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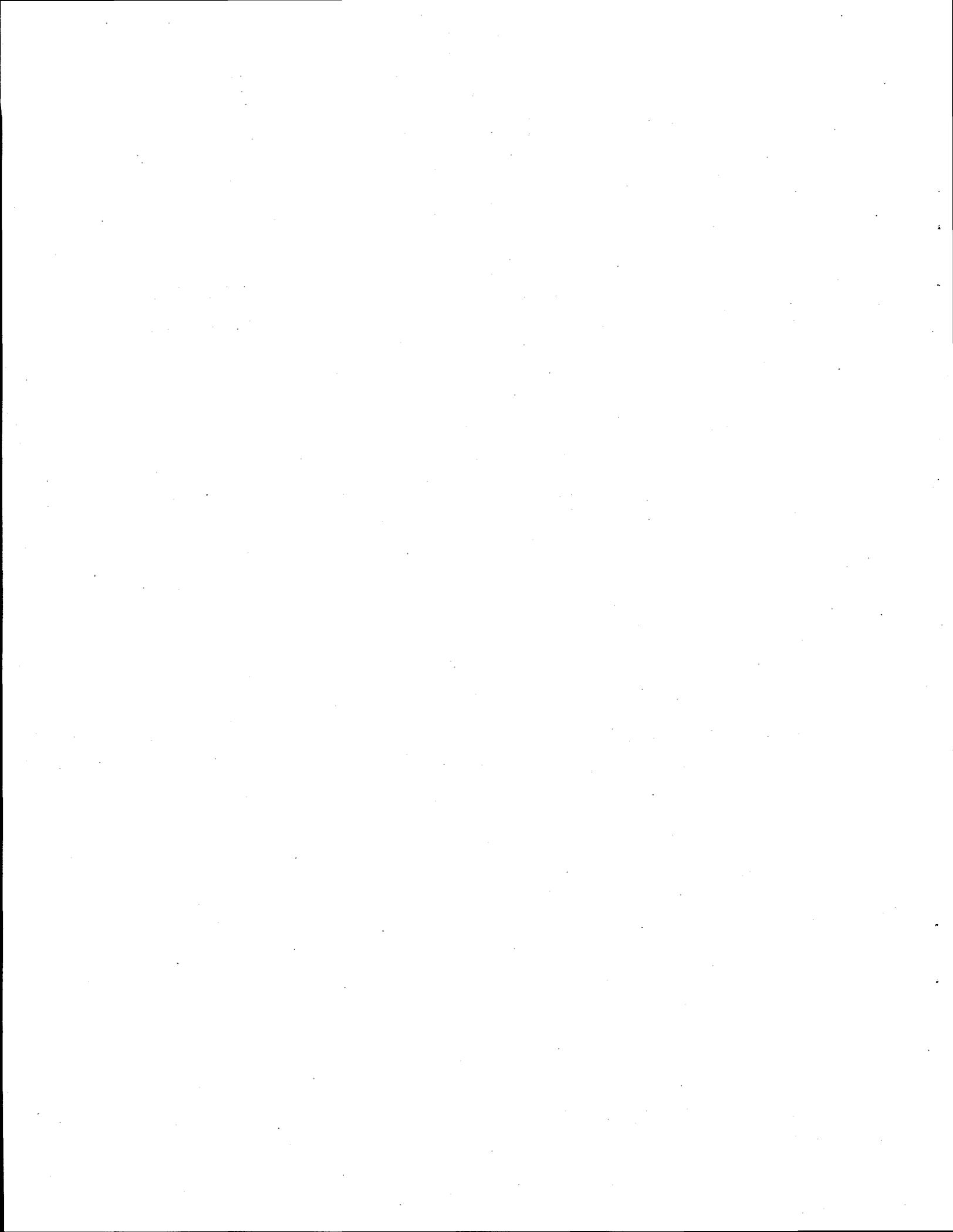
**Thermal Decomposition of
Radiation-Damaged Polystyrene**

J. Abrefah
G. S. Klinger

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Pacific Northwest National Laboratory
Richland, Washington 99352



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Summary

The radiation-damaged polystyrene material ("polycube") used in this study was synthesized by mixing a high-density polystyrene ("Dylene Fines # 100") with plutonium and uranium oxides. The polycubes were used on the Hanford Site in the 1960s for criticality studies to determine the hydrogen-to-fissile atom ratios for neutron moderation during processing of spent nuclear fuel. Upon completion of the studies, two methods were developed to reclaim the transuranic (TRU) oxides from the polymer matrix.

- burning the polycubes in air at 873 K^(a)
- heating the polycubes in the absence of oxygen and scrubbing the released monomer and other volatile organics using carbon tetrachloride.^(b)

Neither of these methods was satisfactory in separating the TRU oxides from the polystyrene. Consequently, the remaining polycubes were sent to the Hanford Plutonium Finishing Plant (PFP) for storage.

Over time, the high dose of alpha and gamma radiation has resulted in a polystyrene matrix that is highly cross-linked and hydrogen deficient, and a stabilization process is being developed in support of Defense Nuclear Facility Safety Board Recommendation 94-1. Baseline processes involve thermal treatment to pyrolyze the polycubes in a furnace to decompose the polystyrene and separate out the TRU oxides. Thermal decomposition products from this degraded polystyrene matrix were characterized by Pacific Northwest National Laboratory to provide information for determining the environmental impact of the process and for optimizing the process parameters. A gas chromatography/mass spectrometry (GC/MS) system coupled to a horizontal tube furnace was used for the characterization studies. The decomposition studies were performed both in air and helium atmospheres at 773 K, the planned processing temperature. The volatile and semi-volatile organic products identified for the radiation-damaged polystyrene were different from those observed for virgin polystyrene. The differences were in the number of organic species generated and their concentrations.

In the inert (i.e., helium) atmosphere, the major volatile organic products identified (in order of decreasing concentrations) were styrene, benzene, toluene, ethylbenzene, xylene, naphthalene, propane, alpha-methylbenzene, indene, and 1,2,3-trimethylbenzene. In air, the major volatile organic species identified changed slightly, with the addition of benzaldehyde.

(a) Uppington, G. W., and L. E. Bruns. 1967. *Polystyrene-PuO₂ Flowsheet and Start-up Procedure*. ISO-989, General Electric, Richland, Washington.

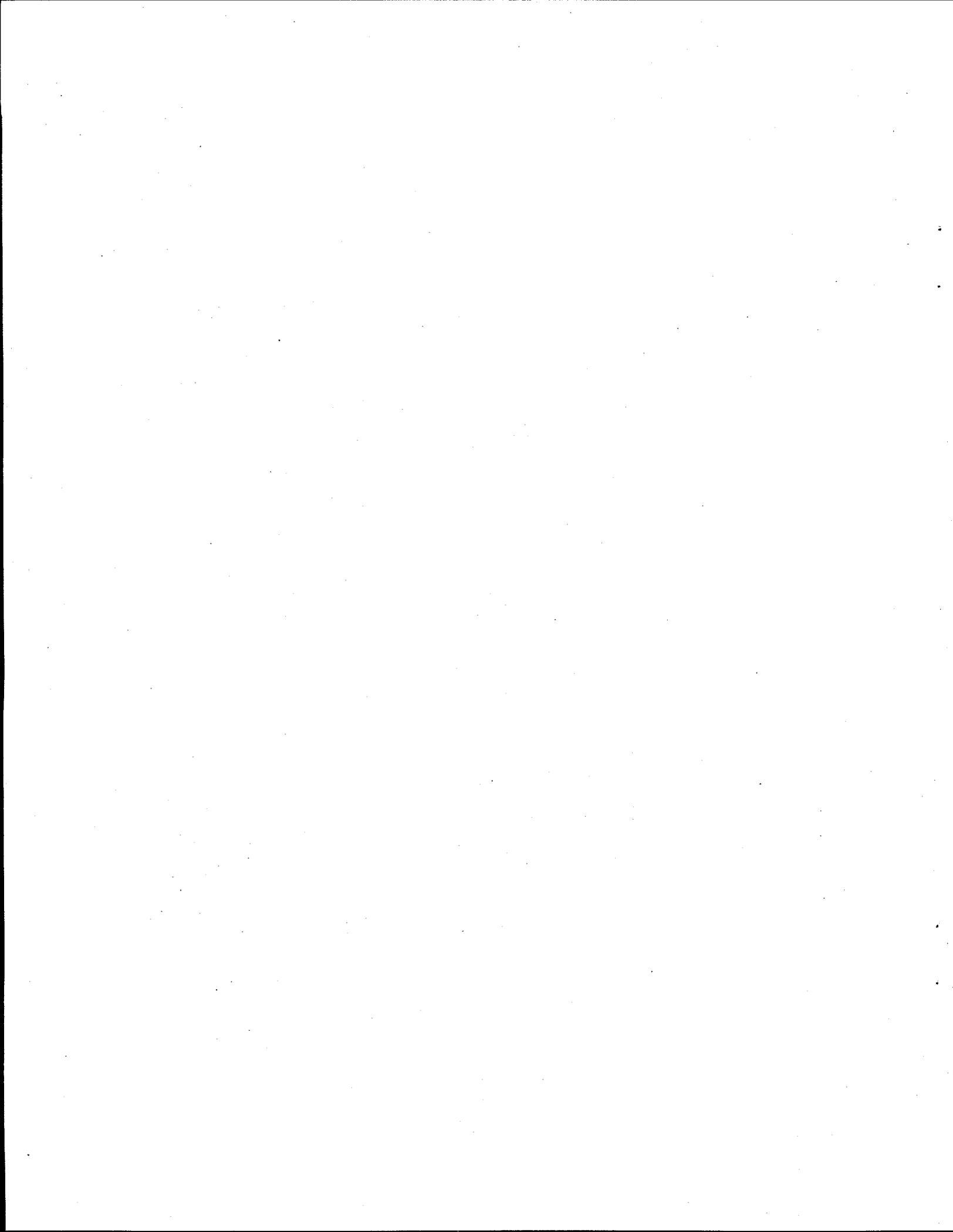
(b) Felt, R. E. 1969. *Plutonium Dioxide Recovery from Polystyrene Cubes by Distillation*. ARH-1391, Atlantic Richfield Hanford Company, Richland, Washington.

The concentrations of the organic species in the inert atmosphere were significantly higher than those for the air atmosphere processing. For example, the concentration of benzene in the inert atmosphere was about two times higher than in air, and xylene in inert was seven times that of the air atmosphere concentration. Overall, 39 volatile organic species were identified in the inert atmosphere compared to 48 species in air. Twenty of the 39 species in the inert conditions were also products in the air atmosphere, and the remaining 19 of the organic species that were identified in the inert atmosphere were not generated during the thermal decomposition in air. Twenty oxidized organic products were identified during thermal processing in air, and 7 (butylbenzene, sec-butylbenzene, naphthalene, 1,2-dihydro, naphthalene 2-methyl-, biphenyl, 1,1'-biphenyl, 3-methyl-, naphthalene, 1-ethyl-) additional organic species were generated due the presence of air.

Both the concentrations and number of the major semi-volatile organic compounds (SVOCs) also showed a significant effect of changing the atmosphere (i.e., inert to air). Thirty-one species (SVOCs) were identified in the inert atmosphere compared to 15 in the air atmosphere. Most of the species that were absent in the air treatment were the heavy molecular weight SVOCs. The reduction in the generation of heavy SVOCs will significantly reduce the plating out that will clog filters and pipelines during thermal processing. The SVOCs that were identified in both atmospheres showed higher concentrations in the inert atmosphere, thereby increasing the potential to form films in the piping. Consequently, the oxidation method may be the most effective and economical process to stabilize the damaged polycubes.

Acknowledgments

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1.0 Introduction

The polycubes stored at the Hanford Plutonium Finishing Plant (PFP) have been identified in a Vulnerability Assessment as material that requires a stabilization process in support of Defense Nuclear Facility Safety Board Recommendation 94-1. The baseline plan involves a pyrolysis process to separate out the plutonium and uranium oxides for treatment and packaging for interim storage, in accordance with the Record of Decision, issued June 25 1996, for the *Plutonium Finishing Plant Stabilization Final Environmental Impact Statement*, DOE/EIS-0244-F.

The polycubes, which were manufactured at Hanford in the 1960s for use in criticality studies (Lewis and Meng 1996), are a mixture of plutonium and/or uranium oxides and a polystyrene (vinyl benzene) matrix, cast into the shape of "cubes." The "cubes" vary in size, typically ½ in. x 2 in. x 2 in. up to 2 in. x 2 in. x 2 in. The cubes were sealed with a coating of aluminum paint and/or tape (PVC or Shurtape). An estimated 1600 polycubes (calculated 179 kg net weight) are stored at the PFP, packed in vented food cans with five to eight cubes per can to accommodate gas generation by radiolysis.

The polycubes have a fairly high ²⁴⁰Pu content, and the 7 to 8 Rad/hr contact dose rate presents a challenge for handling. Significant hazards associated with unstabilized polycubes arise from the polystyrene matrix, which generates hydrogen gas due to radiolysis. In addition, some cans of polycubes may contain fines; sufficient data have not been available to assess the hazards associated with the fines.

Baseline processes considered to stabilize the degrading polycubes involve a thermal treatment that will pyrolyze them in a furnace at 773 K to decompose and vaporize the polystyrene. Designing a thermal treatment process must take into account which organic species will be generated during pyrolysis. In particular, identifying products generated during thermal decomposition of the polycubes will provide information that will

- enable accurate estimates of the flammable organic species concentrations in the off-gas stream during testing of larger polycube samples on a TGA/DSC/MS system (Abrefah et al. 2000)
- provide characterization information for environmental effluent analyses during the processing of the polycubes using the PFP muffle furnaces
- identify organic products from pyrolyzing a radiation-damaged polystyrene that can be compared with data from a pure form of polystyrene.

This report describes tests conducted by Pacific Northwest National Laboratory (PNNL) to identify the volatile and semi-volatile organic species that will occur during thermal processing of the PFP polycubes. The experiments and results of tests conducted in air and inert atmospheres are discussed.

2.0 Experimental

The volatile and semi-volatile organic products from the thermal decomposition of polycubes were characterized using a gas chromatography/mass spectrometry (GC/MS) method. Test samples ranging from 0.1 to 1 mg were cleaved from a degraded polycube (Polycube-1504, Figure 2.1) that was one of the polycubes shipped from PFP to PNNL's Radiochemical Processing Laboratory (RPL) for the thermal stabilization studies. The cleaved samples were very small particulates with irregular shapes, and may have different fractions of organic phase to plutonium oxide ratios.

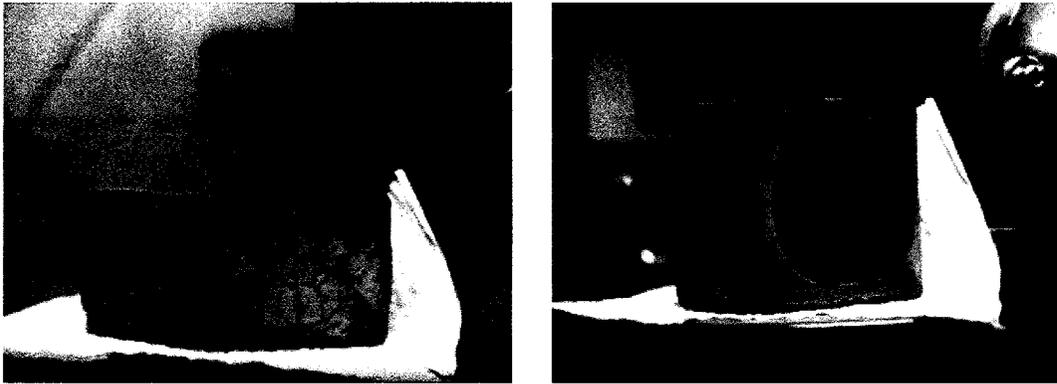


Figure 2.1. Polycube-1504 Sent from PFP to PNNL for the Thermal Stabilization Studies

2.1 GC/MS System

The products from pyrolyzing the degraded polystyrene were analyzed using a Hewlett Packard Model 5890/5989 GC/MS system with methodology similar to USEPA SW-846 methods 8260, 8270, and/or 8275. These methods cover the range of organic compounds from gases, such as butane, through polynuclear aromatic hydrocarbons, such as benzo(a)pyrene. A schematic of the GC/MS system is shown in Figure 2.2. The system consists of a heating cell, a GC/MS, and a sparge gas supply. Separate analyses were performed for volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs).

Typically, pyrolysis gas chromatography (PyGC) is performed using a pyrolysis probe or a pyrolysis autosampler. Since it was expected that pyrolysis of the polycube material will produce highly dispersible aerosol particles, a single-use pyrolysis cell and a heated filter were used to reduce radiological contamination. A horizontal tube furnace was used to heat samples of the polycube in helium and air atmospheres to a maximum temperature of 773 K. The VOCs and SVOCs were analyzed using the methods discussed below.

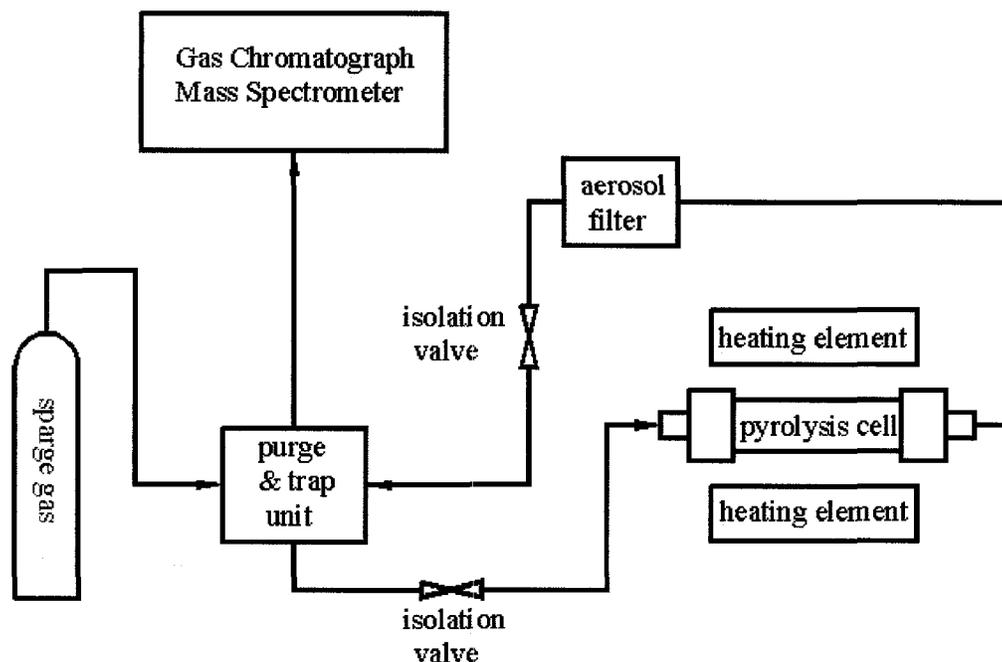


Figure 2.2. Schematic of the GC/MS Pyrolysis System

2.1.1 Volatile Products

The volatile products were analyzed using a standard purge and trap autosampler. The sparging vessel was substituted with a pyrolysis cell made to accommodate milligram-sized solid samples, and to allow for rapid, controlled heating of the sample. Additionally, the system allowed the use of either an inert purge gas, such as helium or argon, or an oxidizing purge gas, such as air. A five-point calibration curve was performed for all compounds (SW-846 analyte list) that included VOCs, such as benzene, toluene, ethylbenzene, xylenes, styrene, n-butylbenzene, sec-butylbenzene, tert-butylbenzene, n-propylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, and p-isopropyltoluene.

2.1.2 Semi-Volatile Products

The pyrolysis experiment for SVOCs was performed using an off-line sample preparation method. The polycube sample was pyrolyzed under the same conditions as in the VOC pyrolysis experiment; however, a solvent-filled sparger was used to trap the pyrolysis products rather than the adsorbent trap used in the VOC purge and trap method. This allowed for the analysis of higher boiling point constituents, such as acenaphthene, acenaphthylene, acetophenone, etc. Many higher boiling point compounds cannot be quantitatively recovered from a solid adsorbent trap; hence, methylene chloride was used as the trapping solvent. The sparger containing the solvent was cooled in a methanol-dry ice bath to reduce evaporation of the methylene chloride while the pyrolysis purge gas flow was being sampled.

2.2 Identification and Quantitation of Uncalibrated Compounds

A computerized search of the National Institute for Standards and Technology mass spectral database and/or interpretation of the mass spectrum fragmentation pattern was used to identify any compounds that were detected but were not part of the calibrated analyte list. Analytes that were not part of the calibration mixture were quantified by comparing the peak response with that of the most closely eluting internal standard.

3.0 Results

As described in Section 2.0, the products of thermal decomposition of a degraded polystyrene (polycube) matrix were characterized using a horizontal tube furnace for heating the polycube samples to a temperature of 773 K. A GC/MS system was used for identifying the VOCs and SVOCs. In addition, a comparison test was performed using a virgin polystyrene sample.

3.1 Polycube Volatile Organic Compounds

The VOCs released and identified by the GC/MS system when a polycube sample (about 0.2 mg) was heated to 773 K are listed in Table 3.1. Table 3.1 also lists the 48 VOCs and their normalized (i.e., normalized to the initial sample weight) concentrations. The concentrations given for the "non-targeted" species were based on internal calibrations and, therefore, may not be representative of their true concentrations. Twenty species in Table 3.1 contain oxygen in the molecular structure, suggesting they are products of either direct oxidation of the polystyrene or gas phase reaction of oxygen (i.e., air) and some of the organic products from pyrolysis. Figure 3.1 shows the chromatogram obtained when the polycube decomposed in the air atmosphere, with indication numbers for some of the species listed in Table 3.1.

Styrene monomer is by far the VOC with the highest concentration in the off-gas stream, followed by similar concentrations of benzene, toluene, benzaldehyde, ethylbenzene, and acetophenone. The total organic species was about 5 weight percent of the polycube sample's initial weight. This observation is far below the organic fractions identified for large polycube test samples in a thermogravimetric system (TGA/DSC/MS) by Abrefah et al. (2000).

The VOCs identified when treating a polycube sample in an inert (i.e., helium) atmosphere are given in Table 3.2 with their normalized concentrations. The number of species identified in the helium environment was 39 compared to the 48 products for thermal treatment in an air atmosphere. Styrene has the highest concentration in the off-gas stream, similar to the results in air. Figure 3.2 shows the chromatogram of species identified. The numbers on the peaks correspond to the numbers in Table 3.2. Thirteen of the VOCs identified in the inert atmosphere treatment that were considered to be major species were styrene, benzene, toluene, ethylbenzene, naphthalene, propane, alpha-methylstyrene, indene, xylene, 1,2,3-trimethylstyrene, benzene, 1-ethenyl-4-methyl, isopropylbenzene and, 1-methyl-1H-indene, in a decreasing order of concentrations.

The concentrations of the VOCs in the off-gas stream for polycube decomposition in the inert atmosphere are higher than their counterparts for the air treatment. The major species concentration ratios for inert to air atmospheres range from 2.1 (benzene) to 4.8 (naphthalene). These major species constitute about 85 weight percent of the total weight of VOCs identified during polycube pyrolysis in the inert atmosphere. The concentrations of benzene, toluene, and ethylbenzene are very close to each other, but styrene is about a factor of 2.2 greater. The concentrations of the four major species (i.e., styrene, benzene, toluene, and ethylbenzene) make up about 59 weight percent of the VOCs.

Table 3.1. VOCs of Polycube Decomposition in Air at 773 K

#	Compound (target)	Chemical Formula	Molecular Weight	CAS #	RT	Area	Concentration	
							ng on col.	ng/mg
1	Benzene	C ₆ H ₆	78	71-43-2	11.834	7E06	793.7	3968.5
2	Toluene	C ₇ H ₈	92	108-88-3	15.031	5E06	664.16	3320.8
3	Ethylbenzene	C ₈ H ₁₀	106	100-41-4	17.606	2E06	561.21	2806.0
4	Xylene(m & p)	C ₈ H ₁₀	106	106-42-3	17.799	4.93E05	60.34	301.7
5	Xylene (o)	C ₈ H ₁₀	106	95-47-6	18.509	77615	19.15	95.7
6	Styrene	C ₈ H ₈	104	100-42-5	18.554	4E06	1697.66	8488.3
7	Butylbenzene	C ₁₀ H ₁₄	134	104-51-8	22.226	65544	27.07	135.3
8	Sec-Butylbenzene	C ₁₀ H ₁₄	134	135-98-8	21.203	1.35E05	14.3	71.5
9	4-Isopropyltoluene	C ₁₀ H ₁₄	134	99-87-6	21.367	49270	6.86	34.3
10	Isopropylbenzene	C ₉ H ₁₂	120	98-82-8	19.161	9.88E05	113.69	568.4
11	Naphthalene	C ₁₀ H ₈	128	91-20-3	25.798	1E06	186.28	931.4
12	Propylbenzene	C ₉ H ₁₂	120	103-65-1	19.901	8.14E05	81.5	407.5
13	1,2,3-Trimethylbenzene	C ₉ H ₁₂	120	108-67-8	20.049	6.26E05	85.64	428.2
SUBTOTAL								21557.6
#	Compound (non-target)	Chemical Formula	Molecular Weight	CAS #	RT	Area	Concentration	
							ng on col.	ng/mg
14	Furan	C ₄ H ₄ O	68	110-00-9	6.667	220658	8.14	40.7
15	2-Propenal	C ₃ H ₄ O	56	107-02-8	6.874	678338	25.03	125.2
16	Methane, isocyano-	C ₂ H ₃ N	41	593-75-9	7.748	335165	12.37	61.8
17	Furan, 2-methyl-	C ₅ H ₆ O	82	534-22-5	9.791	125483	4.63	23.2
18	3-Buten-2-one	C ₄ H ₆ O	70	78-94-4	10.102	837494	30.9	154.5
19	2-Propenoic acid, 2-methyl-, methyl ester	C ₅ H ₈ O ₂	100	80-62-6	13.388	704584	26	130
20	2-Cyclopenten-1-one	C ₅ H ₆ O	82	930-30-3	17.946	433718	16	80
21	Phenylethyne	C ₈ H ₆	102	536-74-3	18.228	434698	16.04	80.2
22	2-Cyclopenten-1-one, 2-methyl-	C ₆ H ₈ O	96	1120-73-	19.545	278281	10.27	51.3
23	Benzene, propyl-	C ₉ H ₁₂	120	103-65-1	19.901	2E06	65.55	327.8
24	alpha-Methylstyrene	C ₉ H ₁₀	118	98-83-9	20.611	5E06	200.32	1001.6
25	Benzaldehyde	C ₇ H ₆ O	106	100-52-7	20.952	2E07	562.14	2810.7
26	Benzofuran	C ₈ H ₆ O	118	271-89-6	21.411	3E06	94.35	471.8
27	Benzene, 1-propenyl-	C ₉ H ₁₀	118	637-50-3	21.767	3E06	94.6	473
28	Phenol	C ₆ H ₆ O	94	108-95-2	22.345	4E06	140.11	700.6
29	Indene	C ₉ H ₈	116	95-13-6	22.478	2E06	77.43	387.2
30	Benzeneacetaldehyde	C ₈ H ₈ O	120	122-78-1	22.863	2E06	71.61	358
31	Acetophenone	C ₈ H ₈ O	120	98-86-2	23.382	1E07	529.8	2649
32	Phenol, 2-methyl-	C ₇ H ₈ O	108	95-48-7	23.619	1E06	53.4	267
33	Benzeneacetaldehyde, alpha-methyl-	C ₉ H ₁₀ O	134	93-53-8	24.019	494718	18.26	91.3
34	Phenol, 3-methyl-	C ₇ H ₈ O	108	108-39-4	24.182	216334	7.98	39.9
35	1H-Indene, 1-methyl-	C ₁₀ H ₁₀	130	767-59-9	24.701	855872	31.58	157.9
36	1H-Indene, 3-methyl-	C ₁₀ H ₁₀	130	767-60-2	24.908	447599	16.52	82.6
37	Naphthalene, 1,2-dihydro	C ₁₀ H ₁₀	130	447-53-0	25.116	592539	21.87	109.3

Table 3.1. (contd)

#	Compound (non-target)	Chemical Formula	Molecular Weight	CAS #	RT	Area	Concentration		
38	Azulene	C ₁₀ H ₈	128	275-51-4	25.175	985027	36.35	181.7	
39	1-Propanone, 1-phenyl-	C ₉ H ₁₀ O	134	93-55-0	25.309	2E06	73.96	369.8	
40	Benzoic Acid, methyl ester	C ₈ H ₈ O ₂	136	93-58-3	25.471	1E06	37.86	189.3	
41	Ethanone, 1- (3-methylphenyl)-	C ₉ H ₁₀ O	134	585-74-0	25.575	676291	24.96	124.8	
42	2-Naphthalenol	C ₁₀ H ₈ O	144	135-19-3	26.45	298133	11	55	
43	Naphthalene, 1-methyl-	C ₁₁ H ₁₀	142	90-12-0	27.962	958655	35.38	176.9	
44	Benzene, (1,2-dimethoxyethyl)-	C ₁₀ H ₁₄ O ₂	166	4013-37-0	28.006	1E06	46.39	232	
45	Naphthalene, 2-methyl-	C ₁₁ H ₁₀	142	91-57-6	28.347	1E06	45.88	229.4	
46	Biphenyl	C ₁₂ H ₁₀	154	92-52-4	29.533	2E06	68.38	341.9	
47	1,1'-Biphenyl, 3-methyl-	C ₁₃ H ₁₂	168	643-93-6	29.666	431147	15.91	79.5	
48	Naphthalene, 1-ethyl-	C ₁₂ H ₁₂	156	1127-76-0	30.007	115064	4.25	21.2	
SUBTOTAL								12676.1	
TOTAL								48169.6	
Sample Initial weight = 0.20 mg									

Table 3.2. VOCs of Polycube Decomposition in Helium at 773 K

#	Compound (target)	Chemical Formula	Molecular Weight	CAS #	RT	Area	Concentration		
							ng on col.	ng/mg	
1	Benzene	C ₆ H ₆	78	71-43-2	11.879	8.9E06	1039.24	8449.1	
2	Toluene	C ₇ H ₈	92	108-88-3	15.107	7.0E06	1002.84	8153.1	
3	Ethylbenzene	C ₈ H ₁₀	106	100-41-4	17.668	3.0E06	923.81	7510.6	
4	Xylene(m & p)	C ₈ H ₁₀	106	106-42-3	17.876	2.1E06	258.6	2102.5	
5	Xylene (o)	C ₈ H ₁₀	106	95-47-6	18.571	236654	58.39	474.7	
6	Styrene	C ₈ H ₈	104	100-42-5	18.63	6.1E06	2294.4	18653.6	
7	4-Isopropyltoluene	C ₁₀ H ₁₄	134	99-87-6	21.43	142770	19.88	161.6	
8	Isopropylbenzene	C ₉ H ₁₂	120	98-82-8	19.222	1.0E06	116.55	947.6	
9	Naphthalene	C ₁₀ H ₈	128	91-20-3	25.856	3.2E06	552.75	4493.9	
10	Propylbenzene	C ₉ H ₁₂	120	103-65-1	19.963	1.0E06	101.27	823.3	
11	1,2,4- Trimethylbenzene	C ₉ H ₁₂	120	95-63-6	20.644	201308	25.84	210.1	
12	1,2,3- Trimethylbenzene	C ₉ H ₁₂	120	108-67-8	20.111	1.5E06	199.58	1622.6	
SUBTOTAL								53602.7	

Table 3.2. (contd)

#	Compound (non-target)	Chemical Formula	Molecular Weight	CAS #	RT	Area	Concentration	
							ng on col.	ng/mg
13	Propane	C ₃ H ₈	44	74-98-6	3.842	1.0E07	349.99	2845.4
14	1-Propene, 2-methyl-	C ₄ H ₈	56	115-11-7	4.493	961614	32.5	264.2
15	1,3-Butadiene	C ₄ H ₆	54	106-99-0	4.656	2.6E06	88.73	721.4
16	1-Buten-3-yne, 2-methyl	C ₅ H ₆	66	78-80-8	7.736	2.9E06	97.55	793.1
17	1,3-Cyclohexadiene	C ₆ H ₈	80	592-57-4	10.873	480769	16.25	132.1
18	1,3,5-Hexatriene, (Z)-	C ₆ H ₈	80	2612-46-6	11.066	331440	11.2	91.1
19	1,3-Hexadien-5-yne	C ₆ H ₆	78	10420-90- 3	11.229	620492	20.97	170.5
20	Phenylethyne	C ₈ H ₆	102	536-74-3	18.305	779958	26.36	214.3
21	Benzene, propyl-	C ₉ H ₁₂	120	103-65-1	19.963	2.2E06	75.39	612.9
22	alpha-Methylstyrene	C ₉ H ₁₀	128	98-83-9	20.674	9.9E06	335.14	2724.8
23	Benzaldehyde	C ₇ H ₆ O	106	100-52-7	21.0	3.1E06	105.97	861.6
24	Benzene, 1-ethenyl- 4-methyl	C ₉ H ₁₀	128	622-97-9	21.074	4.3E06	146.96	1194.8
25	Benzene, 1-ethenyl- 3-methyl	C ₉ H ₁₀	128	100-80-1	21.178	2.3E06	76.59	622.7
26	Benzofuran	C ₈ H ₆ O	118	271-89-6	21.474	2.5E06	83.42	678.2
27	Benzene, 1-propenyl	C ₉ H ₁₀	128	637-50-3	21.815	2.5E06	83.7	680.5
28	Benzene, 1,3-diethyl-	C ₁₀ H ₁₄	134	141-93-5	22.229	597033	20.18	164.1
29	Indene	C ₉ H ₈	116	95-13-6	22.54	8.8E06	296.37	2409.5
30	Benzene, 1-ethenyl- 4-ethyl-	C ₁₀ H ₁₂	132	3535-07-7	23.043	1.6E06	53.68	436.4
31	Benzene, 2-ethenyl-1,3- dimethyl-	C ₁₀ H ₁₂	132	2039-90-9	23.251	1.7E06	57.61	468.3
32	Benzene, (1-methyl- 4-methylenepropyl)-	C ₁₀ H ₁₂	132	2039-93-2	23.636	676158	22.85	185.8
33	Benzene, diethenyl-	C ₁₀ H ₁₀	130	1321-74-0	23.828	912263	30.83	250.7
34	1H-Indene, 1-methyl-	C ₁₀ H ₁₀	130	767-59-9	24.76	3.4E06	116.61	948.0
35	1H-Indene, 3-methyl-	C ₁₀ H ₁₀	130	767-60-2	24.953	2.6E06	88.3	717.9
36	Naphthalene, 1,2-dihydro	C ₁₀ H ₁₀	130	447-53-0	25.16	1.2E06	39.43	320.6
37	Azulene	C ₁₀ H ₈	128	275-51-4	25.22	1.7E06	55.98	455.1
38	Naphthalene, 1-methyl-	C ₁₁ H ₁₀	142	90-12-0	28.016	576347	19.48	158.4
39	Naphthalene, 2-methyl-	C ₁₁ H ₁₀	142	91-57-6	28.416	597462	20.19	160
SUBTOTAL								19282.4
TOTAL								72885.1
Sample Initial Weight = 0.123 mg								

Data File: /vca/000223/00022307.D
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Sample Info: PFP polycube #4
Purge Volume: 0.2
Column phase: DB-624 75m x 2.55um

Instrument: hpl.i
Operator: GS Klinger
Column diameter: 0.45

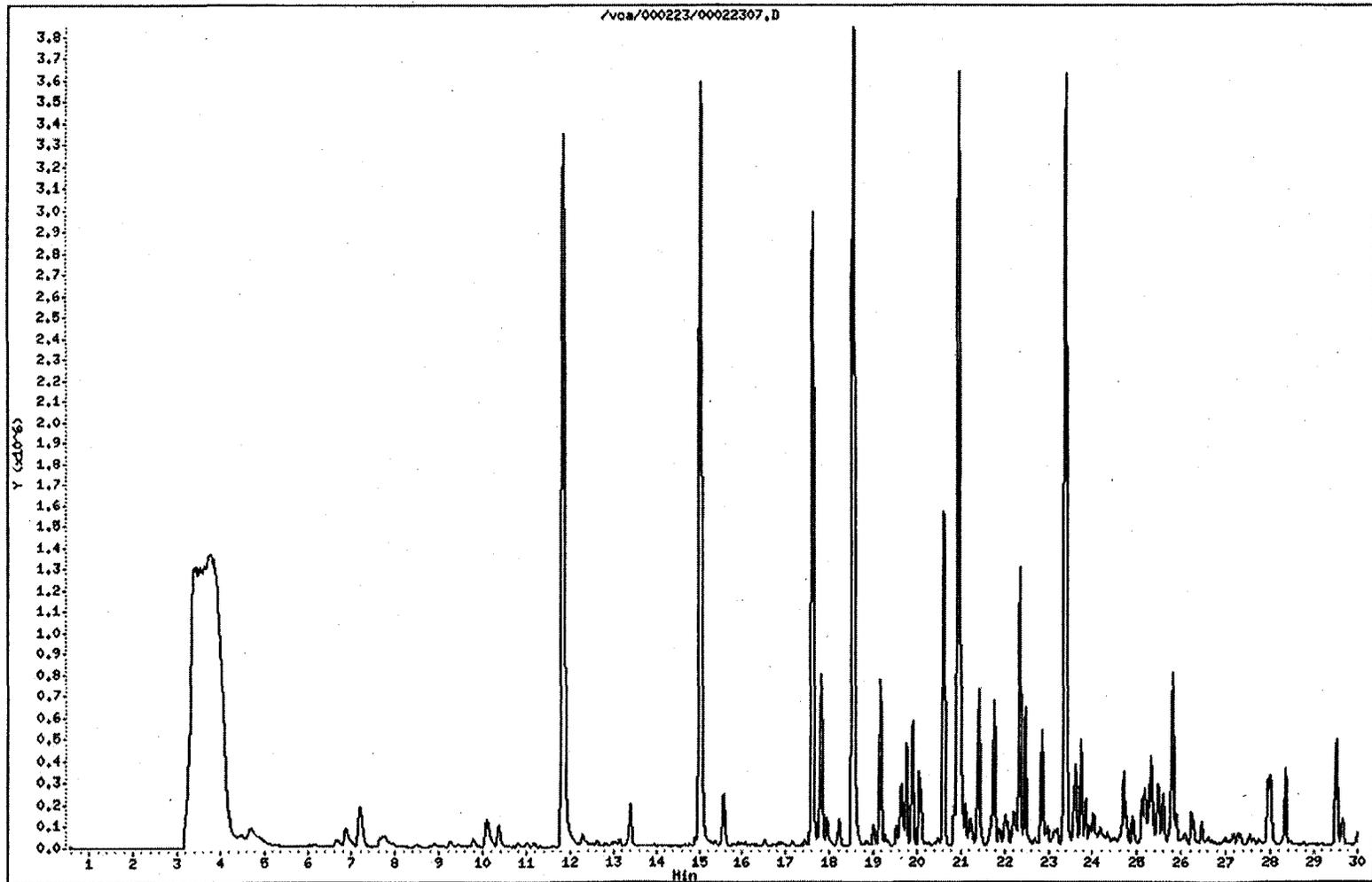


Figure 3.1. Spectrum of VOCs for Polycube Decomposition in Air at 773 K

Data File: /voa/000223/00012709.D

Date : 14-FEB-2000 15:01

Client ID:

Sample Info: furnace test - 5 ug polystyrene in boat

Purge Volume: 0.0

Column phase: DB-624 75m x 2.55um

Instrument: hp1.1

Operator: GS Klinger

Column diameter: 0.45

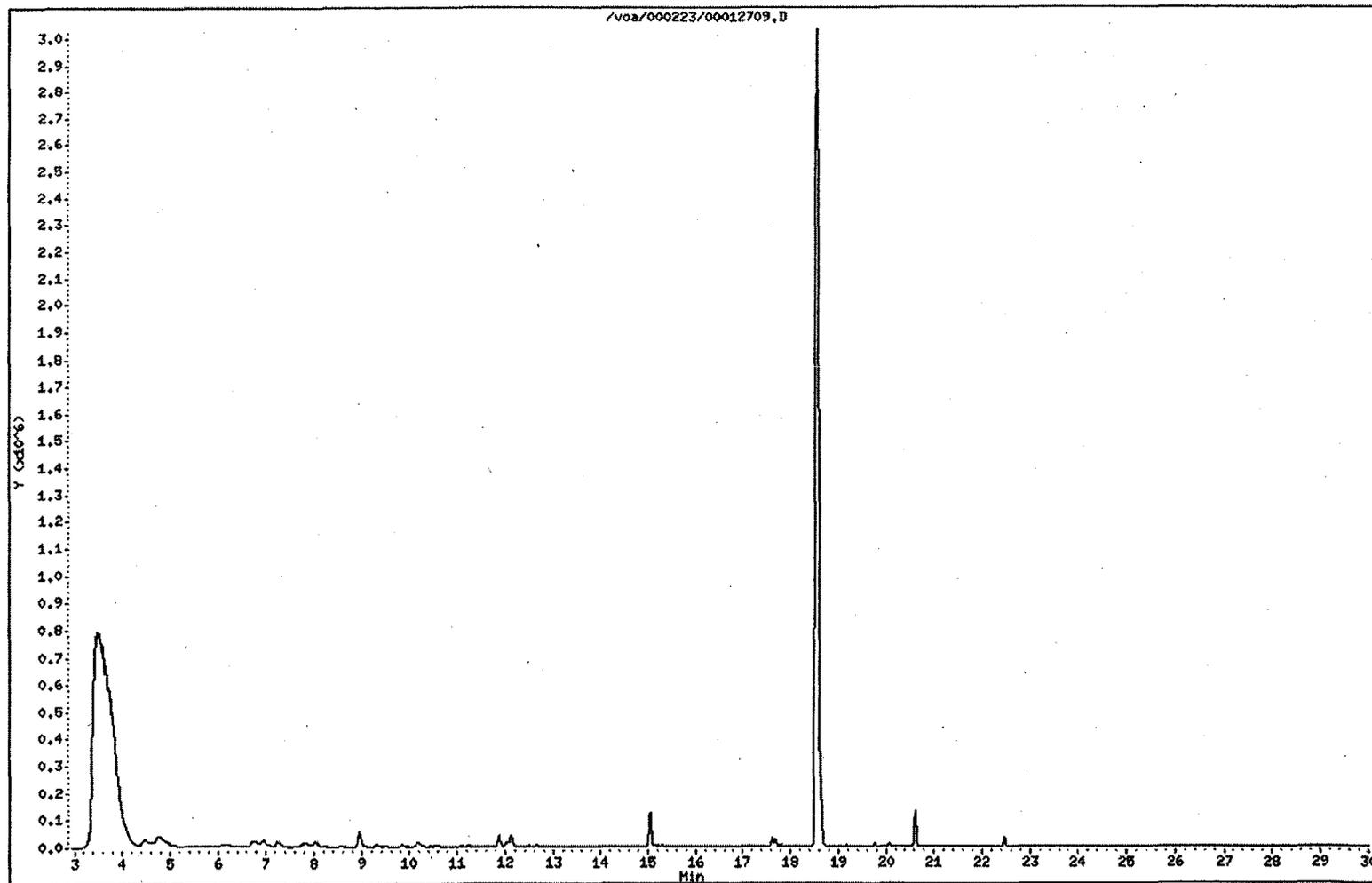


Figure 3.2. Spectrum of VOCs for Polycube Decomposition in Helium at 773 K

3.2 Polystyrene Volatile Organic Compounds

The identified VOCs for pyrolyzing a virgin polystyrene in an inert atmosphere at 773 K are listed in Table 3.3. Figure 3.3 shows the total ion chromatogram of the VOCs identified. Styrene monomer is by far the highest concentration volatile organic product. The other major VOCs (i.e., toluene, ethylbenzene, xylene, etc.) identified for polycube decomposition at the same experimental conditions appeared as minor products for the virgin polystyrene.

Table 3.3. VOCs of Virgin Polystyrene Decomposition in Helium at 773 K

#	Compound (target)	Chemical Formula	Molecular Weight	CAS #	RT	Area	Concentration	
							ng on col.	ng/mg
1	Benzene	C ₆ H ₆	78	71-43-2	11.883	57512	6.69	1337.6
2	Toluene	C ₇ H ₈	92	108-88-3	15.049	60402	8.71	1742.6
3	Ethylbenzene	C ₈ H ₁₀	106	100-41-4	17.624	10279	3.18	636.2
4	Xylene(m & p)	C ₈ H ₁₀	106	106-42-3	17.802	1633	0.20	40.0
5	Styrene	C ₈ H ₈	104	100-42-5	18.557	3.6E06	1362.65	272531.0

Sample Weight = 5 microgram

3.3 Polycube Semi-Volatile Organic Compounds

The SVOCs for polycube thermal treatment in both air and inert atmosphere conditions are listed in Tables 3.4 and 3.5, respectively. The concentrations of most of the species that were identified in the two atmospheres showed similar behavior to that observed in the VOC tests. Again, the concentrations of styrene, ethylbenzene, and alpha-methylbenzene that appeared in the SVOC testing showed a significant decrease in concentrations when the reaction atmosphere was switched from inert to air conditions. Tables 3.4 and 3.5 show that the total number of SVOCs decreased from 31 (inert) to only 15 (air), even though four oxygenated species were generated in the air atmosphere. The data for decomposition in argon (i.e., inert) in Table 3.5 show oxygenated compounds (phenol, bezaldehyde, and acetophenone) as identified products, suggesting that the gas atmosphere was not completely inert. Argon was used to provide the inert atmosphere because it was available.

The chromatograms for both SVOC runs are shown in Figures 3.4 and 3.5 for air and inert atmospheres, respectively. The air treatment chromatogram in Figure 3.4 shows a limited identified species compared to the inert atmosphere chromatogram in Figure 3.5. Most species in Figure 3.5 were barely discernible, and yet they were positively identified products. The low signal intensities for the SVOCs made it difficult to positively identify one product during the air testing ("unknown" in Table 3.4) and another product in the inert atmosphere ("unknown" in Table 3.5).

Data File: /voa/000223/00012709.D
Date : 14-FEB-2000 15:01
Client ID:
Sample Info: furnace test - 5 ug polystyrene in boat
Purge Volume: 0.0
Column phase: DB-624 75m x 2.55um

Instrument: hp1.i
Operator: GS Klinger
Column diameter: 0.45

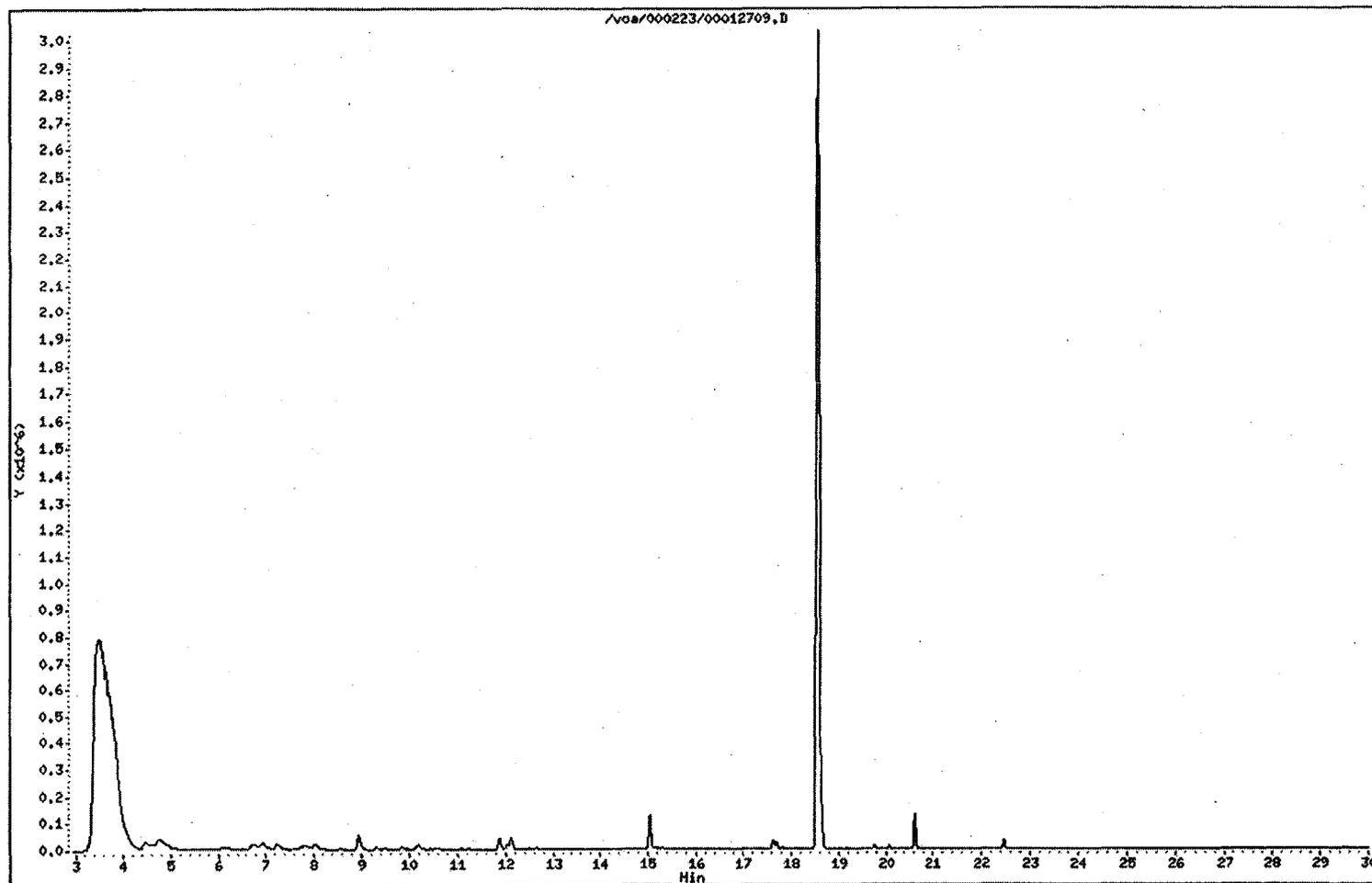


Figure 3.3. Spectrum of VOCs for Polystyrene Decomposition in Helium at 773 K

Table 3.4. SVOCs of Polycube Decomposition in Air at 773 K

#	Compound (non-target)	Chemical Formula	Molecular Weight	CAS #	RT	Concentration	
						ng on col.	ng/mg
1	Ethylbenzene	C ₈ H ₁₀	106			7.44	1018.89
2	Benzene, 1,2-dimethyl-	C ₈ H ₁₀	106	95-47-6	7.663	0.63	86.29
3	Styrene	C ₈ H ₈	104	100-42-5	8.335	25.2	3452.57
4	Benzene, (1-methylethyl)-	C ₉ H ₁₂	120	98-82-8	9.270	1.05	143.55
5	Benzene, 2-propenyl	C ₉ H ₁₀	118	300-57-2	9.896	0.65	89.55
6	Vinyl Ether	C ₄ H ₆ O	70	109-93-3	9.976	0.58	79
7	Benzene, propyl	C ₉ H ₁₂	120	103-65-1	10.102	0.54	74.53
8	Benzaldehyde	C ₇ H ₆ O	106	100-52-7	10.364	9.11	1247.45
9	alpha-Methylstyrene	C ₉ H ₁₀	118	98-83-9	10.831	2.45	336.13
10	Benzene, tert-butyl-	C ₁₀ H ₁₄	134	98-06-6	11.07	1.02	140.36
11	Benzofuran	C ₈ H ₆ O	118	271-89-6	11.195	1.6	219.45
12	Unknown	N/A	N/A	N/A	11.446	1.8	246.3
13	Indene	C ₉ H ₈	116	95-13-6	12.358	0.79	108.04
14	Acetophenone	C ₈ H ₈ O	120	98-86-2	12.893	0.31	41.86
15	Bibenzyl	C ₁₄ H ₁₄	182	103-29-7	21.142	0.51	69.33
Sample Initial Weight = 0.73 mg							

Table 3.5. SVOCs of Polycube Decomposition in Argon at 773 K

#	Compound (target)	Chemical Formula	Molecular Weight	CAS #	RT	Area	Concentration		
							ng on col.	ng/mg	
1	Phenol	C ₆ H ₆ O	94	108-95-2	10.99	24191	3.67	477.26	
2	Naphthalene	C ₁₀ H ₈	128	91-20-3	15.389	43713	3.21	417.36	
3	2-Methylnaphthalene	C ₁₁ H ₁₀	142	91-57-6	17.736	16850	1.9	246.22	
SUBTOTAL								1140.84	
#	Compound (non-target)	Chemical Formula	Molecular Weight	CAS #	RT	Area	Concentration		
							ng on col.	ng/mg	
4	Ethylbenzene	C ₈ H ₁₀	106	100-41-4	7.356	709455	37.29	4842.89	
5	Benzene, 1,2-dimethyl-	C ₈ H ₁₀	106	95-47-6	7.663	79262	4.17	541.06	
6	p-Xylene	C ₈ H ₁₀	106	106-42-3	8.335	89311	4.69	609.66	
7	Styrene	C ₈ H ₈	104	100-42-5	8.335	1674405	88.01	11429.85	
8	Benzene, (1-methylethyl)-	C ₉ H ₁₂	120	98-82-8	9.27	150457	7.91	1027.05	
9	Benzene, 1-propenyl-, (E)-	C ₉ H ₁₀	118	300-57-2	9.896	56351	2.96	384.66	
10	Benzene, propyl	C ₉ H ₁₂	120	103-65-1	10.102	60125	3.16	410.43	
11	Benzene, 1-ethyl-3-methyl-	C ₉ H ₁₂	120	620-14-4	10.295	51525	2.71	351.72	
12	Benzaldehyde	C ₇ H ₆ O	106	100-52-7	10.364	148335	7.8	1012.57	
13	alpha-Methylstyrene	C ₉ H ₁₀	118	98-83-9	10.831	295348	15.52	2016.11	
14	Benzene, tert-butyl-	C ₁₀ H ₁₄	134	98-06-6	11.07	56887	2.99	388.32	
15	Benzene, 2-propenyl-	C ₉ H ₁₀	118	300-57-2	11.173	59040	3.1	403.02	
16	Benzene, 1-ethenyl-3-methyl-	C ₉ H ₁₀	118	100-80-1	11.298	19580	1.03	133.66	
17	Unknown	N/A	N/A	N/A	11.446	34731	1.83	237.08	
18	Benzene, 1-ethenyl-4-methyl-	C ₉ H ₁₀	118	622-97-9	11.936	70136	3.69	478.76	
19	Indene	C ₉ H ₈	116	95-13-6	12.358	141667	7.45	967.05	
20	1,2,3,4,5,8-Hexahydronaphthal	C ₁₀ H ₁₄	134	36231-13-7	12.608	43137	2.27	294.46	
21	Acetophenone	C ₈ H ₈ O	120	98-86-2	12.893	198579	10.44	1355.54	
22	1H-Indene, 1-methyl-	C ₁₀ H ₁₀	130	767-59-9	14.614	71668	3.22	417.69	
23	Benzene, 1-cyclobuten-1-yl-	C ₁₀ H ₁₀	130	3365-26-2	14.956	40403	1.81	235.48	
24	Naphthalene, 1-methyl-	C ₁₁ H ₁₀	142	90-12-0	17.462	47263	2.12	275.46	
25	Biphenyl	C ₁₂ H ₁₀	154	92-52-4	18.886	55572	2.69	350.00	
26	Diphenylmethane	C ₁₃ H ₁₂	168	101-81-5	19.718	23201	1.12	145.76	
27	1,1'-Biphenyl, 4-methyl-	C ₁₃ H ₁₂	168	644-08-6	20.584	29122	1.41	182.95	
28	Bibenzyl	C ₁₄ H ₁₄	182	103-29-7	21.142	100104	4.84	628.89	
29	Benzene, 1,1'-(1,3-propanediyl)	C ₁₅ H ₁₆	196	1081-75-0	23.079	78875	4.21	546.21	
30	Imidazo[1,5-a]pyridine, 3-pheny	C ₁₃ H ₁₀ N ₂	194	35854-46-7	24.242	17969	0.96	124.44	
31	2-Phenylnaphthalene	C ₁₆ H ₁₂	204	35465-71-5	27.375	23835	1.27	165.06	
SUBTOTAL								29955.83	
TOTAL								31096.67	
Sample Initial weight = 0.77 mg									

Data File: /HPCHEH/1/DATA/000303.B/00030304.D
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 Client ID:
 Sample Info: polycube sample #7
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 Column phase: J&W DB-5MS

Instrument: hp1.i
 Operator: GS Klinger
 Column diameter: 0.25

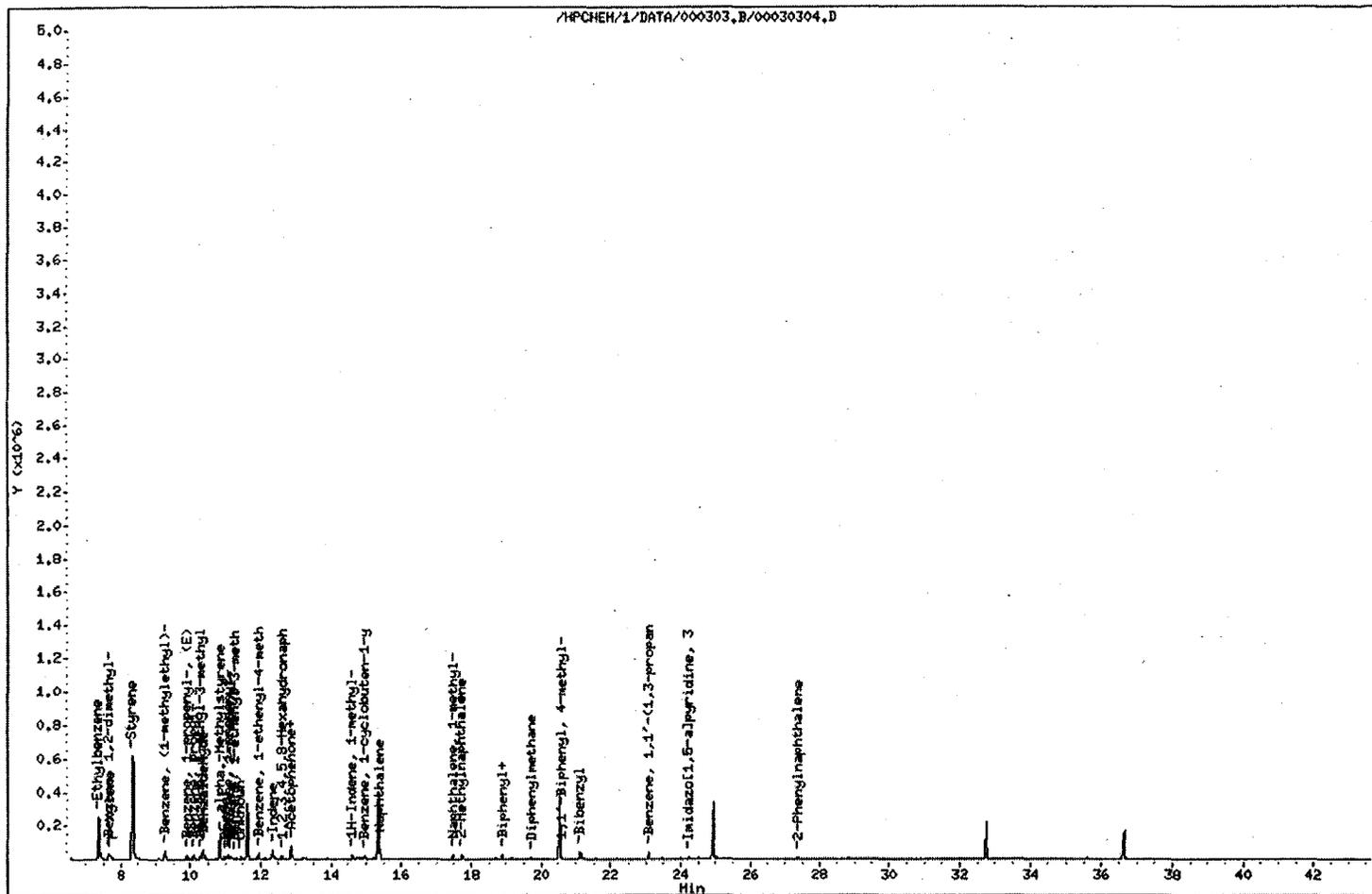


Figure 3.5. Spectrum of SVOCs for Polycube Decomposition in Helium at 773 K

3.12

4.0 Discussion

Results for thermal decomposition of the degraded polystyrene show a number of volatile and semi-volatile organic compounds that varied in concentrations and a number of species that were identified for the two atmospheres studied. The studies were performed at a constant temperature of 773 K to determine the species and their concentrations during polycube processing. Also at this temperature, the pyrolysis products were expected to be at their maximum levels. The data for the VOCs and SVOCs identified in Section 3.0 are discussed below.

4.1 Polycube Volatile Organic Compounds

The two reaction processes (i.e., oxidation and pyrolysis) in the air atmosphere generated the 48 organic species identified in Table 3.1. These species include 20 oxygen-containing compounds that resulted from direct oxidation of the polystyrene matrix, in accordance with Gol'dberg et al. (1975). The three main oxidation products of water, carbon monoxide (CO), and carbon dioxide (CO₂) that were reported by Abrefah et al. (2000) and Barney (2000) could not be monitored during this study because of their high background in the off-gas stream. Thirteen of the species identified had high enough concentrations to be considered major reaction products (Table 4.1).

As noted earlier, styrene monomer is by far the VOC with the highest concentration in the off-gas stream, followed closely by concentrations of benzene, toluene, benzaldehyde, ethylbenzene, and acetophenone. These VOCs constitute about 60 weight percent of the total species observed; the five species (styrene, benzene, toluene, benzaldehyde, and ethylbenzene) that were monitored during the TGA testing of the polycubes by Abrefah et al. (2000) were confirmed by these results to be the main products in the off-gas stream that should serve as the baseline in determining flammability issues. The latter constitutes about 45 weight percent of the organic products. The only flammable species in Table 4.1 that should be added in the further evaluation of treating the polycubes by the direct oxidation process is acetophenone. Benzaldehyde as an oxidative organic product was positively identified during the TGA studies, but three additional oxidative organic species (acetophenone, phenol, and benzofuran) were among the list in Table 4.1 that were not considered in the data of the TGA results. The identification of acetophenone, benzofuran, and phenol agrees with the results for polystyrene oxidation in air reported by Gol'dberg et al. (1975).

Thirteen major VOCs for the inert atmosphere decomposition of polycubes are listed in the Table 4.2 in decreasing order of concentration. The concentrations of these VOCs in the off-gas stream for polycube decomposition in the inert atmosphere are higher than their counterparts for air treatment. The ratios of inert to air concentrations of these major species range from 2.1 (benzene) to 4.8 (naphthalene). These 13 species constitute about 85 weight percent of the total weight of VOCs identified during polycube pyrolysis in the inert atmosphere. The concentrations of benzene, toluene, and ethylbenzene are similar, but styrene is about a factor of 2.2 greater. The concentrations of the four major species (i.e., styrene, benzene, toluene, and ethylbenzene) make up about 59 weight percent of the VOCs.

Table 4.1. Major VOCs for Polycube Decomposition in Air at 773 K

Compound	Chemical Formula	Molecular Weight	Concentration (ng/mg)
Styrene	C ₈ H ₈	104	8488
Benzene	C ₆ H ₆	78	3968
Toluene	C ₇ H ₈	92	3320
Benzaldehyde	C ₇ H ₆ O	106	2811
Ethylbenzene	C ₈ H ₁₀	106	2806
Acetophenone	C ₈ H ₈ O	120	2649
alpha-Methylstyrene	C ₉ H ₁₀	118	1002
Naphthalene	C ₁₀ H ₈	128	931
Phenol	C ₆ H ₆ O	94	701
Isopropylbenzene	C ₉ H ₁₂	120	568
Benzofuran	C ₈ H ₆ O	118	472
1,2,3-Trimethylbenzene	C ₉ H ₁₂	120	428
Propylbenzene	C ₉ H ₁₂	120	408

Table 4.2. Major VOCs for Polycube Decomposition in Helium at 773 K

Compound	Chemical Formula	Molecular Weight	Concentration (ng/mg)
Styrene	C ₈ H ₈	104	18654
Benzene	C ₆ H ₆	78	8449
Toluene	C ₇ H ₈	92	8153
Ethylbenzene	C ₈ H ₁₀	106	7511
Naphthalene	C ₁₀ H ₈	128	4494
Propane	C ₃ H ₈	44	2845
alpha-Methylstyrene	C ₉ H ₁₀	118	2825
Indene	C ₉ H ₈	116	2410
Xylene	C ₆ H ₆ O	94	2103
1,2,3-Trimethylbenzene	C ₉ H ₁₂	120	1623
Benzene, 1-ethenyl-4-methyl	C ₉ H ₁₀	128	1195
Isopropylbenzene	C ₉ H ₁₂	120	948
1H-Indene, 1-methyl	C ₁₀ H ₁₀	130	948

Figure 4.1 is a bar chart plot illustrating the decreasing trend for the VOC concentrations when the reaction atmosphere was switching from inert to air. The decrease in concentrations of the major organic products suggests that a large fraction of the polystyrene matrix was oxidized during the treatment in air, forming water, CO, and CO₂ that were not monitored during this study. The four oxidation products listed in Table 4.1 constitute only a fraction of the concentration decrease when the atmosphere was changed from inert to air.

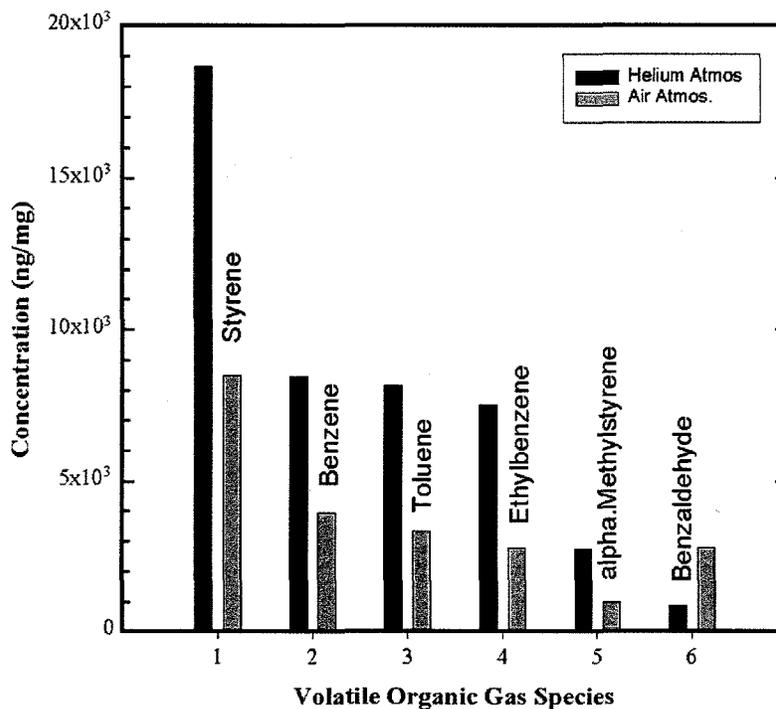


Figure 4.1. Comparison of Polycube VOCs in Air and Inert Atmospheres

The concentrations of all the major volatile organic products formed decreased by a factor of about 0.5 when the atmosphere was changed from pure inert conditions to air. This was likely due to the parallel oxidation reaction of the polycube with the air atmosphere plus the pyrolytic decomposition of the organic phase.

The virgin polystyrene, on the other hand, generated very few organic products, with the vast majority being the styrene monomer. A comparison of the organic products for the virgin polystyrene (in an inert atmosphere) and the polycube is given in Figure 4.2. Styrene concentration for the virgin polystyrene was at least an order of magnitude greater than the highest value for the polycube decomposition in an inert atmosphere. The data show that the cross-linkage significantly alters the distribution and number of VOCs generated when a radiation-damaged polystyrene is thermally processed.

4.2 Polycube Semi-Volatile Organic Compounds

The major SVOC species (Figure 4.3) for polycube decomposition in the two atmospheres (i.e., air and inert) did show significant changes in concentrations for the species identified, such as styrene, ethylbenzene, alpha-methylstyrene, and benzene,(1-methylethyl). These species showed a decrease in concentration similar to the observations for the VOC experiments. The reason for the decrease was

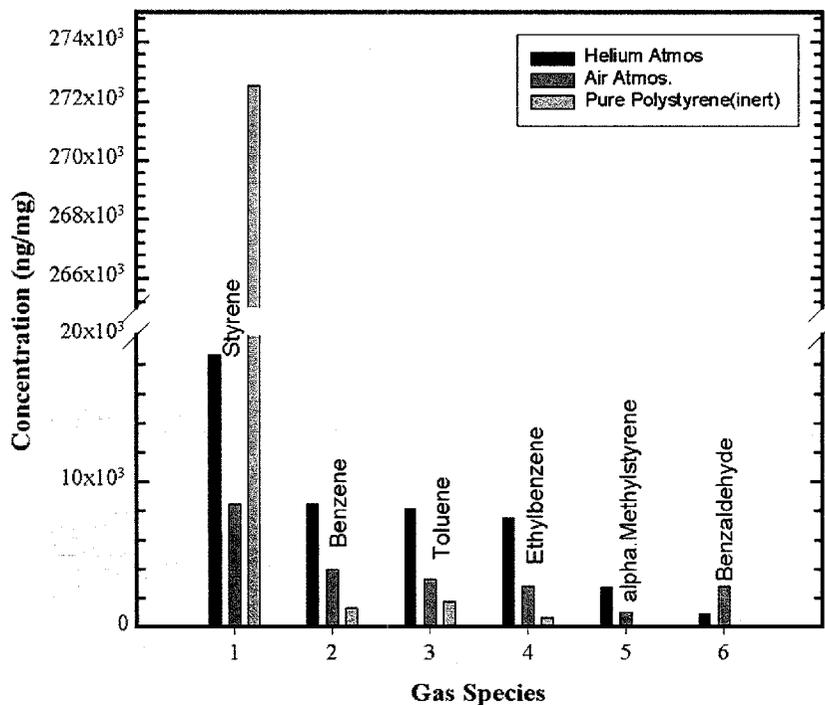


Figure 4.2. Comparison VOCs of Polycube and Virgin Polystyrene (inert atmosphere)

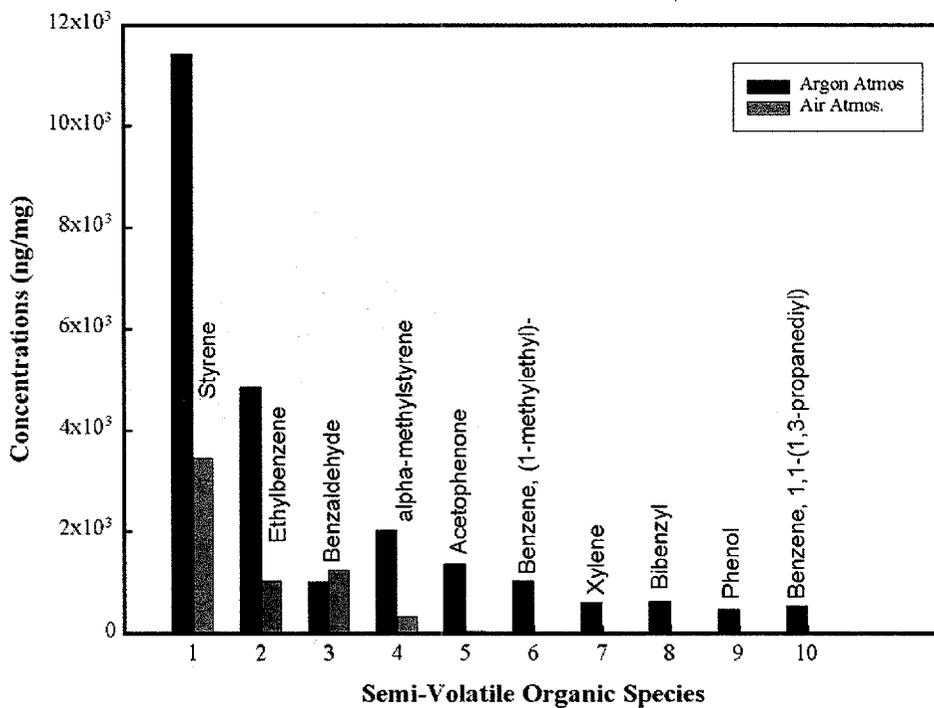


Figure 4.3. Comparison of SVOCs of Polycube in Air and Inert Atmospheres

again the oxidation reaction in air that occurred as a parallel reaction to pyrolysis. The results indicate that the radiation damage to the polystyrene matrix has rendered the polycube amenable to an oxidation process that generates less SVOCs.

The number of heavy molecular weight SVOCs that have the potential for plugging filters and gas lines decreased when the decomposition atmosphere was switched from inert to air. Thus, an air atmosphere can be considered the optimum condition to stabilize the degraded polystyrene matrix, provided the flammable species concentrations stay below their lower flammability limits.

5.0 Conclusions

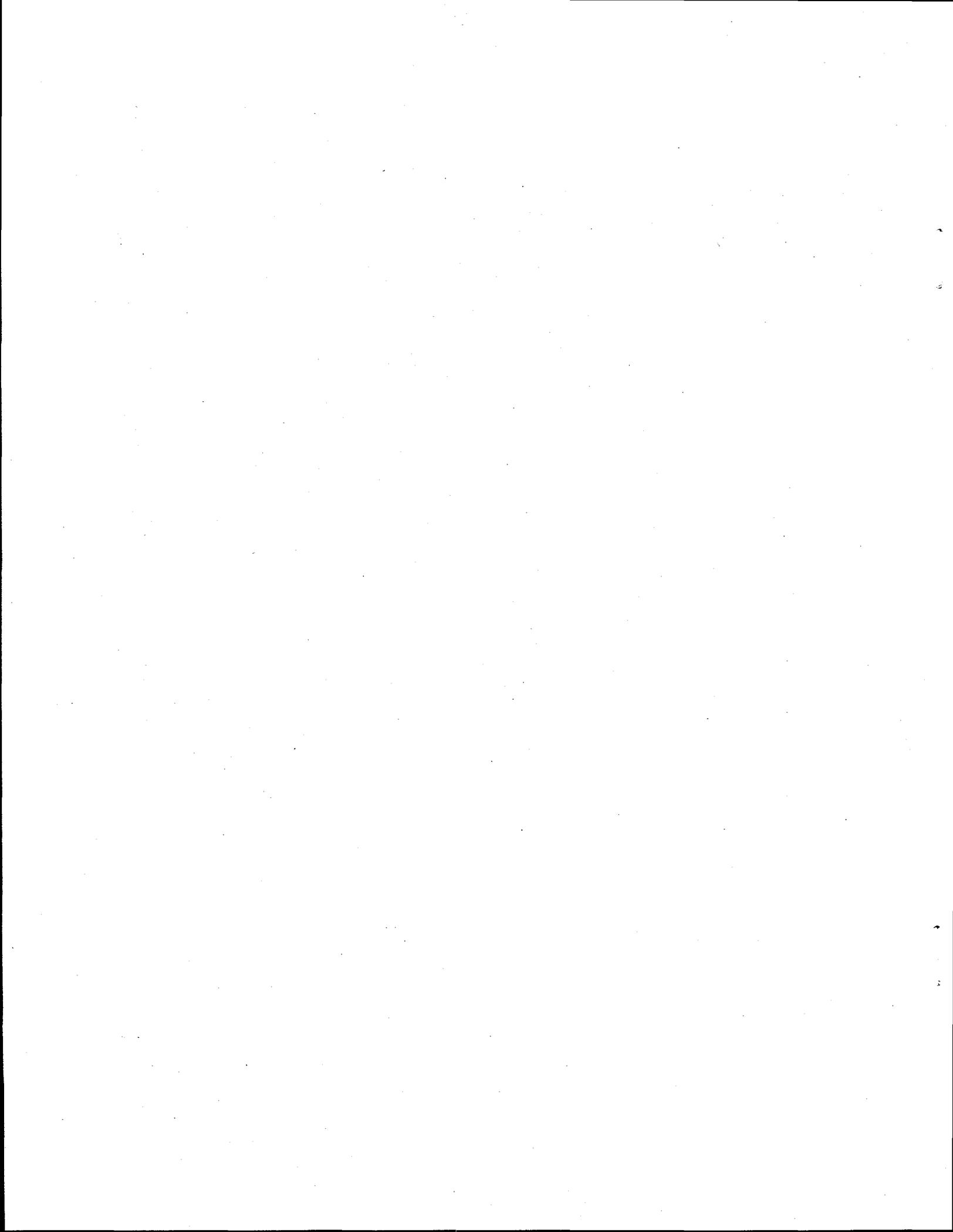
The major volatile organic species identified for polycube decomposition at 773 K were

- styrene, benzene, toluene, benzaldehyde, ethylbenzene, acetophenone, alpha-methylstyrene, and naphthalene in an air atmosphere, and
- styrene, benzene, toluene, ethylbenzene, naphthalene, propane, alpha-methylstyrene, indene, xylene, and 1,2,3-trimethylbenzene in an inert atmosphere.

The normalized concentrations of VOCs in the inert atmosphere were significantly higher than corresponding values in the air atmosphere, suggesting that the oxidation reaction decreases the concentrations of flammable organic species in the off-gas stream.

The concentrations and the number of major SVOCs that were identified and quantified significantly changed from the inert (argon) to the air atmosphere. Thus, the oxidation process may eliminate the heavy molecular species from the SVOCs that have the potential to plug up filters during polycube processing.

The depletion of hydrogen together with the cross-linked polystyrene matrix resulting from radiation damage significantly affect both the products and their concentrations in the off-gas stream when the damaged polystyrene is thermally decomposed.



6.0 References

Abrefah, J., P. J. MacFarlan, and R. L. Sell. 2000. *Polycube Oxidation and Factors Affecting the Concentrations of Gaseous Products*. PNNL-13166, Pacific Northwest National Laboratory, Richland, Washington.

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Lewis, W. S., and C. D. Meng. 1996. *Location Assessment for the Polycube Pyrolysis Process*. WHC-SD-CP-TI-203, Westinghouse Hanford Company, Richland, Washington.

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