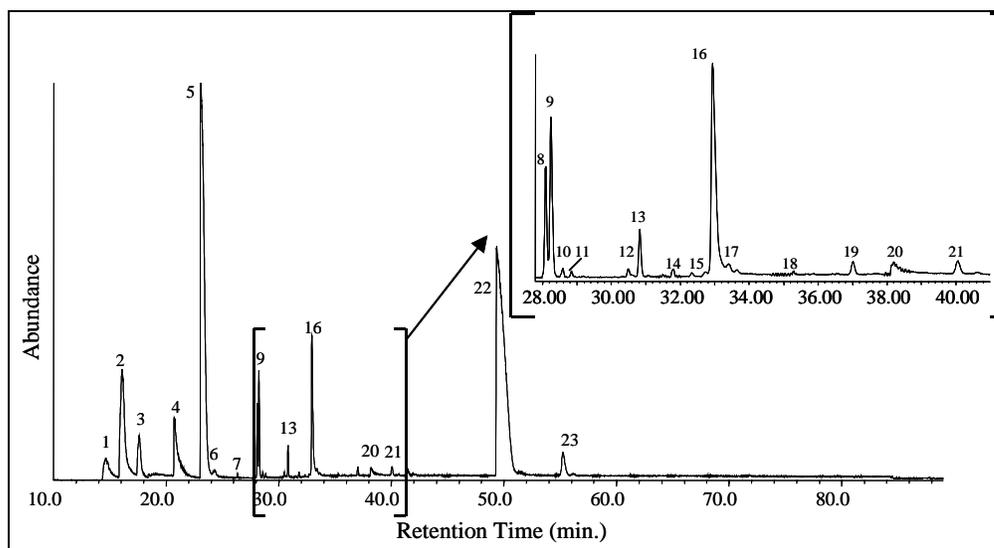
Figure 8. LMW pyrogram of di-n-propyladipate using Configuration A (Filename: DA824.d).

Table 5. Identification of numbered peaks in Figure 8 (LMW by-products from di-n-propyladipate pyrolysis).

Peak #	Compound	Formula	MW	% Area
1	carbon monoxide	CO	28	2.6
2	carbon dioxide	CO_2	44	10.3
3	ethene	C_2H_4	28	2.7
4	water	H_2O	18	4.5
5	propene	C_3H_6	42	30.4
6	1-propyne	C_3H_4	40	0.6
7	ethylene oxide	C_2H_4O	44	0.1
8	2-methyl-1-propene	C_4H_8	56	1.1
9	1,3-butadiene	C_4H_6	54	1.8
10	2-methyl-1-propene	C_4H_8	56	0.1
11	1-butene	C_4H_8	56	0.1
12	2-propenal	C_3H_4O	56	0.1
13	propanal	C_3H_6O	58	0.5
14	1,3-pentadiene	C_5H_8	68	0.1
15	1-pentene	C_5H_{10}	70	0.04
16	1-propanol, acetic acid	C_3H_8O, $C_2H_4O_2$	60	4.4
17	cyclopentene	C_5H_8	68	0.07
18	3-buten-2-one	C_4H_6O	70	0.01
19	1,5-hexadiene	C_6H_{10}	82	0.02
20	2-propenoic acid	$C_3H_4O_2$	72	0.05

Peak #	Compound	Formula	MW	% Area
21	benzene	C_6H_6	78	0.2
22	cyclopentanone	C_5H_8O	84	36.5
23	2-cyclopenten-1-one	C_5H_6O	82	1.5
			Total Area	97.8

NDPA

NDPA is unique among AA2 components as it is the only additive containing aromatic groups. Figure 9 and Table 6 are the pyrogram and by-product identification for pyrolysis of NDPA. Nitric oxide and water are the major peaks followed by carbon monoxide, phenol, and benzene. Furan is present as in AA2 and NC. The light gases and water dominate the by-products, but the major pyrolysate peaks of NDPA are in the HMW fraction (see **HMW Pyrolysis Results** later in this chapter).
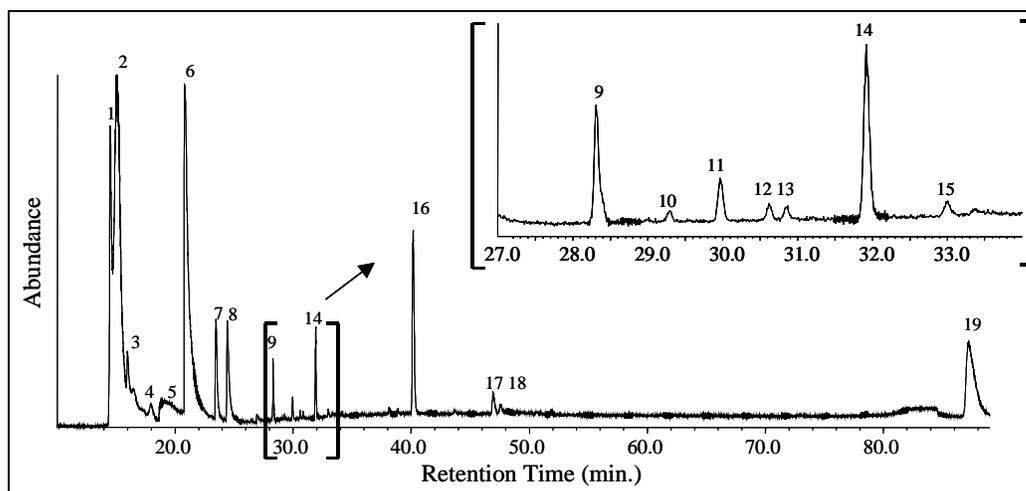
Figure 9. LMW pyrogram of NDPA using Configuration A (Filename: NDPA829.d).

Table 6. Identification of numbered peaks in Figure 9 (LMW by-products from NDPA pyrolysis).

Peak #	Compound	Formula	MW	% Area
1	carbon monoxide	CO	28	9.4
2	nitric oxide	NO	30	32.5
3	carbon dioxide	CO_2	44	0.8
4	acetylene	C_2H_2	26	1.1
5	water	H_2O	18	2.7
6	water	H_2O	18	21.5
7	hydrogen cyanide	HCN	27	2.8
8	methanol	CH_4O	32	3.4
9	1-buten-3-yne	C_4H_4	52	0.8
10	propiolonitrile	C_3HN	51	0.1
11	acetonitrile	C_2H_3N	41	0.3
12	2-propenal	C_3H_4O	56	0.2
13	furan	C_4H_4O	68	0.2

Peak #	Compound	Formula	MW	% Area
14	2-propenenitrile	C_3H_3N	53	1.3
15	3-penten-1-yne	C_5H_6	66	0.3
16	benzene	C_6H_6	78	5.0
17	pyridine	C_5H_5N	79	0.9
18	2,4-pentadienenitrile	C_5H_5N	79	0.5
19	phenol	C_6H_6O	94	8.9
			Total Area	92.7

Candelilla wax

Due to the persistent nature of triacetin on the PoraPLOT Q column, it was believed that candelilla wax would demonstrate similar, if not increased, contamination problems using Configuration A and may irreversibly damage the column. In addition, candelilla wax is the smallest constituent of AA2 (0.1 percent) by weight and is not expected to contribute an interesting or relevant subset of LMW compounds. Therefore, this compound was not pyrolyzed under these conditions.

Heavy Molecular Weight Pyrolysis Results

AA2

Analysis of the HMW pyrolysate for AA2 is shown in Figure 10. This experiment had a longer run time than that shown in the timing figure due to a longer wait period before probe firing to ensure the entrant air peak had eluted. Table 7 identifies the numbered peaks from Figure 10. The light gases make up almost 90 percent of the by-products; several of the species observed in the light gas fraction (Figure 4 and Table 1) are also seen in this analysis. This configuration does not separate these compounds well; the long trailing peak from 14 to 16 min interferes with separation and identification of all other species eluting over this same time period. Numerous aromatic and unsaturated ring compounds are identified, including compounds containing a heteroatom in the ring. Notable is the presence of four original compounds from the composition of AA2: triacetin, NG, di-n-propyladipate, and NDPA. These compounds have enough thermal stability and volatility that a detectable fraction escapes the pyrolysis chamber without degradation. The presence of NG is most surprising; it was expected that this highly energetic compound would readily and quickly decompose into light gases. Based on this data, it may be predicted that pyrolytic pockets in the incinerator would produce the wide variety of by-products listed in Table 7 as PIC and POHC from an input feed of AA2.
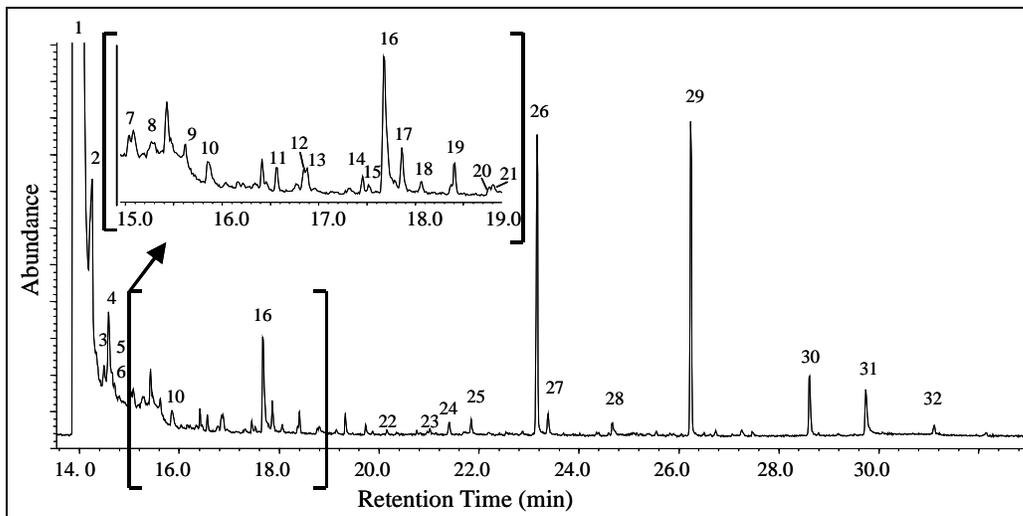
Figure 10. HMW pyrogram of AA2 using Configuration B (Filename: 9100AD.d).

Table 7. Identification of numbered peaks in Figure 10 (HMW by-products from AA2 pyrolysis).

Peak #	Compound	Formula	MW	% Area
1	LMW gases, 2-propenal	C_3H_4O	56	89.9
2	acetic acid	$C_2H_4O_2$	60	0.2
3	2-butenal	C_4H_6O	70	0.6
4	methyl formate	$C_2H_4O_2$	60	0.03
	benzene	C_6H_6	78	
5	2-propanoic acid	$C_3H_4O_2$	72	0.03
6	acetic acid, 2-propenyl ester	$C_5H_8O_2$	100	0.1
7	pyridine	C_5H_5N	79	0.3
8	toluene	C_7H_8	92	0.2
9	3-furancarboxaldehyde	$C_5H_4O_2$	96	0.1
10	2-furancarboxaldehyde	$C_5H_4O_2$	96	0.2
11	styrene	C_8H_8	104	0.1
12	cyclopentanone	C_5H_8O	84	0.1
13	p-benzoquinone	$C_6H_4O_2$	108	0.1
14	isocyanatobenzene	C_7H_5NO	119	0.1
15	benzaldehyde	C_7H_6O	106	0.04
16	phenol	C_6H_6O	94	1.0
17	benzonitrile	C_7H_5N	103	0.2
18	benzofuran	C_8H_6O	118	0.1
19	benzoxazole	C_7H_5NO	119	0.2
20	hydroxybenzaldehyde	$C_7H_6O_2$	122	0.1
21	indene	C_9H_8	116	0.1
22	2-nitrophenol	$C_6H_5NO_3$	139	0.03
23	naphthalene	$C_{10}H_8$	128	0.1
24	quinoxaline	$C_8H_6N_2$	130	0.1
25	isoquinoline	C_9H_7N	129	0.1
26	triacetin	$C_9H_{14}O_6$	218	2.3
27	NG	$C_3H_5N_3O_9$	227	0.2
28	2-ethenylquinoline	$C_{11}H_9N$	155	0.1

Peak #	Compound	Formula	MW	% Area
29	di-n-propyladipate	$C_{12}H_{22}O_4$	230	2.3
30	phenazine	$C_{12}H_8N_2$	180	0.6
31	carbazole	$C_{12}H_9N$	167	0.5
32	NDPA	$C_{12}H_{10}N_2O_2$	214	0.1
			Total Area	100.0

Nitrocellulose

Figure 11 and Table 8 show the HMW species generated from pyrolysis of NC. Again, this pyrogram shows the large tailing peak of the LMW species that do not separate well under these experimental conditions. NC exhibits the expected behavior for an energetic compound; specifically, rapid and nearly complete conversion into light gases upon experiencing high temperatures. Many of the small peaks are not identified due to low abundance, interference from the tailing background, and possibly the absence of these pyrolytic by-products from the mass spectral library. Only 2-furancarboxalde is observed in both experimental configurations.
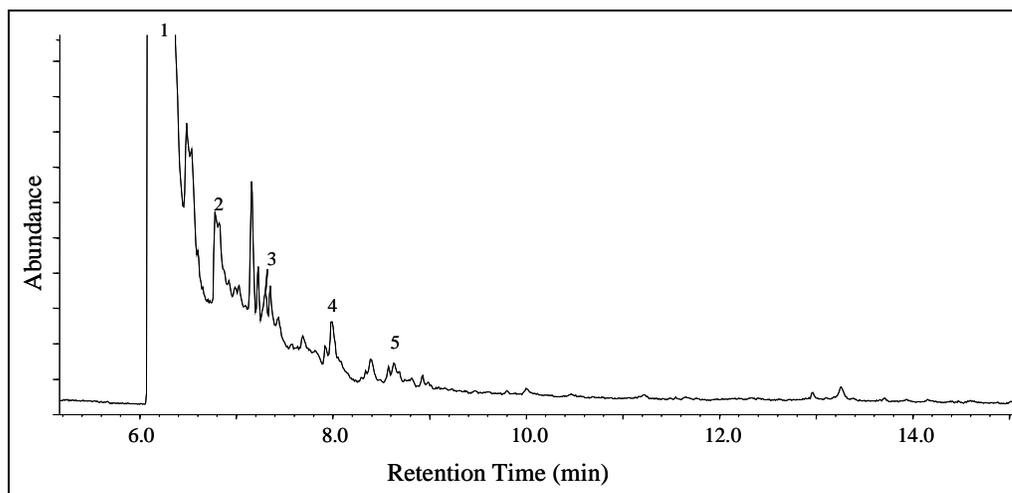
Figure 11. HMW pyrogram of NC using Configuration B (Filename: ncjrnl.d).

Table 8. Identification of numbered peaks in Figure 11 (HMW by-products from NC pyrolysis).

Peak #	Compound	Formula	MW	% Area
1	LMW gases	-	-	96.9
2	2-methyl-2-butenal	C_5H_8O	84	1.6
3	2-furancarboxaldehyde	$C_5H_4O_2$	96	0.2
4	2(5H)-furanone	$C_4H_4O_2$	84	0.8
5	2H-pyran-2-one	$C_5H_4O_2$	96	0.5
			Total Area	100.0

Nitroglycerin

Figure 12 and Table 9 shows the pyrolytic results from NG using Configuration B. As with AA2, this particular experiment allowed more time to elapse before pyrolysis to permit the air peak to elute. NG is highly energetic and it shares a common behavior with NC. The majority of the pyrolysate (96.1 percent) is composed of light gases that are better analyzed with Configuration B. The figure shows an expansion of the abundance scale to show the four identifiable peaks. NG again illustrates its surprising thermal stability with a substantial presence in the pyrolysate. NG has one of the higher vapor pressures for energetic compounds (Yinon and Zitrin 1993). Despite the high temperature of pyrolysis, NG is capable of volatilizing and eluting through the column before transformation into other compounds.
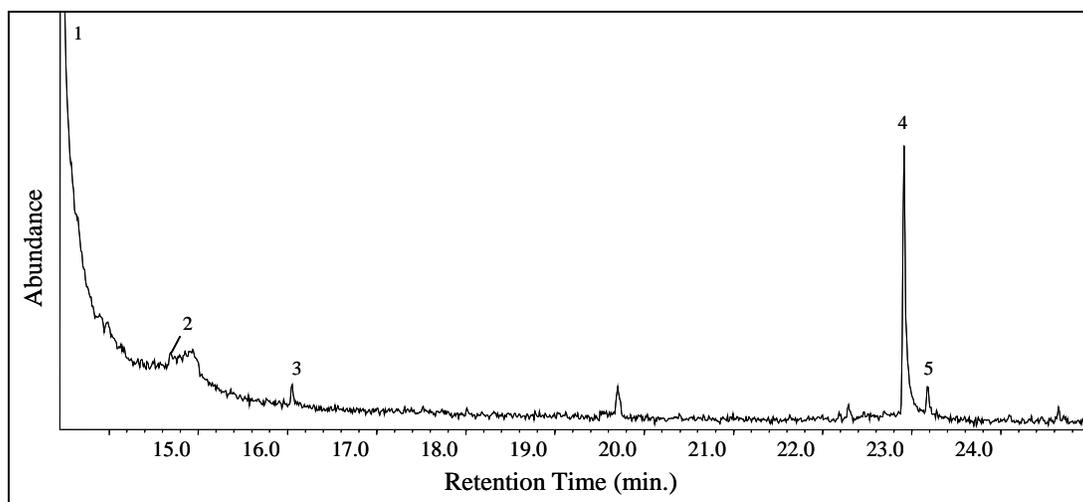

Figure 12. HMW pyrogram of NG using Configuration B (Filename: 9100ng).

Table 9. Identification of numbered peaks in Figure 12 (HMW by-products from NG pyrolysis).

Peak #	Compound	Formula	MW	% Area
1	LMW gases	-	-	96.1
2	toluene	C_7H_8	92	0.2
3	styrene	C_8H_8	104	0.3
4	NG	$C_3H_5N_3O_9$	227	3.1
5	propanoic acid, 2-methyl,-3-hydroxy	$C_{12}H_{24}O_3$	216	0.4
	-2,4,4-trimethylpentyl ester			
			Total Area	100.0

Triacetin

Triacetin is a compound that is not thermally sensitive. Its pyrogram is shown in Figure 13, and Table 10 lists the identified products. It produces only a small amount of light gases while a large amount reaches the detector unaffected despite experiencing the 900 °C environment. In agreement with Configuration B data, ace-

tic acid is the major by-product. Many of the unidentified products are transformations of the triacetin structure into smaller fragments containing ester, ether, and carbonyl groups. The common 43 amu peak is due to the CH3C=O fragment.
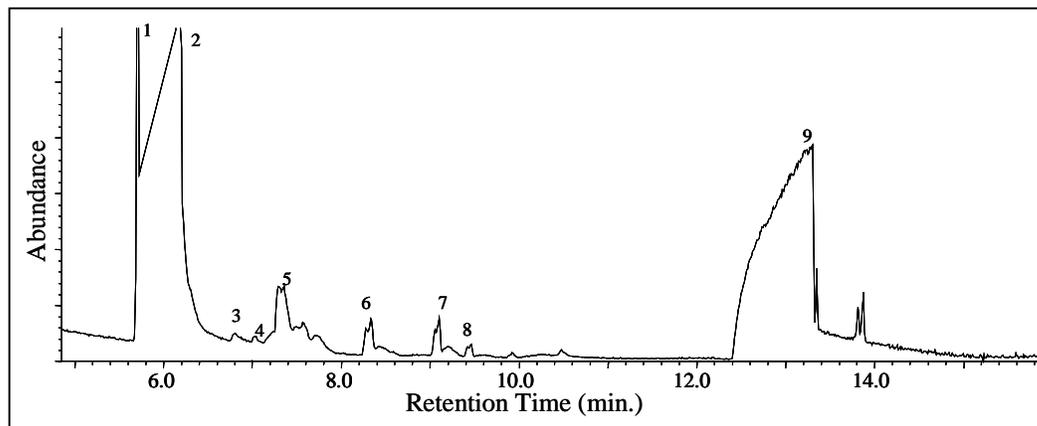
Figure 13. HMW pyrogram of triacetin using Configuration B (Filename: triacta.d).

Table 10. Identification of numbered peaks in Figure 13 (HMW by-products from triacetin pyrolysis).

Peak #	Compound	Formula	MW	% Area
1	LMW gases	-	-	4.7
2	acetic acid	$C_2H_4O_2$	60	74.5
3	2,3-butanedione	$C_4H_6O_2$	86	0.4
4	acetic acid ethenyl ester	$C_4H_6O_2$	86	0.2
5	98, 68, 40 amu	-	-	3.9
6	116, 74, 43 amu	-	-	12.0
7	116, 115, 73, 61, 43 amu	-	-	3.7
8	116, 115, 73, 61, 43 amu	-	-	0.5
9	triacetin	$C_9H_{14}O_6$	218	-
			Total Area	100.0

Di-n-propyladipate

This compound behaves similarly to triacetin. The pyrogram is shown in Figure 14, and Table 11 identifies the numbered peaks. Peaks 1, 2, and 3 co-elute so the values given for the % Area may not be accurate. Pyrolysis of di-n-propyladipate produces a small amount of light gases, acetic acid, and cyclopentanone as major by-products and a large amount of the adipate as undegraded material. Di-n-propyladipate has a similar structure to triacetin with the presence of ester groups but, unlike triacetin, the adipate pyrolytically forms aromatic species such as naphthalene and indene. This formation is likely a result of the adipate containing longer contiguous carbon-carbon bond chain lengths.
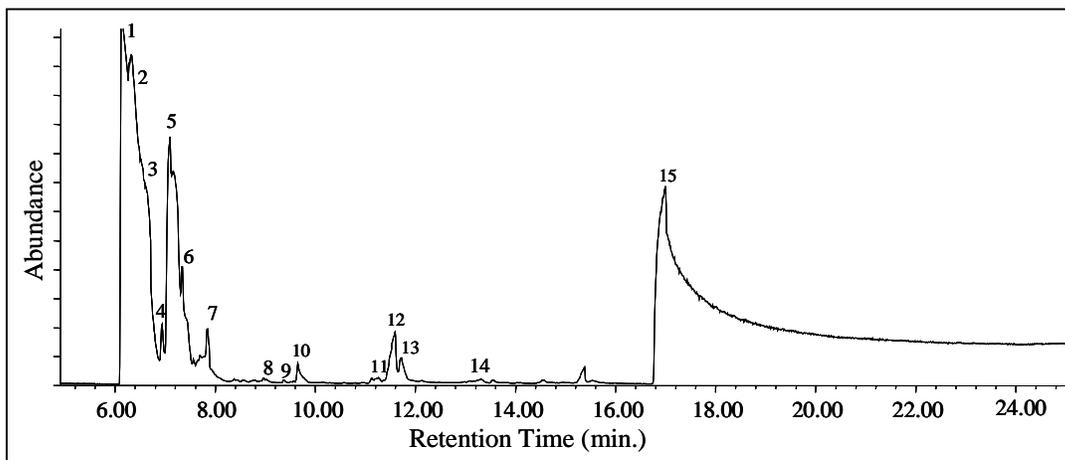
Figure 14. HMW pyrogram of di-n-propyladipate using Configuration B (Filename: dpadpt.a).

Table 11. Identification of numbered peaks in Figure 14 (HMW by-products from di-n-propyladipate pyrolysis).

Peak #	Compound	Formula	MW	% Area
1	LMW gases	-	-	63.1
2	acetic acid	$C_2H_4O_2$	60	2.3
3	benzene	C_6H_6	78	2.5
4	toluene	C_7H_8	92	0.7
5	cyclopentanone	C_5H_8O	84	23.2
6	2-cyclopenten-1-one	C_5H_6O	82	0.05
7	styrene	C_8H_8	104	2.2
8	benzofuran	C_8H_6O	118	0.05
9	1-ethenyl-3-methylbenzene	C_9H_{10}	118	0.1
10	indene	C_9H_8	116	0.7
11	1-methyl-1H-indene	$C_{10}H_{10}$	130	0.3
12	cyclopentanone	C_5H_8O	84	3.4
13	naphthalene	$C_{10}H_8$	128	0.7
14	2-methylnaphthalene	$C_{11}H_{10}$	142	0.4
15	di-n-propyladipate	$C_{12}H_{22}O_4$	230	-
			Total Area	100.0

NDPA

This compound is the only component of AA2 that has aromatic structure. The pyrogram of NDPA in Figure 15 shows the most complex pyrolysate of any AA2 constituent based on the sheer number of peaks. Table 12 lists the identified peaks in the figure. All by-products contain aromatic ring structures. The largest aromatic by-products noted using Configuration B, benzene and phenol, are also observed in this pyrogram. The major pyrolysis species observed in this experiment are phenazine and carbazole. Many by-products contain a heteroatom in the ring structure as well.
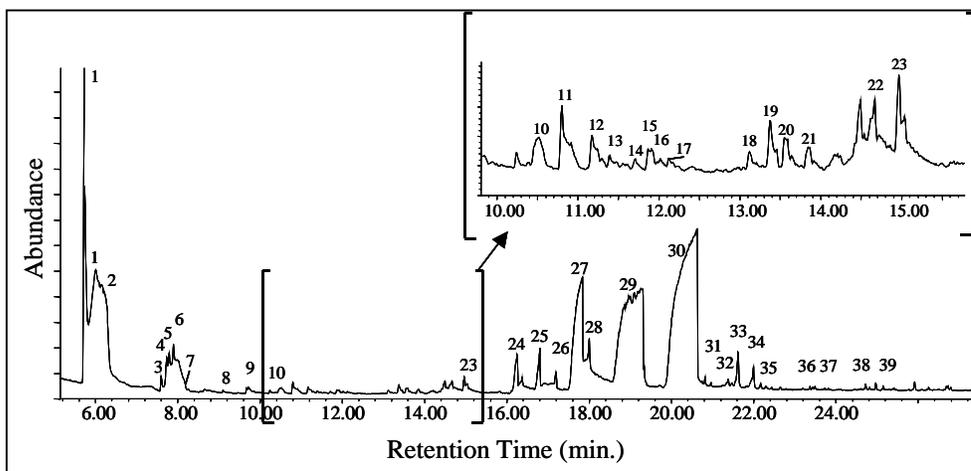
Figure 15. HMW pyrogram of NDPA using Configuration A (Filename: ndpa2.d).

Table 12. Identification of numbered peaks in Figure 15 (HMW by-products from NDPA pyrolysis).

Peak #	Compound	Formula	MW	% Area
1	LMW gases	-	-	27.7
2	benzene	C_6H_6	78	3.4
3	isocyanatobenzene	C_7H_5NO	119	0.3
4	phenol	C_6H_6O	94	0.5
5	aniline	C_6H_7N	93	0.4
6	benzonitrile	C_7H_5NO	103	6.7
7	benzoxazole	C_7H_5NO	119	0.03
8	nitrobenzene	$C_6H_5NO_2$	123	0.1
9	2-nitrophenol	$C_6H_5NO_3$	139	0.4
10	azulene	$C_{10}H_8$	128	0.4
11	quinoxaline	$C_8H_6N_2$	130	0.6
12	isoquinoline	C_9H_7N	129	0.3
13	2-aminobenzonitrile	$C_7H_6N_2$	118	0.1
14	4-methylquinoline	$C_{10}H_9N$	143	0.1
15	indole	C_8H_7N	117	0.2
16	3-isoquinolinamine	$C_9H_8N_2$	144	0.04
17	2-methylquinoline	$C_{10}H_9N$	143	0.05
18	biphenyl	$C_{12}H_{10}$	154	0.1
19	o-nitroaniline	$C_6H_6N_2O_2$	138	0.3
20	4-phenylpyrimidine	$C_{10}H_8N_2$	156	0.3
21	2-ethenylquinoline	$C_{11}H_9N$	155	0.2
22	2-naphthalenecarbonitrile	$C_{11}H_7N$	153	1.2
23	dibenzofuran	$C_{12}H_8O$	168	0.7
24	diphenylamine	$C_{12}H_{11}N$	169	1.3
25	5H-indeno-[1,2-b]-pyridine	$C_{12}H_9N$	167	1.3
26	9H-pyrido-[3,4-b]-indole	$C_{11}H_8N_2$	168	0.4
27	phenazine	$C_{12}H_8N_2$	180	18.4
28	2-aminodiphenyl ether	$C_{12}H_{11}NO$	185	0.9

Peak #	Compound	Formula	MW	% Area
29	carbazole	$C_{12}H_9N$	167	30.7
30	NDPA	$C_{12}H_{10}N_2O_2$	214	-
31	2-phenazinol	$C_{12}H_8N_2O$	196	0.1
32	phenazine-5-oxide	$C_{12}H_8N_2O$	196	0.3
33	phenoxazine	$C_{12}H_9NO$	183	1.1
34	3-nitrocarbazole	$C_{12}H_8N_2O_2$	212	0.9
35	4-dibenzofuranamine	$C_{12}H_9NO$	183	0.1
36	9-phenyl-9H-carbazole	$C_{18}H_{13}N$	243	0.05
37	benzo(a)phenazine	$C_{16}H_{10}N_2$	230	0.04
38	2,2'-biquinoline	$C_{18}H_{12}N_2$	256	0.1
39	9-phenyl-9H-carbazole	$C_{18}H_{13}N$	243	0.1
			Total Area	100.0

Candelilla Wax

Analysis of waxes has a history of application in the field of art and cultural materials. Use of wax as a media in these areas has necessitated development of techniques to analyze and characterize the wax (Wampler 1995). Due to its complex array of constituents, the pyrogram of a wax is complex. Figure 16 shows the pyrogram of candelilla wax. Table 13 gives a general identification of the numbered peaks. The shape and features of the pyrogram agree well with a pyrogram given for this wax in the literature (Wampler 1995, page 135). According to the Aldrich catalog, candelilla wax is a mixture of monoesters (C_{40} to C_{62}) (28-29 wt %), alcohols, sterols, and resins (12-14 wt %), and hydrocarbons (C_{29} to C_{33}) (50-60 wt %). A substantial peak (#1) in the pyrogram is due to lighter weight species that would separate well under the conditions of Configuration A. The dominant recognizable feature, however, is the regular series of triplets that are commonly observed during pyrolysis of polymers. The triplet comprises the diene, the alkene (the dominant peak), and the alkane for a particular carbon number (Wampler 1995). Candelilla wax produces peaks beginning at a carbon number of nine (nonene, peak 6) up to a carbon number of 30 (triacontane, peak 35). The triplet features are not well resolved for the higher carbon number peaks. The percent area listed for a hydrocarbon combines the area under all three peaks.

The large fraction of HMW by-products produced from pyrolysis of candelilla wax shows that caution is well served in omitting this material from analysis using Configuration A. Prolonged contamination, clogging, and perhaps irreversible degradation of the PoraPLOT Q column may have occurred. Memory effects of the wax were persistent in this configuration for many blank runs despite elevated temperatures of all system components.
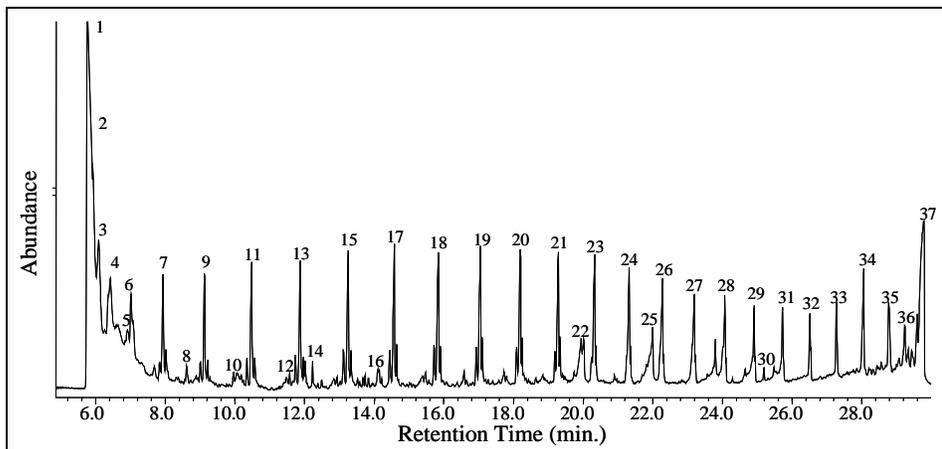
Figure 16. HMW pyrogram of candelilla wax using Configuration A (Filename: cadwax.d).

Table 13. Identification of numbered peaks in Figure 16 (HMW by-products from candelilla wax pyrolysis).

Peak #	Compound	Formula	MW	% Area
1	LMW gases	-	-	35.2
2	2-methyl-1-pentene	C_6H_{12}	84	0.3
3	benzene	C_6H_6	78	1.3
4	toluene	C_7H_8	92	1.8
5	xylene	C_8H_{10}	106	0.3
6	C_9 hydrocarbons	C_9H_{18}	126	1.2
7	C_{10} hydrocarbons	-	-	2.2
8	indene	C_9H_8	116	0.3
9	C_{11} hydrocarbons	-	-	1.7
10	1-methylindene	$C_{10}H_{10}$	130	0.8
	naphthalene	$C_{10}H_8$	128	
11	C_{12} hydrocarbons	-	-	2.3
12	1,1-dimethyl-1H-indane	$C_{11}H_{12}$	144	0.4
13	C_{13} hydrocarbons	-	-	2.5
14	1-methyl-naphthalene	$C_{11}H_{10}$	142	0.3
15	C_{14} hydrocarbons	-	-	2.6
16	biphenylene	$C_{12}H_8$	152	0.5
17	C_{15} hydrocarbons	-	-	2.9
18	C_{16} hydrocarbons	-	-	2.8
19	C_{17} hydrocarbons	-	-	3.0
20	C_{18} hydrocarbons	-	-	3.0
21	C_{19} hydrocarbons	-	-	2.6
22	hexadecanoic acid	$C_{16}H_{32}O_2$	256	2.1
23	C_{20} hydrocarbons	-	-	2.3
24	C_{21} hydrocarbons	-	-	2.2
25	octadecanoic acid	$C_{18}H_{36}O_2$	284	2.1
26	C_{22} hydrocarbons	-	-	1.9
27	C_{23} hydrocarbons	-	-	1.9
28	C_{24} hydrocarbons	-	-	3.2

Peak #	Compound	Formula	MW	% Area
29	C_{25} hydrocarbons	-	-	2.0
30	bis(2-ethylhexyl)phthalate	$C_{24}H_{38}O_4$	390	0.1
31	C_{26} hydrocarbons	-	-	1.7
32	C_{27} hydrocarbons	-	-	1.3
33	C_{28} hydrocarbons	-	-	1.2
34	C_{29} hydrocarbons	-	-	2.0
35	C_{30} hydrocarbons	-	-	1.3
36	408, 393 amu	-	-	0.6
37	436 amu	-	-	6.3
			Total Area	100.0

Discussion

Table 14 summarizes and compares the pyrolytic products from AA2 and its con-
stituents. All of the AA2 by-products are listed followed by the constituent that also
produces this compound during pyrolysis. Out of nearly 60 AA2 pyrolytic byprod-
ucts, only 6 are not produced by one or more of the constituents. These six may
originate from homogeneous interactions between gaseous by-products of different
constituents or may be a result of heterogeneous reactions between a gaseous by-
product and unreacted solid residue left in the pyrolysis chamber. All six species
are very minor and trace compounds based on the % Area values in Tables 1 and 7
with the largest being formamide at 0.2 percent of the total area of LMW products
from AA2. Chemical interactions among the by-products are therefore not a major
source of novel by-products during thermal degradation of AA2. This observation
means that the set of by-products produced from AA2 has the following additive
property:

  [By-products from AA2 pyrolysis] = Sum [By-products from AA2 constituent pyrolysis]

It is possible that the rapid removal of the gaseous products from the pyrolysis
chamber by the helium carrier gas prevents subsequent reactions. Furthermore,
the organometallic salt is the only AA2 constituent not pyrolyzed individually. It
apparently contributes no gaseous organic by-products and has no marked effect on
the pyrolytic degradation mechanisms of any other AA2 constituents.

Most of the LMW pyrolytic by-products of AA2 are also produced by more than one
of the constituents. The light permanent gases and water are common to the pyro-
lysis of all five constituents but, surprisingly, 2-propanol and benzene are common
as well. Pyrolysis of NC alone can duplicate most of the AA2 pyrolytic by-products,
indicating this component of AA2 as the primary origin of the LMW fraction. The

other four contribute equally to the total LMW fraction with nearly 14 separate by-products each.

Table 14. Compounds from pyrolysis of AA2 followed by the AA2 component that also produces this compound during pyrolysis.

LMW By-Products Compound	AA2 Component of Origin[a]					HMW By-Products Compound	AA2 Component of Origin[a]					
carbon monoxide, nitric oxide	1	2	3	4	5	LMW gases, 2-propenal	1	2	3	4	5	6
carbon dioxide	1	2	3	4	5	acetic acid	1		3	4		
acetylene	1	2	3		5	2-butenal			3			
ethane			3			methyl formate	1					
water	1	2	3	4	5	benzene	1	2	3	4	5	6
formaldehyde	1	2				2-propanoic acid				4		
hydrogen cyanide	1	2			5	acetic acid, 2-propenyl ester			3			
propene	1	2	3	4		pyridine					5	
1,2-propadiene	1		3			toluene	1	2	3	4		6
1-propyne				4		3-furancarboxaldehyde						
methanol	1				5	2-furancarboxaldehyde	1					
ethylene oxide	1	2	3	4		styrene		2		4		
methyl formate	1					cyclopentanone				4		
1-buten-3-yne	1		3	4	5	p-benzoquinone						
1,3-butadiene	1	2				isocyanatobenzene					5	
formamide						benzaldehyde						
acetonitrile	1				5	phenol					5	
formic acid	1	2				benzonitrile					5	
2-propenal	1	2	3	4	5	benzofuran				4		
furan	1				5	benzoxazole					5	
propanal	1			4		hydroxybenzaldehyde						
acetone	1	2	3			indene				4		6
2-propenenitrile	1	2				2-nitrophenol					5	
formic acid, 2-propenyl ester						naphthalene				4		6
acetic acid	1		3	4		quinoxaline					5	
3-buten-2-one	1		3	4		isoquinoline					5	
benzene	1	2	3	4	5	triacetin			3			
acetic acid, 2-propenyl ester			3			NG		2				
pyridine					5	2-ethenylquinoline					5	
cyclopentanone				4		di-n-propyladipate				4		
2-furancarboxaldehyde	1					phenazine					5	
phenol					5	carbazole					5	
						NDPA					5	

[a] The AA2 component of origin is (1) NC, (2) NG, (3) triacetin, (4) di-n-propyladipate, (5) NDPA, and (6) candelilla wax.

HMW by-products show a different behavior. Many of these AA2 by-products are produced by only one of the components. Therefore, the production of any one of these by-products during high temperature degradation can be eliminated by removing all presence of the originating constituent in AA2. NDPA produces a bulk of these HMW species. In fact, besides the presence of the POHC NG, all of the nitrogen-containing HMW species from pyrolysis of AA2 originate from the NDPA. Substituting a "greener" non-nitrogen-containing chemical for NDPA would alleviate production of these species.

It is not surprising that NC and NG contribute so many pyrolytic by-products and that the majority of these are in the LMW fraction. These two compounds comprise nearly 90 percent of AA2 with NC at 46.5 to 52.5 percent by weight and NG at approximately 38.8 percent by weight. Triacetin (2.7 percent), NDPA (1.5 to 2.5 percent) and di-n-propyladipate (1.6 percent), however, are minor components that even so are the sole origin of many of the by-products in AA2. As expected, the candelilla wax contributes little (only 0.1 percent by weight); the regular hydrocarbon series of wax pyrolysis was not observed.

Numerous pyrolytic products from the constituents are not observed in the AA2 pyrograms. As indicated earlier, this is most likely a concentration effect. A 2-mg sample of AA2 contains only 50 μg triacetin or NDPA and 2 μg candelilla wax. Pyrolysis of these minute amounts of sample will not produce appreciable peaks. Examination of the LMW pyrograms indicates good agreement of by-products between AA2 and the constituents. For NC, any pyrolytic by-product larger than 0.5 percent area is also present in the AA2 pyrograms. The exception is ethyl acetate at 1.4 percent area. Similarly, even minor peaks in the pyrogram of NG are also present in the AA2 pyrogram except for ethylenediamine (0.4 percent area). The largest peak in the triacetin pyrogram not present in the AA2 pyrogram is 1-butene (1 percent area); for di-n-propyladipate, it is ethane (2.7 percent area); and for NDPA, it is pyridine (0.9 percent area).

The HMW pyrograms do not display the same quality agreement as the LMW pyrograms. The broad unresolved envelope of peaks in the HMW pyrogram of NC (Figure 11) appears to be reproduced in the HMW pyrogram of AA2 (Figure 10) but the peaks identified in Table 8 are not detected. Only the minor propanoic acid ester by-product of NG is not also produced by AA2. Many of the di-n-propyladipate are present, but most of the minor pyrolytic products for triacetin, NDPA, and candelilla wax are not detected in the pyrogram of AA2.

The number of LMW and HMW by-products can be added for each constituent of AA2. NC contributes 25 by-products that are present in the AA2 pyrograms; NG = 16, triacetin = 18, di-n-propyladipate = 20, NDPA = 23, and candelilla wax = 5.

Perhaps more important is the unique contribution each constituent makes to the AA2 set of by-products. NC produces two compounds by pyrolysis that are also produced by AA2 pyrolysis (methyl formate and 2-furancarboxaldehyde) and are not produced by any other constituent. Therefore, NC is clearly the origin for these two compounds when AA2 is pyrolyzed and, conversely, elimination of NC would eliminate the production of these two compounds. The numbers for the other constituents are NG = 1, triacetin = 4, di-n-propyladipate = 5, NDPA = 12, and candelilla wax = 0. Clearly, the minor and trace constituents, and in particular, NDPA, play an inordinately important role in the production of pyrolysis products by AA2.

Pyrolysate Origins

Ideal incineration results in complete degradation of organic compounds; specifically, complete oxidation to carbon dioxide and water. Zones close to burning areas can be heated by conduction, convection, or radiation and, together with a lack of oxidant, pyrolytic processes take over in these zones and lead to PIC. Pyrolysate and undecomposed small molecules (POHC) can escape by volatilization, distillation, and aerosol formation (Moldoveanu 1998). Pyrolysis experiments can determine the compounds that are likely to be present (POHC and PIC) and the origin of each compound.

At least seven primary reaction mechanisms are frequently observed during pyrolysis:
- Elimination reactions eject a small component from the molecule and are frequently the mechanism by which water is produced from compounds containing hydroxyl groups.
- Fragmentation is the breakdown of the molecular main chain, usually a first step in polymer pyrolysis.
- Extrusion reactions are best described by the reaction M-A-B producing M-A + B.
- Eliminations involving free radicals again produces a small component from the molecule but the ejected fragment is a free radical capable of initiating further reactions. This mechanism can explain the formation of unsaturated bonds and aromatic species from aliphatic compounds.
- Bond rearrangements can occur (M-A-B to A-B-M) and are characterized by the lack of a leaving group.
- Oxidation and reduction chemistry is common, although with a lack of oxidant, reduction reactions are more likely.
- Substitutions (M-A + B to M-B + A) and additions (M + A to M-A) are possible.

These types of reactions can form complex multi-ring structures and larger pyrolytic products from smaller initial compounds. Generally, however, these reactions are driven by the production of compounds that are more stable at higher temperatures. Other less common or specialized reactions are also observed. More detail on these pyrolytic reaction mechanisms can be found in Moldoveanu (1998). One key element leading to the further complexity of pyrolysis is that any of the by-products can become initial compounds in further pyrolytic breakdown by any of the mechanisms given earlier.

Using the available pyrolytic mechanisms, the production of nearly any observed by-product can be described. Many mechanistic pathways for the same product are common and numerous mechanisms are required to account for all products (Conley 1970). Comprehensive analysis of all observed by-products is beyond the scope of this report and would fall completely into the realm of conjecture. Rapid time-resolved experiments are required to uncover the evolution of reactions and the structure of intermediates. In addition, care must be taken to immediately separate the gaseous by-products from any remaining solid residue and the heat source to minimize interactions between by-products and eliminate the possibility of homogeneous and heterogeneous secondary reactions (Phillips, Orlick, and Steinberger 1955). This care was not taken in these experiments, yet the results remain applicable to incineration conditions since the careful conditions described above clearly do not occur in the rotary kiln. In fact, the data shown earlier supports the statement that, when composite materials such as AA2 are pyrolyzed, each component can be considered to have started the pyrolysis process independently (Moldoveanu 1998). The components of AA2 and their by-products show little interaction during pyrolysis.

Nitrocellulose

Previous work on the thermal decomposition of NC produced the following gaseous by-products: NO, CO_2, CO, N_2O, N_2, H_2O, NO_2, HCN, CH_2O, HONO, CH_4, C_2H_4O, C_3H_4O, and C_3H_6O (Urbanski 1964; Oyumi and Brill 1986; Wolfram et al. 1955; Kaur et al. 1986). The work reported here observed all of these components except N_2, NO_2, and HONO, which are either short-lived reactive species that do not survive the chromatographic process, or not well separated from the other large permanent gas peaks. Many more products were observed in this work, possibly a result of other heterogeneous and secondary reactions that are not primary pyrolysis reactions. The NC polymer can undergo both fragmentation of the backbone and elimination reactions to produce many of the light gases listed earlier. Pyrolysis of cellulose shows more products than NC (Moldoveanu 1998) because the energetic nature of NC promotes rapid breakdown by the exothermic contribution of additional energy. Elimination and addition reactions produce polycyclic aromatic

hydrocarbons (PAH) from cellulose, so the appearance of benzene and toluene from NC is not surprising. Production of any other by-product from NC can be explained by a combination of the mechanisms listed earlier. Furan, for instance, is a by-product of major concern. NC may first undergo rapid elimination of NO_2 groups from the polymer followed by chain scission to monomer units. Oxidation followed by extrusion of CO_2 groups can result in the five-membered unsaturated rings of furan, especially since the glucosidic rings already contain oxygen. The complexity of this mechanism is reflected in the low abundance of furan (Table 2).

Nitroglycerin

Thermal decomposition of NG results in NO, CO, CO_2, N_2, N_2O, H_2, and H_2O (Urbanski 1964). Only N_2 and H_2 are not observed in this work since N_2 likely co-elutes with other light gases and the mass spectrometer cannot measure the low molecular mass of H_2. For NG, rapid elimination of the nitrogen oxides is a likely first step, leaving the three-carbon chain. Fragmentation can produce the formic acid. Reduction of the nitrogen oxides or the nitro groups to amine groups is required to produce ethylenediamine followed by extrusion or elimination of a carbon. Again, addition reactions can produce benzene and toluene from the three-carbon chains.

Triacetin and Di-n-propyladipate

Pyrolysis of triacetin produces acetic acid as the major product due to elimination reactions at three different positions on the molecule. Formation of two acetic acid molecules leaves a remainder of acetic acid, 2-propenyl ester. Elimination of acetaldehyde from this remainder yields the 1-acetyloxy-2-propanone. Di-n-propyladipate can undergo fragmentation reactions to produce propene at two different positions on the molecule. The center portion of the molecule can then fragment and recombine to form propanol and cyclopentanone. It is important to note that neither triacetin nor di-n-propyladipate degrades to form a nitrogen-containing by-product. This observation lends credence to the mass spectral library matching to identify peaks, and it also indicates the integrity of the pyrolysis system from air leaks.

NDPA

NDPA results in the greatest number of pyrolytic by-products with all of the HMW products containing aromaticity. Fragmentation is the most logical first step for the monoaromatic ring compounds followed by radical attack, oxidation, or reduction to form compounds such as phenol, nitrophenol, aniline, and isocyanatobenzene. The primary mechanism, however, is a type of substitution reaction due to the proximity of either the nitro group or the two phenyl groups. A new ring is created between

the phenyl groups that includes the amino nitrogen atom with the elimination of H_2, NO_2, or H_2O to form the dominant species phenazine and carbazole.

Candelilla Wax

Candelilla wax comprises numerous compounds that contain long chains of carbon-carbon bonds. These long chains degrade by random scission to produce free radicals that frequently stabilize by forming terminal double bonds and a new radical species (Wampler 1995). An oligomeric pattern of triplets is observed in the pyrogram in the order diene, alkene, and alkane for each chain of a particular carbon number. The remaining small pyrolytic species are likely the additional components present in the wax.

4 Conclusion

Pyrolysis experiments comparing the behavior of AA2 with the behavior of individual constituents of AA2 provide an excellent example of the additive property that sometimes exists during thermal degradation of composites. The origin of each pyrolytic by-product from AA2 can be deduced by examination of the set of pyrolysis products from each constituent. Many AA2 by-products have a unique constituent of origin, but more by-products originate from several sources. NDPA is the single source of most HMW species, most nitrogen-containing products, and most aromatic by-products. Elimination of NDPA from AA2 would have the greatest impact in reducing the number and toxicity of by-products from thermal degradation processes with AA2.

Previous work on PIC origin during incineration pinpointed pyrolytic pockets as the source of all PIC. This data set of degradation products from pyrolysis of AA2 may be viewed as the predicted list of PIC emanating from these pockets and POHC that have sufficient thermal stability to survive non-optimal incineration conditions. Future work will compare these data to incineration emission data to assess the value of bench-scale pyrolysis as a predictive method.

References

Behrens, R., Jr., *J. Phys. Chem.*, 94, (1990), p 6706.

Botcher, T.R. and C.A. Wight*, J. Phys. Chem.*, 97 (1993).

Brill, T.B. and K.J. James, *Chem. Rev.*, 93 (1993a).

Brill, T.B. and K.J. James, *J. Phys. Chem.*, 97 (1993b).

Conley, R.T., *Thermal Stability of Polymers*, Volume 1, Marcel Dekker, Inc., NY, 1970.

Dellinger, B., D.L. Hall, J.L. Graham, S.L. Mazer, W.A. Rubey, and M. Malanchuk, EPA Project Summary, EPA/600/S2-86/006, July 1986.

Dellinger, B., P.H. Taylor, and D.A. Tirey, EPA Project Summary, EPA/600/S2-90/039, May 1991.

Duvall, D.S., W.A. Rubey, and J.A. Mescher, EPA Project Summary, EPA/600/9-80/011, March 1980.

Fisher, E.M. and C.P. Koshland, *Combust. Flame*, 90 (1992).

Graham, J.L., D.L. Hall, and B. Dellinger, *Environ. Sci. Technol.*, 20 (1986).

Kaur, B., R.K. Jain, I.S. Gur, and H.L. Bhatnagar, *J. Anal. Appl. Pyrol.*, 9 (1986).

Koshland, C.P. and M.J. Thomson, *Combust. Sci. Technol.*, 85 (1992).

Kubota, N. and S. Sakamoto, *Prop. Explos. Pyrotech.*, 14 (1989).

Lee, W-J., B. Cicek, and S.M. Senkan, *Environ. Sci. Technol.*, 27 (1993).

Maksimov, Y.Y., *Russ. J. Phys. Chem.*, 45 (1971), p 441.

Moldoveanu, S.C., *Analytical Pyrolysis of Natural Organic Polymers, Techniques and Instrumentation in Analytical Chemistry* – Volume 20, Elsevier, NY, 1998.

National Research Council (NRC), *Prudent Practices for Disposal of Chemicals from Laboratories,* National Academy Press Washington, DC, 1983, Chapter 9.

Oyumi, Y. and T. Brill, Combust. Flame, 66 (1986).

Oyumi, Y., Y. Mitarai, and H. Bazaki, *Prop. Explos. Pyrotech.*, 18 (1993).

Phillips, R.W., C.A. Orlick, and R. Steinberger, *J. Phys. Chem.*, 59 (1955).

Sidhu, S., N. Kasti, P. Edwards, and B. Dellinger, *Chemosphere*, 42 (2001), p 499.

Smith, J.D., R. Vandell, and E.M. Hixson, *Combust. Sci. Technol.*, 101 (1994).

Stratta, J.M. and Associates, Inc. and Life Systems, Inc., *Open Burning-Open Detonation Waste Generation Survey and Alternatives Research Study*, Report for the U.S. Army Construction Engineering Research Laboratory, August 1993.

Subsinsky, M.A. Life Systems, Inc., *Identification and Quantification of Energetic Waste Incinerators and Air Emissions from Energetic Waste Incineration*, Report for the U.S. Army Construction Engineering Research Laboratory, November 1993.

Tanada, T. N., J. Velazquez, N. Hemmi, and T.A. Cool, *Combust. Sci. Technol.*, 101 (1994).

Taylor, P.H. and B. Dellinger, *Environ. Sci. Technol.*, 22 (1988).

Taylor, P.H., B. Dellinger, and C.C. Lee, *Environ. Sci. Technol.*, 24 (1990).

Taylor, P.H., B. Dellinger, and D.A. Tirey, Int. *J. Chem. Kinet.*, 23 (1991).

Taylor, P.H., D.A. Tirey, W.A. Rubey, and B. Dellinger, *Combust. Sci. Technol.*, 101 (1994).

Tirey, D.A., P.H. Taylor, J. Kasner, and B. Dellinger, *Combust. Sci. Technol.*, 74 (1990).

Tirey, D.A., R.C. Striebich, B. Dellinger, and H.E. Bostian, *Haz. Waste and Haz. Mat.*, 8, (1991).

Urbanski, T., *Chemistry and Technology of Explosives*, Volume 2, Pergamon Press, NY, 1964.

Vitovec, W., C.P. Koshland, D. Lucas, and R.F. Sawyer, *Combust. Sci. Technol.*, 116-117 (1996).

Wampler, T.P., *Applied Pyrolysis Handbook*, Marcel Dekker, Inc., NY, 1995.

Wolfram, M.L., J.H. Frazer, L.P. Kuhn, E.E. Dickey, S.M. Olin, D.O. Hoffman, R. S. Bower, A. Chaney, E. Carpenter, and P. McWain, *J. Am. Chem. Soc.*, 77 (1955).

Yinon, J. and S. Zitrin, *Modern Methods and Applications in Analysis of Explosives*, Wiley, NY, 1993.

Young, C.M. and K.J. Voorhees, *Chemosphere*, 23 (1991).

Young, C.M. and K.J. Voorhees, *Chemosphere*, 24 (1992).

CERL Distribution

Chief of Engineers
    ATTN: CEHEC-IM-LH (2)

U.S. Army Environmental Center
    ATTN: SFIM-AEC-TS

Engineer Research and Development Center (Libraries)
    ATTN: ERDC, Vicksburg, MS
    ATTN: Cold Regions Research, Hanover, NH
    ATTN: Topographic Engineering Center, Alexandria, VA

Defense Tech Info Center 22304
    ATTN: DTIC-O

    7
    7/01

REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY) 10-2001	2. REPORT TYPE Final	3. DATES COVERED (From - To)

4. TITLE AND SUBTITLE Pyrolytic Decomposition Studies of AA2, A Double-Base Propellant	5a. CONTRACT NUMBER
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) Donald M. Cropek, Patricia A. Kemme, and Jean M. Day	5d. PROJECT NUMBER 622720D048
	5e. TASK NUMBER EP-UC5
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Engineer Research and Development Center (ERDC) Construction Engineering Research Laboratory (CERL) P.O. Box 9005 Champaign, IL 61826-9005	8. PERFORMING ORGANIZATION REPORT NUMBER ERDC/CERL TR-01-66

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Corps of Engineers 441 G Street, NW Washington, DC 20314-1000	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES
Copies are available from the National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.

14. ABSTRACT

Pyrolysis is the thermal decomposition of a substance into a variety of by-products, usually in the absence of oxygen. This work details pyrolytic studies on AA2, a double-base propellant, currently being incinerated during Army demilitarization operations.

Pyrolysis experiments comparing the behavior of AA2 with the behavior of individual constituents of AA2 provide an excellent example of the additive property that sometimes exists during thermal degradation of composites. The origin of each pyrolytic by-product from AA2 can be deduced by examining the set of pyrolysis products from each constituent. Good matching between pyrolytic and incineration data can support using laboratory pyrolysis to predict incineration behavior.

Samples of original AA2 from an Army installation were collected for analysis. In addition, chemical standards were obtained for the major components of AA2. All samples and standards were subjected to pyrolysis and the by-products were analyzed by gas chromatography/mass spectrometry.

15. SUBJECT TERMS

demilitarization	energetic materials (EM)	pyrolysis
AA2	hazardous waste disposal	munitions waste

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Dr. Donald M. Cropek
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified	SAR	46	19b. TELEPHONE NUMBER (include area code) (217) 373-7445