

**Task 15  
Thermal Depolymerization of  
Plastics -- PDU Testing**

**Topical Report**

January 1996

Work Performed Under Contract No.: DE-FC21-93MC30098

For  
U.S. Department of Energy  
Office of Fossil Energy  
Morgantown Energy Technology Center  
Morgantown, West Virginia

By  
University of North Dakota  
Energy & Environmental Research Center  
Grand Forks, North Dakota

**MASTER**

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January 1996

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## **THERMAL DEPOLYMERIZATION OF PLASTICS PDU TESTING**

### **EXECUTIVE SUMMARY**

The process development unit (PDU) test program is part of an ongoing effort at the Energy & Environmental Research Center (EERC) to expand the base of knowledge for the thermal depolymerization of plastics process. This phase of the development effort, initiated after successful completion of a bench-scale program, has concentrated on maximizing liquid yield. The purposes of the PDU program were 1) to demonstrate the process on a commercially scalable unit, 2) to produce quantities of product that could be used to initiate discussions with potential end users, and 3) to gather engineering and yield data.

Experimentation consisted of eleven test points on the PDU and seven on the continuous fluid-bed reactor (CFBR) bench-scale unit. Initial PDU tests (P035-P039) were carried out using a base blend, which consists of 60% high-density polyethylene (HDPE), 20% polypropylene (PP), and 20% polystyrene (PS) virgin resin pellets. Test P039 used base blend with 5% polyvinyl chloride (PVC). The base blend decomposed to produce a flowable liquid, with liquid yields ranging from 33% to 45%. The next series of tests, P040-P044, used a postconsumer plastics feed. This material did not decompose as readily as the base blend and formed a very waxy, heavy liquid, with "liquid" yields ranging from 18% to 63% (low liquid yields are the result of using excess air in the natural gas burner in some tests in an attempt to increase gas residence time). After several marginally successful attempts at producing a lighter liquid, a decision was made to discontinue PDU testing until a better understanding of the conditions necessary to produce a satisfactory liquid was attained. Possible explanations considered for the heaviness of the liquids made from postconsumer material included 1) insufficient gas residence time, 2) CaO fines carryover and suspension in product liquids, 3) the presence of quantities of nonplastic substances on the postconsumer material influencing decomposition, 4) formation of calcium terephthalate or other organic acid-calcium compounds from polyethylene terephthalate (PET) decomposition, or 5) coking of PET. Analysis of the liquids and solid residuals from the tests indicated that insufficient gas residence time was the cause of the heavier-than-expected liquid product. To verify this and to find a range of acceptable gas residence times, a series of tests was run on the bench-scale CFBR unit. Of secondary concern were whether or not steam was an important variable and the effect of CaO concentration. Most work prior to the PDU program was performed without steam. Earlier work was done on the CFBR, which has indirect heaters. The PDU, on the other hand, relies on a natural gas-fired burner for process heat. A byproduct of the natural gas burner is water. Two levels of CaO (5% and 15%) were tested in the CFBR to examine CaO concentration effect. A significant gas residence effect was observed, both on gas and liquid quality.

Based on the bench-scale studies, the gas residence time required to produce liquids of suitable quality from postconsumer plastics at 625°C was found to be approximately 23 seconds. PDU tests reported here were carried out at gas residence times of between 14 and 19 seconds. (The 19-second test employed excess air in the burner to burn some of the feed for process heat and, therefore, has a low liquid yield.) Note that the required residence time is

dependent on decomposition temperature and feed material. In order to allow for future PDU operation over the desired range of gas residence times, the bottom two sections of the PDU were increased from 8-in. inner diameter (ID) to 10-in. ID by removing 2 in. of the refractory.

Additionally, the pneumatic transport system was replaced with a dual auger arrangement, similar to that of the CFBR.

A pair of fluid-bed consultants was retained to evaluate the PDU program. Their suggestions were incorporated into the test plans laid out at the start of the program. A short report issued by these consultants is attached as an appendix.

# THERMAL DEPOLYMERIZATION OF PLASTICS

## PDU TESTING

### 1.0 INTRODUCTION

Presently, some types of plastics (mainly polyethylene terephthalate [PET] and high-density polyethylene [HDPE]) are collected and recycled to plastics of that same type by chemical or mechanical methods. These methods of recycling require relatively clean, homogeneous streams. Processes to recycle PET or HDPE exist mainly because large enough quantities of feed are available at a sufficiently low price to make the process economic. For many types of plastics, delivery of sufficient quantities (collection, sortation, preparation, and transportation) to a process dedicated solely to the recycling of that plastic is presently economically prohibitive. In order to recycle large quantities of postconsumer plastics, processes that are able to accept mixed streams are necessary. Methods to form usable products with minimal processing of postconsumer plastics also exist, such as plastic lumber and trash bag manufacturing, but have limited markets when compared to the abundance of plastic available for recycling. Traditional recycling processes such as these are an important part of the overall recycling effort but cannot process all types of plastics streams and do not accept sufficient quantities of material to achieve the higher recycling level desired for plastics. As an additional recycling option, several groups around this country and in Europe are examining methods of thermal decomposition (sometimes referred to as thermal depolymerization, chemical recycling, tertiary recycling, or feedstock recycling) of mixed-plastic streams. A range of hydrocarbon liquid and gaseous products are available from this type of process, many of which have potentially large markets. The products of thermal depolymerization can be used for the manufacture of new plastics or of various other hydrocarbon-based products. Recycling mixed-plastic streams presents many challenges. Postconsumer plastics streams are highly heterogeneous. Because of the many applications of plastics, numerous additives, both inorganic and organic, are present. Contaminants from use by the consumer will be mixed with the plastics (e.g., paint, paint thinner, food, metals, paper, adhesives). Processes to recycle postconsumer plastics will need to account for all of these factors.

Thermal depolymerization process development began at the Energy & Environmental Research Center (EERC) with a bench-scale program that ran from September 1992 to June 1993 (1). Testing conducted in a 1-4-lb/hr continuous fluid-bed reactor (CFBR) unit using individual virgin resins and resin blends was intended to determine rough operating parameters and product yields and to identify product stream components. Process variables examined included temperature and bed material, with a lesser emphasis on gas fluidization velocity and feed material mix. Following successful completion of the study using virgin resins, postconsumer plastics were tested. Next, a short program was completed that examined the use of CaO in a postreactor fixed bed for chlorine removal.

The follow-up to the bench-scale projects, described here, covers testing on a 100-lb/hr process development unit (PDU). Several bench-scale tests performed as new questions arose

from the PDU program will also be covered. The purposes of the PDU program are to 1) prove the concept on a commercially scalable unit, 2) identify engineering challenges, 3) gather engineering and yield data for scaleup, and 4) generate quantities of products for qualification and evaluation by end users.

While the overall objective of efforts at the EERC is to quantitatively and qualitatively determine the potential slate of products from the thermal depolymerization of plastics as a function of process variables, this phase of the PDU program has focused on maximizing the yield of hydrocarbon liquid product.

## 2.0 TEST EQUIPMENT

Experiments described here were performed in both the 100-lb/hr PDU and the 1-4-lb/hr CFBR. The CFBR (Figure 1) consists of a 1-4-lb/hr fluid-bed reactor, gas conditioning train, solids feed system, and condensation train. The reactor is rated to 825°C and 175 psi and is indirectly heated. The bottom section is 33 in. long and has a nominal 3-in. ID. The top section is 17.5 in. long and has a 4-in. ID. The primary means of solids removal is a top bed drain leg, located at the junction of the 3-4-in. sections. Solids are introduced through a bottom, side port via a dual auger system. The top, horizontal auger meters feed material from the feed hopper. The metered feed material gravity drops to a second auger, which is at 60° from horizontal. The angled auger runs very fast and delivers the feed material quickly into the bottom of the reactor before melting can occur. The condensation train consists of a series of

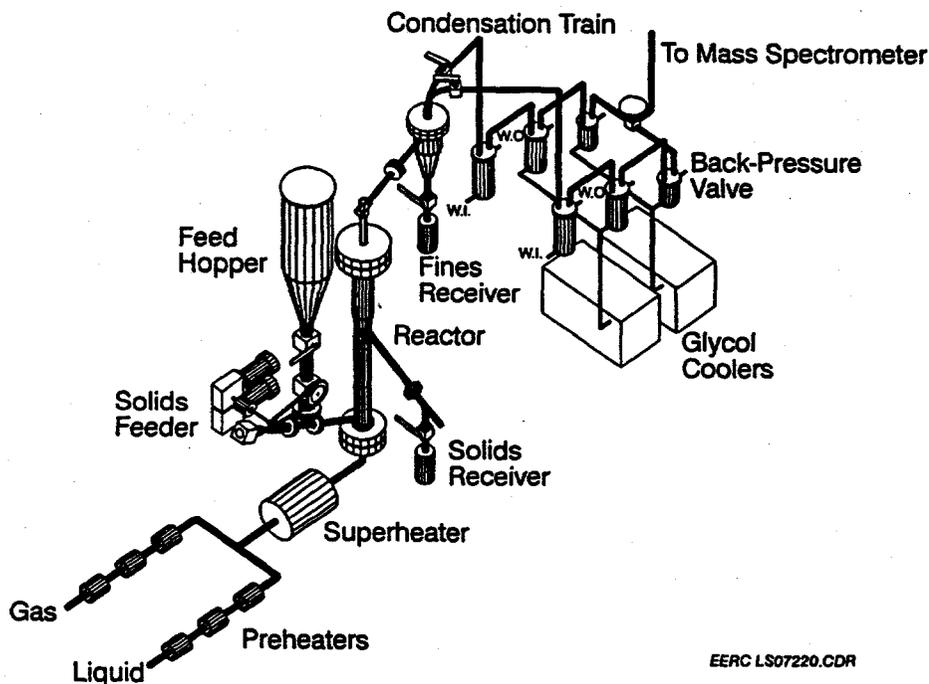


Figure 1. CFBR.

## Thermal Depolymerization of Plastics

three indirectly cooled condensation pots. The first of these pots is water-cooled, and the second and third are glycol-cooled.

The PDU fluid-bed reactor, solids feed system, gas conditioning system, and condensation train are shown in Figure 2. The fluid-bed reactor consists of four 5-foot-long refractory-lined sections. The first two sections have 8-in. IDs, and the second two have 16-in. IDs. Feed is introduced to the system either through the bottom center of the reactor, using a pneumatic transport line, or through a bottom, side port, also using the pneumatic transport system. The condensation train of the PDU consists of a sieve tower, followed by a series of two water venturi scrubbers. Both the sieve tower and the venturis use condensed product liquids as cooling fluids. Gas is analyzed by gas chromatography (GC) grab bag samples and by on-line analyzers for both the PDU and CFBR.

### 3.0 FEED MATERIALS

Three feed material mixes were used in the tests described here. "Base blend" refers to a mix of virgin resin pellets composed of 60% HDPE, 20% polystyrene (PS), and 20% polypropylene (PP). Two postconsumer blends were tested. Both blends were procured from Quality Checked of Paynesville, Minnesota. The first postconsumer blend consisted mainly of HDPE, with small amounts of PP and PS present, based on historical assay provided by Quality Checked. The second blend consisted of approximately 59.2% HDPE, 20.1% PET, 0.6% polyvinyl chloride (PVC), 10.7% PP, 4.7% PS, and 4.7% low-density polyethylene (LDPE). This analysis was provided by Southwest Research Corporation of San Antonio. A description of the method used is found in Appendix H. It should be noted that the postconsumer material is highly heterogeneous and that only one sample was analyzed. While some care was taken to submit a representative sample, no accuracy for the analytical method has been established. Bed materials used were sand and CaO. The sand was 20 × 40 mesh. CaO was procured from Cutler-Magner of Duluth, Minnesota, and was sized to -1/4 in. An analysis for the CaO is given in Table 1.

TABLE 1

#### Rockport High-Calcium Lime (typical analysis)<sup>a</sup>

Calcium Oxide (total)	CaO	95.00%
Calcium Oxide (available)	CaO	92.00%
Magnesium Oxide	MgO	1.20%
Silica	SiO <sub>2</sub>	0.95%
Iron Oxide	Fe <sub>2</sub> O <sub>3</sub>	0.34%
Aluminum Oxide	Al <sub>2</sub> O <sub>3</sub>	0.20%
Sulfur	S	0.05%
Phosphorus Pentoxide	P <sub>2</sub> O <sub>5</sub>	0.02%
Manganese	Mn	0.02%
Titanium Oxide	TiO <sub>2</sub>	0.02%
LOI <sup>b</sup>		1.51%

<sup>a</sup> From Cutler-Magner Company, Duluth, MN.

<sup>b</sup> Loss on ignition.

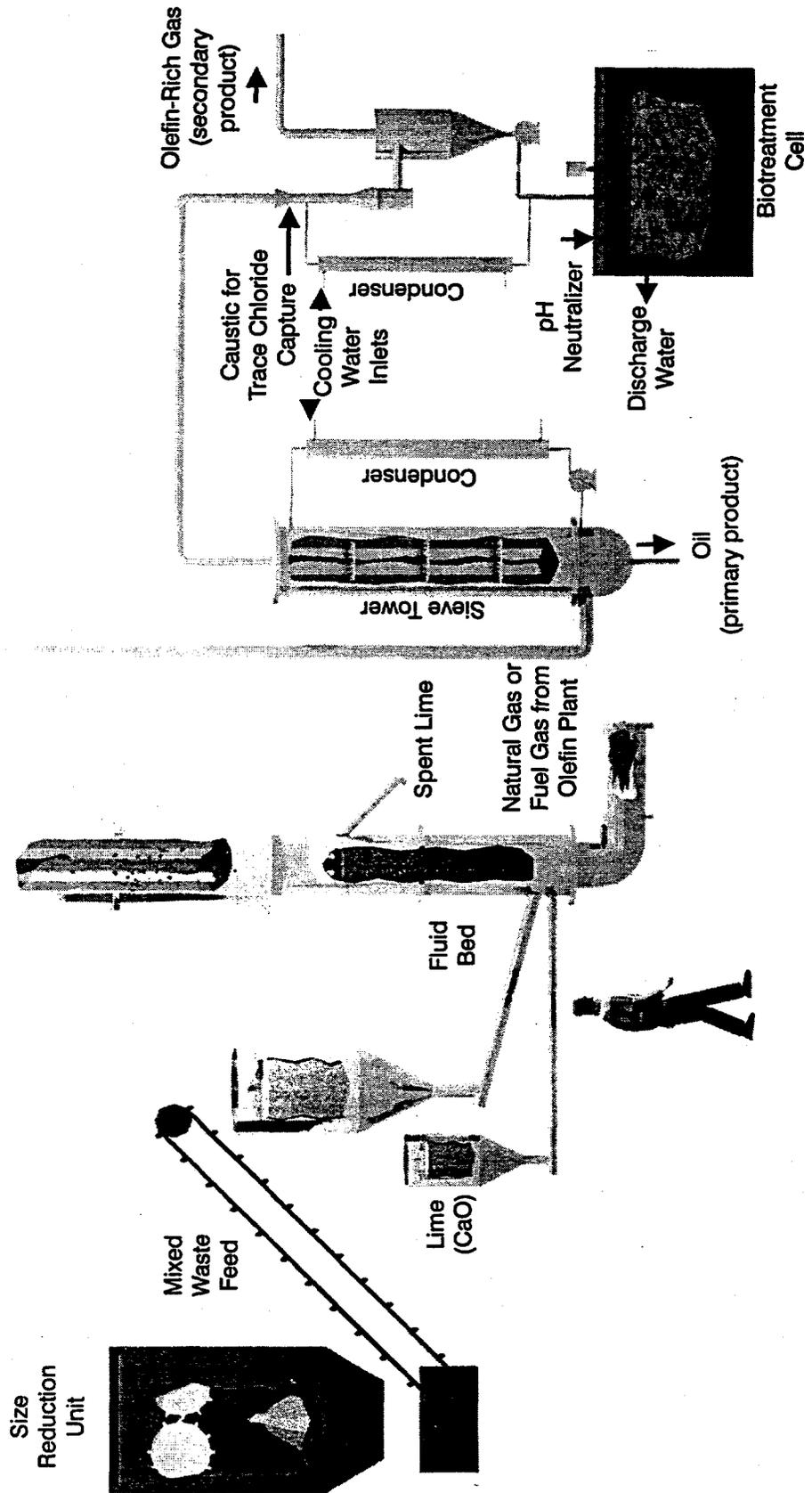


Figure 2. Schematic of PDU.

EERC BN12009E.CDR

#### **4.0 EXPERIMENTAL CONSIDERATIONS**

Experiments on the PDU consisted of 11 test conditions, as shown in Table 2. The first few tests in the series were intended to begin with the easiest process conditions, and with complicating factors gradually added in subsequent tests. Conditions or factors seen as potentially difficult were CaO as a bed material, PVC in the feed, high PET postconsumer plastics, and low decomposition temperatures. Feed introduction was also considered as a potential difficulty.

CaO is used for chlorine capture when PVC or other chlorine-containing plastics are present. One difficulty anticipated with CaO was attrition in the bed, due to the higher fluidization velocities of the PDU relative to the CFBR (where data used for design of PDU tests originated). The PDU does have two cyclones for fines removal, but since little information was yet available on the degree of attrition, the adequacy of these cyclones was unknown. Attrition is a concern, because CaO fines in the product liquids are difficult to remove and add a unit operation (cost) to the process.

While CaO was shown to be quite efficient in chlorine removal in the bench-scale tests, the PDU has a much higher partial pressure of CO<sub>2</sub> than the CFBR. The CFBR is indirectly heated, while the PDU relies on a direct-fired natural gas burner for process heat. CO<sub>2</sub> from the burner may react with CaO to form CaCO<sub>3</sub>. CaCO<sub>3</sub> has been shown to be ineffective for chlorine capture (1).

Postconsumer plastics containing high levels of PET (> 10%) had been observed to cause processing difficulties (1). This is especially true when PET is decomposed without adequate steam/PET ratios (2). Because of limits on quench train cooling capacity, only approximately 30 lb/hr steam could be fed.

Low-temperature tests will result in waxy liquids. The PDU, originally designed for a coal pyrolysis project, was modified (condensation and feed systems) for processing plastics. Prior to the first test with plastics, these modifications had yet to be tested.

Several problems were possible with feeding postconsumer plastic. At the suggestion of fluid-bed scaleup consultants, the point of feed introduction to the process was changed so that material entered through the center of the bed. The change to center feed introduction occurred prior to testing with postconsumer plastics. Feeding to the bottom, center of the bed enables a less complicated model of the system (for scaleup considerations) to be constructed. Center feed implies pneumatic transport in the existing reactor configuration. The plastic, sized to - ¼ in., is difficult to move, having no angle of repose. An additional constraint is imposed by the need to keep the transport tube as small as possible, so as to minimize the amount of cold transport gas added to the system.

#### **5.0 ANALYTICAL METHODS AND DATA REDUCTION**

Table 3 lists analytical methods used to qualify various products. Standard methods are noted as such. Nonstandard methods and variations on standard methods are detailed in Appendix B.

TABLE 2  
Summary of Test Conditions

Run Number	Feed Mix	Temperature, °C	Pressure, psig	Bed Material	Steam, lb/hr	Feed Rate, lb/hr	Gas Fl. Vel., ft/s	Feed Duration, hr	Balance Period, hr
P035	BB <sup>a</sup>	495	20	Sand	30	100	5	2.25	--
P036	BB	625	40	Sand	30	80	4	8.5	3
P037	BB	625	35	Sand	0	100	4	6.0	2.5
P038	BB	625	45	CaO	30	100	4	18.5	8
P039	BB/PVC <sup>b</sup>	625	45	CaO	30	100	4	5	1.5
P040	PC-1 <sup>c</sup>	625	30	Sand	30	85	4	5.5	--
P041-A	PC-2 <sup>d</sup>	575	35	Sand	30	100	4	2	--
P041-B	PC-2	625	35	Sand	30	100	4	9	6
P042	PC-2	625	45	Sand	30	50	4.5	24	16
P043	PC-2	625	45	Sand	30	50	4.5	3	--
P044	PC-2	590	50	Sand	0	70	3.6	15	8

<sup>a</sup> Base blend: 60% HDPE, 20% PS, 20% PP.

<sup>b</sup> 95% base blend, 5% PVC.

<sup>c</sup> Postconsumer blend #1 - mainly HDPE, < 1% PS, < 1% PP possible, based on historical assay by Quality Checked.

<sup>d</sup> Postconsumer blend #2 - 59.2% HDPE, 20.1% PET, 0.6% PVC, 10.7% PP, 4.7% PS, and 4.7% LDPE.

TABLE 3

Sample Description	Analytical Methods	
	Measurement	Method
Plastic Feedstock	V, Ni, Fe, Cu Cl	EPA Method 3051, 6010 ASTM D808-91 <sup>d</sup>
Product Gas	Moisture, fixed carbon, volatiles, ash H <sub>2</sub> , CO <sub>2</sub> , CO, CH <sub>4</sub> , N <sub>2</sub> , C <sub>3</sub> H <sub>6</sub> , C <sub>3</sub> H <sub>8</sub> , I-butane, n-butane, 1-butene, t-2-butene, I-pentane, c-2-butene, n-pentane, C <sub>2</sub> H <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , O <sub>2</sub>	ASTM D3172-89 <sup>a</sup> GC (Appendix B)
Organic Liquids	Boiling point distribution Component analysis Total chlorine Organic chlorine Terephthalic acid V, Ni, Fe, Cu Cl Cyanide	GC-FID <sup>b</sup> (Appendix B) GC-MS <sup>c</sup> ASTM D808-91 <sup>d</sup> GC-AED <sup>e</sup> (Appendix B) See Appendix B EPA Method 3051, 6010 ASTM D808-91 <sup>d</sup> Standard Method 4500 American Public Health Association
Water	Cyanide  Chlorine	Standard Method 4500 American Public Health Association EPA Method 3000
Solids (spent bed material + ash)	Moisture, fixed carbon, volatile, and ash content V, Ni, Fe, Cu Cl Total chlorine	ASTM D3172-89 <sup>a</sup> EPA Method 3051, 6010 ASTM D808-91 <sup>d</sup> Bomb digestion followed by ion chromatography

<sup>a</sup> The thermogravimetric analysis (TGA) proximate analysis used is slightly different from the ASTM specification. In the TGA method, when the sample is heated to 110°C for the moisture analysis determination, the sample is held at 110°C until weight loss ends, whereas the ASTM method specifies a 1-hour hold time. This is justified since the sample size used in the TGA method is small (< 100 mg) compared to that used for non-TGA tests (1000 mg).

<sup>b</sup> Gas chromatography-flame ionization detection.

<sup>c</sup> Gas chromatography-mass spectrometry.

<sup>d</sup> Modified slightly to allow chlorine quantification using ion chromatography instead of silver chloride precipitation.

<sup>e</sup> Gas chromatography-atomic emission detection.

Appendix C details the material balance procedure used. Material balance sheets for all applicable tests are given in Appendix C also. Water and gas yields are combined, as the natural gas burner produces both gas and water, and measurements of gases entering the process are made prior to the burner. Ratios of air to  $\text{CH}_4$  varied, but are indicated for each test.

## 6.0 PDU RESULTS

### 6.1 Summary

Table 4 summarizes all completed tests and conditions, and summarizes key operational notes on the performance of the system. Feeding plastics to the system through the pneumatic transport tube was initially troublesome. Several times, plastic melted in the tube, blocking flow. Another problem encountered was long pieces of plastic bridging across the tube diameter. Although the plastics had been classified to  $\frac{1}{4}$  in., some longer slivers of plastic passed through the screens. This problem could be minimized by several passes through a classifier, but this additional feed preparation adds cost and does not wholly ensure the elimination of oversized pieces. Loss of feed to such an endothermic process results in significant system upset. When feed is lost, temperature rapidly increases in the reactor. While process controls are in place to prevent temperature runaway, the increase that results during the response time is unacceptable. At around  $850^\circ\text{C}$ , the plastics in the bed will experience severe coking. After several attempts at modification to the pneumatic transport configuration (P037-P044), the feed system was modified so that an auger was used to deliver the feed material into the bottom side of the reactor (Figure 2), similar to the feed system of the bench-scale unit.

Chlorine concentration of the various streams from Runs P039 and P041 are given in Table 5. Chlorine balances are unavailable for these tests, but as Table 5 shows, chlorine concentration for liquids from P039 is  $<0.1$  ppm and for P041, 430 ppm.

The change in volatile content of the bed material, as measured by TGA proximate analysis, gives a measure of conversion of  $\text{CaO}$  to  $\text{CaCO}_3$  (Table 6). Volatile content for the starting and ending bed material samples for both of these tests is lost after  $800^\circ\text{C}$ , indicating  $\text{CO}_2$  evolution. Therefore this can be used as a measure of  $\text{CO}_2$  absorption. While no conclusions can be made as to why chlorine content of the P039 product liquids is lower than the P041 product liquid chlorine content (numerous differences exist between the two tests, including different feed compositions, points of feed introduction, starting bed material, and temperature), it can be observed that more of the bed material from P041 is  $\text{CaCO}_3$ , compared with the bed material from P039.

Although PET was present in the postconsumer plastics, difficulties in processing this feed material did not appear to result from its presence. While all PDU tests with PET present were carried out over  $575^\circ\text{C}$ , no significant coking was observed. No streams with PET concentrations over 20% were tested.

TABLE 4  
Operational Summary of PDU Tests

Run No.	P035	P036	P037	P038	P039	P040	P041A	P041B	P042	P043	P044
Feed Mix	Bb <sup>b</sup>	BB	BB	Bb <sup>b</sup>	BB/PVC <sup>c</sup>	PC1 <sup>d</sup>	PC2 <sup>e</sup>	PC2	PC2	PC2	PC2
Temperature, °C	495	625	625	625	625	625	575	625	625	625	590
Starting Bed Material	Sand	Sand	Sand	CaO	CaO	Sand	Sand	Sand	Sand	Sand	Sand
Liquid Character	Wax <sup>f</sup>	Fluid	Fluid	Fluid	Fluid	Fluid	Wax	Viscous <sup>g</sup>	Viscous-Solid	Viscous	Viscous
Reactor Bed	Black with no agglomeration <sup>h</sup>										
Feed Position	Side ½ in.	Side ½ in.	Side ½ in.	Side ¾ in.	Side ¾ in.	Side ¾ in.	Bottom 1 in.	Bottom 1 in.	Bottom 1 in.	Bottom 1 in.	Bottom 1 in.
Shutdown Status	Quench <sup>i</sup>	Feed <sup>j</sup>	Feed <sup>k</sup>	Scheduled <sup>l</sup>	Feed <sup>m</sup>	Feed <sup>n</sup>	Equip. <sup>o</sup>	Equip. <sup>p</sup>	Feed <sup>q</sup>	Equip. <sup>r</sup>	Equip. <sup>s</sup>
HCN	NA	NA	NA	NA	NA	Unknown	Yes	Yes	Yes	Yes	Yes

<sup>a</sup> 5% sand as bed makeup.  
<sup>b</sup> 5% CaO added as bed makeup.  
<sup>c</sup> 95% base blend, 5% PVC; 10% CaO added as bed makeup.  
<sup>d</sup> Postconsumer blend #1; mainly HDPE, with <1% PP and <1% PS possible; 5% CaO as bed makeup, based on historical assay.  
<sup>e</sup> Postconsumer blend #2; 59.2% HDPE, 20.1% PET, 0.6% PVC, 10.7% PP, 4.7% PS, 4.7% LDPE; 15% CaO as bed makeup.  
<sup>f</sup> Liquid consistency was waxy.  
<sup>g</sup> Liquid consistency was much more viscous than previously seen.  
<sup>h</sup> Approximately 0.5% carbon produced by substoich combustion in burner.  
<sup>i</sup> Wax buildup in the quench system.  
<sup>j</sup> Plastic melting in the feed tube.  
<sup>k</sup> Testing continued to next set of conditions with no interruption.  
<sup>l</sup> Air compressor malfunction.  
<sup>m</sup> Loss of feed tube coolant.  
<sup>n</sup> Computer reset causing emergency shutdown procedure initiation.  
<sup>o</sup> Overheating of reactor shell due to a refractory gap.

TABLE 5

Chlorine Analysis and Balance for P039

	Cl Concentration, ppm	
	P039	P041
Feed Material	25,000	28,000
Bed Material	54	8300
Solids Receiver	13	4000
Secondary Cyclone	3.2	NA
Organic Liquids	<0.1	430

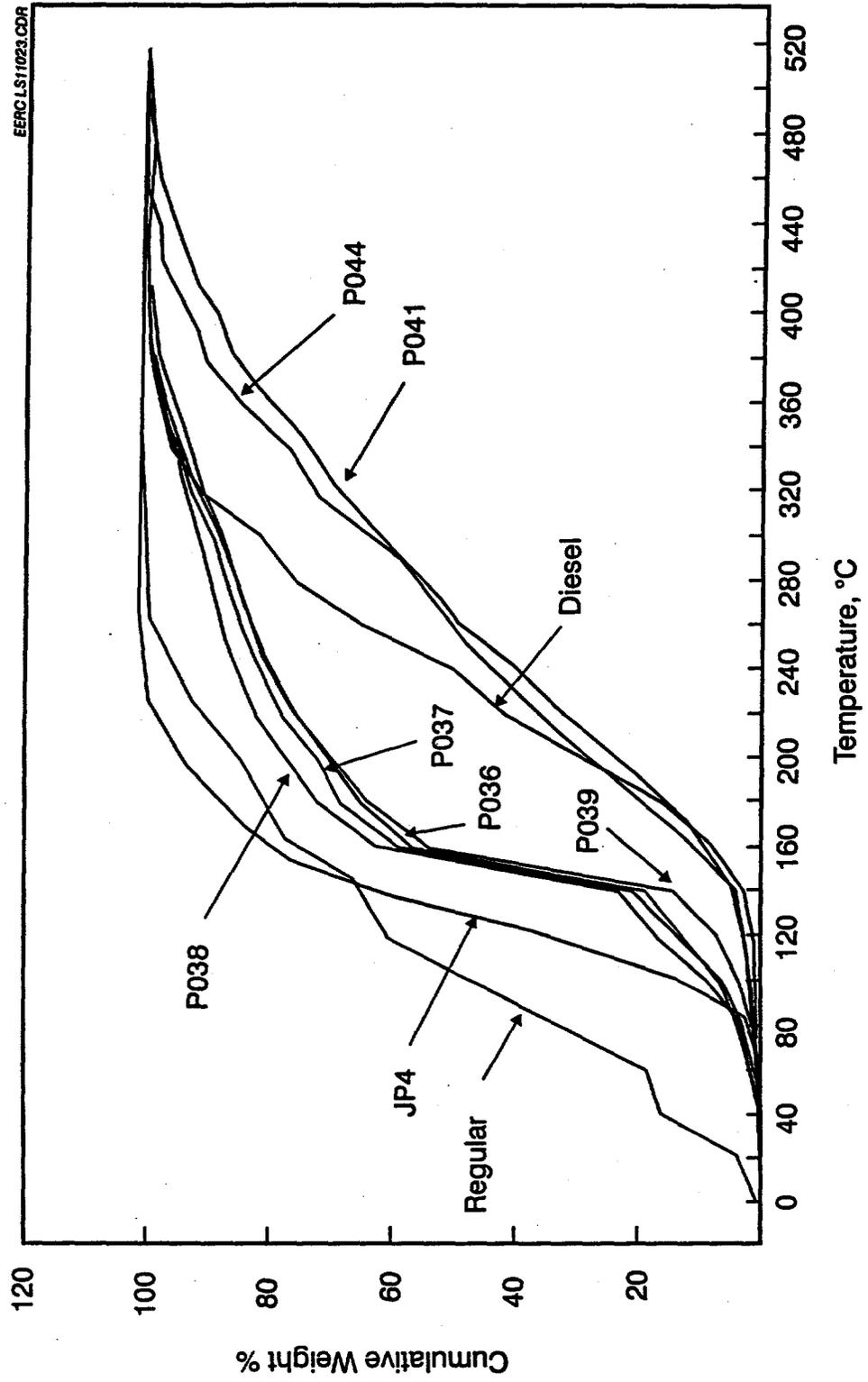
TABLE 6

CaO Conversion

		Start	End
P038	% Volatile	1.94	29
	% CaCO <sub>3</sub>	4.4	65
P039	% Volatile	1.94	20
	% CaCO <sub>3</sub>	4.4	45
P041 Solids Receiver	% Volatile	1.94	13
	% CaCO <sub>3</sub>	4.4	30
P041 Bed Material	% Volatile	1.94	27
	% CaCO <sub>3</sub>	4.4	62

Simulated boiling point distributions for Tests P036-P039, P041, and P044 are shown in Figure 3, along with some common fuels for comparison. Liquids from the tests using postconsumer plastics were noticeably heavier those produced from the base blend. Possibilities considered for the heaviness of the liquids made from postconsumer material included 1) insufficient solids residence time (due to the presence of PET), 2) CaO fines carryover, 3) formation of calcium terephthalate or other organic acid-calcium compounds (from PET decomposition), 4) insufficient gas residence time, 5) coking, and 6) presence of materials in the postconsumer mix that affect decomposition of the mix. Analysis of the liquids and solid residuals from the tests (especially P042) indicated that gas residence time was the most likely cause of the heavier-than-desired liquid product. To clarify gas residence time effect, a series of tests were run on the bench-scale CFBR unit. A residence effect was observed, both on gas and liquid quality, and is discussed briefly in Section 9.0.

Also of concern was whether or not steam is an important variable. Most work prior to the PDU program was performed without steam. Earlier work was done on the CFBR, which has indirect heaters. The PDU, on the other hand, relies on a natural gas-fired burner for



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Figure 3. Simulated boiling point distribution.

process heat, a by-product of which is water. While steam was added in some CFBR tests involving PET, the effect of steam on liquid production from other plastics was not studied. CFBR work indicated that a high steam content is desirable when PET is present. Steam was added to the PDU in some tests, mainly in order to determine condensation train heat load capability. In anticipation of a maximum 30% PET content, 30 lb/hr of steam was used. Based on the residence time study (Section 9.0), it appears that steam has a beneficial effect, producing a lighter boiling point distribution for a given gas residence time at 625°C.

While the PDU and CFBR have been seen to produce similar yields in the pyrolysis of coal, some difference exist, mainly in gas residence times and fluidization velocities. Gas residence time on the PDU can be simulated in the CFBR, but will be at different gas fluidization velocities. The PDU maintains higher fluidization velocities for a given gas residence time, relative to the CFBR. While the two units have similar length-to-diameter ratios (L/Ds), 15 for the PDU and 11 for the CFBR (bottom section measurement), the (heated) cyclones and piping to the condensation train on the PDU are longer than on the CFBR.

## 6.2 Week 1

Operating conditions and product yields for tests run during Week 1 are shown in Table 7. P035 was performed at a temperature of 495°C. As expected, processing at this temperature produced a waxy liquid, and heavy wax formation was observed in the condensation train. The system was shut down after 2.25 hours to clean out the quench train. Plastics feed was occasionally interrupted during this test because of plugging in the feed tube.

Temperature was increased to 650°C in the next test (P036) and fluidization velocity decreased, in an attempt to lighten product liquids. This test went well, and a 3-hour balance period was completed. The balance period was terminated when the feed tube plugged. The feed tube was cleared, the feed material rescreened to eliminate large pieces of feed that had passed through the first screening, and Run P037 begun. Feed was maintained for P037 for approximately 6 hours, during which a 2-hour balance period was completed. As with P036, the balance period was terminated prematurely because of feed tube plugging.

The condensation train of the PDU consists of a sieve tower and two water spray quench venturi scrubbers. Initial plans called for organic liquids to be condensed mainly in the sieve tower, light organics and some water in the first water scrubber, and water in the second water scrubber. The sieve tower uses cooled, condensed, process liquids as a cooling fluid. For start-up, mixed xylenes, with a 2% by weight anisole tracer, were used in the sieve tower. During operation, it was discovered that that level was difficult to maintain in the sieve tower and that a constant sieve tower outlet temperature was maintained (approximately 95°C). Upon reflection, it became apparent that a water/xylene azeotrope was forming. In addition, many of the organic components produced from thermal depolymerization of plastics form azeotropes with water. In subsequent tests, water was used as a start-up fluid for both the sieve tower and water scrubbers. Xylene was used in Tests P035-P037. Xylene is subtracted from all simulated boiling point distributions for these tests (by use of the tracer fluid). After Run P037, water was used as a start-up fluid for both the sieve tower and the water scrubbers.

TABLE 7

Shakedown (Week 1) Tests

Test Conditions			
Run Number	P035	P036	P037
Feed Mix <sup>a</sup>	Base blend with 5% sand	Base blend with 5% sand	Base blend with 5% sand
Bed Material	Sand	Sand	Sand
Temperature °C	495	650	625
Pressure, psig	20	40	30
Fluidization Velocity, ft/s <sup>b</sup>	5	4	4
Steam, lb/hr	30	30	0
Feed Rate, lb/hr	100	80	100
Duration of Feed, hr <sup>c</sup>	2.25	8.5	6.0
Balance Period, hr <sup>d</sup>	0	3	2.5
Product Yields, wt%			
Liquid	Not available (NA)	33	26
Gas + Water <sup>e</sup>	NA	64	74
Solids	NA	3	0
C <sub>2</sub> <sup>-</sup> + C <sub>3</sub> <sup>-</sup> + C <sub>4</sub> <sup>-</sup> Yield	NA	41	46

<sup>a</sup> 5% by weight of the feed material was sand for bed makeup.

<sup>b</sup> Fluidization velocity is based on incoming gas only. Gas produced during the reaction is not accounted for.

<sup>c</sup> Duration of feed refers to the length of time over which plastics were fed to the unit for the specified test.

<sup>d</sup> A balance period is the length of continuous time over which steady-state material balance information is collected.

<sup>e</sup> A natural gas burner is used for process heat, which generates combustion gases and water. Gas composition exiting the burner is not measured.

Simulated boiling point distributions for Tests P036 and P037 are shown in Figure 3, along with some common fuels for comparison. Tabular listings of product liquid components are given in Table 8.

TABLE 8

Tabular Listings of Product Liquid Components					
GC Simulated Distillation Data, Start-Up Fluid-Free, 5-20-94					
BPI, °C	Retention Index	Retention Time, min	ID	P036 WS1+2 Balance	P037 WS1+2 Balance
65.4	589.0	8.623	C6 olefin	0.6	1.6
83.7	650.3	10.623	Benzene	1.7	3.6
95.1	689.1	11.886	C7 olefin	0.7	2
114.0	757.7	13.968	toluene	4.3	8.4
122.6	789.1	14.909	C8 olefin	0.9	2
139.2	854.4	16.730	Ethylbenzene	4.9	8
146.4	883.2	17.518	Styrene	35.5	42
147.9	889.2	17.685	C9 olefin	1.1	1.6
167.7	973.3	19.826	C1 styrene	2.8	2.8
171.4	989.3	20.231	C10 olefin	2	2.4
182.8	1040.1	21.435	Indene	1	1.2
193.7	1089.3	22.584	C11 olefin	1.3	1.2
213.4	1186.3	24.705	Naphthalene	1	1.2

### 6.3 Week 2

Test points completed in Week 2 are shown in Table 9. After successfully processing base blend in sand, CaO was used (P038) as a bed material. Some concern existed over the possible attrition of CaO, since the fluidization velocity in the PDU is much higher than in the CFBR. While some fines carryover was observed, this did not prove to be of significance. The feed tube was increased in diameter to  $\frac{3}{4}$  in. (it was  $\frac{1}{2}$  in. for P035-P037) for P038, in an attempt to eliminate the feed tube plugs experienced in previous runs. With the  $\frac{3}{4}$ -in. tube, feed was maintained for 18.5 hours, and an 8-hour balance period completed. After completion of the 8-hour run, system parameters were changed so that P039 could be run.

P039 used a 5% PVC/95% base blend mixture as feed material. A soda ash solution (pH 12) was added to the second water scrubber to capture HCl released during PVC decomposition. This test was terminated after 5 hours because of bed agglomeration. Upon dropping the bottom of the reactor, it was found that three of the six nozzles on the gas distributor plate had eroded or corroded away. This plate is located at the bottom of the bed, immediately after the natural gas burner. The three possible explanations considered for the nozzle failure were corrosion (from PVC), erosion (from high transport velocities), or corrosion (because of a rich burner). As mentioned, the feed material for this test was introduced via the side of the reactor. (Figure 2). The high velocity of the pneumatically transported feed material caused impingement on the distributor plate, which may have, over time, eroded away sufficient metal to cause the failure. This test was the first to introduce PVC into the system. One scenario envisioned PVC decomposition to HCl at the bottom of the bed, before thorough mixing with the CaO bed material. An alternative scenario considered was that PVC decomposed at the bottom of the bed and that the CaO in this region may have been

TABLE 9

Week 2 Tests

Test Conditions			
Run Number	P038	P039	P040
Feed Mix	Base blend (BB) with 5% sand as bed makeup)	BB/PVC (95/5) (with 5% CaO as bed makeup)	Postconsumer <sup>a</sup> (with 5% CaO as bed makeup)
Bed Material	CaO	CaO	Sand
Temperature °C	625	625	625
Pressure, psig	44	36	40
Fluidization Velocity, ft/s <sup>b</sup>	4	4	4
Steam, lb/hr	30	30	30
Feed Rate, lb/hr	100	100	75
Duration of Feed, hr <sup>c</sup>	18.5	5	5.5
Balance Period, hr <sup>d</sup>	8	1.5	0
Product Yields, wt%			
Liquid	53	NA	NA
Gas + Water	47	NA	NA
Solids	0	NA	NA
C <sub>2</sub> <sup>-</sup> + C <sub>3</sub> <sup>-</sup> + C <sub>4</sub> <sup>-</sup>	31	NA	NA

<sup>a</sup> Mostly HDPE, some PP, PS.

<sup>b</sup> Fluidization velocity is based on incoming gas only. Gas produced during the reaction is not accounted for.

<sup>c</sup> Duration of feed refers to the length of time over which plastics were fed to the unit for the specified test.

<sup>d</sup> A balance period is the length of continuous time over which steady state material balance information is collected.

converted to CaCO<sub>3</sub> from the relatively high concentrations of CO<sub>2</sub>. CaCO<sub>3</sub> has been observed to be ineffective in chlorine capture during thermal depolymerization (1). The HCl, at temperatures in excess of 625°C, would attack the stainless steel distributor plate. The third scenario examined as a possibility was that the stainless steel of the distributor plate was insufficient for the high temperatures it experienced. Normally, a Hastalloy plate is used for this application. Because of changing the feed location to the side of the unit, an older plate, made of stainless steel, was used. In an attempt to lower the fluidization gas (and lengthen gas residence time), the burner was run slightly lean. Temperature at the plate was estimated to be approximately 982°–1093°C (1800°–2000°F). This temperature is not overly problematic in a reducing atmosphere. In order to determine which of the possible reasons considered was responsible for the distributor plate failure, proximate analyses were taken of material on the

plate and further up in the bed, and an SEM analysis was performed on the metal which had flaked off from the plate. The proximate analyses, shown in Table 10, indicate that very little carbonate material is present in the area of the distributor plate, but the bed material higher up (around TC 305) has large quantities of volatile matter (likely carbonate) present. The SEM analysis (listed in tabular form in Appendix D) indicated no chlorine at all, but did indicate several highly oxidized species. The conclusion was, therefore, that the high oxygen content of the burner corroded the plate to the point of failure.

P040 was the first test in the PDU using postconsumer plastics as a feed material. This particular postconsumer plastics feed stream consisted mainly of polyethylenes, with the possibility of some (< 1%) PP and PS present. During this test, numerous feed problems were experienced, and the test was terminated so that the feed system could be reconfigured.

### 6.3.1 Product Liquids

Component analyses for Tests P038 and P039 are given in Table 11. Styrene, from polystyrene decomposition, is found in high concentrations in both samples. Figure 3 shows the simulated boiling point distributions for these two tests, along with those from gasoline and diesel fuel as comparisons.

### 6.3.2 Chlorine Analyses

Chlorine concentration of the various streams from Run P039 are given in Table 12. Methods used for chlorine analysis and their accuracies are given in Appendix B.

## 6.4 Week 3

### 6.4.1 Summary

Week 3 tests conditions and yields are listed in Table 13. These two tests used a postconsumer plastics blend that reportedly consisted of 59.2% HDPE, 10.7% PP, 4.7% LDPE, 4.7% PS, 20.1% PET, 0.6% PVC, based on results of a solvent dissolution method described in Appendix A.

TABLE 10

Proximate Analyses for P039 Bed Material Samples, wt%

Sample	Moisture	Volatile Matter	Fixed Carbon	Ash
Agglomerate on distributor plate	0.0	0.2	0	99.8
Agglomerate at TC 304	0.0	0.6	0	99.4
Agglomerate at TC 305	0.7	21.7	0	77.6
Agglomerate above TC 305	0.2	30.8	0	69.0

TABLE 11

Component Analyses for P038-P039					
GC Simulated Distillation Data, 5-20-94					
(No organic acids detected under GC conditions used)					
				P038	P039
				WS1+2	WS1+2
				Balance	Balance
				GW 482	
BPI, °C	Retention Index	Retention Time, min	ID	GC area%	GC area%
65.4	589.0	8.623	C6 olefin	0.8	0.6
83.7	650.3	10.623	Benzene	1.5	0.8
87.2	662.2	11.009	C6 olefin	0.3	0.2
91.1	675.5	11.441	C6 olefin	0.3	0.2
95.1	689.1	11.886	C7 olefin	0.9	0.7
114.0	757.7	13.968	Toluene	4.8	2.7
122.6	789.1	14.909	C8 olefin	1.2	1.0
139.2	854.4	16.730	Ethylbenz.	5.1	3.2
146.4	883.2	17.518	Styrene	39.0	35.2
147.9	889.2	17.685	C9 olefin	1.5	1.5
154.9	918.3	18.442	C3 benzene	0.7	0.6
159.3	937.5	18.926	MW 118	0.5	0.5
162.0	948.8	19.209	C3 benzene	0.7	0.6
167.7	973.3	19.826	C1 styrene	3.3	3.1
168.5	976.9	19.908	C10 olefin		
171.4	989.3	20.231	C10 olefin	2.7	3.0
175.7	1008.2	20.691	C4 benzene	0.6	0.5
177.9	1018.1	20.922	C1 styrene	0.9	0.8
182.8	1040.1	21.435	Indene	1.0	0.9
184.0	1045.5	21.550			
191.3	1078.3	22.327	C11 olefin	0.6	0.9
193.7	1089.3	22.584	C11 olefin	1.9	2.3
196.0	1099.7	22.826	nC11	0.3	
206.1	1149.9	23.915	C1 indene	0.6	0.6
211.8	1178.4	24.532	C12 olefin		0.8
213.4	1186.3	24.705	Naphthalene	0.9	1.0
214.0	1189.3	24.770	C12 olefin	1.3	1.7
215.8	1198.6	24.958	nC12		
231.5	1279.1	26.602	C13 olefin	0.5	0.8
233.5	1289.4	26.812	C13 olefin	1.1	1.4

Continued . .

Table 11 (continued)

BPI, °C	Retention Index	Retention Time, min	ID	GC area%	GC area%
235.3	1298.5	26.983	nC13		
239.0	1319.3	27.392	C1 naphth.	0.3	
249.7	1379.8	28.540	C14 olefin	0.6	1.0
251.5	1389.7	28.727	C14 olefin	1.0	1.3
253.2	1399.5	28.913	nC14	0.2	0.3
267.2	1480.5	30.354	C15 olefin	0.3	0.6
268.9	1490.3	30.528	C15 olefin	0.8	1.2
270.6	1499.7	30.695	nC15	0.2	0.3
283.7	1581.1	32.067	C16 olefin	0.3	0.6
285.2	1590.6	32.226	C16 olefin	0.6	0.9
286.7	1599.7	32.380	nC16	0.1	0.2
299.3	1681.6	33.686	C17 olefin	0.3	0.5
300.8	1690.8	33.833	C17 olefin	0.4	0.7
302.2	1699.7	33.975	nC17	0.1	0.2
314.1	1781.9	35.223	C18 olefin	0.3	0.5
315.4	1790.7	35.357	C18 olefin	0.4	0.7
316.6	1799.1	35.485	nC18	0.1	0.3
328.1	1882.3	36.680	C19 olefin	0.2	0.4
329.3	1890.9	36.803	C19 olefin	0.4	0.7
330.5	1899.2	36.922	nC19	0.1	0.5
341.6	1982.8	38.069	C20 olefin	0.2	0.4
342.7	1990.9	38.180	C20 olefin	0.3	0.5
344.0	2000.8	38.314	nC20	0.3	0.8
354.7	2084.5	39.391	C21 olefin	0.2	0.4
355.8	2092.6	39.495	C21 olefin	0.2	0.4
356.7	2100.4	39.595	nC21	0.0	0.3
367.0	2184.3	40.657	C22 olefin	0.1	0.4
367.9	2191.8	40.751	C22 olefin	0.2	0.4
368.8	2199.1	40.843	nC22	0.0	0.6
378.3	2284.7	41.867	C23 olefin	0.1	0.3
379.1	2291.9	41.953	C23 olefin	0.2	0.3
379.9	2299.0	42.038	nC23	0.0	0.5
389.4	2384.6	43.070	C24 olefin	0.1	0.3
390.2	2391.8	43.157	C24 olefin	0.2	0.3
390.9	2397.9	43.231	nC24		0.5
400.3	2486.8	44.351	C25 olefin	0.1	0.2
401.1	2494.1	44.442	C25 olefin	0.2	0.3
401.7	2499.7	44.513	nC25		0.1
412.1	2597.7	45.749	C26 olefin	0.1	0.2
412.9	2605.4	45.846	C26 olefin	0.1	0.2
			Total	82.5	83.9

TABLE 12

Chlorine Analyses for P039

	Cl Concentration, mg/g
Feed Material	5000
Bed Material	54
Solids Receiver	13
Secondary Cyclone	3.2
Organic Liquids	<0.1
Water	200 mg/L

TABLE 13

Week 3 Tests

Test Conditions		
Run Number	P041-A	P041-B
Feed Mix	Postconsumer with 15% CaO	Postconsumer with 15% CaO
Bed Material	Sand	Sand
Temperature, °C	575	625
Pressure, psig	40	40
Fluidization Velocity, ft/s <sup>a</sup>	4	4
Steam, lb/hr	30	30
Feed Rate, lb/hr	100	100
Duration of Feed, hr <sup>b</sup>	2	9
Balance Period, hr <sup>c</sup>	0	6
Product Yields, wt%		
Liquid	NA	63
Gas + Water	NA	22
Solids	NA	15
C <sub>2</sub> <sup>-</sup> + C <sub>3</sub> <sup>-</sup> + C <sub>4</sub> <sup>-</sup>	NA	35

<sup>a</sup> Fluidization velocity is based on incoming gas only. Gas produced during the reaction is not accounted for.

<sup>b</sup> Duration of feed refers to the length of time over which plastics were fed to the unit for the specified test.

<sup>c</sup> A balance period is the length of continuous time over which steady-state material balance information is collected.

Prior to the start of P041, the 1/2-in. feed tube was replaced with a 3/4-in. tube, in an attempt to eliminate the persistent feed tube plugging problems experienced throughout the first two weeks of testing. Additionally, feed was introduced into the bottom of the reactor, as per the suggestion of the fluid-bed scaleup consultants. A water jacket was added to the feed tube so that the plastic feed would not melt in the tube before reaching the bed. Initial tests used 3/8-in. feed material. This size of postconsumer plastic flake produced severe bridging in the feed system. The 3/8-in. material would not flow from a vertical 4-in. pipe into the feed hopper. The feed was subsequently resized to 1/4 in., and attempts at feeding continued. While periodic plugging of the feed tube was experienced during this run, the test was terminated because a leak developed in the water jacket of the cooling tube surrounding the feed tube. This significant repair caused testing to be terminated for the remainder of the week.

#### 6.4.2 Liquids

A simulated boiling point distribution for a composite sample from P041 is given in Figure 3, and component analysis for the test is given in Table 14.

#### 6.4.3 HCN

During Test P041, hydrogen cyanide (HCN) was detected in the product gas stream and in the vents from the water scrubber collection barrels. A sodium bicarbonate solution was maintained in the water scrubbers in anticipation of HCN formation. Actual HCN levels are not known, as the meter used for detection has an upper detection limit of 100 ppm, and all readings were off scale. HCN levels in the liquid product was measured to be 1.16 mg/L, and in the liquid "sludge" (heavier liquid layer), HCN was measured to be 10.7 µg/g.

#### 6.4.4 Metals

Several streams from P041 were analyzed for metals content to gain insight into the distribution of metals during thermal decomposition. Analyses for those streams tested are given in Table 15.

TABLE 14

Component Analysis for P041				
GC Simulated Distillation Data, 5-20-94				
(no organic acids detected under GC conditions used)				
				P041
				Balance
BPI, °C	Retention Index	Retention Time, min	ID	GC area %
65.4	589.0	8.623	C6 olefin	0.2
83.7	650.3	10.623	Benzene	0.6
87.2	662.2	11.009	C6 olefin	0.1
91.1	675.5	11.441	C6 olefin	0.1

Continued . . .

Thermal Depolymerization of Plastics Table 14 (continued)

BPI, °C	Retention Index	Retention Time, min	ID	GC area %
95.1	689.1	11.886	C7 olefin	0.3
114.0	757.7	13.968	Toluene	0.5
122.6	789.1	14.909	C8 olefin	0.6
139.2	854.4	16.730	Ethylbenzene	0.4
146.4	883.2	17.518	Styrene	1.6
147.9	889.2	17.685	C9 olefin	1.2
154.9	918.3	18.442	C3 benzene	
159.3	937.5	18.926	MW 118	0.2
162.0	948.8	19.209	C3 benzene	0.1
167.7	973.3	19.826	C1 styrene	
168.5	976.9	19.908	C10 olefin	0.8
171.4	989.3	20.231	C10 olefin	3.5
175.7	1008.2	20.691	C4 benzene	
177.9	1018.1	20.922	C1 styrene	
182.8	1040.1	21.435	Indene	0.2
184.0	1045.5	21.550		1.7
191.3	1078.3	22.327	C11 olefin	1.1
193.7	1089.3	22.584	C11 olefin	4.0
196.0	1099.7	22.826	nC11	0.6
206.1	1149.9	23.915	C1 indene	
211.8	1178.4	24.532	C12 olefin	1.6
213.4	1186.3	24.705	Naphthalene	
214.0	1189.3	24.770	C12 olefin	3.6
215.8	1198.6	24.958	nC12	0.7
231.5	1279.1	26.602	C13 olefin	1.8
233.5	1289.4	26.812	C13 olefin	3.5
235.3	1298.5	26.983	nC13	0.8
239.0	1319.3	27.392	C1 nphthn.	
249.7	1379.8	28.540	C14 olefin	3.2
251.5	1389.7	28.727	C14 olefin	3.7
253.2	1399.5	28.913	nC14	0.5
267.2	1480.5	30.354	C15 olefin	1.6
268.9	1490.3	30.528	C15 olefin	3.0
270.6	1499.7	30.695	nC15	0.6
283.7	1581.1	32.067	C16 olefin	1.6
285.2	1590.6	32.226	C16 olefin	2.4
286.7	1599.7	32.380	nC16	0.5
299.3	1681.6	33.686	C17 olefin	1.4
300.8	1690.8	33.833	C17 olefin	2.0
302.2	1699.7	33.975	nC17	0.4
314.1	1781.9	35.223	C18 olefin	1.4
315.4	1790.7	35.357	C18 olefin	2.0
316.6	1799.1	35.485	nC18	0.3
328.1	1882.3	36.680	C19 olefin	1.3

Continued . . .

Table 14 (continued) *Thermal Depolymerization of Plastics*

BPI, °C	Retention Index	Retention Time, min	ID	GC area %
329.3	1890.9	36.803	C19 olefin	1.9
330.5	1899.2	36.922	nC19	0.4
341.6	1982.8	38.069	C20 olefin	1.3
342.7	1990.9	38.180	C20 olefin	1.6
344.0	2000.8	38.314	nC20	0.4
354.7	2084.5	39.391	C21 olefin	1.2
355.8	2092.6	39.495	C21 olefin	1.5
356.7	2100.4	39.595	nC21	0.3
367.0	2184.3	40.657	C22 olefin	1.1
367.9	2191.8	40.751	C22 olefin	1.3
368.8	2199.1	40.843	nC22	0.3
378.3	2284.7	41.867	C23 olefin	1.0
379.1	2291.9	41.953	C23 olefin	1.2
379.9	2299.0	42.038	nC23	0.4
389.4	2384.6	43.070	C24 olefin	0.9
390.2	2391.8	43.157	C24 olefin	1.1
390.9	2397.9	43.231	nC24	0.4
400.3	2486.8	44.351	C25 olefin	0.8
401.1	2494.1	44.442	C25 olefin	1.0
401.7	2499.7	44.513	nC25	0.2
412.1	2597.7	45.749	C26 olefin	0.7
412.9	2605.4	45.846	C26 olefin	0.9
413.1	2609.3	45.885	nC26	0.2
422.0	2697.8	47.259	C27 olefin	0.7
422.6	2704.6	47.374	C27 olefin	0.8
423.1	2709.0	47.453	nC27	0.2
431.5	2797.7	49.022	C28 olefin	0.6
432.1	2804.4	49.152	C28 olefin	0.7
432.5	2808.7	49.240	nC28	0.2
440.4	2897.8	51.052	C29 olefin	0.5
441.0	2904.9	51.196	C29 olefin	0.6
441.5	2909.9	51.298	nC29	0.1
450.8	3014.2	53.419	C30 olefin	0.4
451.4	3021.6	53.570	C30 olefin	0.5
451.9	3027.5	53.690	nC30	0.1
462.8	3149.8	56.177	C31 olefin	0.4
463.6	3158.6	56.357	C31 olefin	0.4
477.1	3309.8	59.432	C32 olefin	0.3
478.0	3319.8	59.635	C32 olefin	0.3
493.9	3498.6	63.272	C33 olefin	0.2
494.9	3510.6	63.516	C33 olefin	0.2
513.8	3722.8	67.833	C34 olefin	0.2
515.0	3735.6	68.093	C34 olefin	0.2
			Total	83.2

TABLE 15

P041 Metals and Cl Analyses					
	V, $\mu\text{g/g}$	Ni, $\mu\text{g/g}$	Fe, $\mu\text{g/g}$	Cu, $\mu\text{g/g}$	Cl, mg/g
Plastics Feed	<5	<10	200	<10	28
CaO	5.44	<10	2170	<10	0.052
Product Oils (WS 1&2)	<5	<10	200	<10	28
Water (WS 1&2)	NA <sup>a</sup>	NA	NA	NA	910 mg/L
Water (sieve tower)	NA	NA	NA	NA	360 mg/L
Bed Material	NA	NA	NA	NA	8.3
Solids Receiver	NA	NA	NA	NA	4.0

<sup>a</sup> Not analyzed.

### 6.5 Week 4

After the cooling jacket for the feed tube was modified for Week 4 to include an expansion joint, a 16-hr balance period was completed for P042. Conditions and yields for this test and for P043 are shown in Table 16. Slight feed tube plugging was observed in P042, but did not force interruption of the test. Two incidents were recorded, in which it was believed

TABLE 16

Week 4 Tests		
Test Conditions		
Run Number	P042	P043
Feed Mix	Postconsumer w/15% CaO	Postconsumer w/15% CaO
Bed Material	Sand	Sand
Temperature, °C	625	625
Pressure, psig	45	45
Fluidization Velocity, ft/s <sup>a</sup>	4.5	4.5
Steam, lb/hr	32	30
Feed Rate, lb/hr	50	50
Duration of Feed, hr <sup>b</sup>	23	3
Balance Period, hr <sup>c</sup>	16	--
Product Yields, wt%		
Liquid	27	NA
Gas + Water	73	NA
Solids	0	NA
C <sub>2</sub> <sup>-</sup> + C <sub>3</sub> <sup>-</sup> + C <sub>4</sub> <sup>-</sup>	24	NA

<sup>a</sup> Fluidization velocity is based on incoming gas only. Gas produced during the reaction is not accounted for.

<sup>b</sup> Duration of feed refers to the length of time over which plastics were fed to the unit for the specified test.

<sup>c</sup> A balance period is the length of continuous time over which steady-state material balance information is collected.

that the feed tube plugged momentarily, but material broke through, and the test was continued. Two 8-hr balance periods were completed. At the start of the third 8-hr balance period, the feed tube plugged, and the test was terminated to clean out the feed system. The feed system was cleaned out, and testing resumed at the same conditions (P043). "Liquids" produced from P042 were quite heavy, and several analytical tests were run to determine the cause of the poor liquid quality. Several theories were put forth, including 1) the possibility of terephthalic or other organic acid formation, 2) CaO fines carryover, 3) incomplete decomposition (short gas residence time), 4) unknown substances entering the process with the postconsumer feed (e.g., paper) that do not decompose at the same conditions as the plastics, and 5) coking. As a start, proximate analyses of the liquid from P042 were performed. Results of these analyses are shown in Table 17, and Figure 4 shows the volatile decomposition temperature profile of the sample. The proximate analyses indicate a high amount of ash. Some fixed carbon is indicated, but this may be generated by the analytical procedure, which measures volatiles by heating the sample to 950°C prior to the fixed-carbon measurement. The high ash level in initial proximate analyses could have been explained by either the presence of CaO fines, coked material, or organic acids. TGA, as well as a THF (tetrahydrofuran) solubility (to check the fines level) and organic acids quantification were also performed on a composite sample. Details of these analyses are given in Appendix E. This more in-depth analysis indicated about 40% partially reacted polymer material, about 3% organic acid content, and less than 5% highly carbonized (coked) material. Based on these findings, insufficient gas residence time was judged to be the primary reason for the unsatisfactory liquid character.

Early in Test P043, the computer controlling the PDU was inadvertently shut off, initiating an emergency shutdown procedure. The depressurization that occurred during the emergency shutdown caused liquids in the quench to surge, coating pipes downstream of the cooling train and up to the flare. When the system was restarted, the organics coating these pipes started to produce a mist over the parking lot of the EERC. When the misting problem was discovered, testing was terminated so that these pipes could be thoroughly cleaned out. In the event of any such future disturbances, two coke scrubbers were placed after the condensation system to remove any entrained vapors that might escape the quench train.

As with P041, HCN was detected at levels higher than the upper detection limit for the HCN meter during P042. This is a concern, since the bicarbonate solutions in the water scrubbers should have captured most of the HCN generated.

TABLE 17

P042 Sieve Tower Proximate Analyses

	Sample No. 1	Sample No. 2	Sample No. 3
Moisture, wt%	17.95	31.98	32.13
Volatile Matter, wt%	38.04	36.35	47.91
Fixed Carbon, wt%	5.65	5.11	4.97
Ash, wt%	38.36	26.57	14.99

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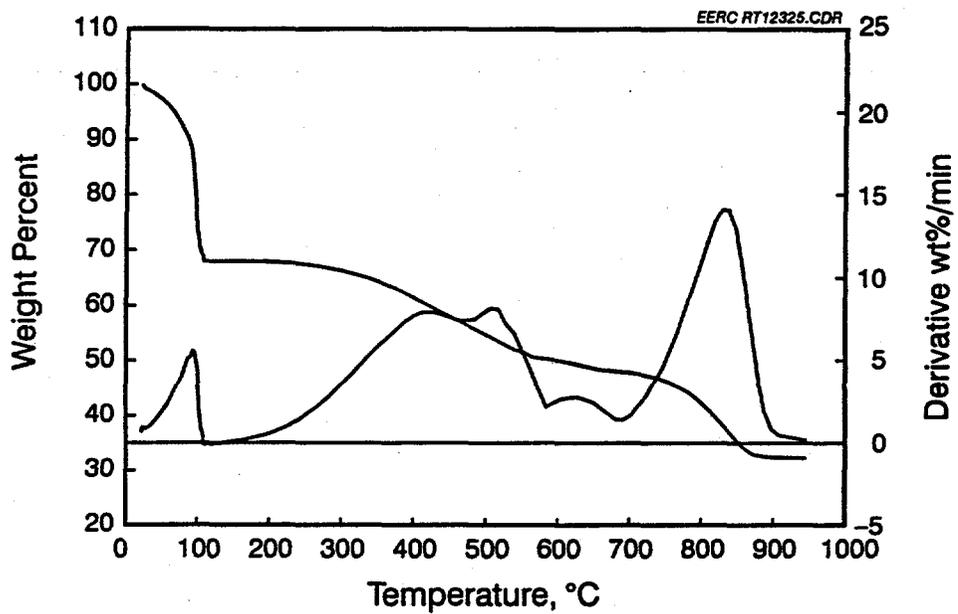
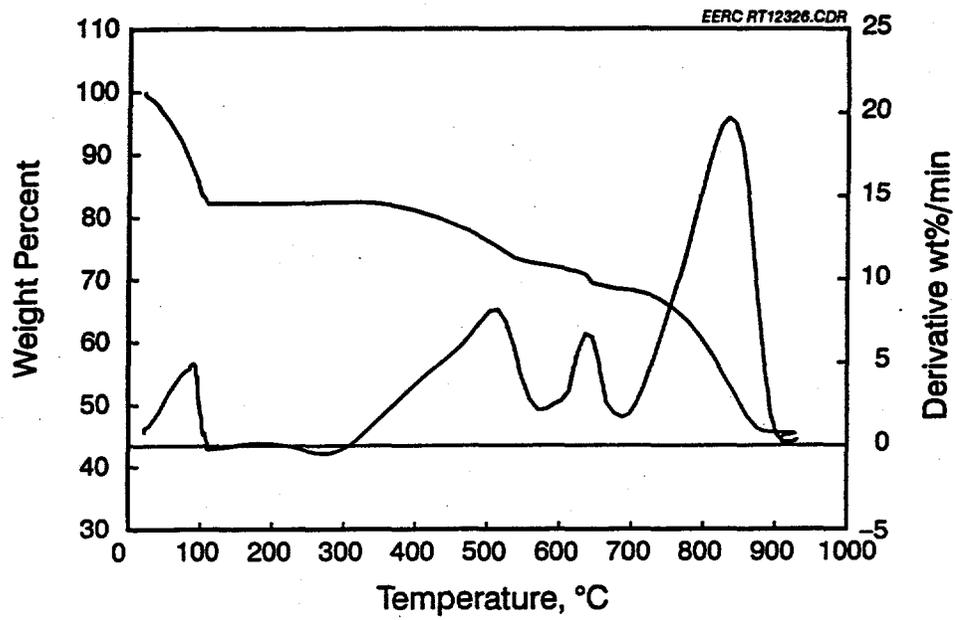


Figure 4. TGA profiles of three samples of P042 liquids recovered from sieve tower.

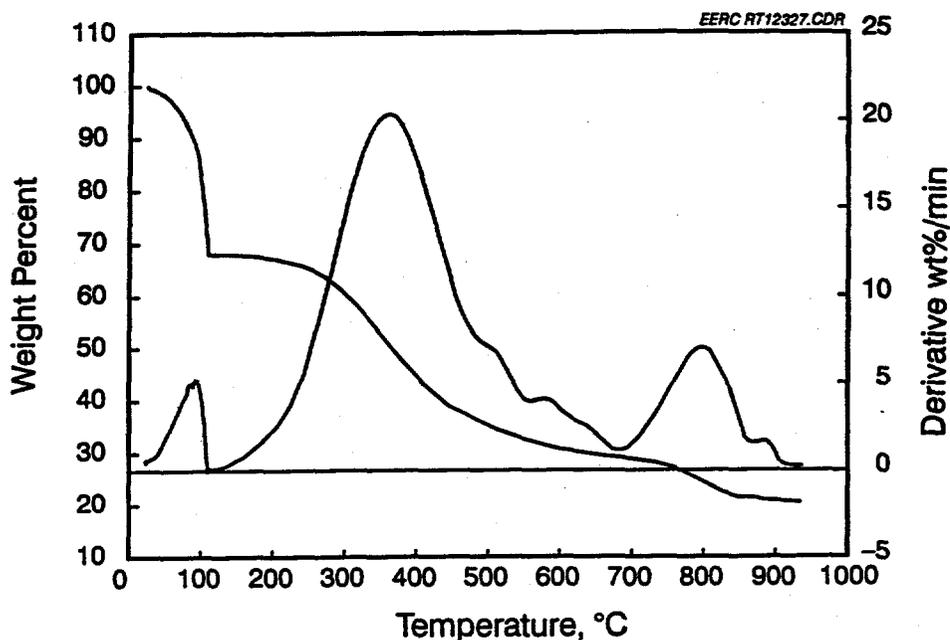


Figure 4. Continued.

## 6.6 Week 5

### 6.6.1 Summary

Conditions and yields for the last test in this phase of this phase of the PDU program, P044, are shown in Table 18. This test went well, with no feed problems experienced. An uneventful 8-hr balance period was completed. After completion of the balance period, the test was terminated because of unacceptably high skin temperatures on the bottom section of the reactor. The high skin temperatures were due to refractory failure in the vicinity of a recently replaced thermowell, located on the lower bottom section. It is thought that vapor from the burner gas channeled through a crack in the refractory in this area.

### 6.6.2 Liquids

A simulated boiling point distribution for P044 is shown in Figure 3, and a component analysis is given for the product liquids in Table 19. Liquid yields are low for this test, as excess air was added to lower the fluidization velocity (and increase gas residence time) by burning some feed material for heat.

## 7.0 COMPOSITE LIQUIDS

A composite sample of product liquids was analyzed to determine the appropriateness of sending the material to a refinery. The simulated boiling point distribution is shown in

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Figure 5. Since Runs P035–P037 used xylene as a start-up fluid for the quench system, the region where xylene boils is disproportionately represented. Figure 5 also shows what this distribution would be if the xylene had not been added. The xylene content was calculated, based on the concentration of anisole, which was added to the xylene as a tracer. Significant properties of the composite liquids are given in Table 20, and Table 21 is a component breakdown of the composite liquids.

TABLE 18

Week 5 Tests	
Test Conditions	
Run Number	P044
Feed Mix	Postconsumer with 7% CaO
Bed Material	Sand
Temperature, °C	590
Pressure, psig	50
Fluidization Velocity, ft/s <sup>a</sup>	3.4
Steam, lb/hr	0
Feed Rate, lb/hr	68
Duration of Feed, hr <sup>b</sup>	15
Balance Period, hr <sup>c</sup>	8
Product Yields, wt%	
Liquid	18
Gas + Water	79
Solids	4
$C_2^= + C_3^= + C_4^=$	16

<sup>a</sup> Fluidization velocity is based on incoming gas only. Gas produced during the reaction is not accounted for.

<sup>b</sup> Duration of feed refers to the length of time over which plastics were fed to the unit for the specified test.

<sup>c</sup> A balance period is the length of continuous time over which steady-state material balance information is collected.

TABLE 19

Product Liquid Analysis for P044				
Identification	BPI, °C	Retention Index	Retention Time, min	P044 Conc., %
C <sub>6</sub> H <sub>12</sub>	65.2	588.6	8.610	0.17
Benzene	83.7	650.3	10.620	0.40
C7 or C8	87.1	661.9	11.000	NI
C7 or C8	95.0	688.9	11.876	0.37

Continued . . .

Table 19 (continued)

Identification	BPI, °C	Retention Index	Retention Time, min	P044 Conc., %
Toluene	114.0	757.3	13.955	0.50
C <sub>8</sub> H <sub>16</sub>	122.6	788.9	14.900	0.81
Ethylbenzene	139.0	853.7	16.702	0.54
<i>m</i> -, <i>p</i> -Xylene	141.1	862.1	16.933	0.42
Styrene	145.7	880.2	17.428	0.97
<i>o</i> -Xylene	147.0	885.6	17.575	0.38
C <sub>9</sub> H <sub>18</sub>	147.9	889.2	17.673	1.90
C <sub>10</sub> H <sub>20</sub>	171.4	989.3	20.219	4.35
Indene	182.8	1040.2	21.424	0.37
	184.0	1045.6	21.550	1.45
C <sub>11</sub> H <sub>22</sub>	193.8	1089.6	22.574	3.98
C <sub>11</sub> H <sub>24</sub>	196.1	1100.2	22.822	1.34
C1 Indene	206.1	1150.1	23.902	0.46
C1 Indene	207.2	1155.5	24.019	0.46
Naphthalene	213.4	1186.7	24.695	0.38
C <sub>12</sub> H <sub>24</sub>	214.0	1189.7	24.760	3.33
C <sub>12</sub> H <sub>26</sub>	216.1	1200.2	24.987	1.46
C <sub>13</sub> H <sub>26</sub>	233.7	1290.1	26.805	3.45
C <sub>13</sub> H <sub>28</sub>	235.9	1301.6	27.035	1.81
C1 Naphthalene	239.1	1320.0	27.384	0.40
	250.0	1381.2	28.545	1.07
C <sub>14</sub> H <sub>28</sub>	251.6	1390.4	28.720	3.30
C <sub>14</sub> H <sub>30</sub>	253.3	1400.3	28.907	1.56
C <sub>15</sub> H <sub>30</sub>	269.0	1490.6	30.520	3.13
C <sub>15</sub> H <sub>32</sub>	270.6	1500.2	30.691	1.62
	283.7	1581.6	32.060	0.83
C <sub>16</sub> H <sub>32</sub>	285.2	1591.0	32.218	2.65
C <sub>16</sub> H <sub>34</sub>	286.7	1600.3	32.375	1.61
	290.8	1626.5	32.796	0.49
	299.4	1682.2	33.680	0.85
C <sub>17</sub> H <sub>34</sub>	300.8	1691.3	33.825	2.44
C <sub>17</sub> H <sub>36</sub>	302.2	1700.2	33.967	1.44
	314.2	1782.7	35.215	0.74
C <sub>18</sub> H <sub>36</sub>	315.4	1791.3	35.346	2.29

Continued . . .

Table 19 (continued)

Identification	BPI, °C	Retention Index	Retention Time, min	P044 Conc., %
C <sub>18</sub> H <sub>38</sub>	316.7	1800.1	35.478	1.31
C <sub>19</sub> H <sub>38</sub>	329.4	1891.7	36.793	2.26
C <sub>19</sub> H <sub>40</sub>	330.6	1900.2	36.915	1.36
C <sub>20</sub> H <sub>40</sub>	342.8	1992.0	38.171	1.93
C <sub>20</sub> H <sub>42</sub>	343.9	2000.2	38.283	1.34
C <sub>21</sub> H <sub>42</sub>	355.8	2092.8	39.485	1.73
C <sub>21</sub> H <sub>44</sub>	356.8	2100.6	39.586	1.19
C <sub>22</sub> H <sub>44</sub>	368.0	2192.6	40.740	1.56
C <sub>22</sub> H <sub>46</sub>	368.9	2200.1	40.834	1.17
C <sub>23</sub> H <sub>46</sub>	379.2	2293.0	41.942	1.30
C <sub>23</sub> H <sub>48</sub>	380.0	2300.3	42.028	1.05
C <sub>24</sub> H <sub>48</sub>	390.3	2392.9	43.142	1.10
C <sub>24</sub> H <sub>50</sub>	391.1	2400.2	43.230	0.89
				71.94

BPI = GC boiling point index.

Conc. = Concentration.

NI = Not identified.

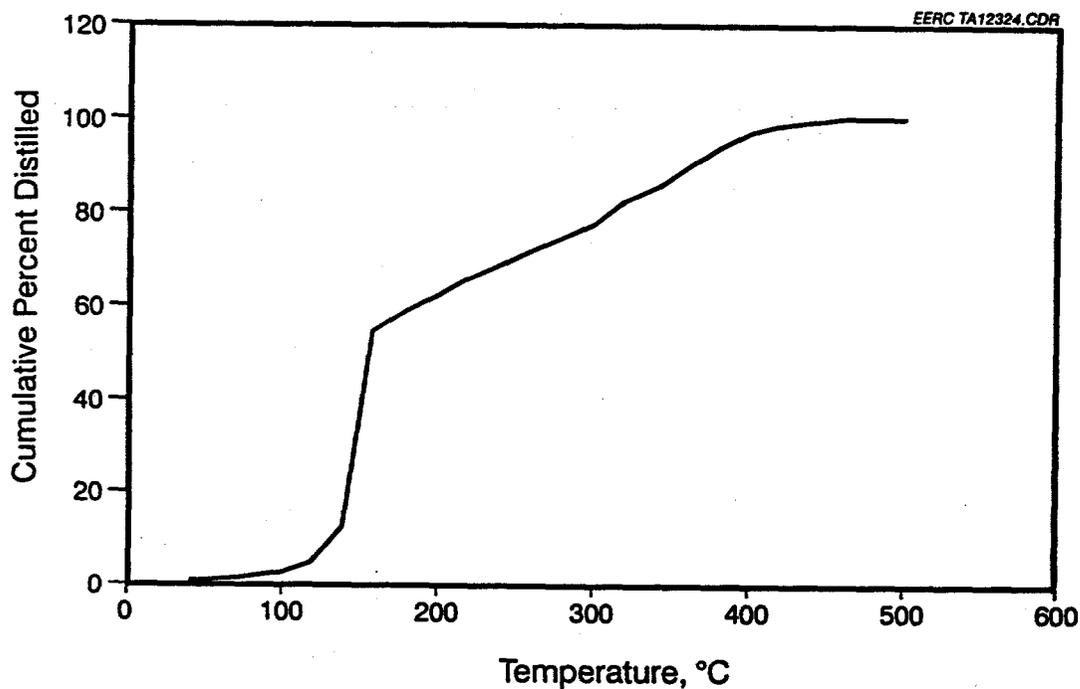


Figure 5. Simulated boiling point distribution and boiling point distribution minus xylene.

TABLE 20

Properties of Plastics Decomposition Liquids Composite Sample	
Flashpoint	32°C
Specific Gravity @ 20°C	0.91
	Concentration, µg/g
Chlorine	43
Fluorine	<30
Bromine	<30
Iron	30.5
Copper	<10
Vanadium	<5
Nickel	<10
	Concentration, wt%
Sulfur	0.03
Nitrogen	0.55

TABLE 21

Analysis of Big Reactor Composite Depolymerization Liquids			
Sampled from 500-gal Steel Tank on 7-27-94			
Sample is about 60% aromatics, 40% olefins and aliphatics.			
	BPI, °C	Retention Time, min	Conc., area%
C <sub>6</sub> H <sub>12</sub>	65.0	8.549	0.22
Benzene	83.3	10.540	0.49
C <sub>7</sub> H <sub>14</sub>	94.8	11.806	0.31
Toluene	113.5	13.869	1.48
C <sub>8</sub> H <sub>16</sub>	122.2	14.820	0.43
Ethylbenzene	138.6	16.624	6.49
<i>m</i> -, <i>p</i> -Xylene	140.9	16.869	19.37
Styrene	145.4	17.360	14.50
<i>o</i> -Xylene	146.6	17.500	5.83
C <sub>9</sub> H <sub>18</sub>	147.4	17.586	0.74
Anisole	150.1	17.876	0.73
C3 Benzene	154.3	18.340	0.32

Continued . . .

Thermal Depolymerization of Plastics Table 21 (continued)

	BPI, °C	Retention Time, min	Conc., area%
C1 Styrene	167.1	19.715	1.35
C <sub>10</sub> H <sub>20</sub>	170.9	20.125	1.36
C1 Styrene	177.3	20.815	0.40
Indene	182.2	21.323	0.49
C <sub>11</sub> H <sub>22</sub>	193.2	22.476	1.15
nC11	195.5	22.725	0.18
C1 Indene	205.5	23.800	0.36
naphthalene	212.7	24.585	0.67
C <sub>12</sub> H <sub>24</sub>	213.4	24.660	1.01
nC12	215.5	24.885	0.25
C <sub>13</sub> H <sub>26</sub>	233.0	26.700	1.03
nC13+C1			
naphthalene	235.1	26.921	0.50
Biphenyl	249.2	28.430	0.79
C <sub>14</sub> H <sub>28</sub>	250.9	28.614	1.07
nC14	252.6	28.804	0.37
C <sub>15</sub> H <sub>30</sub>	268.2	30.413	1.07
nC15	269.9	30.583	0.30
C <sub>16</sub> H <sub>32</sub>	284.4	32.110	0.98
nC16	285.9	32.266	0.28
C <sub>17</sub> H <sub>34</sub>	300.0	33.715	0.94
nC17	301.4	33.859	0.28
C <sub>18</sub> H <sub>36</sub>	314.6	35.237	1.02
nC18	315.8	35.367	0.36
C <sub>19</sub> H <sub>38</sub>	328.5	36.682	0.98
nC19	329.7	36.803	0.40
C <sub>20</sub> H <sub>40</sub>	341.9	38.060	0.85
nC20	343.0	38.173	0.92
C <sub>21</sub> H <sub>42</sub>	355.1	39.371	0.82
nC21	356.1	39.471	0.30
C <sub>22</sub> H <sub>44</sub>	367.2	40.625	0.68
nC22	368.1	40.719	0.42
C <sub>23</sub> H <sub>46</sub>	378.4	41.826	0.65
nC23	379.2	41.911	0.51
C <sub>24</sub> H <sub>48</sub>	389.4	43.015	0.65
nC24	390.2	43.101	0.55
C <sub>25</sub> H <sub>50</sub>	400.5	44.281	0.47
nC25	401.2	44.368	0.22
C <sub>26</sub> H <sub>52</sub>	412.3	45.661	0.37
nC26	413.1	45.753	0.16
Total Identified			76.07

## 8.0 RESIDUALS

All available bed material, solids receiver, and primary and secondary cyclone analyses are listed in Table 22. Of particular interest is the  $\text{CaCO}_3$  content of the starting and ending bed material. Conversion of  $\text{CaO}$  to  $\text{CaCO}_3$  is of interest because the carbonate is ineffective for chlorine capture. Proximate analysis was performed by TGA. This method allows for identification of the volatile material. If volatile material is evolved exclusively above about  $850^\circ\text{C}$ , it is assumed to be  $\text{CO}_2$  evolution. If a sharp weight loss is observed at  $560^\circ\text{C}$ , the weight loss is assumed to be due to the evolution of water (from  $\text{Ca}[\text{OH}]_2$ ). These evolutions are shown on the TGA graphs in Appendix F.

## 9.0 CFBR RESIDENCE TIME STUDY

In order to gain a better understanding of the effect of residence time on liquid yields and boiling point distribution, a series of tests were performed in the CFBR. Conditions of these tests and major product yields are shown in Table 23. All tests used postconsumer

TABLE 22

Residual Analyses						
Run Number	Description	Proximate Analysis, wt% (as-rec.)				Chlorine ppm
		Moisture	Volatile	Fixed Carbon	Ash	
All Runs	CaO sorbent		1.94		98.06	52
P035	Bed material	0.00	0.10	0.00	99.87	
	Secondary cyclone	0.00	0.66	0.00	99.24	
P036	Bed material	0.00	0.01	0.00	99.99	
	Solids receiver	0.00	0.43	0.00	99.53	
P037	Bed material	0.00	0.38	0.00	99.61	
P038	Solids receiver	0.00	28.49	0.00	70.35	
	Secondary cyclone	0.10	17.11	5.59	77.20	
P039	Bed material	0.10	20.07	0.00	79.93	54,000
	Solids receiver	0.30	39.03	0.00	60.67	13,000
	Secondary cyclone	0.20	25.57	9.45	64.78	3200
P041	Bed material	0.00	29.08	0.00	72.62	8200
	Solids receiver	0.10	13.99	0.00	86.67	4000
P043	Bed material	0.15	20.16	0.94	78.75	

TABLE 23

Residence Time Study Results							
Run No.	M413	M414	M415	M416	M417	M418	M419
Residence Time, sec	18	23	44	42	22	13	19
Temperature °C	625	625	625	625	625	625	575
Pressure, psig	35	35	35	35	35	35	35
Steam	Yes	Yes	Yes	No	No	No	No
CaO, wt%	15	5	15	15	15	15	15
Product Yields, wt%							
Liquid	29	29	33	24	37	82	84
Gas + Water	71	71	67	75	63	18	16
C <sub>2</sub> <sup>=</sup> + C <sub>3</sub> <sup>=</sup>	17	17	28	31	16	11	9

plastics for a feed material (same composition as Tests P041-P044). Most of the tests were performed at 625°C, as this temperature had been selected as typical for liquid production. A range of residence times were examined. Figure 6 shows the simulated boiling point distributions of the tests and for P044. Figure 7 shows the effect of residence time on liquid, gas, and C<sub>2</sub><sup>=</sup> + C<sub>3</sub><sup>=</sup> yield.

M415 and M416 represent tests with and without steam, all other conditions being roughly equivalent. The test with steam had a slightly lighter boiling point distribution, and a higher liquid yield.

M413 was run under conditions similar to P044. The product liquids of these two tests have nearly identical boiling point distributions. To find residence times that produced satisfactory liquid quality, a series of residence times were run (M416, M417, and M418), with all other conditions being roughly equivalent. As seen in Figure 7, liquid yield decreases with increased residence time at 625°C, and gas yield correspondingly increases. While liquid yield decreases with increased residence time, the liquid boiling point distribution shifts toward lighter products, as seen in Figure 6. These tests seem to indicate that residence time, like temperature, can be used to shift liquid yields and character, although the effect appears to be less dramatic than with temperature. Tests M418 (13 seconds) and M419 (19 seconds), 50°C in temperature apart, had roughly equal liquid yields and boiling point distributions fairly close together.

Table 24 shows a component breakdown for M413-M419, based on GC-FID chromatograms. Of interest is the shift with residence time of aliphatic/olefins to aromatics in the liquids.

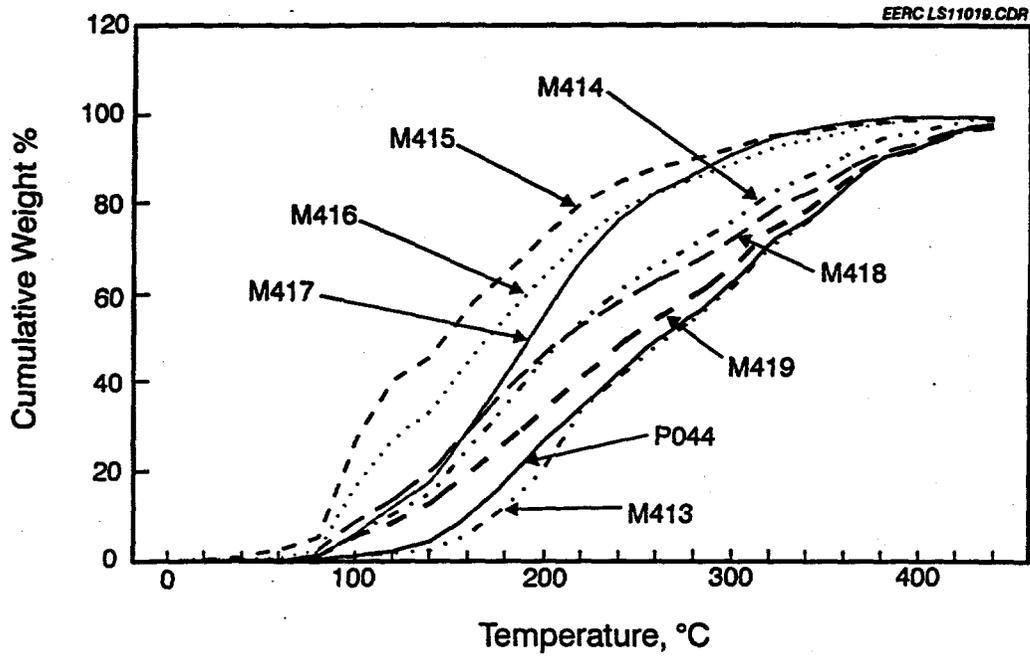


Figure 6. Simulated boiling point distribution for residence time series.

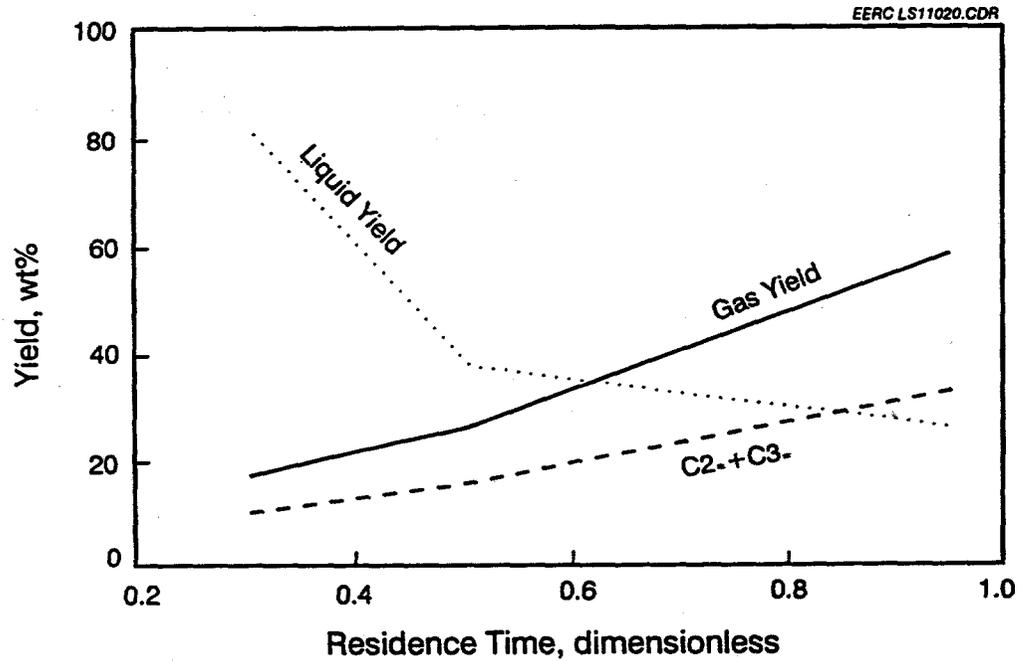


Figure 7. Residence time, dimensionless.

## 10.0 SUMMARY

The purposes of the PDU program are to 1) prove the fluid-bed thermal depolymerization of plastics conceptually on a commercially scalable unit, 2) identify engineering problems, 3) gather engineering data for scaleup, and 4) generate quantities of product for end-user qualification and evaluation. This first-phase effort has necessarily emphasized proof of concept and identification of engineering problems. The original system configuration and process conditions worked well for plastics of limited composition (i.e., the "base blend"), but longer gas residence times are necessary for processing postconsumer plastics, which have higher levels of PET and polyethylenes. In order to provide for longer gas residence times, the refractory in the bottom two sections of the PDU was removed and repoured to a 10-in. ID. Also, the pneumatic feed system was replaced with a dual auger arrangement, similar to that of the CFBR. This eliminates the large volume of cold transport gas used in the pneumatic method of feed introduction. No tests have been attempted in the PDU since completion of the modifications.

CaO attrition was not observed to be problematic at the fluidization velocities examined. Some CaO is converted to CaCO<sub>3</sub>, although the suitability of CaO for chlorine remediation is not yet decided. No operational problems were observed when CaO was used as a bed material.

PET levels of 20% caused no apparent operation difficulties. It is recommended that higher levels be tested.

Bench-scale tests indicate that gas residence time has an effect on both liquid quality and quantity, although to a lesser extent than process temperature. An earlier study (1) observed an effect on liquid quality, but minimal effect on yield. It should be noted that the tests described here cover a much wider range of residence times. This effect has been studied over a limited temperature range. At 625°C with steam, gas residence time needs to be above about 23 seconds to produce liquids of satisfactory quality.

## 11.0 REFERENCES

1. Sharp, L.L.; Ness, R.O.; Aulich, T.A.; Randall, J.C. "Thermal Depolymerization of Plastics," presented at the Canadian Chemical Engineering Conference, Ottawa, Canada, Oct. 3-6, 1993.
2. Sharp, L.L. "Thermal Recycling of 3M Products," final report for 3M Specialty Film Division/3M Traffic Control Division and U.S. DOE DE-FC21-93MC30098; EERC Publication 94-EERC-09-04, Dec. 1994.

TABLE 24

Residence Time Study Component Analysis

Component	BPI, °C	M413		M414		M415		M416		M417		M418		M419	
		wt%	% Yield	wt%	% Yield	wt%	% Yield	wt%	% Yield	wt%	% Yield	wt%	% Yield	wt%	% Yield
		18 seconds, steam		23 seconds, steam		44 seconds, steam		42 seconds		22 seconds		13 seconds		19 seconds, 575°C	
		wt%	% Yield	wt%	% Yield	wt%	% Yield	wt%	% Yield	wt%	% Yield	wt%	% Yield	wt%	% Yield
		Aromatics													
Benzene	83.7	0.51	0.15	2.91	0.84	16.87	5.57	11.48	2.87	3.52	1.30	3.17	2.60	2.18	1.83
Toluene	114.0	0.54	0.16	3.45	1.00	11.38	3.76	8.68	2.17	5.10	1.89	2.64	2.16	1.73	1.45
Ethylbenzene	139.0	0.38	0.11	1.67	0.48	3.08	1.02	3.26	0.82	2.86	1.06	1.20	0.98	1.11	0.93
<i>m</i> -, <i>p</i> -Xylene	141.1	0.38	0.11	1.63	0.47	2.77	0.91	2.60	0.65	2.37	0.88	1.11	0.91	0.73	0.61
Styrene	145.7	0.82	0.24	2.76	0.80	3.87	1.28	3.27	0.82	3.06	1.13	1.86	1.53	1.15	0.97
<i>o</i> -Xylene	147.0	0.22	0.06	1.10	0.32	1.78	0.59	2.05	0.51	2.12	0.78	0.73	0.60	0.57	0.48
Indene	182.8	0.29	0.08	1.03	0.30	1.90	0.63	1.84	0.46	2.52	0.93	0.50	0.41	0.37	0.31
C1 Indene	206.1	1.21	0.35	1.17	0.34	1.51	0.50	1.67	0.42	2.20	0.81	0.51	0.42	0.70	0.59
C1 Indene	207.2	1.10	0.32	1.01	0.29	1.39	0.46	1.42	0.36	2.09	0.77	0.49	0.40	0.54	0.45
Naphthalene	213.4	0.56	0.16	1.30	0.38	1.97	0.65	2.29	0.57	3.11	1.15	0.39	0.32	0.39	0.33
C1 Naphthalene	239.1	0.45	0.13	0.71	0.21	0.90	0.30	1.07	0.27	1.58	0.58	0.32	0.26	0.43	0.36
Total Aromatics Identified		6.46		18.75		47.41		39.62		30.55		12.91		9.89	
		Olefins and Aliphatics													
Component	BPI	M413	M414	M415	M416	M417	M418	M419							
C <sub>6</sub> H <sub>12</sub>	65.2	0.10	0.03	0.56	0.16	1.47	0.49	0.93	0.23	0.45	0.17	1.06	0.87	0.79	0.66
C7 or C8	87.1	NI	0.00	0.25	0.07	1.06	0.35	0.43	0.11	0.18	0.07	0.38	0.31	0.26	0.22

Continued . . .

Thermal Depolymerization of Plastics

Table 24 (continued)

Component	BPI	M413	M414	M415	M416	M417	M418	M419						
C7 or C8	95.0	0.16	1.05	0.31	1.71	0.57	1.34	0.34	0.87	0.32	1.67	1.37	1.16	0.98
C <sub>8</sub> H <sub>16</sub>	122.6	0.36	1.83	0.53	1.64	0.54	1.70	0.42	1.52	0.56	2.44	2.00	1.69	1.42
C <sub>9</sub> H <sub>18</sub>	147.9	1.08	2.94	0.85	1.60	0.53	2.03	0.51	2.34	0.86	3.08	2.52	2.22	1.86
C <sub>10</sub> H <sub>20</sub>	171.4	3.53	5.25	1.52	3.19	1.05	4.00	1.00	5.14	1.90	4.52	3.71	3.56	2.99
C <sub>11</sub> H <sub>22</sub>	193.8	3.27	4.00	1.16	1.80	0.59	2.53	0.63	3.22	1.19	3.34	2.74	3.54	2.97
C <sub>11</sub> H <sub>24</sub>	196.1	0.54	1.03	0.30	0.68	0.22	0.94	0.24	1.38	0.51	1.10	0.90	1.38	1.16
C <sub>12</sub> H <sub>24</sub>	214.0	2.98	3.10	0.90	1.49	0.49	2.06	0.51	2.43	0.90	2.59	2.12	3.20	2.69
C <sub>12</sub> H <sub>26</sub>	216.1	1.05	1.10	0.32	0.73	0.24	0.99	0.25	1.43	0.53	1.10	0.90	1.55	1.30
C <sub>13</sub> H <sub>26</sub>	233.7	3.16	2.98	0.86	1.56	0.52	1.89	0.47	2.25	0.83	2.52	2.06	3.34	2.81
C <sub>13</sub> H <sub>28</sub>	235.9	1.14	1.68	0.49	1.67	0.55	1.97	0.49	2.96	1.09	1.34	1.10	1.86	1.56
C <sub>14</sub> H <sub>28</sub>	251.6	3.24	2.71	0.79	1.18	0.39	1.53	0.38	1.60	0.59	2.30	1.89	3.09	2.60
C <sub>14</sub> H <sub>30</sub>	253.3	0.63	1.13	0.33	0.72	0.24	0.82	0.21	1.14	0.42	1.11	0.91	1.55	1.30
C <sub>15</sub> H <sub>30</sub>	269.0	3.04	2.49	0.72	1.05	0.35	1.36	0.34	1.44	0.53	2.24	1.84	2.94	2.47
C <sub>15</sub> H <sub>32</sub>	270.6	0.81	1.11	0.32	0.86	0.28	1.03	0.26	1.36	0.50	1.15	0.94	1.58	1.32
C <sub>16</sub> H <sub>32</sub>	285.2	2.76	2.19	0.63	0.80	0.26	1.06	0.27	0.96	0.35	2.01	1.65	2.53	2.13
C <sub>16</sub> H <sub>34</sub>	286.7	0.82	0.97	0.28	0.66	0.22	0.71	0.18	0.95	0.35	1.26	1.03	1.65	1.39
C <sub>17</sub> H <sub>34</sub>	300.8	2.68	1.96	0.57	0.66	0.22	0.89	0.22	0.72	0.27	1.89	1.55	2.29	1.92
C <sub>17</sub> H <sub>36</sub>	302.2	0.70	0.79	0.23	0.50	0.17	0.54	0.14	0.64	0.24	1.00	0.82	1.38	1.16
C <sub>18</sub> H <sub>36</sub>	315.4	2.67	1.84	0.53	0.56	0.18	0.78	0.20	0.56	0.21	1.80	1.48	2.13	1.79
C <sub>18</sub> H <sub>38</sub>	316.7	0.67	0.76	0.22	0.54	0.18	0.54	0.13	0.60	0.22	0.94	0.77	1.25	1.05
C <sub>19</sub> H <sub>38</sub>	329.4	2.54	1.68	0.49	0.47	0.15	0.75	0.19	0.56	0.21	1.73	1.42	2.07	1.74
C <sub>19</sub> H <sub>40</sub>	330.6	0.71	0.74	0.21	0.54	0.18	0.51	0.13	0.55	0.20	0.95	0.78	1.26	1.06
C <sub>20</sub> H <sub>40</sub>	342.8	2.17	1.35	0.39	0.34	0.11	0.55	0.14	0.30	0.11	1.44	1.18	1.71	1.44
C <sub>20</sub> H <sub>42</sub>	343.9	0.79	0.78	0.23	0.62	0.20	0.59	0.15	0.67	0.25	0.97	0.79	1.24	1.04
C <sub>21</sub> H <sub>42</sub>	355.8	1.93	1.22	0.35	0.31	0.10	0.49	0.12	0.25	0.09	1.34	1.10	1.56	1.31
C <sub>21</sub> H <sub>44</sub>	356.8	0.55	0.57	0.16	0.31	0.10	0.36	0.09	0.28	0.10	0.80	0.65	1.10	0.92
C <sub>22</sub> H <sub>44</sub>	368.0	1.70	1.01	0.29	0.20	0.07	0.39	0.10	0.15	0.06	1.19	0.97	1.36	1.14
C <sub>22</sub> H <sub>46</sub>	368.9	0.52	0.55	0.16	0.49	0.16	0.41	0.10	0.32	0.12	0.80	0.66	1.05	0.88
C <sub>23</sub> H <sub>46</sub>	379.2	1.46	0.86	0.25	0.18	0.06	0.33	0.08	0.19	0.07	1.05	0.86	1.23	1.03
C <sub>23</sub> H <sub>48</sub>	380.0	0.54	0.50	0.15	0.49	0.16	0.40	0.10	0.34	0.12	0.71	0.59	1.02	0.86
C <sub>24</sub> H <sub>48</sub>	390.3	1.24	0.72	0.21	0.12	0.04	0.27	0.07	NI	0.00	0.87	0.72	1.00	0.84
C <sub>24</sub> H <sub>50</sub>	391.1	0.42	0.49	0.14	0.46	0.15	0.39	0.10	0.32	0.12	0.67	0.55	0.87	0.73
Totals		49.96	14.49	52.19	15.14	30.64	10.11	35.50	8.87	14.08	53.38	43.77	60.42	50.75

**APPENDIX A**  
**SOLVENT DISSOLUTION ANALYSIS METHOD**

**Amoco Chemical Company**

Research and Development Department  
Post Office Box 3011  
Naperville, IL 60566-7011  
708-420-5111

November 12, 1992

Mr. B. Bryant Slimp, Jr.  
Lyondell Petrochemical Company  
One Houston Center, Suite 1600  
1221 McKinney Street  
Houston, TX 77253-3646

Dear Bryant:

Attached to this letter is a copy of the analytical method that we developed at Amoco to analyze waste plastic samples in order to determine the types and amounts of plastics present and the associated organic and inorganic impurities. I've also attached some recent analyses in order to give you an idea of the capability of the method.

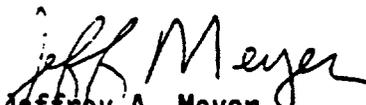
We developed this method with the intent of getting as much data as possible using classical analytical procedures. These include weighing, dissolving, precipitating, drying and reweighing. The only instrumental techniques involved are x-ray fluorescence (XRF) and inductively coupled plasma (ICP) spectroscopy for the metals and non-metals determination.

We have received samples in two different forms; one is from a curbside pickup program and the other is from recycling companies. The former were plastic garbage bags of intact plastic containers or other packaging material. In this case we first did an inventory of the bag contents by weight and type (see Tables I and II); then we reduced the entire sample by cutting and grinding to a uniform particle size from which we could remove a reasonably homogeneous sample (visual criteria) for analysis. The samples from commercial recyclers were already ground up and homogenized so getting a reasonably homogeneous sample was the main analysis issue.

The method was tested using a known polymer mixture and the data are shown in Table III. Table IV shows the results from six repeat analysis of a sample of plastics waste from a recycler in New Jersey. Table V shows data on five bags of plastic waste from the Chicago recycling pick up program. Table VI shows an analysis for metals and non-metals.

We can discuss the method further at our next Tertiary Recycling Committee, Feedstock Definition Team meeting. Please send this report and attachments to the other team members as you see fit.

Sincerely,

  
Jeffrey A. Meyer  
Naperville, C-1

JAM/djd  
Attachments

## ANALYTICAL METHOD FOR POLYMER WASTE STREAMS

### Scope

This method will quantitatively and qualitatively analyze a polymer waste stream for polymers, metals, and nonmetals. The method involves using XRF, ICP, and FTIR spectroscopy along with a solvent separation technique.

### Summary

Municipal and industrial polymer waste, in the form of curb-side pick-up or washed and chopped chips, can be sampled and analyzed by this method. The sample should be of a representative size, which can be from 500 g. for an industrial sample, to 15 kilograms of municipal curb-side polymer waste. The sample is reduced to particles approximately 1 cm x 1 cm by sawing, chopping, and grinding, if needed. Analyses by XRF, ICP, and FTIR are performed on the bulk sample. The sample is extracted with water and XRF and ICP analyses are completed on the extract. The particles from the water extract are dried, and a solvent(o-xylene) separation into polymer types is performed. ICP, XRF, and FTIR analyses are completed on the six fractions and the weights are obtained after drying. All results are reported in a standard format. If there is a particular component in the sample of interest then the analysis can be customized to accommodate analysis for that particular component. A flow chart and sample report format are included in this method for reference purposes (Figures 2 and 3).

### Apparatus

- 1 Temperature Controller
- 2 Thermometers 0 - 200°C
- 3 Condensers
- 3 Resin Kettles (4 neck)
- 1 Stirring Motor
- 1 Shaft and Blade for above
- 1 Glass Joint (water cooled) for Stirrer
- Beakers (600 ml)
- Vials and Jars (Several sizes for fractions)
- XRF, ICP, and FTIR Analysis Available
- Screen 40 to 60 Mesh
- o-xylene (99% Eastman-Kodak)

### Sample Prep

Select a representative sample by determining the type of waste stream, municipal/industrial, large/small pieces, few/many polymer types. The larger the variety of polymer types expected in the stream, the larger the

sample should be. For example, a municipal post consumer polymer waste stream may need 15 to 18 kilograms sampled, and a manufacturing waste stream may need 500 grams. Once the sample is selected, it should be inventoried. This is done by listing the contents, weighing each piece, and recording the polymer type if possible. The inventory process should be done using proper safety precautions such as gloves, hood, and if necessary face mask and rubber apron. Caution must be used due to the possibility of broken glass, chemical, and biological hazards present in the sample. Sample preparation will vary according to the size of the pieces and type of polymers in the sample. The goal is to obtain a representative sample chipped into pieces about 1 cm x 1 cm in area and a thickness of 20 mils to 1 cm. However, this is not always possible. Samples of containers must be sawed into strips using a band saw and the strips ground using a rotating blade mill. The result is pieces of various sizes with most being 0.25 cm x 0.50 cm. If pieces of sample are too small (such as powders), they will be drawn into the sample flask, through the screen and separation will not be achieved. Once the sample is ground, mix the particles by shaking them in a large plastic bag.

#### Composite Sample

Once the bulk sample (500g-18kg.) is ground and mixed, 100g is collected and reduced to powder. This is accomplished by cooling the sample with liquid nitrogen and passing it through a Brinkman grinder using a 1.5 pore size screen. This powder is then analyzed for the following elements by XRF and ICP analyses: Cl, P, Zn, S, Mn, Si, Pb, Cr, Fe, Ni, Cu, Co, Na, K, Ca, Al, Ti, Sb. The powder is also sent for ash oxide analysis.

#### Water Wash

Take 100 g of the ground and mixed sample and place it in a 2 liter jar. Add 250 ml of distilled water and shake vigorously for 3 minutes. After shaking, pass liquid through a very coarse filter or fine screen and obtain ICP analysis of the extract for the following metals and nonmetals: Cl, Zn, Mn, Fe, Cu, Na, K, Ca, Al, Ti. Oven dry the solids at 110°C, under vacuum, with a nitrogen purge. These chips will be used for the solvent dissolution analysis.

#### Solvent Dissolution

Refer to Figure 1 for the equipment setup. The first part of the apparatus labeled "Dissolution Assembly" consists of a 500 ml resin kettle equipped with a water cooled condenser and lab stirrer. The kettle is placed in a heating mantle, which in turn is connected to a Eurotherm temperature controller with over-temperature protection. An additional thermocouple connected to a digital display is immersed in the solvent (o-xylene) to monitor the temperature. The separate fractions of the mixed plastic waste are dissolved in this resin kettle. The second portion of the apparatus in Figure 1 is the "Filtration Assembly." It consists of a filtration and transfer tube connected to a vacuum flask, which in turn is connected to a vacuum source. The third portion of the apparatus in

Figure 1 is a set of two resin kettles used to heat the wash solvent to the same temperature as the dissolution kettle, and to heat the next portion of solvent to the next higher temperature for dissolution.

1. After the chips from the water wash are dry, place 20 to 25 grams of them into the resin kettle marked "C".
2. Add 500 ml of o-xylene and stir for 30 minutes at 25°C. Also add 500 ml of o-xylene to each of the other two resin kettles and bring each to temperature.
3. Draw off the o-xylene by applying a vacuum to the sample flask.
4. Transfer this solution to a tared 600 ml beaker.
5. Transfer 500 ml of solvent from resin kettle marked "B" which is set to the same temperature as resin kettle "C".
6. Mix 30 seconds and transfer to a tared 600 ml beaker.
7. Transfer 500 ml of o-xylene from resin kettle "A" which is set for the next higher temperature fraction. This avoids waiting for temperature increases from room temperature. Heat 30 minutes and repeat procedure from 3 through 7 for each temperature fraction (25°C, 75°C, 105°C, 120°C, 138°C).

NOTE: Replenish the o-xylene in each kettle as soon as it is being used. This will minimize the time needed to reach temperature.

8. When the last temperature run is complete, collect the residue in resin kettle "C" as the insoluble.
9. Take the beakers to dryness on a steam bath with nitrogen blowing over them.
10. Weigh The fractions and obtain XRF, ICP and FTIR analyses. (XRF and ICP for Cl, Zn, Pb, Cr, Fe, Ni, Cu, Na, K, Ca, Al, Ti, and FTIR for polymer identification)
11. Assemble all data into a report format such as the example provided (See attached report form). If this is done using a word processor, the form can easily be altered to accept the larger area needed for certain parts of report such as "inventory".

#### Notes

To attain the necessary skill at running this apparatus and setting the temperatures correctly, one should prepare and analyze a known blend of polymers.

In running samples it was noticed that pigments end up with the polymer fraction they were originally associated with. Some additives will be leached into earlier fractions along with plasticizers.

# Dissolution Apparatus

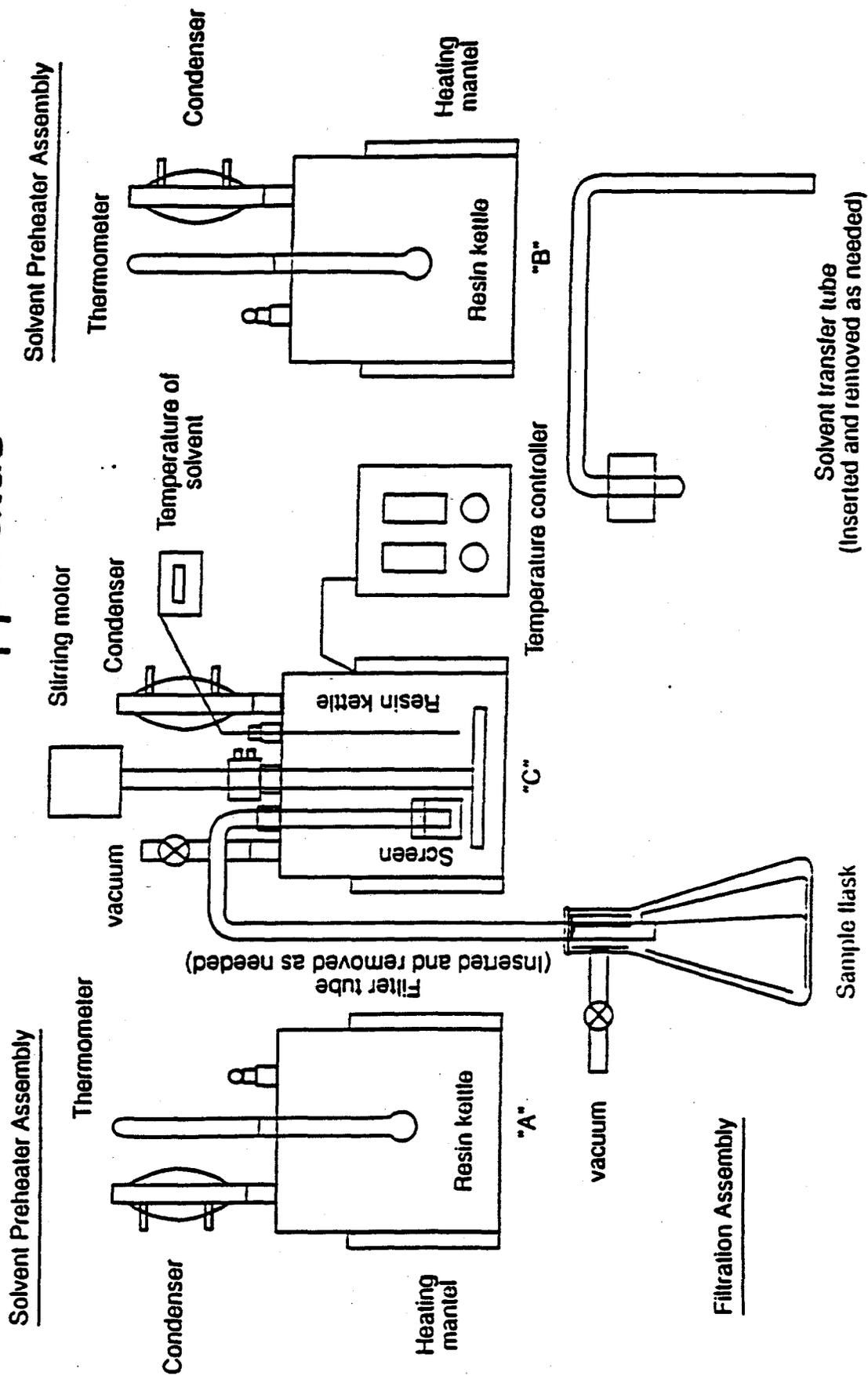


Figure 1.

POLYMER WASTE ANALYSIS FLOW CHART

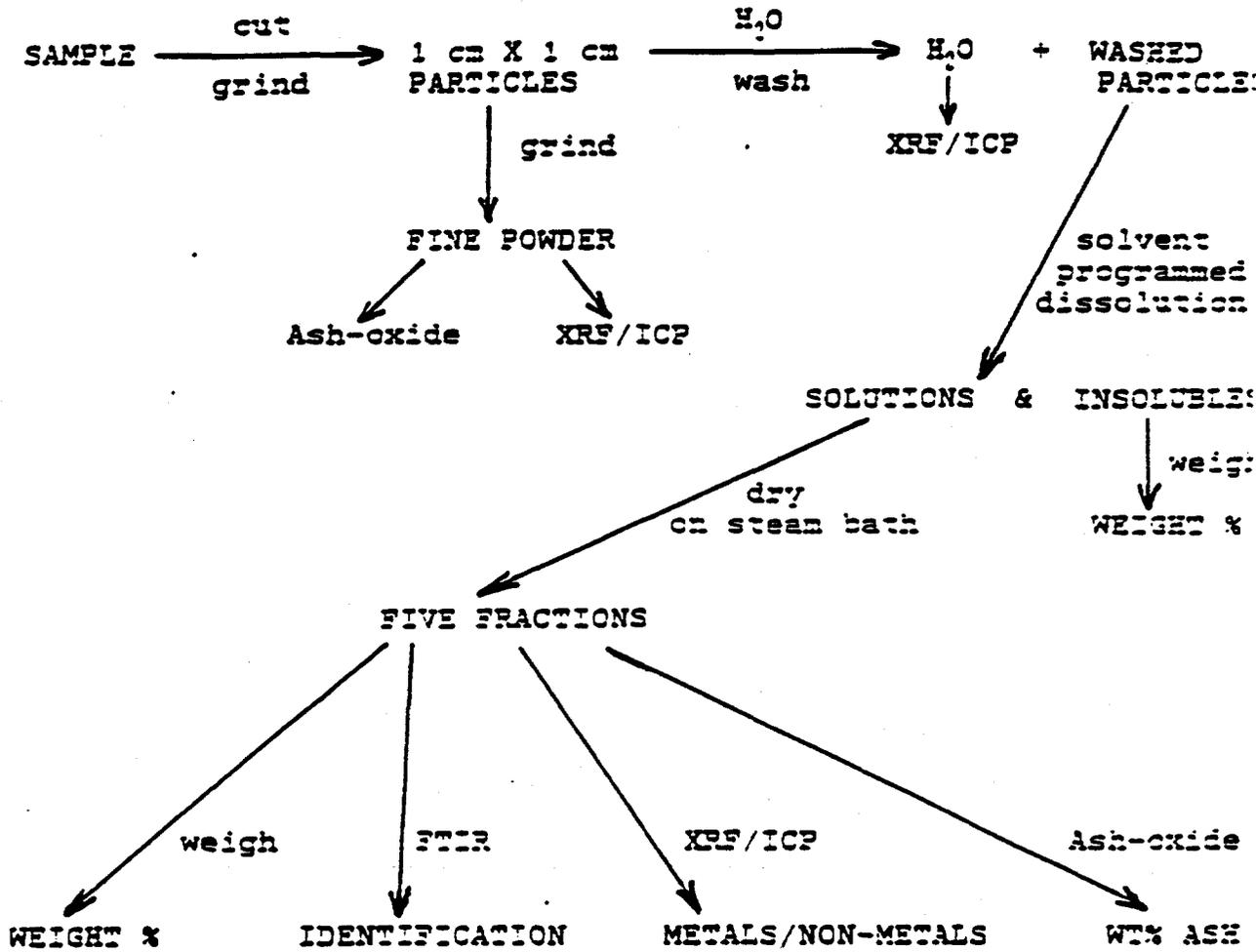


Figure 2.

POLYMER WASTE ANALYSIS REPORT

Client:

CARN:

SAMPLE:

DATE:

Discription/Inventory:

Water Wash:

Cl Zn Mn Fe Cu Na K Ca Al Ti

Composite:

Cl P Zn S Mn Si Pb Cr Fe Ni

Cu Co Na K Ca Al Ti Sb

Ash-Oxide =

Dissolution Results:

<u>PS</u> <u>(25C)</u>	<u>LDPE</u> <u>(75C)</u>	<u>HDPE</u> <u>(105C)</u>	<u>PP</u> <u>(120C)</u>	<u>PVC</u> <u>(138C)</u>	<u>Residue</u>
---------------------------	-----------------------------	------------------------------	----------------------------	-----------------------------	----------------

Elemental Analysis of Fractions:

	<u>Cl</u>	<u>Zn</u>	<u>Pb</u>	<u>Cr</u>	<u>Fe</u>	<u>Ni</u>
Fraction <u>PS</u>						
Fraction <u>LDPE</u>						
Fraction <u>HDPE</u>						
Fraction <u>PP</u>						
Fraction <u>PVC</u>						

Figure 3.

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Fraction Residue

Cu

Na

K

Ca

Al

Ti

Fraction PS

Fraction LDPE

Fraction HDPE

Fraction PP

Fraction PVC

Fraction Residue

FTIR Results:

Fraction PS:

Fraction LDPE:

Fraction HDPE:

Fraction PP:

Fraction PVC:

Fraction Residue:

Comments:

TABLE I

BAG "A" INVENTORY

4 Burnetts Gin bottles	PETE	Green	336.3g
5 All laundry detergent bottles	HDPE	Blue	691.6g
2 Downy Softener bottles	HDPE	Blue	275.2g
5 Spouts from All bottles	HDPE	Natural	81.7g
1 Cheer liquid detergent bottle	HDPE	Blue	119.9g
1 Bumble Bee tuna can	Al	-	9.4g
1 Dole pineapple can & lid	Steel	-	48.2g
- Broken glass	Sl	Clear	104.8g
1 Blue bag (container of above)	?	Blue	45.3g
			<hr/>
			1,712.0g
			<hr/>
			3.8#
			22% PET
			78% PE

TABLE II

BAG "B" INVENTORY

9 Milk bottles	HDPE	Natural	573.8g
2 Vivid bleach bottles	HDPE	Yellow	271.1g
1 Tide detergent bottle	HDPE	Red & Blue	231.1g
1 Green soda bottle	PETE	Green	69.1g
2 Diet Pepsi bottles	PETE	Clear	138.8g
1 Spic & Span pine	PETE	Clear	59.7g
1 Clean & Clear	?	Clear	60.6g
1 Jet Dry	?	Blue	31.9g
1 Triaminicol	?	Clear	34.5g
2 Kool-Aid bottles	LDPE	Red	25.8g
- Red caps	?	Red	17.0g
- Blue caps	?	Blue	9.6g
- Green caps	?	Green	4.9g
- White caps	?	White	16.5g
1 Blue bag (container)	?	Blue	45.2g
- Maggots	?	-	0.5g
			<hr/>
			1,590.0g
			<hr/>
			3.5#
			72% PE
			17% PET
			9% PP/PS

TABLE III

Solvent\* Separation Results

<u>Polymer</u>	<u>Known Blend</u>	<u>Found</u>	<u>Temperature °C</u>
PS	4.76	4.6	25
LDPE	9.46	1.3	75
HDPE	70.5	80.6	105
PP	4.77	3.8	120
PVC	0.99	0.6	138
PET	<u>9.55</u>	<u>9.2</u>	Residue
	100%	100%	

TABLE IV

Polymer Waste AnalysisNew Jersey Tailings

<u>Component</u>	<u>Weight % (6 Analyses)</u>	<u>Range</u>
PS	$0.85 \pm 0.18$	0.65 - 1.2
LDPE	$2.1 \pm 0.6$	1.4 - 2.8
HDPE	$91.2 \pm 2.3$	87.3 - 94.5
PP	$5.5 \pm 2.1$	2.5 - 8.7
PVC	$0.18 \pm 0.07$	0.10 - 0.27
Residue	$0.42 \pm 0.11$	0.26 - 0.51

TABLE V

Dissolution Results in wt. %

<u>Sample</u>	<u>PS</u> <u>(25°C)</u>	<u>LDPE</u> <u>(75°C)</u>	<u>HDPE</u> <u>(105°C)</u>	<u>PP</u> <u>(120°C)</u>	<u>PVC</u> <u>(138°C)</u>	<u>Residue</u>	<u>% Ash</u>
New Jersey 8-20-91	0.88	1.9	89.6	7.1	0.10	0.44	1.1
Chicago Recycling Works							
Bag "A"	0.75	1.0	73.0	0.28	0.12	24.9	1.3
Bag "B"	2.5	1.9	75.8	1.3	0.08	18.4	1.1
Bag "C"	3.3	2.8	92.2	0.43	0.14	1.2	2.5
Bag "D"	18.9	8.1	46.7	15.7	1.6	9.0	2.5
Bag "E"	20.8	6.4	47.7	15.5	2.4	7.1	1.2
North American Plastics Recycling Corp.	8.7	9.8	55.5	16.6	3.2	6.22	1.6

TABLE VI

ELEMENTAL ANALYSES OF HOMOGENIZED NEW JERSEY POST-CONSUMER TAILINGS

ICP RESULTS (Concentrations in ppm):

Ti - 2000	Cr - 42
Ca - 1120	Zn - 37
Na - 810	K - 37
Al - 490	Cu - 30
Pb - 231	Sb - 14
Ni - 122	Mn - 4
Fe - 112	Co - 4

XRF RESULTS (Concentrations in ppm):

<u>1st Analysis</u>		<u>Repeat Analysis</u>	
Cl - 25100 *	P - 275	Cl - 22700 *	P - 233
Si - 1450	Fe - 40	Si - 1240	Fe - 39
Ti - 1250	Cr - 30	Ti - 1320	Cr - 30
Ca - 1120	Zn - 12	Ca - 790	Zn - <5
S - 590	Ni - <2	S - 500	Ni - <2

\* This concentration is beyond the instrument's current calibration and therefore cannot be considered as accurate. The actual Cl concentration may be somewhat different.

**APPENDIX B**  
**ANALYTICAL PROCEDURES**

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**— Simulated Distribution Methods**

## SIMULATED DISTILLATION METHODS

The "Retention Time," "Area %," "Yield %," "wt%," and "Cumulative Area %" values in Table D-1 (using M290 as an example) were obtained directly from the gas chromatography/flame ionization detection (GC/FID) analysis of the sample. The "Boiling Point Index" and "Retention Index" values were calculated from the GC/FID analysis of an alkane standard, which comprises the series of 26 normal alkanes from C<sub>5</sub> (pentane) to C<sub>30</sub>. Boiling points for several of the alkanes are listed in Table D-2. The simulated distillation technique employed for this work uses the boiling points and retention indices (arbitrarily assigned values such that C<sub>5</sub> has a retention index (RI) of 500, C<sub>6</sub> has an RI of 600, C<sub>10</sub> has an RI of 1000, etc.) of the normal alkanes to relate component GC retention time to boiling point and RI. For example, if a compound has a retention time halfway between the retention times of pentane and hexane, the compound will be assigned a boiling point index of 52.5°C (halfway between 36° and 69°C, the boiling points of pentane and hexane, respectively) and an RI of 550 (halfway between 500 and 600, the retention indices of pentane and hexane, respectively).

At least one GC analysis of the alkane standard is performed for every series of sample analyses. If more than eight samples are analyzed, one alkane standard analysis is performed for every eight sample analyses. Each individual alkane in the alkane standard is used as a marker to relate GC retention time to boiling point and retention index. Once this relationship is determined, the GC area count data for each sample is normalized to area percent data, which can then be plotted as a distillation profile showing cumulative percent distilled as a function of temperature, or as a bar graph showing the percentages of sample distillable in 20-degree (or other desired) increments.

Since the simulated distillation technique uses a series of normal alkanes to derive a relationship between GC retention time and boiling point, it will necessarily work best in analyzing samples composed of components similar in chromatographic behavior to alkanes. If a sample contains components that differ in chromatographic behavior from alkanes, the simulated distillation data for the sample may differ somewhat from actual distillation data, depending on the extent of the chromatographic difference. This is shown by the calculated boiling point index of styrene, an aromatic, in Table D-2. While the actual boiling point of styrene is 145.2°C, its calculated boiling point index is about 148.0°C, a difference of about 1.9%. Most of the detected compounds were not identified, since most were present in very small quantities.

In Table D-1, each yield value is calculated as the area % detected for the entire sample times the total liquid yield. Because of this, and because the tables include area % data for only GC/MS-identified compounds, the sum of the area % values at a given retention time will not equal the corresponding cumulative area % value.

Since the GC/FID analysis used in this work provides area count data for every detected component in a sample, the simulated distillation data discussed above are only a portion of the data obtainable using the GC/FID analysis of a plastics decomposition liquid. For more detailed information, component identification templates (for component identification and quantitation in similar liquids) can be produced using GC/MS, GC/AED, and GC coupled with FT-IR analysis. Use of a component identification template enables

the merging of sample analyses together (on the basis of retention time, boiling point index, or retention index) into a database for comparison of different samples and/or tracking changes in individual component concentrations and overall sample composition due to processing condition changes.

TABLE D-1

Polypropylene/Polystyrene GC Analysis at 525°C in CaCO<sub>3</sub> (M290) - CH<sub>2</sub>Cl<sub>2</sub> Injection

Boiling Point Index, °C	Retention Time Index	Retention Time, min	Area %	Cumulative Area %	Yield, wt%	Compound Identification
120.92	781.28	0.95	3.25	3.82	3.06	Toluene
132.98	829.51	1.45	6.00	10.59	5.64	C <sub>9</sub> H <sub>18</sub> (C <sub>9</sub> olefin)
137.06	845.85	1.62	0.71	11.64	0.67	C <sub>2</sub> Benzene
147.97	889.49	2.08	52.80	65.36	49.63	Styrene
166.68	969.03	3.93	2.53	68.53	2.38	C <sub>1</sub> Styrene
185.46	1052.05	6.11	0.30	70.20	0.28	C <sub>2</sub> Styrene
191.15	1077.72	6.79	0.78	71.10	0.73	C <sub>12</sub> H <sub>24</sub>
192.04	1081.72	6.90	0.59	71.70	0.55	C <sub>12</sub> H <sub>24</sub>
202.32	1131.09	8.06	0.96	72.94	0.90	C <sub>5</sub> H <sub>10</sub> + Benzene
202.98	1134.41	8.14	0.56	73.50	0.53	C <sub>5</sub> H <sub>10</sub> + Benzene
232.30	1283.07	11.13	0.35	75.50	0.33	C <sub>14</sub> H <sub>28</sub>
236.01	1302.32	11.49	1.25	76.84	1.18	C <sub>15</sub> H <sub>30</sub>
237.53	1310.92	11.63	1.51	78.35	1.42	MW = 176, C <sub>7</sub> Benzene?
238.98	1319.11	11.77	1.00	79.36	0.94	C <sub>15</sub> H <sub>30</sub>
246.55	1361.85	12.51	0.66	80.24	0.62	C <sub>8</sub> Benzene
270.92	1501.99	14.80	1.05	82.24	0.99	Diphenylethane
273.68	1519.11	15.06	0.38	82.74	0.36	C <sub>18</sub> H <sub>36</sub>
276.32	1535.50	15.30	0.61	83.51	0.57	C <sub>1</sub> Diphenylethane
292.07	1634.66	16.77	0.71	85.51	0.67	Diphenylpropane
302.98	1705.40	17.77	4.84	90.89	4.55	Styrene Dimer
304.76	1717.63	17.94	0.37	91.41	0.35	Diphenylpropene
311.47	1763.91	18.54	0.47	92.36	0.44	C <sub>21</sub> H <sub>42</sub>
327.23	1875.75	20.03	0.52	94.02	0.49	MW = 234
336.21	1942.15	20.88	0.07	94.35	0.07	MW = 204
338.85	1962.06	21.12	0.26	94.65	0.24	MW = 220
346.24	2018.24	21.81	0.25	95.12	0.24	MW = 220

TABLE D-2

## Normal Alkane Boiling Points

<i>N</i> -Alkane Carbon Number	Boiling Point, °C
5	36
6	69
7	98
8	126
9	151
10	174
11	196
12	216
13	235
14	253
15	271
20	344
25	402
30	450

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**— Organic and Chlorine Determination (GC- AED)**

## TOTAL AND ORGANIC CHLORINE DETERMINATION

To determine chlorine distribution, total chlorine and organic chlorine are determined by analyses, while inorganic chlorine is calculated by their difference.

### Total Chlorine Content of Liquid Products

The method used in product liquid total chlorine determination is based on ASTM Method D808-91, "Standard Test Method for Chlorine in New and Used Petroleum Products (Bomb Method)." The primary difference between the method used and ASTM D808-91 is that the ASTM method utilizes precipitation of chloride from solution for chloride quantitation. Chloride quantitation by ion chromatography is less labor-intensive and provides accurate, reproducible results. Total chlorine is determined as follows: An approximate 0.5-g sample is obtained for combustion in a Parr bomb apparatus. The weighed sample is sealed in the bomb along with a solution of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$ , and the bomb is pressurized with oxygen to 28 atmospheres. The sample is then ignited electronically with a platinum firing wire and combusted. After a cooldown period for condensation of vapors, the bomb is opened, and the sample is removed for chloride analysis by ion chromatography.

Table B-1 is a list of several other ASTM chlorine analysis methods. After review of these methods, ASTM Method D808-91 was deemed most appropriate for these samples.

### Total Chlorine Content of Solid Products

Total chlorine determination of solids (CaO filter sorbent) was determined by first washing the sorbent with acid to remove chlorine. Chlorine is then quantified with ion

TABLE B-1

#### ASTM Chlorine/Chloride Analysis Methods

D 2384-83	Standard Test Methods for Traces of Volatile Chlorides in Butane-Butene Mixtures
E 776-87	Standard Test Method for Forms of Chlorine in Refuse-Derived Fuel
E442-91	Standard Test Method for Chlorine/Bromine/Iodine in Organic Compounds, by Oxygen Flask Combustion
E256-91	Standard Test Method for Chlorine in Organic Compounds, by Sodium Peroxide Bomb Ignition
D1726	Standard Test Method for Hydrolyzable Chlorine Content of Liquid Epoxy Resins
D1847	Standard Test Method for Total Chlorine Content of Liquid Epoxy Resins

chromatography. Chlorine-containing salts, such as calcium chloride, sodium chloride, and potassium chloride, are easily solubilized in water. Quantitation of chlorine in samples of the calcium oxide sorbent used to capture chlorine generated during the decomposition of PVC was performed as follows:

- Weigh out about 1 g of sample into a 100-mL volumetric flask.
- Fill the flask to the 100-mL line with distilled, deionized water.
- Sonicate at room temperature for about 30 minutes.
- Gently swirl, then filter, the mixture.
- Analyze the filtered liquid for total chlorine content using ion chromatography.
- If the chlorine content of the liquid is above the accurate detection level of the instrument, repeat Steps 1-5 using about 100 mg of sample.

### Organic Chlorine Content of Liquid Products

Organic chlorine concentrations were determined using gas chromatography/atomic emission detection (GC/AED) analysis. GC/AED can identify and quantitate chloride in compounds as they elute from a GC column. When a compound leaves the GC column and enters the atomic emission detector, electrons in the atoms that make up the compound are energized by a microwave-induced plasma and excited to higher energy levels. When the electrons return to their stable state, they emit light, which passes into a spectrophotometer. The light is separated by a diffraction grating into wavelengths characteristic of the element selected for analysis (in this case, chlorine, but the instrument can also analyze for hydrogen, carbon, nitrogen, sulfur, oxygen, and several metals and other halogens) and transmit to a photodiode array detector, which can be tuned to monitor a specific range of wavelengths, depending on the element(s) of interest.

To quantitate chlorine, the photodiode array is tuned to monitor the 479-nanometer wavelength, which is characteristic of the energy emission from chlorine atoms. When energy of this wavelength is detected, it is converted into an electrical signal, the intensity of which is proportional to a specific quantity of chlorine atoms. The electrical signal intensity of each detected chlorine-containing compound is directly related to the amount of chlorine contained in the total amount of the compound present. For this reason, GC/AED (by itself) is useful in providing accurate total "gas chromatographable" chloride concentration values, but may or may not provide accurate concentration values for chloride-containing compounds, depending on how many chloride atoms a compound has. For example, if only GC/AED data are used, a compound with two chloride atoms will appear twice as concentrated as an equal amount of a compound with one chloride atom. Quantitating the concentrations of individual chloride-containing species can be done using GC/AED analysis in conjunction with GC/mass spectrometry (GC/MS) analysis to determine a species' degree of chloride substitution. This does not mean the organic chloride level will be inaccurate using GC/AED alone, but rather that a compound with one chlorine will appear less concentrated than a compound with two or more chlorine atoms. Therefore GC/AED alone cannot be used to quantify the chlorinated compound, but can be used to quantify organically associated chlorine of the liquid, overall. In this

work, in which GC/AED alone was used to quantitate total organic chloride, 1-chloronaphthalene was used to calibrate the detector's chloride response.

Because GC/AED is a chromatographic technique, its use in determining organic chloride concentrations is valid for samples that contain no significant quantities of nonchromatographable organic species. Use of the technique in this work is probably worthwhile, since the plastics decomposition liquids analyzed appear to be composed primarily of volatile species.

Chlorine distributions for runs that contained measurable organic chloride are shown in Figures B-1 through B-5.

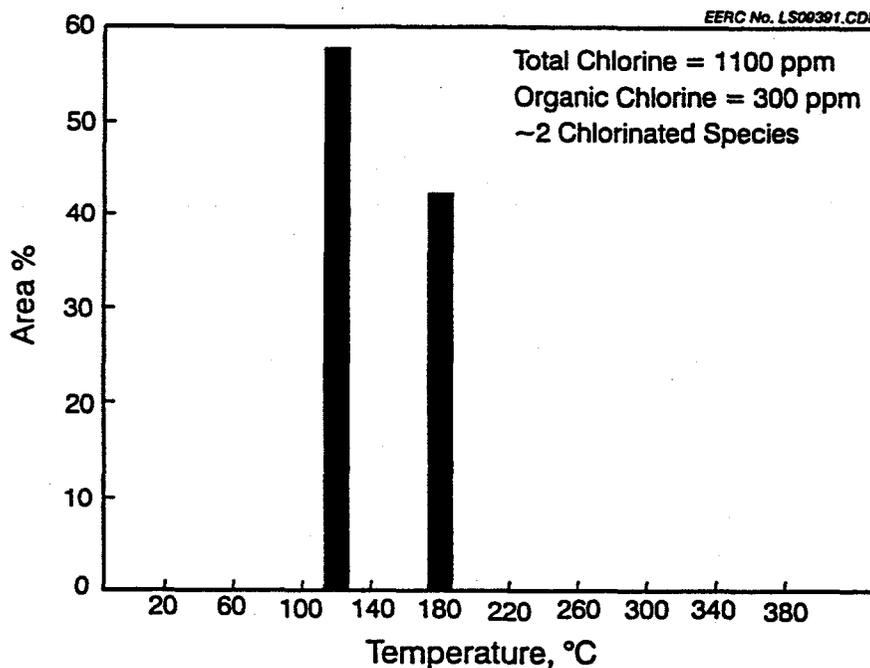


Figure B-1. Organic chlorine distribution for liquids produced at a depolymerization temperature of 440°C (M359).

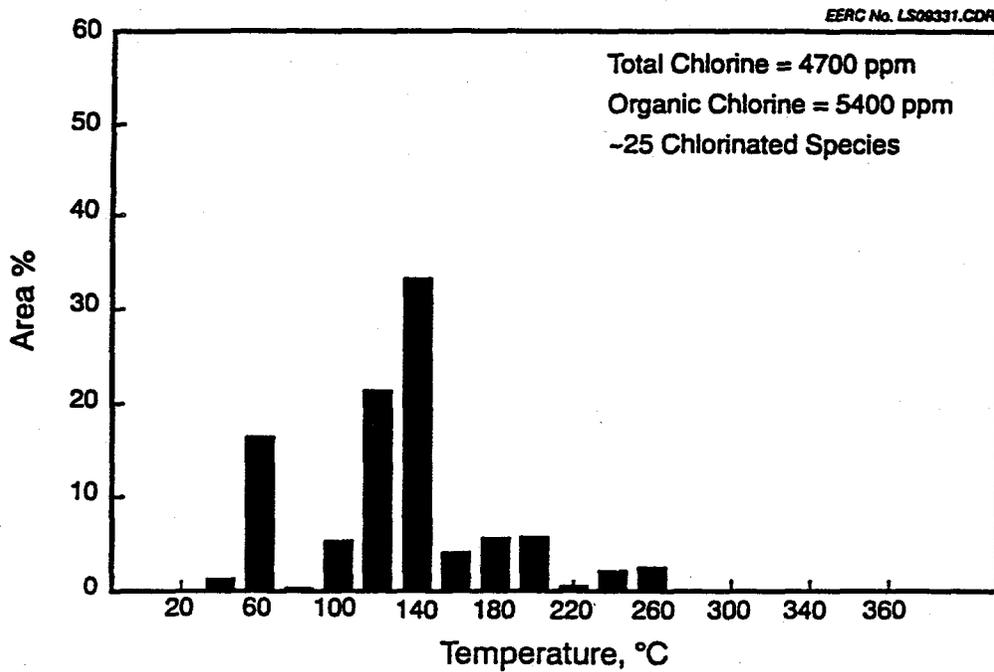


Figure B-2. Organic chlorine distribution for liquids produced at a depolymerization temperature of 540°C (M357).

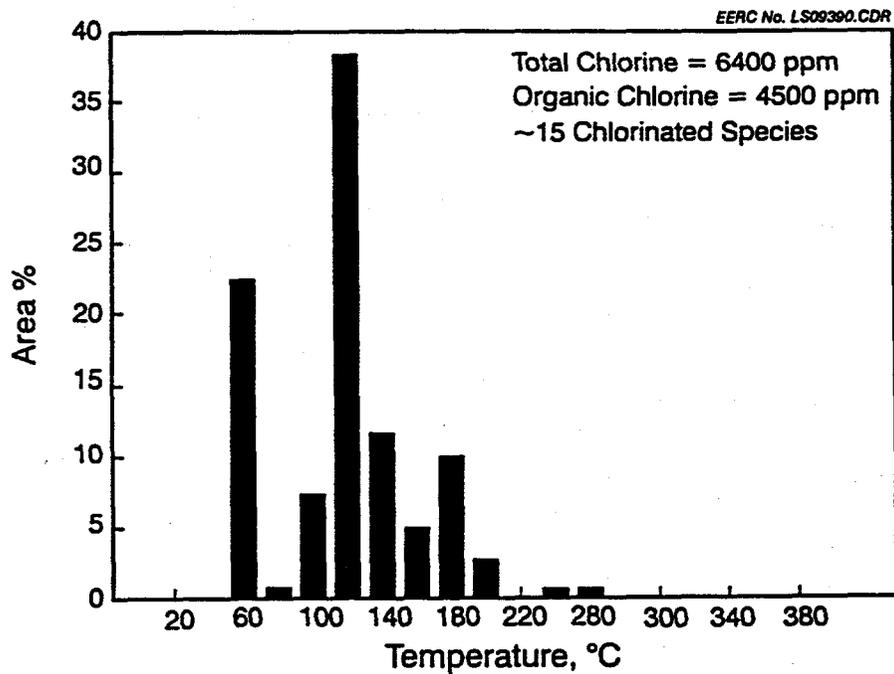


Figure B-3. Organic chlorine distribution for liquids produced at a depolymerization temperature of 540°C (M364).

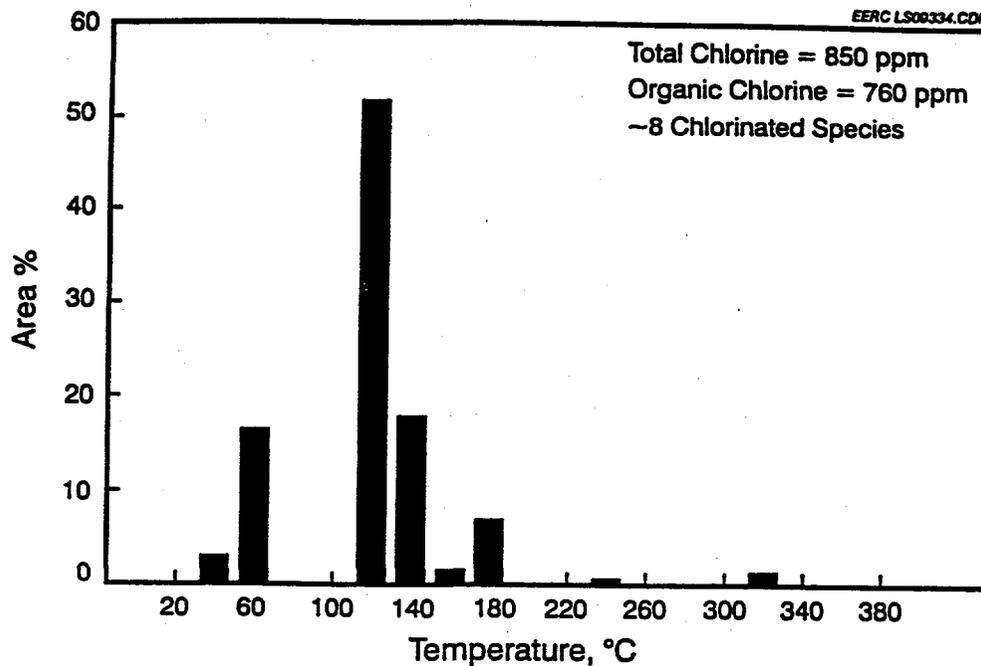


Figure B-4. Organic chlorine distribution for liquids produced at a depolymerization temperature of 440°C and a filter temperature of 340°C (M360).

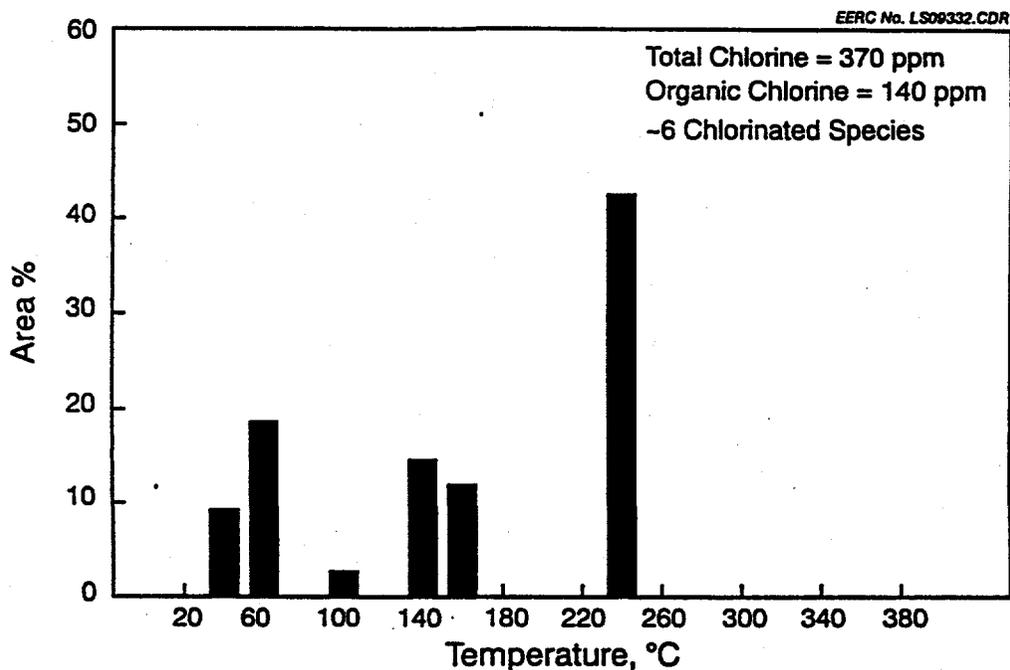


Figure B-5. Organic chlorine distribution for liquids produced at a depolymerization temperature of 540°C and a filter temperature of 340°C (M357).

## GC/AED ORGANIC CHLORINE ANALYSIS OF PLASTICS DECOMPOSITION LIQUIDS DETECTION LIMIT/QUALITY CONTROL STUDY

A study was conducted at the Energy & Environmental Research Center (EERC) in Grand Forks, North Dakota, to determine the detection limit (lowest detectable concentration) of organic chlorine in plastics decomposition liquids using gas chromatography coupled with atomic emission detection (GC/AED). The study consisted of analyzing a base material and three successively less concentrated dilutions of the base material. The results of this limited study indicate a *per-compound* detection limit of about 4 parts per million (ppm) organic chlorine. It must be stressed that the 4-ppm value is an indication of a detection limit and that a more comprehensive study would be required to establish a statistically valid detection limit.

Several decomposition products from both the EERC and the Energy & Environmental Research (EER) Corporation in Irvine, California, were considered as a base material for the study. APC-106 from EER was chosen for the following reasons:

- While many decomposition products are waxy, sludgy materials at room temperature, APC-106 is a liquid with the approximate viscosity of a heavy fuel oil. Liquids can be accurately sampled, mixed, and solubilized without heat, which eliminates the possibility of boiling away volatile chlorine species.
- APC-106 has been analyzed for organic chlorine twice at the EERC and at least once at Core Laboratories in California; all three analyses provided similar results:

EERC 1 11,300 ppm  
EERC 2 10,300 ppm  
Core 1 11,000 ppm

- APC-106 has a wide concentration range of chlorine-containing species. In the two EERC analyses, APC-106 was found to be composed of about 30 organic chlorine-containing species, ranging in concentration from less than 1.0% to about 24% of the total organic chlorine content.

Table C-1 provides results of the two EERC analyses of APC-106, and the following table provides results of triplicate analyses of the three APC-106 dilutions. The following definitions apply to both tables:

IS1/IS2	Area counts of Internal Standard 1 (2-chloronaphthalene) divided by area counts of Internal Standard 2 (1-chloronaphthalene)
IS1+IS2	Area counts of Internal Standard 1 plus area counts of Internal Standard 2
Total-IS	Total area counts minus IS1+IS2
ISTD, g	Weight of Internal Standard in grams

Sx, g	Weight of sample in grams
Cl, ppm	Organic chlorine content in parts per million
BPI, °C	Boiling point index (calculated boiling point based on relationship of GC retention time to boiling point for the series of normal alkanes from C <sub>5</sub> to C <sub>15</sub> )
RT	GC retention time
AC	GC area counts

Table C-1 indicates the reproducibility of the analysis technique. In both analyses, the same five compounds (with boiling point indices of 47°, 86°, 113°, 126°, and 153°C) accounted for about 70% of the total organic chlorine. Regarding the internal standard (ISTD), the original intent was to use 1-chloronaphthalene, but analysis revealed that 2-chloronaphthalene was present as an impurity in the 1-chloronaphthalene. This turned out to be advantageous, because it enabled calculation of an area count ratio (IS1/IS2) for the two compounds. If this ratio is consistent over the course of a series of analyses, it indicates that 1) neither species is present in the samples (this is required for overall quantitative accuracy—if chloronaphthalene is found in a sample, a different ISTD must be used in the analysis of that sample) and 2) the instrument is providing accurate and reproducible area count data.

In Table C-1, the two analyses are merged to allow easy comparison of area count data. Gaps in the columns indicate that the instrument detected a compound in one analysis but did not find the same compound in the other analysis. These errors are because of judgement differences in establishing a baseline from which to integrate the AED response for chlorine-containing compounds. As shown in the table, none of these inconsistently present compounds accounts for more than 2% of the total organic chlorine content, and the cumulative effect of all of them is 3.1% for APC-106a and 4.8% for APC-106b. Also of significance in the analysis of the base material are the ISTD area count values of 399 and 297 for APC-106a and APC-106b, respectively, and the weight ratio of ISTD to sample ( $0.011/1.010 = 0.011$ ). These numbers will be compared to their counterparts in the analysis of the base material dilutions.

In order to prepare dilutions of the base material, a liquid was needed in which the base material was soluble at room temperature. Because the base material was produced from a feedstock containing 10% PVC in a mixture of polyethylene (PE), polypropylene (PP), and polystyrene (PS), it was determined that a dilution liquid made from a similar feedstock would have the best solubilization capability. The dilution liquid (DL) was prepared by mixing 6 mL of a PP decomposition product (EERC-M269) with 14 mL of a 50% PE/50% PS decomposition product (EERC-M291). The three base material dilutions were prepared as follows:

- No. 1      0.5 mL (0.418 g) APC-106 was added to 4.5 mL (3.743 g) DL.
- No. 2      About 0.05 mL (0.056 g) APC-106 was added to 5.0 mL (4.121 g) DL.
- No. 3      0.010 g APC-106 was added to about 8 mL (6.890 g) DL.

Based on the average of the three base material analyses, the chlorine content of the base material is about 10,900 ppm. Therefore, assuming good mixing and solubilization of the base material in the DL (which seems reasonable because of lack of visual evidence of precipitation or cloudiness), the chlorine content of the three dilutions should be about 1100 ppm, 150 ppm, and 16 ppm, respectively, for No. 1, No. 2, and No. 3 ( $\mu\text{g/g}$  and ppm are equivalent—see Table C-2). Table C-2 shows the merged results of the triplicate analyses of the three dilutions. To avoid any effects of analysis repetition, the dilutions were analyzed in the order shown in the table (APC-1 through APC-9).

The table shows that in all three analyses of No. 1 and No. 2, the analyzed chlorine content was higher than the calculated value. The reason for this is unknown and would require more testing to determine, but comparison of the three analyses of No. 1 and the three analyses of No. 2 shows that in both cases the greatest chlorine content error is associated with the smallest ISTD area count value. This indicates valid relationship between the accuracy of analyzed chlorine content and the magnitude of the ISTD area count value and the establishment of a minimum ISTD area count value. Based on the available data, it appears that reasonable accuracy should be possible, provided the ISTD area count value for an analysis exceeds 1800. This does not mean that if the ISTD area count is below 1800 the analysis will not be accurate; it means that the chance for inaccuracy is greater. In the case of the base material analyses, it must be remembered that the ISTD-to-sample ratio was about 0.011, whereas with the dilution analyses, the ISTD-to-sample ratios were about 0.013 (0.011/0.824), a difference of about 22%. Also, three separate analyses of the base material, using two different samples, yielded three similar chlorine content values.

Of the three analyses of Dilution No. 3 (the least concentrated), only APC-4 detected a response for a compound other than the two ISTDs. The ISTD area count for APC-4 was 1868, while the other two area count values were less than 500. A small ISTD area count is indicative of a small GC injection volume, the reason for which may involve sample viscosity and the small inside diameter of the injection needle. However, this should not be a problem—if an injection size is small, the analysis can be repeated until a representative sample (as defined by an ISTD area count of over 1800) is injected.

The following rationale was used to yield an indication of the detection limit of the GC/AED method for organic chlorine analysis:

Based on the average base material total organic chlorine content of 10,900, the concentration of the most concentrated component (BPI of 47°C) of the base material was calculated to be 2600 ppm. The concentration of this component in Dilution No. 3 (assuming proper mixing and solubilization) was calculated to be about 4 ppm. Because this 4-ppm component was detected in a representative sample injection, it seems reasonable to assume that the detection limit is at least 4 ppm (per component), provided an adequate sample volume is injected (as defined by an ISTD area count value of at least 1800).

Concerning the use of GC/AED to quantitate organic chlorine in APC plastics decomposition liquids, the primary implication of this limited study is that the technique will detect chlorine-containing species present at concentrations of 4 ppm or higher. Hence, the possibility exists that if a product contains 100-ppm organic chlorine distributed among 40 compounds, none of which individually comprise more than 3 ppm

of the total organic chlorine content, the technique may yield an organic chlorine content of zero for this product. However, this is unlikely, because in analyses of products from both the EERC and EER Corporation, the same five components normally account for about 50% to 70% of the organic chlorine content. In products with lower chlorine contents (from 200 to 1000 ppm), these same five components appear to account for about 70% to 90%. While it is possible that product liquids with lower organic chlorine contents have lower degrees of chlorine compound speciation, it is more likely that at lower organic chlorine levels, fewer species are present in above-detection-limit concentrations. In a hypothetical analysis, if only the above-mentioned five compounds were detected, all at concentrations of 4 ppm, the analyzed organic chlorine content of 20 ppm would probably account for less than the actual content, which would probably range from about 25 to 50 ppm.

In addition to enabling quantitation of total organic chlorine, GC/AED data provides useful information regarding product volatility. In comparing samples analyzed at different times, it is important to remember that GC boiling point indices can vary by about 3°C, because of differences in chromatographic conditions and the use of different alkane mixtures for boiling point calibration.

TABLE C-1

## Analytical Reproducibility

Base Material						
		APC-106a		APC-106b		
IS1/IS2		0.140		0.142		
IS1+IS2		399		297		
Total-IS		1833		1245		
ISTD, g		0.011		0.011		
Sx, g		1.010		1.010		
Cl, ppm		11307		10318		

Organic Chlorine Boiling Point Distribution						
		APC-106a		APC-106b		
BPI, °C	RT	AC	A%	RT	AC	A%
47	1.33	447	24.4	1.28	303	24.3
53	1.47	6	0.3			0.0
64			0.0	1.71	13	1.0
68			0.0	1.82	22	1.8
73			0.0	1.96	6	0.5
81	2.65	14	0.8	2.55	15	1.2
86	2.99	151	8.2	2.89	111	8.9
91			0.0	3.20	6	0.5
102			0.0	4.09	9	0.7
104	4.35	67	3.7	4.24	55	4.4
113	5.12	280	15.3	5.00	209	16.8
118	5.59	84	4.6	5.48	59	4.7
119	5.73	10	0.5			0.0
126	6.37	288	15.7	6.25	151	12.1
129	6.59	44	2.4	6.47	27	2.2
133	6.97	16	0.9	6.87	11	0.9
133	7.05	12	0.7	6.93	10	0.8
136	7.27	23	1.3	7.15	13	1.0
139	7.57	42	2.3	7.45	20	1.6
139	7.64	6	0.3	7.51	4	0.3
140	7.65	8	0.4			0.0
146	8.25	22	1.2	8.13	10	0.8
150	8.66	17	0.9	8.54	16	1.3
153	8.92	126	6.9	8.79	93	7.5
154	9.06	33	1.8	8.94	21	1.7
164	10.01	13	0.7	9.88	6	0.5

(continued...)

TABLE C-1 (continued)

BPI, °C	Base Material					
	RT	AC	A%	RT	AC	A%
165	10.10	8	0.4			0.0
173	10.81	17	0.9			0.0
173	10.83	14	0.8	10.68	5	0.4
175	10.99	11	0.6	10.86	8	0.6
180	11.54	8	0.4			0.0
184	11.85	4	0.2			0.0
187	12.15	15	0.8	12.02	16	1.3
194			0.0	12.68	4	0.3
199	13.23	47	2.6	13.10	22	1.8
247	17.80	49	IS	17.65	37	IS
247	17.87	350	IS	17.72	260	IS

TABLE C-2

Dilution Analyses

Dilution:	No. 1, 1100 Fg/g			No. 2, 150 Fg/g			No. 3, 16 Fg/g							
	APC3-3	APC3-6	APC3-9	APC3-2	APC3-5	APC3-8	APC3-1	APC3-4	APC3-7					
IS1/IS2	0.137	0.136	0.141	0.133	0.135	0.139	0.128	0.140	0.135					
IS1 + IS2	2485	301	2393	2076	4928	654	132	1868	487					
TotalBIS	1087	170	1029	131	296	48	0	6	0					
ISTD, g	0.012	0.012	0.012	0.011	0.011	0.011	0.011	0.011	0.011					
Sx, g	0.825	0.825	0.825	0.808	0.808	0.808	0.838	0.838	0.838					
Cl, ppm	1341	1732	1319	194	185	226	0	10	0					
BPI, EC	RT	AC	RT	AC	RT	AC	RT	AC	RT	AC				
47	1.36	206	1.37	55	1.36	193	1.38	23	1.37	42	1.38	11	1.38	6
					2.52	6								
	2.62	8			2.61	8								
86	2.97	82	2.99	18	2.97	69	2.98	15	2.97	18				
	3.68	8							2.83	5				
	4.15	6			4.14	13								

(continued)

TABLE C-2 (continued)

Dilution:	No. 1, 1100 µg/g						No. 2, 150 µg/g						No. 3, 16 µg/g							
	RT	AC	RT	AC	RT	AC	RT	AC	RT	AC	RT	AC	RT	AC	RT	AC	RT	AC	RT	AC
104	4.31	49	4.34	12	4.30	56			4.32	11										
	4.61	10																		
113	5.08	154	5.10		5.07	145	5.11	24	5.10	49	5.12	14								
	5.21	9																		
	5.27	4							5.26	8										
									5.32	2										
118	5.53	51	5.55	7	5.52	46	5.54	7	5.54	10										
	5.65	2			5.64	5														
126	6.32	126	6.34	28	6.31	123	6.35	18	6.33	34	6.36	8								
	6.52	14			6.51	12			6.52	2										
	7.20	12			6.88	9														
	7.50	31	7.51	6	7.50	18	7.51	3												
	7.79	11			7.19	14														
	8.19	10																		
	8.61	13			8.60	16														
153	8.86	86	8.87	10	8.85	83	8.89	16	8.88	26	8.88	15								
	8.99	21			8.99	25	9.01	5	9.00	14										
	9.92	36			9.91	23														
	10.74	22			10.01	13														
					10.73	20			10.74	22										

(continued...)

TABLE C-2 (continued)

Dilution:		No. 1, 1100 µg/g										No. 2, 150 µg/g										No. 3, 16 µg/g				
BPI, °C	RT	AC	RT	AC	RT	AC	RT	AC	RT	AC	RT	AC	RT	AC	RT	AC	RT	AC	RT	AC	RT	AC	RT	AC	RT	
	10.90	17			10.90	16																				
	11.10	7																								
	11.46	12			11.47	11																				
	12.08	16			11.76	9							12.07	11												
199	13.15	64	13.32	2	13.14	50	13.16	11	13.15	25																
					15.29	11																				
					15.70	2																				
					16.45	4																				
					16.55	6	16.57	9	16.56	17																
					17.44	9																				
247	17.72	299	17.71	36	17.71	295	17.73	244	17.73	585	17.71	80	17.73	15	17.72	230	17.71	58								
247	17.81	2186	17.78	265	17.80	2098	17.81	1832	17.83	4343	17.79	574	17.81	117	17.80	1638	17.78	429								

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**— Terephthalic Acid Quantification**

## TEREPHTHALIC ACID QUANTIFICATION

The terephthalic acid (TA) analysis method (West, J.C., *Analytical Chemistry* 1975, 47, 1708, and Knapp, D.R., *Handbook of Analytical Derivatization Reactions*, John Wiley & Sons, 1979; p. 221) used in this project is a two-step process consisting of 1) esterification of TA to its methyl ester, dimethyl terephthalate (DMT) and 2) quantitation of DMT using GC-FID. Accurate quantitation requires construction of a calibration curve based on gas chromatography-flame ionization detection (GC-FID) analysis of a series of analytical standards representative of a DMT concentration range that "brackets" the DMT concentration value yielded by the analytical sample. Because the molar ratio of DMT to TA is 1:1, wt% TA in a sample can be calculated based on the weight ratio of DT to TA (194:166). In addition to TA, the method will convert other carboxylic acids present in a sample to their respective methyl esters, which can then also be quantitated in the same manner. Work to date has indicated that benzoic acid is the only other carboxylic acid present in greater than trace amounts in any of the samples tested. In order to ensure sample homogeneity (and representative results), all derivatizations should be performed using material obtained from a sample that has been thoroughly mixed with an electric blender. The standard operating procedure (SOP) used for TA derivatization is as follows:

### Standard Operating Procedure for Ta Derivatization

1. The condensate sample is blended (to ensure homogeneity) for at least 2 minutes using a laboratory blender.
2. An approximate 75- to 100-milligram (mg) aliquot of the blended sample is weighed into a 50-milliliter (mL) flask, 1.0 mL of methanol and 1.0 mL of tetramethylammonium hydroxide (TMAH) are added, and the mixture is refluxed for 10-15 minutes (min) or until all solids are dissolved.
3. Ten mL of dimethyl formamide (DMF) and 1 mL of internal standard (*n*-octadecane in dichloromethane) are added, and the solution is mixed.

**Warning: Extreme Caution Should Be Employed in the Use of Methyl Iodide, as it Has the Potential of Producing Severe Narcosis.**

4. One mL of methyl iodide ( $\text{CH}_3\text{I}$ ) is added, the solution is mixed, and tetramethylammonium iodide precipitate (formed in the reaction of TMAH with any carboxylic acid [s] present) is separated by centrifugation.
5. An aliquot of the supernatant is analyzed for TA quantitation using GC-FID.

The SOP for DMT quantitation, which is performed using an HP 5890A gas chromatograph equipped with a Petrocol capillary column, is as follows:

## Standard Operating Procedure for Dmt Quantitation

1. An internal standard (ISTD) solution is prepared by dissolving a known weight of *n*-octadecane into a known volume of dichloromethane to produce a 100- $\mu\text{g}/\text{mL}$  solution of *n*-octadecane.
2. Stock solutions containing 1200, 600, 250, 100, 50, and 25  $\mu\text{g}/\text{mL}$  of DMT, each also containing 100  $\mu\text{g}/\text{mL}$  of *n*-octadecane ISTD, are prepared.
3. One  $\mu\text{L}$  of each solution is injected into the GC and analyzed, using the following temperature program and GC conditions:

Initial temperature: 30°C

30° to 40°C @ 0.5°C/min

40° to 300°C @ 2°C/min

Carrier gas: H<sub>2</sub> @ 3 mL/min at 25°C

Makeup gas: N<sub>2</sub>

Split ratio: 40:1

4. Data gathered from these analyses will be used to generate a calibration table (from which a DMT response factor is calculated—see Step 6) that is stored on the hard drive of the GC computer. A calculation program can then be used to compute DMT amount (in grams) in a sample using the calibration table, the ISTD amount, and DMT and ISTD area count data for the sample.
5. To check the accuracy of the calibration table, two DMT solutions of known concentration will be prepared and analyzed.
6. Calculation of DMT amount in a sample is performed as follows:

$$\text{amt}_{\text{DT}} = \left( \frac{(\text{ac}_{\text{DMT}})(\text{rsp}_{\text{DMT}})}{(\text{ac}_{\text{ISTD}})(\text{rsp}_{\text{ISTD}})} \right) (\text{amt}_{\text{ISTD}}) \quad [\text{Eq. 1}]$$

where: ac = area counts

amt = amount, in grams

rsp = response factor (calibration amt/calibration ac)

7. Calculation of TA amount is then performed as follows:

$$\text{amt}_{\text{TA}} = (\text{amt}_{\text{DMT}})(166:194) \quad [\text{Eq. 2}]$$

where: 166:194 = TA:DMT molar weight ratio in grams/mole

8. Calculation of TA concentration is then performed as follows:

$$\text{conc}_{\text{TA}} = [(\text{amt}_{\text{TA}})/(\text{amt}_{\text{sample}})](100\%) \quad [\text{Eq. 3}]$$

To investigate the accuracy of the method, 0.0172 g of TA (Aldrich Chemicals, 18,536-1, 98% purity) was derivatized and analyzed. The calculated yield of TA was 0.0159 g, which indicates (assuming an initial TA weight of 0.0169 g, owing to 98% purity) a recovery of about 94%.

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**— Gas Analysis**

## GAS ANALYSIS

Light olefins quantitation in balance-period gas samples is performed using a gas chromatography (GC) analysis method developed and published by Hewlett-Packard Company to provide "rapid determinations of fixed gases and light hydrocarbons in various refinery type gas mixtures, including minor concentrations of C<sub>6</sub> + hydrocarbons." A complete description of the method is provided in "Refinery Gas Analyzer 18900C Option 816, Gas Chromatograph 5880A, "Hewlett-Packard Company, 1983. Samples can be injected into the GC from either a pressurized sample cylinder or gas bag. Samples for this project were injected into the GC from gas bags according to the following standard operating procedure (SOP).

### Standard Operating Procedure for Injection of Gas Bag Samples

1. Attach gas bag to stainless steel sample inlet line with short piece of "Tygon" tubing.
2. Open gas bag valve.
3. Apply gentle pressure on gas bag for 2 minutes (this action will result in purging about 200 cubic centimeters of gas through the GC sample loops).
4. Close gas bag valve and press GC sample injection button to activate sample loop valves and initiate analysis.

The gas analysis provides mole percent (mol%) concentration values for a specific set of gas compounds, including each of the light olefins of interest in this project, hydrogen, nitrogen, oxygen, carbon dioxide, carbon monoxide, and other hydrocarbons. Other outputs from the analysis include calculated heating value, calculated average molecular weight, and calculated "air-basis" specific gravity (defined as the ratio of the density of a particular gas to the density of air at standard temperature and pressure), obtained using the gas compound concentration data and published air-basis specific gravity values. In addition to the steps described in the above SOP for gas sample injection, each gas bag is tested for leaks during a "nitrogen rinse" as described in the following SOP for gas sample collection.

### Standard Operating Procedure for Gas Sample Collection

1. Attach a gas bag to the house nitrogen line with Tygon tubing, open gas bag valve, fill gas bag to slightly under capacity with nitrogen, and close gas bag valve.
2. Attach full gas bag to house vacuum line with Tygon tubing, open bag valve, evacuate bag completely, and close bag valve.
3. Repeat Steps 1 and 2.
4. Fill bag with nitrogen a third time according to Step 1 and check bag (including valve) thoroughly for leaks. If a leak is detected, dispose of bag, obtain a new bag, and begin SOP again, starting with Step 1.

5. If no leaks are detected, evacuate bag according to Step 2.
6. Attach nitrogen-rinsed bag to reactor system gas-sampling line with Tygon tubing.
7. Open gas bag valve, open reactor system vacuum valve, and evacuate sampling line and gas bag as a unit.
8. Close vacuum valve, open reactor system sampling valve, and fill gas bag with product gas.
9. Close reactor system sampling valve, close gas bag valve, remove gas bag from reactor system gas-sampling line, and deliver sample to gas analysis lab.

A single-point calibration of the GC for the light olefins analysis is performed using the three calibration gas mixtures (Cal-1, Cal-2, and Cal-4) listed in the accompanying "Calibration Gas Concentrations" table. Calibration is performed for each of the 21 components (analytes) listed in the table. The calibration procedure is described in "5880A Gas Chromatograph, Volume 5: Integration and Methods," Hewlett-Packard Company, 1979. All calibrations are performed using certified standard-grade calibration gas (cal gas) mixtures from Matheson Company, Houston, Texas. As shown in the cal gas listings, the calibration concentrations of the C<sub>2</sub>, C<sub>3</sub>, and C<sub>4</sub> olefins to be quantitated range from 0.731 mol% for acetylene to 1.08 mol% for 1,3-butadiene. Based on analyses performed in past EERC work, concentration ranges for these light olefins in depolymerization product gases normally range from about 0.5 to 1.5 mol% for the C<sub>4</sub> olefins and from about 1 to 5 mol% for the C<sub>2</sub> and C<sub>3</sub> olefins.

Calibration Gas Concentrations

Cal-1      Cal-2      Cal-3      Cal-4

1	Helium (He)	0.956			
2	Hydrogen (H <sub>2</sub> )	29.47			
3	Carbon Dioxide (CO <sub>2</sub> )	10.10	2.99		
4	Propane (C <sub>3</sub> H <sub>8</sub> )	0.981			
5	Propylene (C <sub>3</sub> H <sub>6</sub> )		0.986		
6	Acetylene (C <sub>2</sub> H <sub>2</sub> )				0.731
7	iso-Butane (i-C <sub>4</sub> )	0.483			
8	Carbonyl Sulfide (COS)			0.205	
9	n-Butane (n-C <sub>4</sub> )	0.496			
10	Hydrogen Sulfide (H <sub>2</sub> S)			0.972	
11	1-Butene (1-Bu)		0.963		
12	iso-Butylene (i-Bu)				1.02
13	trans-2-Butene (t-2-Bu)		0.949		
14	iso-Pentane (i-C <sub>5</sub> )	0.495	0.993		
15	cis-2-Butene (c-2-Bu)		0.958		
16	n-Pentane (n-C <sub>5</sub> )	0.492			
17	1,3-Butadiene (1,3-BDN)				1.08
18	Ethylene (C <sub>2</sub> H <sub>4</sub> )		1.04		
19	Ethane (C <sub>2</sub> H <sub>6</sub> )	0.975			
20	Oxygen (O <sub>2</sub> )	0.984			5.06
21	Nitrogen (N <sub>2</sub> )	7.03	70.791	98.823	92.109
22	Methane (CH <sub>4</sub> )	7.49	20.33		
23	Carbon Monoxide (CO)	40.048			

**APPENDIX C**

**MATERIAL BALANCE PROCEDURES  
SUMMARIES AND METHODS DESCRIPTION  
MATERIAL BALANCE CALCULATION METHODS**

## MATERIAL BALANCE SUMMARIES AND METHODS DESCRIPTION MATERIAL BALANCE CALCULATION METHODS

Figure G-1 is a material balance sheet for M268. This sheet will be used to help to explain how yields were calculated.

Components listed are polymer/solids (a generic reference to the component fed), water, condensables (organic liquids), and gas. The organic liquid section is broken down further as boiling point cuts. The gas section is also broken down further, by components. The first column, marked "Grams In," contains the grams of material fed to the process, broken down by component. For example, 3628 grams of PP and 2537 grams of nitrogen were fed over the material balance period for M268. The next column is "Grams Out," again broken down by component. The third column is "Yields." Yields for each component are calculated by dividing grams out of a component minus grams in by the grams of polymer fed. For example, the calculation of total liquid (cond.) yield for this run would be as follows:

$$\frac{\text{Liquid grams out} - \text{liquid grams in}}{\text{Polymer fed}} = \frac{(3052.9 - 0)}{3628.0} = 84.1\%$$

All columns are totalled at the bottom of the sheet. In this case, 6165.0 g of total material were fed to the process, and 5806.8 g of total material were collected. This corresponds to a 94.2% material closure, shown below the grams-out total. The yields do not add up to 100% because the material balance is not 100%. These two numbers are not the same (94.2 and 90.1) because the yield calculation is based on polymer fed and the material balance number is based on total material fed and collected. The last column is labeled "N Yields." This column takes the difference between the material fed and the material collected and distributes it to one or more of the three product streams, based on tie elements. A tie element is a portion of a stream that does not take part in a reaction or is "inert." The only tie elements in these balances is nitrogen. Nitrogen into the system must equal nitrogen out of the system. No significant solid material or unreacted polymer was collected, so it was not available for use as a tie. In the case of M268, the difference between total material fed and total product collected is 358.2 grams. Five % of this "missing" mass is assigned to the gas stream and 95% to the liquid stream. This 5% was based on the nitrogen balance in the gas stream, which allowed the nitrogen in to equal the nitrogen out. Five percent, or 17.9 g, is distributed to the gas stream on a molar, or volume, basis. Since this is distributed on a molar basis, the mass assigned to the gas stream must be put on a molar basis by dividing by the average molecular weight of the gas, 28.79.

$$\frac{17.9}{28.79} = 0.6217 \text{ mol}$$

Propylene is 2.3% of the product gas stream, so 2.3% of the 0.6217 moles is given to propylene.

$$\begin{aligned} 0.6217 \text{ mol} \times 2.3\% &= 0.0143 \text{ mol propylene} \\ 0.0143 \text{ mol} \times 42 \text{ g/g-mol} &= 0.60 \text{ g propylene} \end{aligned}$$

The normalized (N) yield for propylene is as follows:

$$\frac{\text{Gas grams out} - \text{gas grams in} + \text{normalization quantity}}{\text{Grams PP fed}} = \frac{(92.4 - 0) + (0.60)}{3628.0} = 2.6\%$$

For the product liquids, there were 3052.9 grams collected. This equates to a yield of 84.1%.

$$\frac{3052.9}{3628.0} \times 100\% = 84.1\%$$

95% of the mass loss ( $0.95 \times 358.2 = 340.3$ ) has been assigned to the liquid stream in this run. The normalized yield becomes:

$$\frac{\text{Liquid grams out} - \text{liquid grams in} + \text{normalization quantity}}{\text{Grams PP fed}} = \frac{(3052.9 - 0 + 340.3)}{3628.0} \times 100\% = 93.5\%$$

The assignment of percentages to streams is shown in the lower left corner of the yields summary sheet.

	Gms In	Gms Out	Yields	N Yields	
Polymer/solids	7256.0	0.0	0.0	0.0	
H2O	0.0	0.0	0.0	0.0	
-----					
Cond. Total		5515.1	76.0	95.3	
ibp-160		0.0	0.0	0.0	
<C10		0.0	0.0	0.0	
BXT		0.0	0.0	0.0	
160-260		0.0	0.0	0.0	
C10-C12		0.0	0.0	0.0	
Phenols		0.0	0.0	0.0	
Cresols		0.0	0.0	0.0	
Naphthal.		0.0	0.0	0.0	
260-360		0.0	0.0	0.0	
C13-C22		0.0	0.0	0.0	
C2-Phenol		0.0	0.0	0.0	
Phytene		0.0	0.0	0.0	
360-460		0.0	0.0	0.0	
C23-C30		0.0	0.0	0.0	
460-600		0.0	0.0	0.0	
Aliphatics		0.0	0.0	0.0	
Phenolics		0.0	0.0	0.0	
-----					
Gas Total	38232.0	37170.9	-14.6	4.7	6.4
H2		1.9	0.0	0.0	0.8
CO2		5.8	0.1	0.1	0.1
C3H8		5.8	0.1	0.1	0.1
C3H6		105.5	1.5	1.5	2.3
i-C4		0.0	0.0	0.0	0.0
Unid.		0.0	0.0	0.0	0.0
n-C4		0.0	0.0	0.0	0.0
Unid.		0.0	0.0	0.0	0.0
1-Bu		29.6	0.4	0.4	0.5
t-2-Bu		0.0	0.0	0.0	0.0
i-C5		0.0	0.0	0.0	0.0
c-2-Bu		0.0	0.0	0.0	0.0
n-C5		152.3	2.1	2.2	1.9
C2H4		0.0	0.0	0.0	0.0
C2H6		15.9	0.2	0.2	0.5
O2		0.0	0.0	0.0	0.0
N2	38232.0	36849.8	-19.0	0.1	0.2
CH4		0.0	0.0	0.0	0.0
C6+		0.0	0.0	0.0	0.0
-----					
Total	45488.0	42686.0	61.4	100.0	
-----					
Mat. Balance		93.8			
-----					
% loss to char1	0				
% loss to char2	0				
% loss to liq	50				
% loss to gas	50				

7/27/93

Run # M266  
 PP  
 Temp. 450 C  
 Pressure 10 psig  
 % H2O 0.0  
 % N2 100.0  
 Bed Material = Sand

SCF

Figure G-1. Examples of material balance sheets.

P036

Temp C	650
Press, psig	42
feedrate, lb/hr	80
runtime, hrs	3
% Sand	5

	IN	OUT	YIELD	N YIELD
plastics in, lbs	228	0	0.0%	0.0%
CaO/sand in, lbs	12	19.9	3.5%	3.5%
water, lbs				
scrubbers	53			
steam	120			
Organic Liquids, lbs	14	89	32.9%	32.9%
<u>Gas</u>				
H2	0	2.3	1.0%	1.0%
CO2	0	128.3	56.3%	55.5%
C3	0	32.1	14.1%	13.9%
C3=	0	39.1	17.2%	16.9%
i-Bu	0	0.0	0.0%	0.0%
i-butyl	0	9.1	4.0%	3.9%
n-bu	0	0.0	0.0%	0.0%
unid	0	6.8	3.0%	2.9%
1-but	0	6.8	3.0%	2.9%
t-2-but	0	2.3	1.0%	1.0%
i-C5	0	0.0	0.0%	0.0%
c-2-but	0	0.0	0.0%	0.0%
n-C5	0	0.0	0.0%	0.0%
C2=	0	31.8	13.9%	13.7%
C2	0	7.3	3.2%	3.2%
O2	199.5	0.0	-87.5%	-87.5%
N2	887.7	899.4	5.2%	-0.0%
CH4	50.8	11.7	-17.1%	-17.2%
CO	0.0	25.0	10.9%	10.8%
avg mol wt		29.7		
Total Gas + Water	1310.9	1471.9	70.6%	63.6%
Total mass	1564.9	1580.8	149.5%	100.0%
material balance		101.0%		
% to gas	100.0%	moles O2/CH4 in =	2.0	
% to liquids	0.0%			
% to solids	0.0%			

P037

Temp C 628  
 Press, psig 36  
 feedrate, lb/hr 100  
 runtime, hrs 2.5  
 % CaO/sand 5

	IN	OUT	YIELD	N YIELD
plastics in, lbs	237.5	0	0.0%	0.0%
CaO/sand in, lbs	12.5	0	-5.3%	0.5%
water, lbs				
scrubbers	320.0			
steam	19.3			
Organic Liquids, lbs	52.0	66.0	5.9%	25.8%
<u>Gas</u>				
H2	0.0	3.8	1.6%	1.6%
CO2	0.0	78.0	32.8%	33.3%
C3	0.0	3.1	1.3%	1.3%
C3=	0.0	46.1	19.4%	19.7%
i-Bu	0.0	0.0	0.0%	0.0%
i-butyl	0.0	7.9	3.3%	3.4%
n-bu	0.0	0.0	0.0%	0.0%
unid	0.0	6.0	2.5%	2.5%
1-but	0.0	7.9	3.3%	3.4%
t-2-but	0.0	2.0	0.8%	0.8%
i-C5	0.0	0.0	0.0%	0.0%
c-2-but	0.0	2.0	0.8%	0.8%
n-C5	0.0	0.0	0.0%	0.0%
C2=	0.0	36.7	15.5%	15.7%
C2	0.0	1.1	0.4%	0.5%
O2	170.9	0.0	-71.9%	-71.9%
N2	744.1	733.2	-4.6%	0.2%
CH4	39.7	14.7	-10.5%	-10.4%
CO	0.0	43.7	18.4%	18.7%
avg mol wt		27.8		
Total Gas + Water	1293.9	1258.1	-15.1%	73.7%
Total mass material balance	1595.9	1324.1	-42.7%	100.0%
		83.0%		
% to gas	5.7%	moles O2/CH4 in =		2.2
% to liquids	89.3%			
% to solids	5.0%			

P038

Temp C	625
Press, psig	44
feedrate, lb/hr	100
runtime, hrs	8
% CaO/sand	5

	IN	OUT	YIELD	N YIELD
plastics in, lbs	760	0	0.0%	0.0%
CaO/sand in, lbs	40.0	18.1	-2.9%	-0.2%
water, lbs				
scrubbers	35.0			
steam	240.0			
Organic Liquids, lbs	0.0	335.0	44.1%	52.7%
<u>Gas</u>				
H2	0	8.8	1.2%	1.2%
CO2	0	298.7	39.3%	39.3%
C3	0	0.0	0.0%	0.0%
C3=	0	102.4	13.5%	13.5%
i-Bu	0	0.0	0.0%	0.0%
i-butyl	0	25.0	3.3%	3.3%
n-bu	0	6.8	0.9%	0.9%
unid	0	15.1	2.0%	2.0%
1-but	0	19.0	2.5%	2.5%
t-2-but	0	3.9	0.5%	0.5%
i-C5	0	0.0	0.0%	0.0%
c-2-but	0	2.6	0.3%	0.3%
n-C5	0	3.4	0.4%	0.4%
C2=	0	70.3	9.2%	9.2%
C2	0	23.6	3.1%	3.1%
O2	543.7	0.0	-71.5%	-71.5%
N2	2646.0	2645.8	-0.0%	-0.0%
CH4	140.7	28.5	-14.8%	-14.8%
CO	0.0	96.4	12.7%	12.7%
avg mol wt		28.6		
Total Gas + Water	3605.4	3866.4	34.3%	47.5%
Total mass	4405.4	4219.4	107.2%	100.0%
material balance		95.8%		
% to gas	0.0%	moles O2/CH4 in =	1.9	
% to liquids	89.0%			
% to solids	11.0%			

P041

Temp C 627  
 Press, psig 35  
 feedrate, lb/hr 100  
 runtime, hrs 2  
 % CaO/sand 15

	IN	OUT	YIELD	N YIELD
plastics in, lbs	170	0	0.0%	0.0%
CaO/sand in, lbs	30	55	14.7%	14.7%
water, lbs				
scrubbers	255.0			
steam	60.0			
Organic Liquids, lbs	0	107	62.9%	62.9%
<u>Gas</u>				
H2	0	1.8	1.0%	1.2%
CO2	0	75.3	44.3%	51.1%
C3	0	3.5	2.1%	2.4%
C3=	0	18.0	10.6%	12.2%
i-Bu	0	0.0	0.0%	0.0%
i-butyl	0	1.5	0.9%	1.0%
n-bu	0	0.0	0.0%	0.0%
unid	0	4.5	2.6%	3.0%
1-but	0	6.0	3.5%	4.1%
t-2-but	0	1.5	0.9%	1.0%
i-C5	0	0.0	0.0%	0.0%
c-2-but	0	0.0	0.0%	0.0%
n-C5	0	0.0	0.0%	0.0%
C2=	0	19.5	11.5%	13.2%
C2	0	4.0	2.4%	2.7%
O2	141.4	0.0	-83.2%	-83.2%
N2	698.7	605.7	-54.7%	-0.3%
CH4	38.1	5.6	-19.1%	-18.6%
CO	0.0	20.2	11.9%	13.7%
avg mol wt		28.7		
Total Gas + Water	1193.2	1114.0	-46.6%	22.4%
<b>Total mass</b>	<b>1393.2</b>	<b>1276.0</b>	<b>49.9%</b>	<b>100.0%</b>
<b>material balance</b>		<b>91.6%</b>		
% to gas	100.0%	moles O2/CH4 in =	1.9	
% to liquids	0.0%			
% to solids	0.0%			

P042

Temp C 625  
 Press, psig 45  
 feedrate, lb/hr 50  
 runtime, hrs 16  
 % CaO/sand 15

	IN	OUT	YIELD	N YIELD
plastics in, lbs	680	0	0.0%	0.0%
CaO/sand in, lbs	120	116.5	-0.5%	-0.5%
water, lbs				
scrubbers	1289.0			
steam	515.2			
Organic Liquids, lbs	0	185	27.2%	27.2%
<u>Gas</u>				
H2	0	4.5	0.7%	0.9%
CO2	0	376.1	55.3%	72.2%
C3	0	3.4	0.5%	0.7%
C3=	0	53.0	7.8%	10.2%
i-Bu	0	0.0	0.0%	0.0%
i-butyl	0	0.0	0.0%	0.0%
n-bu	0	0.0	0.0%	0.0%
unid	0	4.4	0.6%	0.8%
1-but	0	15.2	2.2%	2.9%
t-2-but	0	0.0	0.0%	0.0%
i-C5	0	0.0	0.0%	0.0%
c-2-but	0	0.0	0.0%	0.0%
n-C5	0	0.0	0.0%	0.0%
C2=	0	53.8	7.9%	10.3%
C2	0	12.8	1.9%	2.5%
O2	884.7	0.0	-130.1%	-130.1%
N2	6457.7	4947.6	-222.1%	0.7%
CH4	206.8	21.1	-27.3%	-26.3%
CO	0.0	37.0	5.4%	7.1%
avg mol wt		28.5		
Total Gas + Water	9353.3	8159.0	-175.6%	73.3%
Total mass	10153.3	8460.5	-27.5%	100.0%
material balance		83.3%		
% to gas	100.0%	moles O2/CH4 in =		2.1
% to liquids	0.0%			
% to solids	0.0%			

P044

Temp C	590
Press, psig	49
feedrate, lb/hr	68.3
runtime, hrs	8
% CaO/sand	7

	IN	OUT	YIELD	N YIELD
plastics in, lbs	508.2	0.0	0.0%	0.0%
CaO/sand in, lbs	38.2	57.0	3.7%	3.7%
water, lbs				
scrubbers	160.0			
steam	0.0			
Organic Liquids, lbs	0.0	50.0	9.8%	17.7%
<u>Gas</u>				
H2	0.0	0.5	0.1%	0.1%
CO2	0.0	332.5	65.4%	71.2%
C3	0.0	4.5	0.9%	1.0%
C3=	0.0	29.3	5.8%	6.3%
i-Bu	0.0	0.0	0.0%	0.0%
i-butyl	0.0	0.0	0.0%	0.0%
n-bu	0.0	0.0	0.0%	0.0%
unid	0.0	0.0	0.0%	0.0%
1-but	0.0	8.8	1.7%	1.9%
t-2-but	0.0	0.0	0.0%	0.0%
i-C5	0.0	0.0	0.0%	0.0%
c-2-but	0.0	0.0	0.0%	0.0%
n-C5	0.0	0.0	0.0%	0.0%
C2=	0.0	36.5	7.2%	7.8%
C2	0.0	7.1	1.4%	1.5%
O2	469.3	0.0	-92.3%	-92.3%
N2	3066.5	2819.7	-48.6%	-0.0%
CH4	84.9	11.3	-14.5%	-14.3%
CO	0.0	19.5	3.8%	4.2%
avg mol wt		29.1		
Total Gas + Water	3780.6	3617.7	-32.1%	78.7%
<b>Total mass</b>	<b>4327.0</b>	<b>3724.7</b>	<b>18.5%</b>	<b>100.0%</b>
<b>material balance</b>		<b>86.1%</b>		
% to gas	47.5%	moles O2/CH4 in =		2.8
% to liquids	52.5%			
% to solids	0.0%			

**APPENDIX D**  
**SEM ANALYSIS OF PO39 BED MATERIAL**

NATURAL MATERIALS ANALYTICAL RESEARCH LABORATORY  
SAMPLE ANALYSIS REQUEST  
05/04/94

FUND NO: 4717

NMARL NO: 6686

PI: AULICH

Proprietary? Y

Date Submitted: 05/04/94

Company: APC

Project: PLASTICS DECOMPOSITION

Contact:

~~Sample Description~~

DISTRIBUTOR PLATE BUBBLE CAP DEPOSIT-POSSIBLY CONTAINING  
CHLORIDE

Sample Type: DEPOSIT

Sample Source: PILOT SCALE

Collection Device: REACTOR PLUG

Deposit Location: DISTRIBUTOR PLATE

Coal Name:

Coal Seam:

Coal Mine:

Other Coal Info:

~~Comments~~

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ANALYSIS

SUBMITTED NEEDED

EST. COST NOTES

MORPHOLOGY

05/04/94 05/11/94

\$142.00 DOUBLE STICK TAPE

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## Bubble Cap Deposit Analyses

Label: 6679b.F6.S125.X51.Y153

kV: 15.0 Current: 0.0000nA Take\_off: 40.1 Live Time: 25

Stage: X=15.4919 Y=-30.1190 Z=32.1609 R=-0.00 B=0.02 T=-0.00

Beam: X=25.641uM(3072) Y=2.003uM(2128)

Refit \_Mg-K \_Al-K \_P-K \_S-K \_Cl-K \_K-K \_Ti-K

Refit \_Ba-L

Chi-sqd = 8.71

Analysis With Standards

Element	k-ratio	Net Counts
Na-K	0.00116 +/- 0.00036	83 +/- 26
Mg-K	0.000001 +/- 0.00001	0 +/- 0
Al-K	0.000001 +/- 0.00001	0 +/- 0
Si-K	0.00091 +/- 0.00053	65 +/- 38
P-K	0.000001 +/- 0.00001	0 +/- 0
S-K	0.000001 +/- 0.00001	0 +/- 0
Cl-K	0.000001 +/- 0.00001	0 +/- 0
K-K	0.000001 +/- 0.00001	0 +/- 0
Ca-K	0.14072 +/- 0.00228	4978 +/- 81
Ti-K	0.000001 +/- 0.00001	0 +/- 0
Cr-K	0.03826 +/- 0.00276	573 +/- 41
Fe-K	0.54121 +/- 0.00795	7453 +/- 109
Ba-L	0.000001 +/- 0.00001	0 +/- 0

ZAF Correction 15.00 kV 40.15 deg

No.of Iterations = 3

Element	k-ratio	Z	A	F	Atom %	Wt %	Formula	Compound%
Na-K	0.00116	0.979	3.137	1.000	0.44	0.36	Na2O	0.48
Mg-K	0.00000	0.956	2.243	1.000	0.004	0.000	MgO	0.000
Al-K	0.00000	0.985	1.762	0.999	0.003	0.000	Al2O3	0.000
Si-K	0.00091	0.958	1.471	0.998	0.13	0.13	SiO2	0.27
P-K	0.00000	0.991	1.302	0.997	0.008	0.000	P2O5	0.000
S-K	0.00000	0.966	1.190	0.994	0.004	0.000	S O3	0.000
Cl-K	0.00000	1.010	1.123	0.989	0.0023	0.000	ClO	0.000
K-K	0.00000	1.005	1.048	0.967	0.0019	0.000	K2O	0.000
Ca-K	0.14072	0.981	1.028	0.979	9.76	13.88	CaO	19.43
Ti-K	0.00000	1.077	1.036	0.953	0.0064	0.000	TiO2	0.000
Cr-K	0.03826	1.081	1.015	0.900	2.05	3.78	Cr2O3	5.53
Fe-K	0.54121	1.082	1.008	1.000	29.73	59.00	Fe2O3	84.35
Ba-L	0.00000	1.314	0.984	0.955	0.0035	0.000	BaO	0.000
O-K	---	0.915	2.240	0.998	57.90	32.92	S	---
Total						110.06 %		110.06 %

Na-- 0.1204 Mg-- 0.0001 Al-- 0.0001 Si-- 0.0354  
P -- 0.0000 S -- 0.0000 Cl-- 0.0000 K -- 0.0000  
Ca-- 2.6981 Ti-- 0.0000 Cr-- 0.5654 Fe-- 8.2150  
Ba--0.00000 O --16.0000

95

Label: 6679b.F6.S125.X51.Y153  
 kV: 15.0 Current: 0.0000nA Take\_off: 40.1 Live Time: 25  
 Stage: X=15.9488 Y=-29.8898 Z=32.1609 R=-0.00 B=0.02 T=-0.00  
 Beam: X=3.015uM(2176) Y=0.000uM(1376)

Refit \_Na-K \_Mg-K \_P-K \_S-K \_K-K \_Ti-K \_Ba-L

Chi-sqd = 1.11

Analysis With Standards

Element	k-ratio	Net Counts	
Na-K	0.000001 +/- 0.00001	0 +/-	0
Mg-K	0.000001 +/- 0.00001	0 +/-	0
Al-K	0.00035 +/- 0.00021	26 +/-	16
Si-K	0.00333 +/- 0.00031	239 +/-	22
P-K	0.000001 +/- 0.00001	0 +/-	0
S-K	0.000001 +/- 0.00001	0 +/-	0
Cl-K	0.00070 +/- 0.00051	35 +/-	25
K-K	0.000001 +/- 0.00001	0 +/-	0
Ca-K	0.10085 +/- 0.00191	3568 +/-	68
Ti-K	0.000001 +/- 0.00001	0 +/-	0
Cr-K	0.07439 +/- 0.00317	1115 +/-	48
Fe-K	0.46173 +/- 0.00736	6358 +/-	101
Ba-L	0.000001 +/- 0.00001	0 +/-	0

ZAF Correction 15.00 kV 40.12 deg  
 no. of iterations = 3

Element	k-ratio	Z	A	F	Atom %	Wt %	Formula	Compound%
Na-K	0.00000	0.978	3.132	1.000	0.006	0.000	Na2O	0.000
Mg-K	0.00000	0.954	2.244	1.000	0.004	0.000	MgO	0.000
Al-K	0.00035	0.984	1.762	0.999	0.07	0.06	Al2O3	0.11
Si-K	0.00333	0.956	1.475	0.999	0.53	0.47	SiO2	1.00
P-K	0.00000	0.989	1.304	0.997	0.008	0.000	P2O5	0.000
S-K	0.00000	0.965	1.192	0.995	0.004	0.000	S O3	0.000
Cl-K	0.00070	1.009	1.125	0.990	0.07	0.08	ClO	0.11
K-K	0.00000	1.004	1.049	0.970	0.0021	0.000	K2O	0.000
Ca-K	0.10086	0.979	1.028	0.977	7.84	9.93	CaO	13.90
Ti-K	0.00000	1.075	1.031	0.949	0.0052	0.000	TiO2	0.000
Cr-K	0.07439	1.079	1.013	0.906	4.47	7.37	Cr2O3	10.77
Fe-K	0.46173	1.080	1.010	1.000	28.49	50.38	Fe2O3	72.03
Ba-L	0.00000	1.312	0.980	0.953	0.0025	0.000	BaO	0.000
S-K	---	0.914	2.074	0.998	58.52	29.64 S	---	---
Total						97.93 %		97.93 %

Na-- 0.0001 Mg-- 0.0001 Al-- 0.0192 Si-- 0.1441  
 P-- 0.0000 S-- 0.0000 Cl-- 0.0192 K-- 0.0000  
 Ca-- 2.1428 Ti-- 0.0000 Cr-- 1.2234 Fe-- 7.7903  
 Ba-- 0.00003 O-- 16.0000

Label: 6679b.F6.Si25.X51.Y153

kV: 15.0 Current: 0.0000nA Take\_off: 40.2 Live Time: 25

Stage: X=16.9344 Y=-30.2348 Z=32.1609 R=-0.00 B=0.02 T=-0.00

Beam: X=0.000uM(1552) Y=0.000uM(272)

Refit \_ P-K \_ S-K \_ Cl-K \_ K-K \_ Ti-K \_ Ba-L

Chi-sqd = 12.72

Analysis With Standards

Element	k-ratio	Net Counts	
Na-K	0.00164 +/- 0.00043	118 +/-	31
Mg-K	0.00058 +/- 0.00042	45 +/-	32
Al-K	0.00181 +/- 0.00049	138 +/-	37
Si-K	0.00390 +/- 0.00057	281 +/-	41
P-K	0.000001 +/- 0.00001	0 +/-	0
S-K	0.000001 +/- 0.00001	0 +/-	0
Cl-K	0.000001 +/- 0.00001	0 +/-	0
K-K	0.000001 +/- 0.00001	0 +/-	0
Ca-K	0.14266 +/- 0.00229	5047 +/-	81
Ti-K	0.000001 +/- 0.00001	0 +/-	0
Cr-K	0.02681 +/- 0.00257	402 +/-	39
Fe-K	0.58762 +/- 0.00837	8092 +/-	115
Ba-L	0.000001 +/- 0.00001	0 +/-	0

ZAF Correction 15.00 kV 40.23 deg.

No. of iterations = 3

Element	k-ratio	Z	A	F	Atom %	Wt %	Formula	Compound%
Na-K	0.00164	0.980	3.126	1.000	0.57	0.50	Na2O	0.68
Mg-K	0.00058	0.956	2.242	1.000	0.13	0.13	MgO	0.21
Al-K	0.00181	0.986	1.767	0.999	0.30	0.31	Al2O3	0.60
Si-K	0.00390	0.958	1.477	0.999	0.51	0.55	SiO2	1.18
P-K	0.00000	0.991	1.305	0.997	0.009	0.000	P2O5	0.000
S-K	0.00000	0.967	1.193	0.994	0.0047	0.000	S O3	0.000
Cl-K	0.00000	1.011	1.125	0.990	0.0025	0.000	ClO	0.000
K-K	0.00000	1.006	1.049	0.968	0.0021	0.000	K2O	0.000
Ca-K	0.14267	0.982	1.029	0.979	9.20	14.10	CaO	19.73
Ti-K	0.00000	1.077	1.035	0.953	0.0063	0.000	TiO2	0.000
Cr-K	0.02681	1.081	1.015	0.894	1.32	2.63	Cr2O3	3.85
Fe-K	0.58762	1.083	1.006	1.000	29.94	64.02	Fe2O3	91.53
Ba-L	0.00000	1.314	0.984	0.954	0.0033	0.000	BaO	0.000
O-K	---	0.916	2.211	0.998	58.01	35.53	---	---
Total						117.77 %		117.77 %

Na--	0.1574	Mg--	0.0371	Al--	0.0841	Si--	0.1416
P--	0.0000	S--	0.0000	Cl--	0.0000	K--	0.0000
Ca--	2.5386	Ti--	0.0000	Cr--	0.3647	Fe--	8.2593
Ba--	0.00003	O--	16.0000				

**APPENDIX E**  
**ANALYSIS OF PO42 LIQUIDS**

Preliminary Analysis of P042 Sieve Tower Residue, 6-9-94  
Ted Aulich, 6-10-94

Analyses

- 1) Preliminary THF solubility analysis--50% THF solubles
- 2) Extraction with 0.1 M NaOH--42% base solubles  
Acidification of solubles--3% organic acids  
Possibility of chlorine in base extract?
- 3) TGA Results--32% moisture, 48% volatile matter, 5% fixed carbon, 15% ash

Interpretations

- 1) Comparison of TGA moisture (32%) with base extraction--42% minus 3% organic acids equals 39%; if we have some chlorine in the water, our water value is lower than 39%, which gets us closer to the TGA 32%.
- 2) If, based on TGA, we assume 8% CO<sub>2</sub> (from CaCO<sub>3</sub>--volatiles emitted starting at about 796°C), this equates to about 13% CaO; we have 15% ash based on TGA. Presence of CaCl<sub>2</sub>?
- 3) At temperatures below about 400°C, we are volatilizing individual compounds; at temperatures of about 300 to 600°C, we are decomposing material. The TGA shows that we probably have both volatilization and decomposition happening (volatiles coming off between 200 and 650°C), which means that some of the fixed carbon we see is probably generated during the TGA itself. This means that the 5% referred to as fixed carbon (material that is involatile up to 950°C in an inert atmosphere, but is combustible at 750°C) may be both process- and analysis-derived material.
- 4) If we subtract 8% CO<sub>2</sub>, we are left with 40% volatiles, which probably consist of partially reacted polymer material. Of this 40%, about 11-18% is THF-soluble material (depending on which moisture value--TGA or base extraction--we use).
- 5) The fact that we have very little material volatilizing between 100°C and about 250°C indicates the presence of very little oil in the sample. This supports the TGA moisture value as being representative of water, as opposed to a combination of water and organics that boil at about 100°C.

Preliminary Conclusions

- 1) The volatile organic portion (about 40%) of the sample is comprised primarily of partially reacted polymer material.
- 2) The sample contains about 3% organic acids.
- 3) The sample contains a small amount (probably less than 5%) of highly carbonized (coked) material.

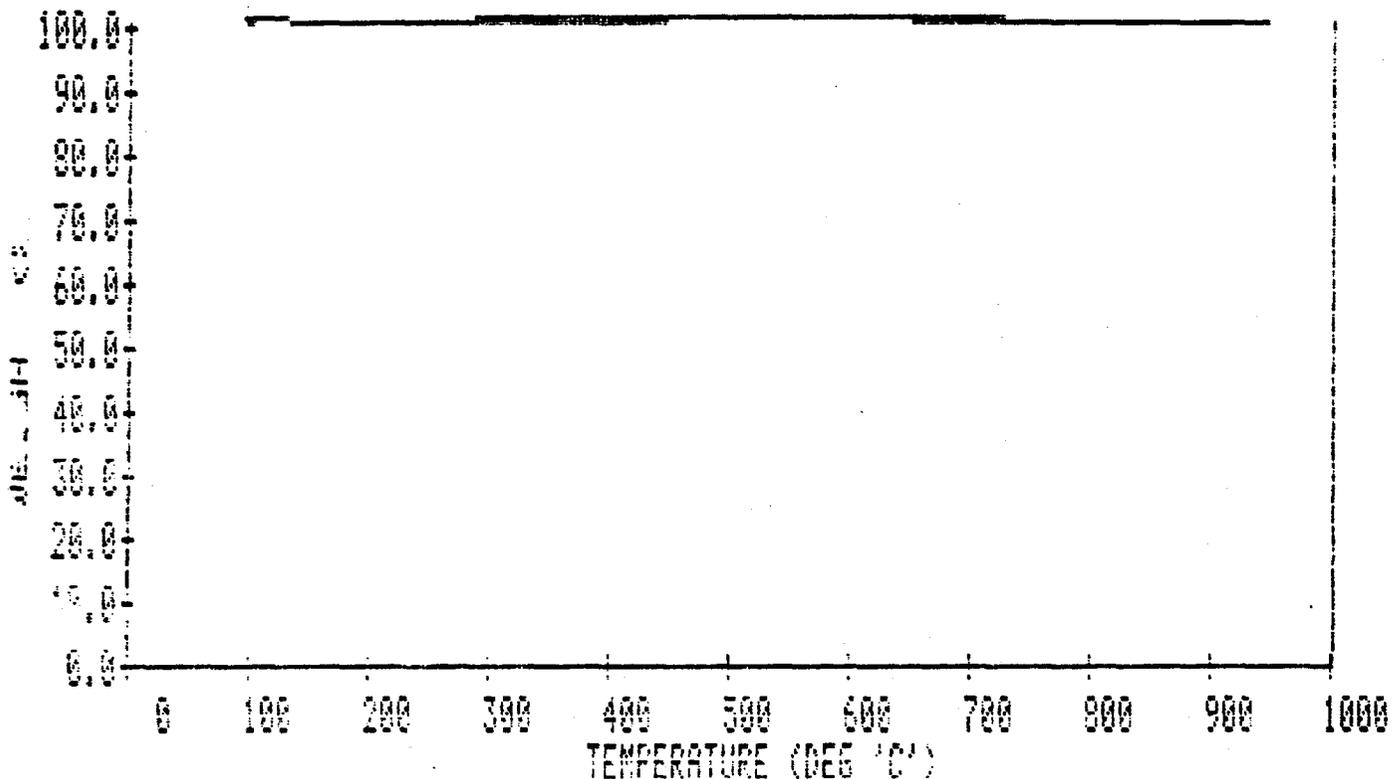
**APPENDIX F**  
**TGA GRAPHS OF PDU SOLIDS**

mac-401 emulation

date : May. 06, 1994

Elapsed Time : 04:48:00

P035 Bed Material



n. #1	Cr. #17	Type: bed mat.	9109	ID: 94-04630-01	Weight:	2.472	Gram(s)
n. #1	Cr. #18	Type: bed mat.	9109	ID: 94-04630-02	Weight:	2.512	Gram(s)
n. #1	Cr. #19	Type: bed mat.	9109	ID: 94-04630-03	Weight:	2.252	Gram(s)

title : mac-401 emulation      Zero Dev : 10      Max Dev : 5

Step	Cvr	Ramp Rate	Final Temp.	Mode/ATM	Step End Mode.	Timeout or % Deviation
1st	--	99 D/M	106 °C	B/N2	Timeout	90 Min.
2nd	ON	99 D/M	950 °C	B/N2	Timeout	7 Min.
3rd	OFF	99 D/M	950 °C	B/O2	Const Wgt	0.05 %

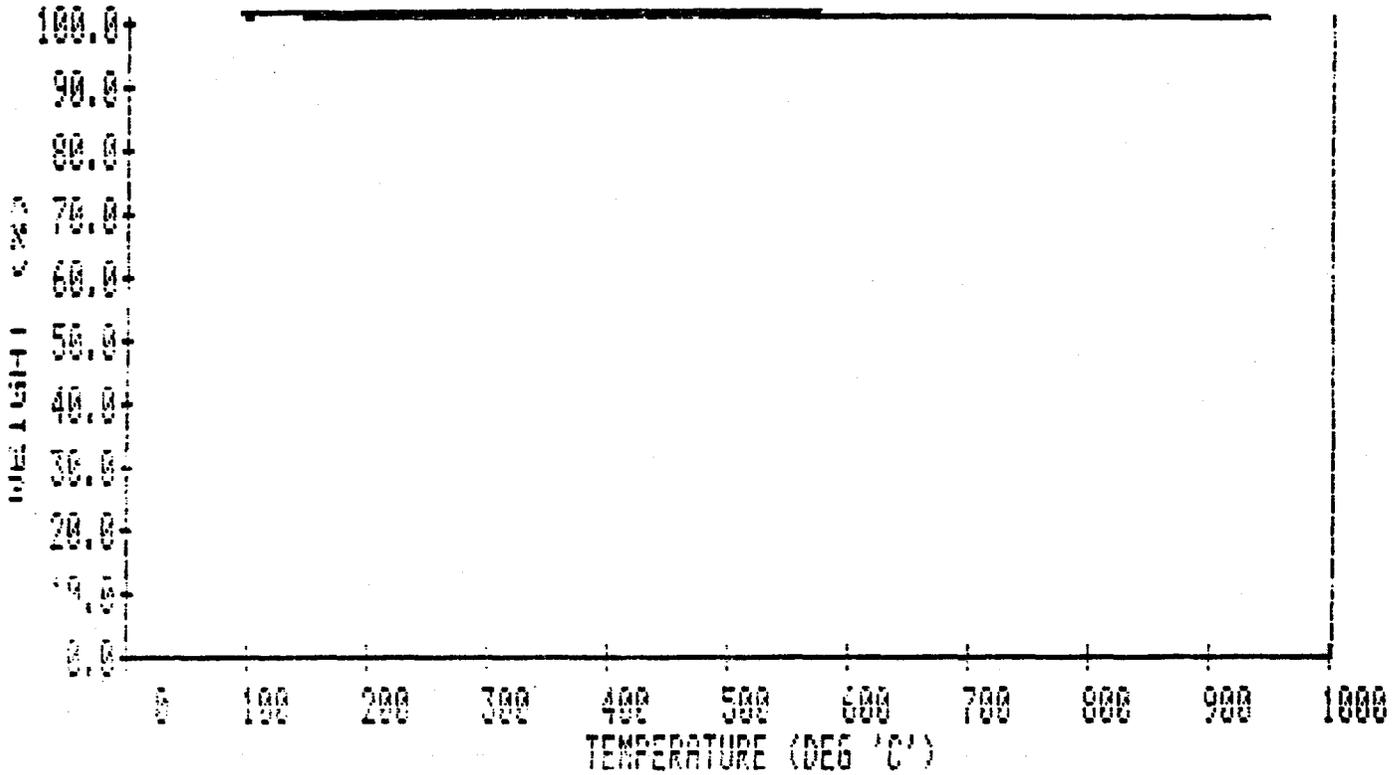
\* VOLATILE calibration used in calculations.

mac-401 emulation

at: May. 06, 1994

Elapsed Time : 04:27:00

P035 Secondary Cyclone



rn.#2 Cr.# 4 Type:sec.cyclone 9110 ID:94-04640-01 Weight: 2.546 Gram(s)  
 rn.#2 Cr.# 5 Type:sec.cyclone 9110 ID:94-04640-02 Weight: 2.472 Gram(s)  
 rn.#2 Cr.# 6 Type:sec.cyclone 9110 ID:94-04640-03 Weight: 2.204 Gram(s)

file : mac-401 emulation Zero Dev : 10 Max Dev : 5

Code	Cvr	Ramp Rate	Final Temp.	Mode/ATM	Step End Mode.	Timeout or % Deviation
1st	--	99 D/M	106 °C	B/N2	Timeout	90 Min.
2nd	ON	99 D/M	950 °C	B/N2	Timeout	7 Min.
3rd	OFF	99 D/M	950 °C	B/O2	Cnst Wgt	0.05 %

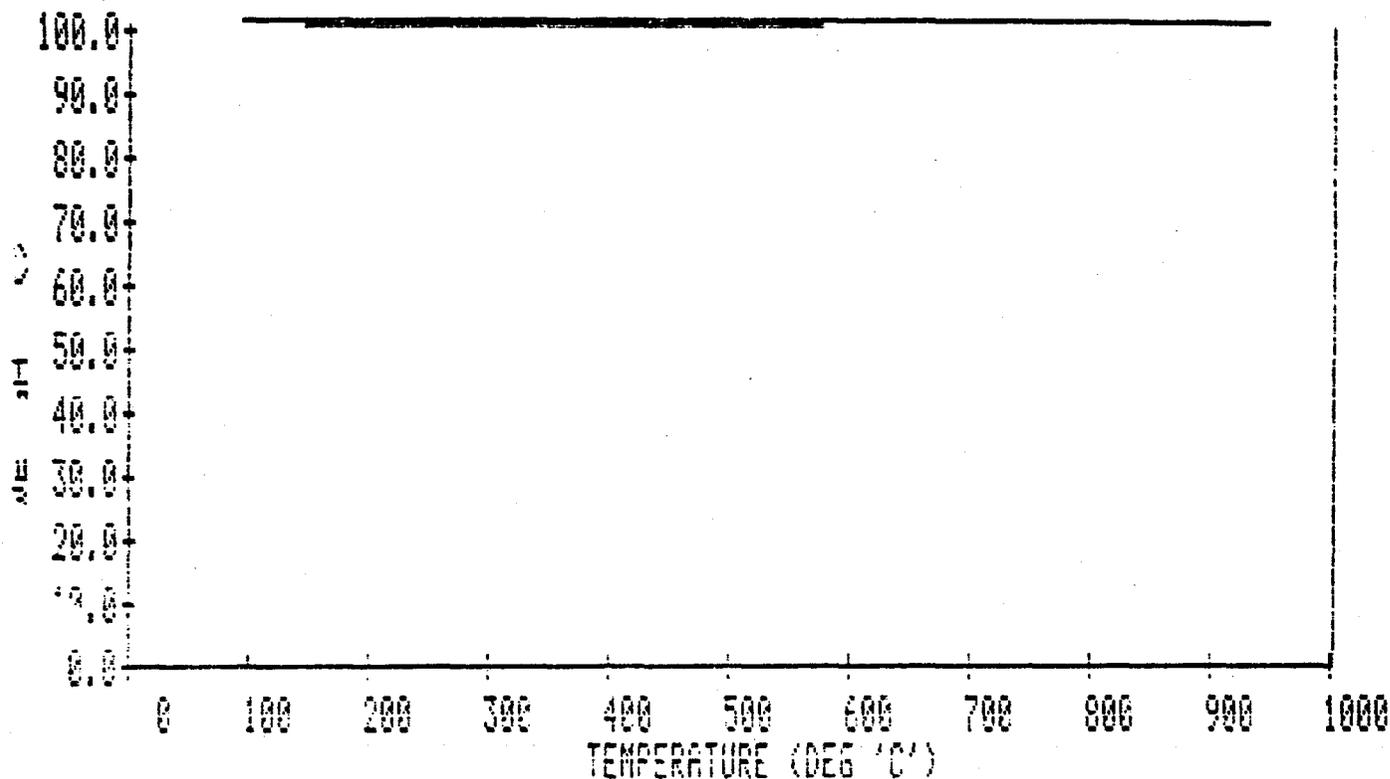
\* VOLATILE calibration used in calculations.

mac-401 emulation

Mon, May 06, 1994

Elapsed Time : 04:27:00

P036 Bed Material



n.#2 Cr.# 8 Type:bed mat. 9111 ID:94-04650-01 Weight: 2.355 Gram(s)  
 n.#2 Cr.# 9 Type:bed mat. 9111 ID:94-04650-02 Weight: 2.029 Gram(s)  
 n.#2 Cr.#10 Type:bed mat. 9111 ID:94-04650-03 Weight: 2.283 Gram(s)

file : mac-401 emulation Zero Dev : 10 Max Dev : E

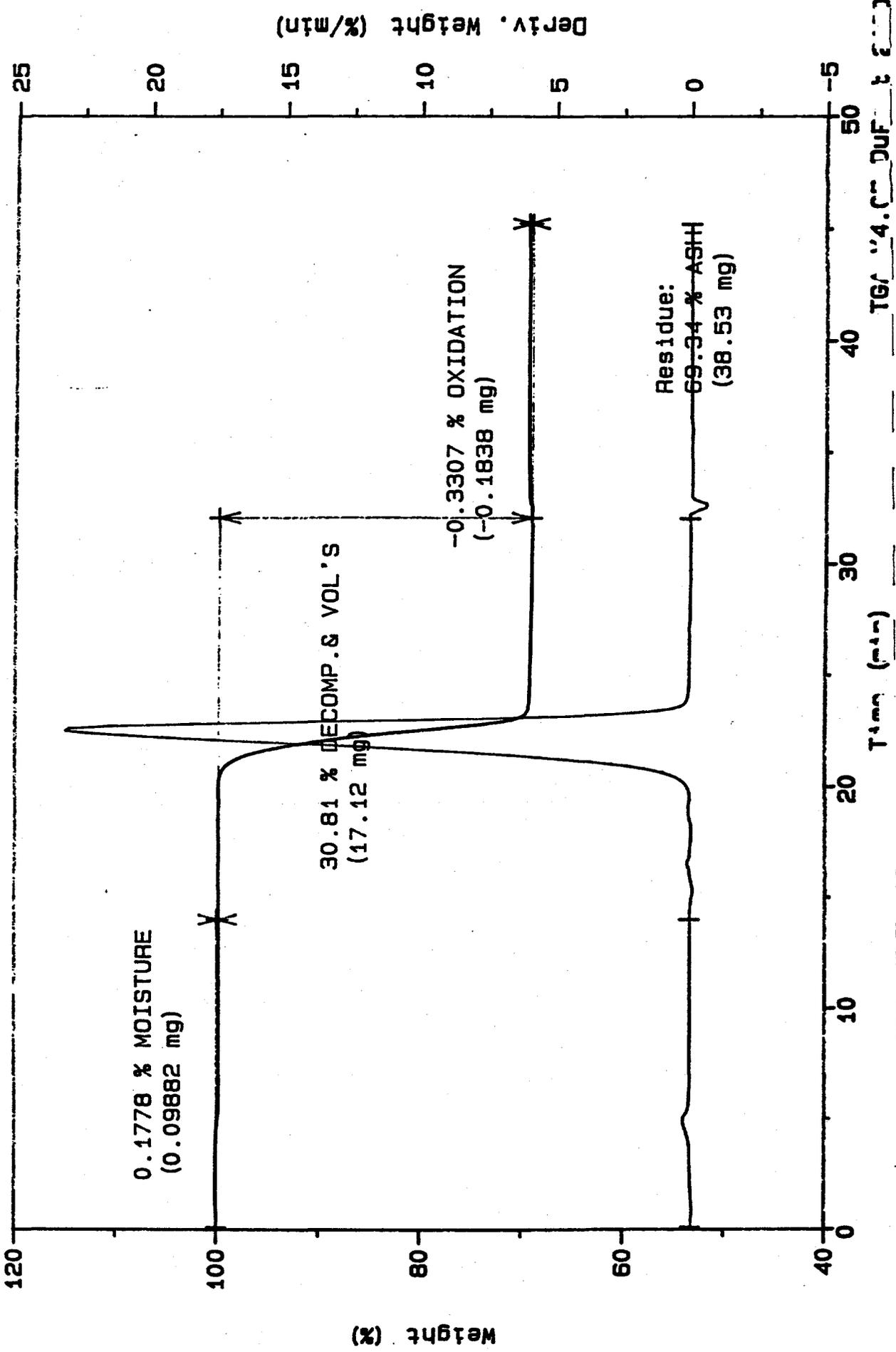
Code	Cvr	Ramp Rate	Final Temp.	Mode/ATM	Step End Mode.	Timeout or % Deviation
1st	--	99 D/M	106 °C	B/N2	Timeout	90 Min.
2nd	ON	99 D/M	950 °C	B/N2	Timeout	7 Min.
3rd	OFF	99 D/M	950 °C	B/O2	Cnst Wgt	0.05 %

\* VOLATILE calibration used in calculations.

Sample: P039: B.M. AGGLOM. ABOVE TC#305  
 Size: 55.5683 mg  
 Method: PROX  
 Comment: PROX. UPON AGGLOM. OF P039'X BED MATER. ABOVE TC305; 4717; 940104

# TGA

File: A:940104.001  
 Operator: KULAS  
 Run Date: 14-Apr-94 00:06



Sample: P039: B.M. AGGLOM.DIST.PLATE

Size: 48.5898 mg

Method: PROX

Comment: PROX.UPON AGGLOM.ON DISTRIBUTOR PLATE

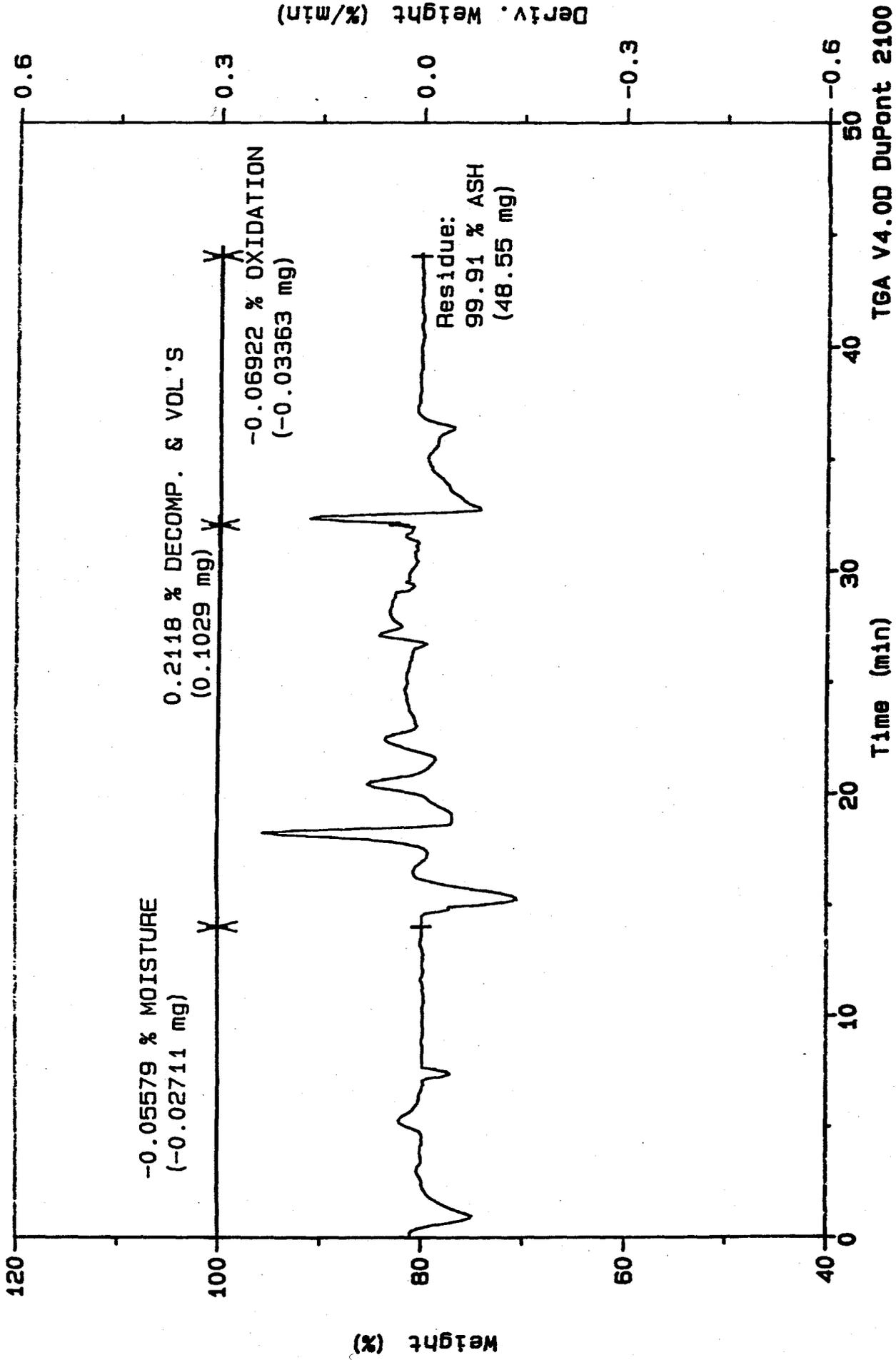
TGA

File: A: 940105.001

Operator: KULAS

Run Date: 14-Apr-94 02:09

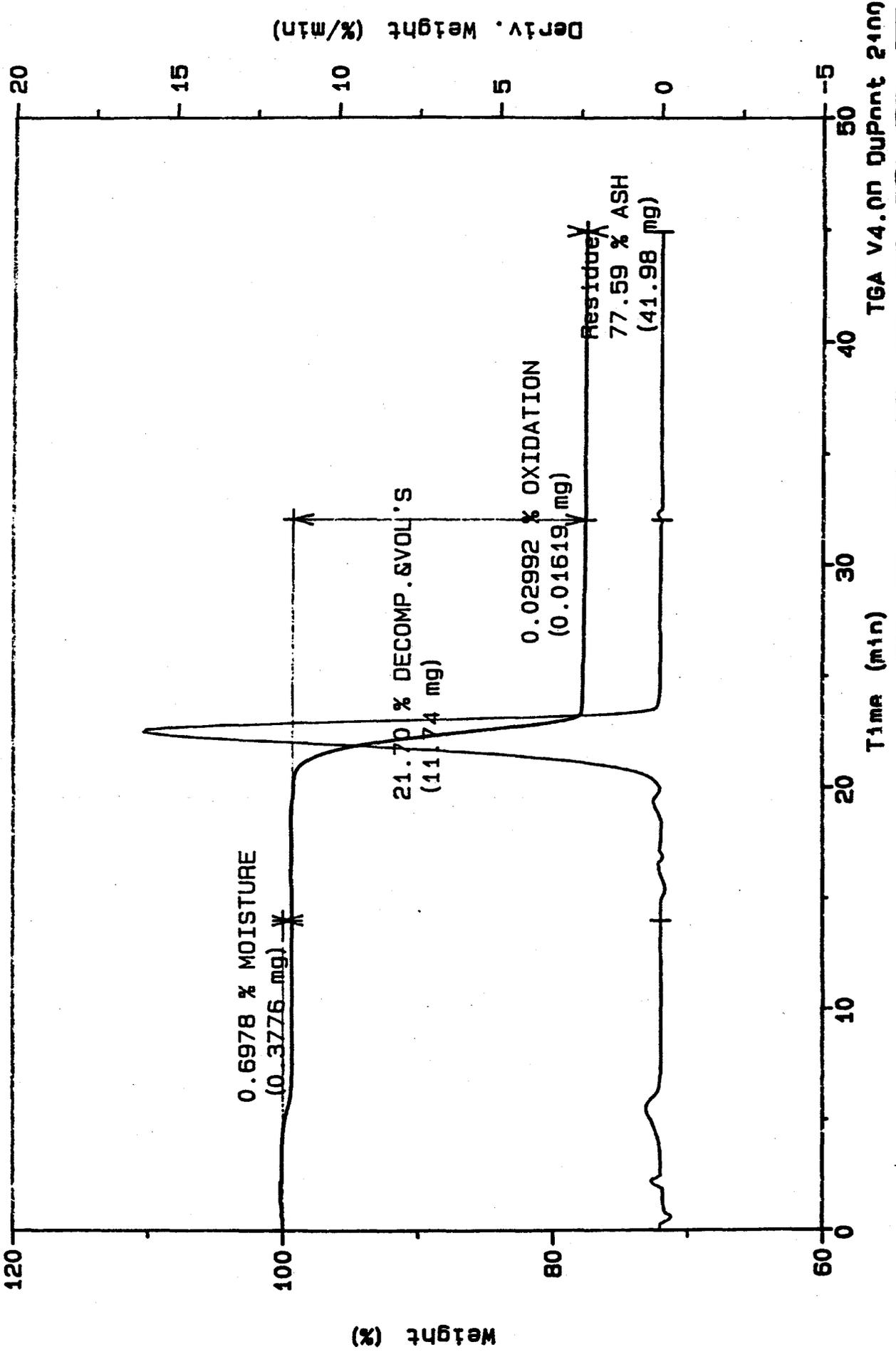
A#4717: 940105



Sample: P039: B.M. AGGLOM. AT TC305  
Size: 54.1099 mg  
Method: PROX  
Comment: PROX. UPON AGGLOM. AT TC305

# TGA

File: A: 940106.001  
Operator: KULAS  
Run Date: 14-Apr-94 03:22  
A#4717: 940106



Weight (%)

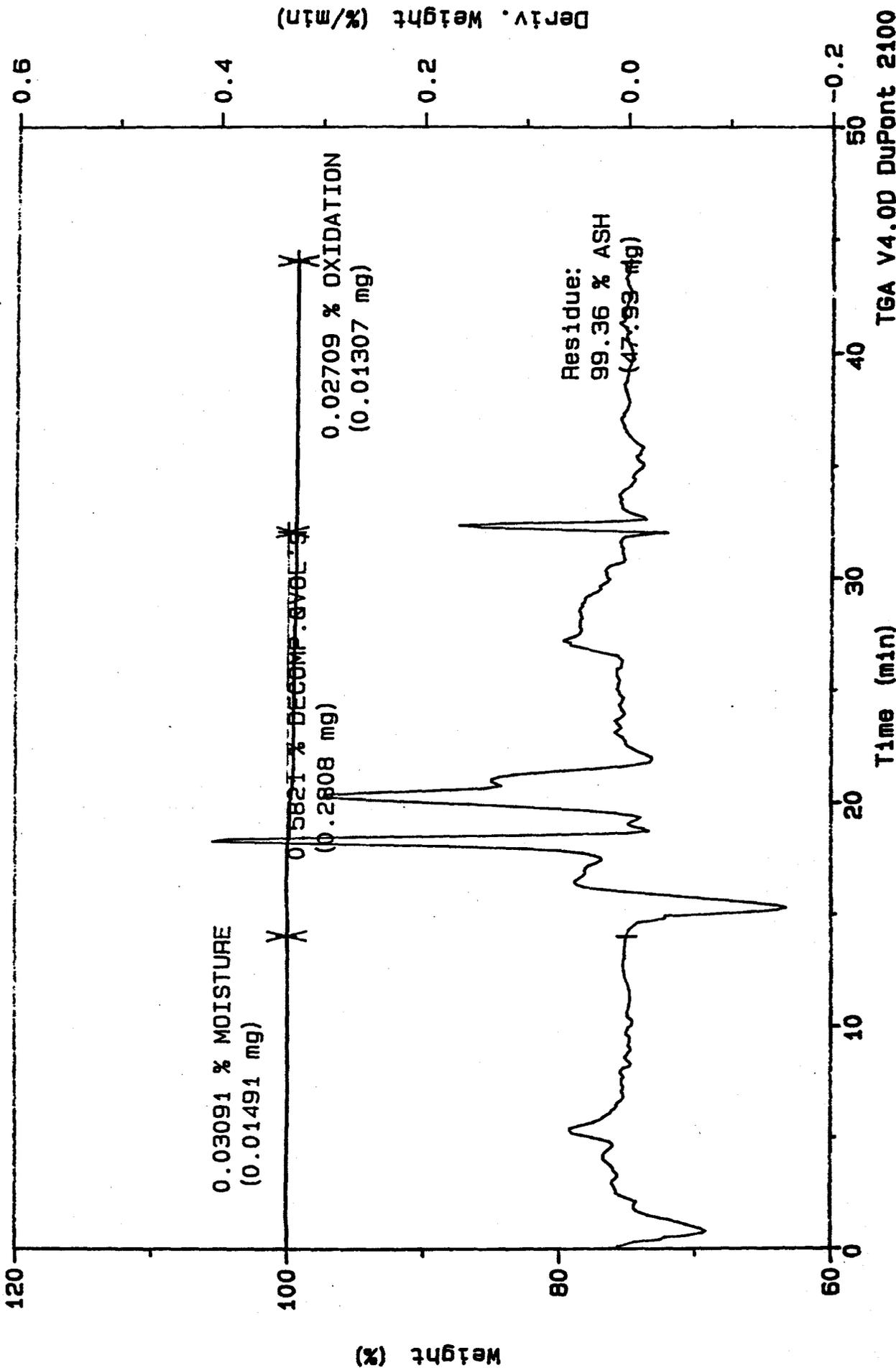
107

Time (min)

TGA V4.00 DuPont 2100

Sample: P039: B.M. AGG.AR TC304: POST-RUN TGA  
 Size: 48.2420 mg  
 Method: PROX  
 Comment: PROX.UPON AGGLOM.AT TC304

File: A:940107.001  
 Operator: KULAS  
 Run Date: 14-Apr-94 20:53  
 A#4717: 940109



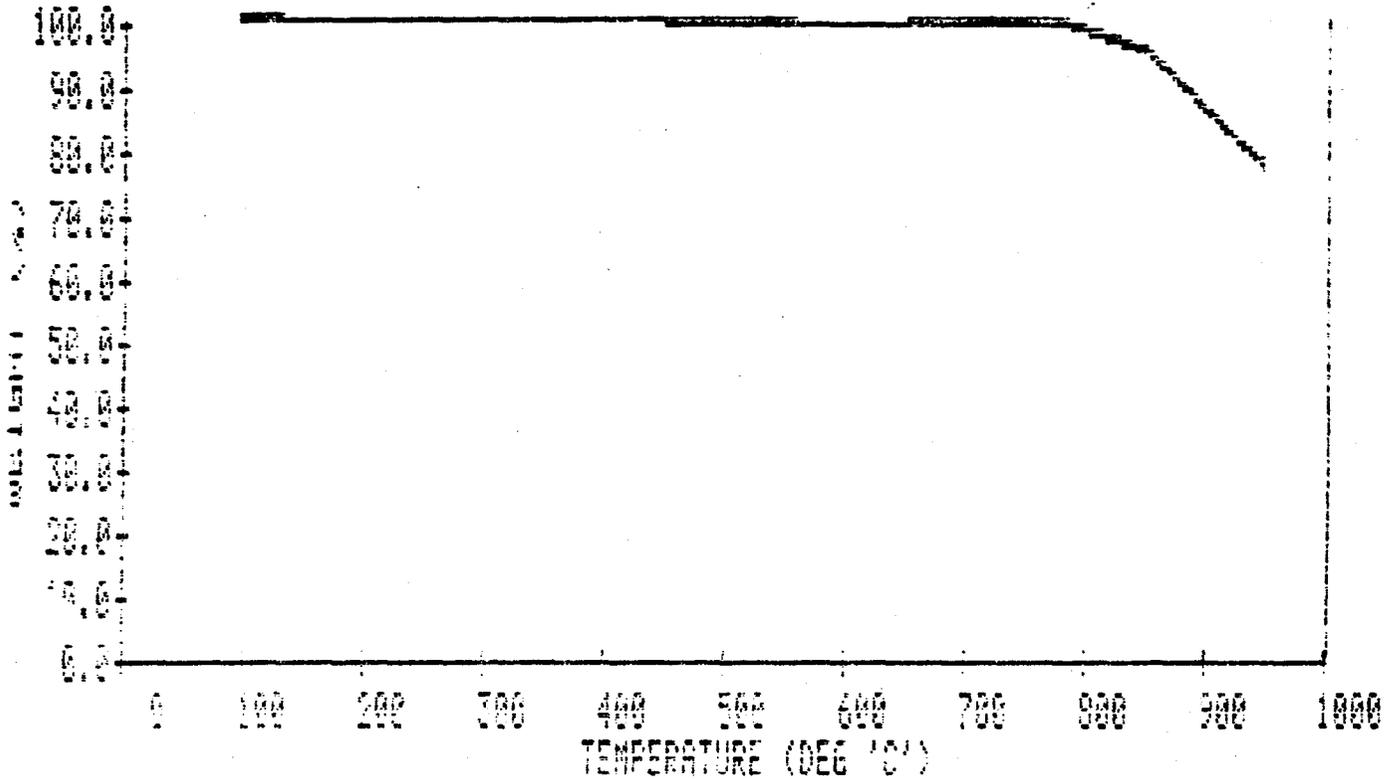
801

mac-401 emulation

Date : May. 06. 1994

Elapsed Time : 04:43:00

P039 Secondary Cyclone



n. #1 Cr. # 6 Type:sec.cyclone 9106 ID:94-04600-01 Weight: 1.008 Gram(s)  
 n. #1 Cr. # 9 Type:sec.cyclone 9106 ID:94-04600-02 Weight: 1.077 Gram(s)  
 n. #1 Cr. #10 Type:sec.cyclone 9106 ID:94-04600-03 Weight: 1.056 Gram(s)

mac-401 emulation Zero Dev : 10 Max Dev : 5

Step	Ctrl	Ramp Rate	Final Temp.	Mode/ATM	Step End Mode.	Timeout or % Deviation
01	--	99 D/M	106 °C	B/NE	Timeout	90 Min.
02	OK	99 D/M	950 °C	B/NE	Timeout	7 Min.
03	OFF	99 D/M	950 °C	B/OE	Const Wgt	0.05 %

\* VOLATILE calibration used in calculations.

Sample: P043- BED MATERIAL - POST RUN

Size: 82.6532 mg

Method: PROX

Comment: PROXIMATE ANALYSIS SHARP'S P043 BED MATERIAL;

File: A: 940274.001

Operator: KULAS

Run Date: 10-Jun-94 04: 13

POST RUN; A#4717

# TGA

