

## Precipitate Hydrolysis Experimental Facility(PHEF) Run 66 And 67 Final Report

by

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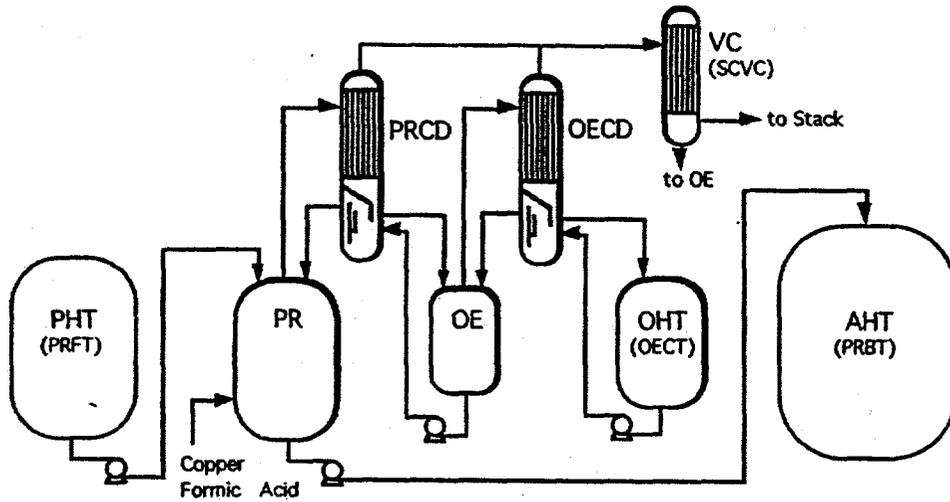
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**PRECIPITATE HYDROLYSIS EXPERIMENTAL FACILITY (PHEF)  
RUN 66 and 67 FINAL REPORT (U)**



**H. B. SHAH  
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Keywords: PHEF, DWPF, SPC, Late Wash,  
Low Nitrite, High Boilers,  
Decanters

Retention Period: Permanent

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RUN 66 AND 67 FINAL REPORT (U)**

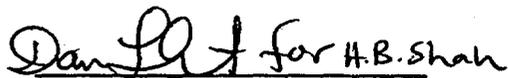
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Publication Date: October 31, 1996

  
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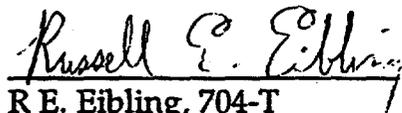
  
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## TABLE OF CONTENTS

Table Of Contents.....	iii
List Of Figures.....	iv
List Of Tables.....	iv
1. Executive Summary.....	1
2. Run Details.....	3
2.1 Pre-Run Preparation	
2.2 Precipitate Hold Tank Ultrasonic Inspection	
2.3 Precipitate Slurry Feed Composition	
2.4 Pre Reaction Heel Composition	
3. Precipitate Slurry Feeding.....	9
3.1 Run 66 Slurry Feeding	
3.2 Run 67 Slurry Feeding	
4. Hold, Heat Up and Aqueous Boil.....	11
5. OE Cycle.....	11
5.1 Run 66 OE Cycle	
5.2 Run 67 OE Cycle	
6. Preliminary Results.....	15
6.1 Run 66 Reaction Kinetics	
6.2 Run 67 Reaction Kinetics	
6.3 High Boiling Organics in Aqueous Product/Aromatic Carbon Removal	
7. Benzene Production.....	19
7.1 Run 66 Benzene Production	
7.2 Run 67 Benzene Production	
8. Temperature Control.....	19
8.1 Run 66 Temperature Control	
8.2 Run 67 Temperature Control	
9. Cooling Coil Fouling Estimates.....	20
10. Run 66 Benzene In PHA.....	21
11. References.....	22

## LIST OF FIGURES

Figure 3.1	Run 66 Feed Flow and Integrated Feed Flow vs Time	10
Figure 3.2	Run 67 Feed Flow and Integrated Feed Flow vs Time	10
Figure 3.3	Run 67 Reactor Pressure and Temperature During Feeding vs Time	11
Figure 5.2.1	Diphenylamine, Biphenyl, and 2-Phenylphenol stripping during Run 67 OE Cycle Aqueous Boil	13
Figure 5.2.2	Phenol, O-Terphenyl and M-Terphenyl Stripping During Run 67 OE Cycle Aqueous Boil	14
Figure 5.2.3	Ln (DPA) vs Time during Run 67 OE cycle Aqueous Boil	14
Figure 5.2.4	Ln (BP) vs Time during Run 67 OE cycle Aqueous Boil	15
Figure 5.2.5	Ln (2-Phenylphenol) vs Time during Run 67 OE cycle Aqueous Boil	15
Figure 8.1	Run 66 Temperature Control during Feeding and Hold	19
Figure 8.2	Run 67 Temperature Control during Feeding and Hold	20
Figure 10.1	Run 66 Benzene Concentration during and after Cooldown	21
Figure 10.2	Run 67 Benzene Concentration during and after Cooldown	21

## LIST OF TABLES

Table 1.1	Run 66 Chronological Data	4
Table 1.2	Run 67 Chronological Data	5
Table 1.3	Run 66/67 Process Parameters	5
Table 2.3.1	Run 66 PHT Pre-feed Composition	6
Table 2.3.2	Run 66 PHT Post Feed Composition	7
Table 2.4.1	Run 66 PR Pre-Reaction heel Composition	8
Table 2.4.2	Run 67 PR Pre-Reaction heel Composition	9
Table 5.1	Run 66 OE Cycle Mass Balance (18 minutes into Aqueous Boil)	11
Table 6.1	Run 66 Phenylboronic Acid Concentration during Feeding and Hold	16
Table 6.2	Run 67 Phenylboronic Acid Concentration during Feeding and Hold	16
Table 6.3.1	Run 66 and 67 High Boiling Organics in the PHA	16
Table 6.3.2	Run 66 Aqueous Product Composition	17
Table 6.3.3	Run 67 Aqueous Product Composition	18

## 1. EXECUTIVE SUMMARY

DATE OF RUN 66: 10/08/93 - 10/09/93 (PR Cycle)  
10/19/93 - 10/29/92 (OE Cycle)

DATE OF RUN 67: 11/04/93 - 11/05/93 (PR Cycle)  
11/17/93 - 11/18/93 (OE Cycle)

During the period from late June to early September of this year, approximately 1600 gallons of precipitate feed stored in the Precipitate Hold Tank (PHT) at PHEF decomposed [1]. This decomposition took place during a two month storage period of the Tetraphenyl borate (TPB) precipitate under a CO<sub>2</sub> blanket. The visual inspection of the tank revealed that a very small amount of TPB solids were left and that there were approximately 100 to 110 gals of benzene/high boilers present in the tank. The resultant decomposition products in the PHT consist of an organic and aqueous phase containing a small quantity of unreacted solids. A path forward was developed to understand TPB decomposition and to determine if the material remaining in the PHT could be processed without adverse effects to the process or equipment [1]. A small scale hydrolysis run with the remaining PHT material was made by Process Technology Development Group of DWPT at TNX.

It was determined from small scale runs and an extensive analyses of the PHT material that the decomposed material was safe to run at PHEF without adversely affecting the process or equipment. The PHT volume was 1592 gallons at the time of decomposition. Two runs (66 and 67) were performed to process the decomposed feed. The main objective of these runs was to process the decomposed precipitate from the PHT. In both the runs copper nitrate was used as the catalyst. Because of the decomposition, the effectiveness of the copper nitrate in catalyzing the destruction of TPB could not be completed.

The significant findings of Run 66 are:

- (1) After 5 hours of aqueous boil, the aqueous product had a Diphenylamine (DPA) concentration of 31 mg/L and the Biphenyl concentration of 8 mg/L. At these concentrations, the high boiling organic mass in the aqueous product included 0.28 lbs of Diphenylamine and 0.07 lbs of Biphenyl.
- (2) Benzene production was 62.1 gallons, with an aromatic removal ratio of 96.26% as measured by liquid chromatography analysis.
- (3) The calculated reactor cooling coil heat transfer coefficient during cooldown was 244 (design basis = 80) PCU/ft<sup>2</sup>/hr/°C @ 55°C. It took 90 minutes to cooldown the reactor contents at cooling water flowrate of 20 gpm and 168 RPM agitator speed. This suggested that minimal high boilers deposition had occurred with the processing of decomposed feed.
- (4) Phenylboronic Acid concentration dropped below 53 mg/L in less than 180 minutes. As such very little PBA was produced because of the decomposed feed.

The Organic Evaporator (OE) cycle was completed in two attempts. In the first attempt, the OE run was interrupted due to a high Evaporator Condenser Decanter (ECD) vapor temperature interlock, approximately 18 minutes into the aqueous boil (AB). The cause of this interlock was determined to be fouling of the ECD tubes by high boiling organics. Several process changes were implemented in an attempt to defoul the condenser tubes. The changes were mainly targeted at running the condenser hot. The increase in CW supply temperature and reduction in CW flow helped to run the condenser hot, to increase the heat transfer efficiency and to melt the high boiling organics from the condenser tubes.

The significant findings of Run 67 are:

- (1) After 5 hours of aqueous boil, the aqueous product had a Diphenylamine (DPA) concentration of 22 mg/L and the Biphenyl concentration of 5 mg/L. At these concentrations, the high boiling organic mass in the aqueous product included 0.18 lbs of Diphenylamine and 0.04 lbs of Biphenyl.
- (2) Benzene production was 30 gallons, with an aromatic removal ratio of 95.75% as measured by liquid chromatography analysis.
- (3) The calculated reactor cooling coil heat transfer coefficient during cooldown was 254 (design basis = 80 ) PCU/ft<sup>2</sup>/hr/°C @ 55°C. It took 92 minutes to cooldown the reactor contents. This suggested that minimal high boiler deposition had occurred during the processing of decomposed feed.
- (4) There was no PBA left in the reactor at the end of the feeding. Therefore, no destruction of PBA took place during the hold cycle.

Run 66 and 67 Run Objectives:

The primary objective of Runs 66 and 67 was to process the decomposed precipitate from the PHT. Baseline data on reaction kinetics, high boiling organics production, benzene generation, copper profile, and offgas generation was collected and analyzed. The run objective parameters are listed in Table 1.3.

A secondary objective of Runs 66 and 67 was to demonstrate Cupric Nitrate as a catalyst in lieu of copper formate. Both runs were made using the old decanter.

## 2. RUN DETAILS

Run 66 and 67 chronological data are listed in Table 1.1 and 1.2.

### 2.1 Pre-Run Preparation

The Reactor Condenser/Decanter (RCD) was not inventoried with "fresh" organic vapor from the Run-65 OE cycle. The RCD is not inventoried in the last couple of runs to see the accumulation of high boilers over the runs and to assess the performance of the old decanter. Run 65 OE water (84 gals) was transferred to the PR via RCD as the PR heel make up volume. No additional Biphenyl was added to the feed.

### 2.2 Precipitate Hold Tank Ultrasonic Inspection

Because of the precipitate decomposition in the tank and the carbon steel TPB storage drum failure in the past, concerns arose over storage of hydrolyzed precipitate in the carbon steel PHT. The nitrite and pH were insufficient to inhibit pitting of carbon steel. The materials committee recommended performing an Ultrasonic Thickness Examination. The Site Services Quality (SSQ) group performed the UT on portions on the bottom of the tank and on areas on the sides of the tank where the liquid level had been maintained. The nominal thickness of the tank is 0.25". The thickness measurements ranged from 0.25 to 0.278". The examination revealed no indications of erosion or corrosion. However, the materials committee recommended processing the precipitate as soon as possible because of the uninhibited conditions in the tank.

### 2.3 Runs 66 And 67 Simulated Precipitate Slurry Feed Composition

The Run 66 and 67 simulated precipitate slurry had a nitrite concentration of 0.0082 and 0.01 M respectively. The TPB concentration was 0.11 wt% (specified was 7.7 wt%) for both the runs. Because of feed (precipitate) decomposition, very small amounts of TPB solids were left and there were approximately 100 to 110 gallons of benzene/high boilers present in the tank. Most of the TPB solids were hydrolyzed to form benzene and high boilers [1]. The PHT and PHA product were both higher in Phenol due to the uncontrolled, slow hydrolysis of the TPB.

The sample analyses for the PHT prior to feeding are listed in Table 2.3.1. The sample analyses for the PHT after feeding are listed in Table 2.3.2. The Run 66 after feed PHT analysis was used for the Run 67 heel and feed preparation. No material was left in the PHT after Run 67 for analysis.

Runs 66 and 67 were the two runs completed with a decomposed late washing precipitate slurry. Antifoam (Surfynol® 420) was added to the PHT prior to the transfer from the W-1 to minimize foaming in the PHT. Since the Run 65 PHT heel contained Surfynol 104E, the surfactant for this batch was a mixture of Surfynol® 420 and 104E.

**TABLE 1.1**  
**RUN 66 CHRONOLOGICAL DATA**

Description	Time(approximate)		Comments
	Start	Stop	
<b>PHT Additions</b>			
W-1 Transfer I	5/28/93		581 gallons added
Surfynol® to PHT	5/28		29 lbs added
W-1 Transfer II	6/4		449 gals added
W-1 Transfer III	6/9		356 gals added
PHT sample			On 6/9,9/7,&9/8
PHT grab sample	9/10		Aqu and org phase
NANO <sub>2</sub> to PHT	10/05		7.42 lbs added
Sodium Titanate to PHT	10/05		150 lbs added
PHT Sample	10/05		Final PHT Sample
<b>PR Additions</b>			
VV system vacuum test	10/04/93		vacuum test
OE water To the PR	10/06		84 gals
Copper addition	10/07		32 lbs added
Formic addition	10/07		225 lbs added
Water addition	10/07		100 gallons added
Sample Pulled	10/07		
Heatup to feed	10/08 0944	10/07 11.00	
Feeding	10/08 1124	10/08 1328	Fed 810 gallons
Five hour hold	10/08 1328	10/08 1848	
Heatup to Aqueous Boil	10/08 1849	10/08 1944	
Aqueous boil	10/08 1945	10/09 0045	AB completed
Cooldown	10/09 0046	10/09 0216	Cooldown completed
<b>First OE Cycle</b>			
Organic Boil in OE	10/19	10/19	OB Complete
Heatup/Aqueous Boil	10/19	10/19	
Aqueous Boil	10/19	10/19	Steam to OE cutoff
Cooldown	10/19	10/19 1100	Cooldown completed
<b>OE Cleaning</b>			
OHT organics to OE	10/22	10/22	47 gals transferred
OE agitation	10/22	10/24	Agitated OE
<b>Second OE Cycle</b>			
Heat up to AB	10/27	10/27	Clean the decanter and the ECD tubes
Aqueous Boil (Steam Flow 60 pph)	10/27		51 min into AB, steam cut off due to HH ECD vapor temp.
Aqueous Boil (Steam Flow 10 pph)	10/27		Continue OE AB
Aqueous Boil (Steam Flow 100 pph)	10/27	10/28	Continue OE AB
OHT to OE Recirc.	10/28		
Aqueous Boil (Steam Flow 200 pph)	10/28	10/29	AB Completed
Cooldown	10/29		Cooldown Complete

**TABLE 1.2**  
**RUN 67 CHRONOLOGICAL DATA**

Description	Time(approximate)		Comments
	Start	Stop	
PHT Additions			
PHT Sample	10/09/93		PHT Sampled
PR Additions			
VV system vacuum test	10/04		Vacuum test
OE water to the PR			None, OE Pump Problem
Copper addition	11/02		32 lbs added
Formic addition	11/02		293 lbs added
Water addition	11/02		136 gallons added
Sample pulled	11/02		PR heel Sampled
Heatup to feed	11/04 0810	11/04 1115	
Feeding	11/04 1115	11/04 1745	Fed 780 gallons
Five hour hold	11/04 1745	11/04 2210	
Heatup to Aqueous Boil	11/04 2210	11/04 2350	
Aqueous boil	11/04 2350	11/05 0456	AB completed
Cooldown	11/05 0457	11/05 0627	Cooldown completed
OE Cycle			
Organic Boil in OE	11/17 0725	10/19	OB Complete
Heatup/Aqueous Boil	11/17	11/17 1045	
Aqueous Boil	11/17 1045	11/18 0745	1275 minutes AB
Cooldown	11/18 0745	11/18 0848	Cooldown completed

**Table 1.3**  
**Run 66 and 67 Parameters**

	Run 66	Run 67	Units
Feed adjustment			
sodium nitrite	0.01	0.008	M
sodium titanate	2000	2000	ppm
TPB	0.11	0.12	wt %
Pre-reaction heel adjustment			
Residual Aqueous Heel	0	0	gallons
Formic Acid	1.747	2.8	M
Process operating parameters			
Feed Temperature	90	90	°C
Hold Cycle Time	300	300	min
CO2 Purge			
During Feeding and Post Feed Purge	50	50	lbs/hr
Five Hour Hold	30	30	lbs/hr
Heat-up to Aqueous Boil	30	30	lbs/hr
Normal	10	10	lbs/hr
Post Feed Purge Time	0.25	0.25	hrs
Aqueous Boil Time	5	5	hrs

**Table 2.3.1**  
**Run 66 PHT Pre Feed Composition**  
**(Sample ID PH-66-001A)**

	Target	Actual
Volume Fed, gallons	800	756
Volume in PHT, gallons		906
Nitrite, M	0.01	0.0082(average)
TPB, wt%	8.4	0.11 (average)
Titanate, ppm	2000	1709

Component	Analytical	Units
Phenylboronic acid	3553	mg/L
Aniline	<1	mg/L
Phenol	2433	mg/L
Nitrobenzene	<1	mg/L
Nitrosobenzene	<1	mg/L
4-Phenylphenol	<1	mg/L
2-Phenylphenol	<1	mg/L
Diphenylamine	24	mg/L
Biphenyl	86	mg/L
o-Terphenyl	86	mg/L
m-Terphenyl	<1	mg/L
p-Terphenyl	<1	mg/L
Chloride	131	ppm
Fluoride	<61	ppm
Titanium (Ti)	141	ppm
Boron	4090	ppm
Iron (Fe)	0.012	wt %
Manganese (Mn)	0.005	wt %
Total wt% solids	7.58	wt %
Insoluble wt% solids	7.45	wt %
Tetraphenylborate (TPB)	0.11(a)	wt %
Tetraphenylborate (TPB)	0.11(b)	wt %
Total base to pH 5.5	0.56	moles/liter
Carbonate	0.215(avg)	moles/liter

**Table 2.3.2**  
**Run 66 PHT Post Feed Composition**  
**(Sample ID PH-66-141 A, B, C)**

Note: PHT post feed sample analysis was used for the Run 67 feed prep and reactor heel make up.

<u>COMPONENT</u>	<u>Analytical</u>	<u>Units</u>
Phenylboronic acid	3960	mg/L
Aniline	<1	mg/L
Phenol	3258	mg/L
Nitrobenzene	<1	mg/L
Nitrosobenzene	<1	mg/L
4-Phenylphenol	<1	mg/L
2-Phenylphenol	94	mg/L
Diphenylamine	108	mg/L
Biphenyl	326	mg/L
o-Terphenyl	6	mg/L
m-Terphenyl	<1	mg/L
p-Terphenyl	<1	mg/L
Titanium (Ti)	151	ppm
Nitrite	463	mg/L
Iron (Fe)	0.015	wt %
Manganese (Mn)	0.005	wt %
Total wt% solids	7.75	wt %
Soluble wt% solids	7.52	wt %
Insoluble wt% solids	0.23	wt %
Tetraphenylborate (TPB)	0.12	wt %

## 2.4 PRE-REACTION HEEL COMPOSITION

### 2.4.1 Run 66

The precipitate reactor heel preparation was within the limits specified. Copper catalyst (in the form of copper nitrate) was added to the heel to achieve a target concentration in the precipitate product of 950 ppm. Formic acid was added to the heel at a target concentration of 2.88 M (lab analysis was 2.95 M) to achieve a concentration in the precipitate product of 0.25 M. The formic acid was added to balance the base, nitrite, TPB, and add .25 M excess acid. A five gallon heel was added from the previous run. The OE water (84 gallons) was transferred to the PR via RCD to make up the heel volume. Process water was added to bring the final volume to 270 gallons. The sample analyses for the PR heel are listed in Table 2.4.1.

**Table 2.4.1**  
**Run 66 PRE-REACTION HEEL COMPOSITION**  
**(Sample # PH 66-004A)**

	Target	Actual
Volume of heel, Gallons	270	270
Formic acid, M	1.49 to 1.81	1.747 (Average)
Copper, ppm	2975	3037 (Average)
Component	Analytical	units
Phenylboronic acid	<1	mg/L
N-Phenylformamide	167	mg/L
Aniline	<1	mg/L
Phenol	1076	mg/L
Nitrobenzene	<1	mg/L
Nitrosobenzene	<1	mg/L
4-Phenylphenol	<1	mg/L
2-Phenylphenol	<1	mg/L
Diphenylamine	<1	mg/L
Biphenyl	39	mg/L
o-Terphenyl	<1	mg/L
m-Terphenyl	<1	mg/L
p-Terphenyl	<1	mg/L
Formate (COOH[1-])	84731	mg/L
Nitrite (NO <sub>2</sub> [1-])	<100	mg/L
Nitrate (NO <sub>3</sub> [1-])	8673	mg/L
Cesium (Cs)	34	ppm
Tot acid (eq pt)	2.80 to pH 7	m
Tot acid (eq pt)	2.80 to pH 7	m
Copper soluble (Cu)	4322	ppm
Boron (b)	323	ppm
Ammonium (NH <sub>4</sub> [1+])	<1	mg/L

### 2.4.2 Run 67

The precipitate reactor heel preparation was within the limits specified. Copper catalyst (in the form of copper nitrate) was added to the heel to achieve a target concentration in the precipitate product of 950 ppm.

Formic acid was added to the heel at a target concentration of 2.33 M (lab analysis was 2.59/2.69 M) to achieve a concentration in the precipitate product of 0.25 M. The formic acid was added to balance the base, nitrite, TPB, and add .25 M excess acid. A five gallon heel was added from the previous run. The OE water (71 gallons) of Run 66 OE cycle was not transferred to the PR via RCD to make up the heel volume because the OE pump had a mechanical problem. Process water was added to bring the final volume to 270 gallons. The sample analyses for the PR heel are listed in Table 2.4.2.

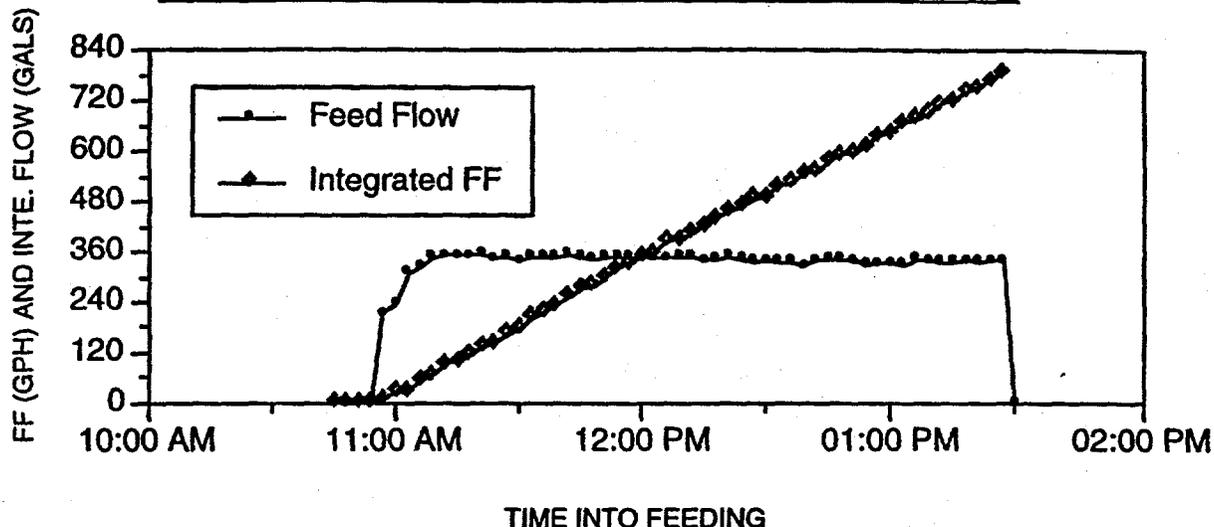
<u>Table 2.4.2</u>		
<u>Run 67 PRE-REACTION HEEL COMPOSITION</u>		
<u>(Sample # PH 67-002A)</u>		
	Target	Actual
Volume of heel, Gallons	270	270
Formic acid, M	2.54	2.8 (Average)
Copper, ppm	3920	3978
<u>Component</u>	<u>Analytical</u>	<u>units</u>
Phenylboronic acid	<1	mg/L
N-Phenylformamide	24	mg/L
Aniline	<1	mg/L
Phenol	860	mg/L
Nitrobenzene	<1	mg/L
Nitrosobenzene	<1	mg/L
4-Phenylphenol	<1	mg/L
2-Phenylphenol	<1	mg/L
Diphenylamine	17	mg/L
Biphenyl	5	mg/L
o-Terphenyl	<1	mg/L
m-Terphenyl	<1	mg/L
p-Terphenyl	<1	mg/L
Formate (COOH[1-])	98622	mg/L
Nitrite (NO2[1-])	<1000	mg/L
Nitrate (NO3[1-])	10851	mg/L
Cesium (Cs)	85	ppm
Tot acid (eq pt)	2.59 to pH 7	mole/liter
Copper soluble (Cu)	3978	ppm
Boron (B)	807	ppm
Ammonium (NH4[1+])	<1	mg/L

### 3. PRECIPITATE SLURRY FEEDING

#### 3.1 Run 66

Feeding was continuous except for two interruptions at the onset, which lasted less than a minute. A graph of feed rate and integrated feed flow vs time is shown in Figure 3.1.

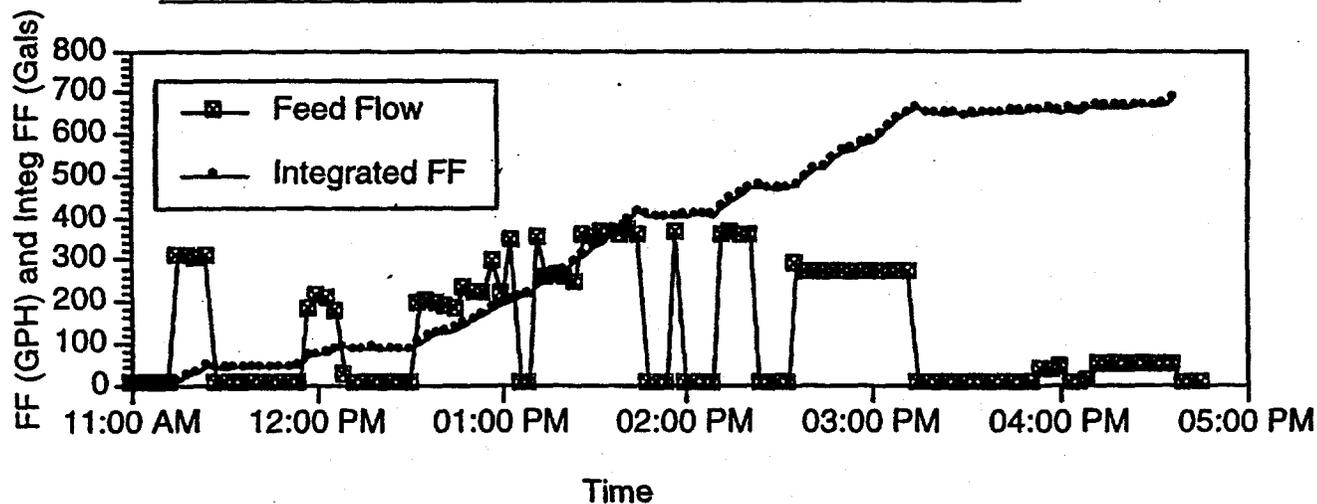
**Figure 3.1**  
**RUN 66 FEED RATE AND INTEGRATED FEED FLOW**



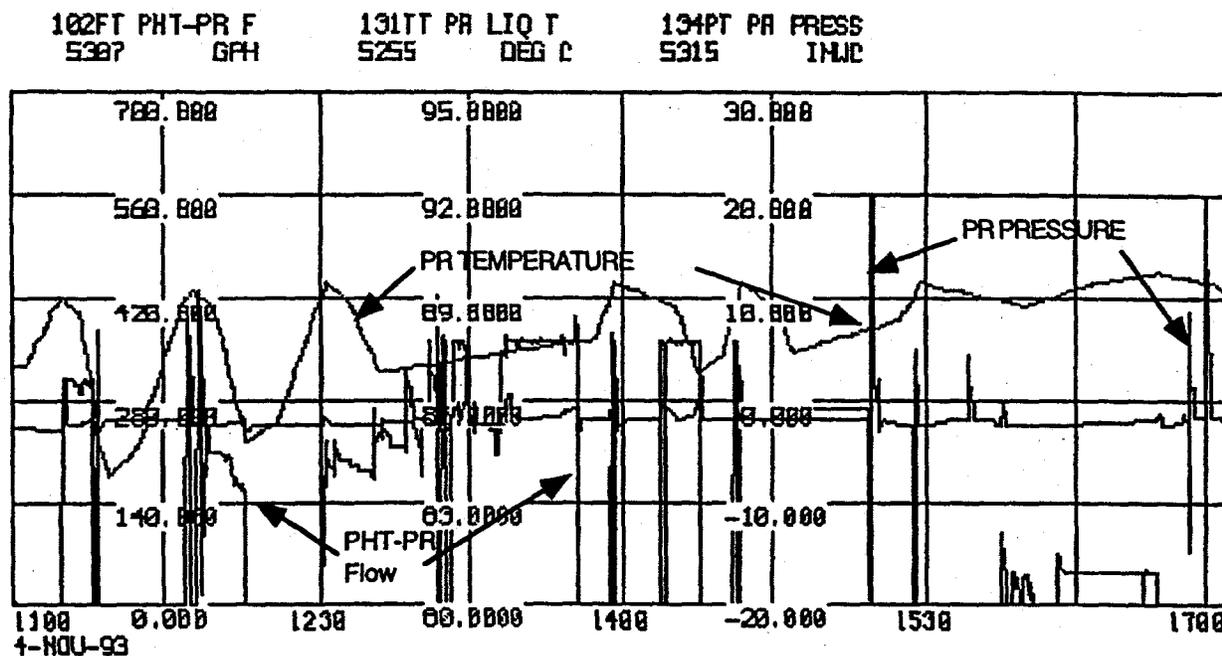
**3.2 Run 67**

The objective of this run is to empty out the PHT completely. Feeding was interrupted a number of times. The interruptions were mainly attributed to high pressure excursions in the reactor or because the reactor temperature dropped below 85°C. The pressure excursions were mainly due to flashing of the separate phase of benzene in the decomposed feed. The PHT was flushed with 30 to 40 gallons of water to clean the insides of the tank. A graph of feed rate and integrated feed flow vs time is summarized in Figure 3.2 and the graph of feed flow, PR Pressure and reactor temperature is summarized in figure 3.3.

**Figure 3.2**  
**RUN 67 FEED RATE AND INTEGRATED FEED FLOW**



**Figure 3.3**  
**REACTOR PRESSURE AND TEMPERATURE DURING FEEDING**



#### **4. RUNS 66 AND 67 FIVE HOUR HOLD, HEATUP, AND AQUEOUS BOILING**

The five hour hold, heat-up and aqueous boil periods all proceeded very smoothly. Temperature control was excellent. No interruptions were experienced during this period.

#### **5. ORGANIC EVAPORATOR CYCLE**

##### **5.1 Run 66**

The OE cycle was completed in two attempts. The first OE run was conducted on October 19 and was interrupted due to a high Evaporator Condenser Decanter (ECD) vapor temperature interlock, approximately 18 minutes into the aqueous boil (AB). The cause of this interlock was believed to be the ECD tubes fouling by high boiling organics. The fouling lowered the heat transfer efficiency of the condenser. During the cooldown it was also noted that the OE cooling coils also fouled based upon the long cooling time. Prior to reinitiation of the OE cycle, approximately 50 gallons of benzene rich organic was transferred from the Organic Hold tank to the OE. The OE was agitated for two days to clean the high boiling organics from the cooling coils. The benzene rich organics functioned as a solvent to dissolve the high boilers.

The cause of the fouling in the ECD was the high content of Biphenyl in the OE at the completion of the organic boil. It is believed that the ECD organic (which had 10 wt% Biphenyl at the completion of the Run 65 OE cycle) was concentrated by evaporation of benzene during the lay up period. When Biphenyl concentration increases above the Biphenyl solubility in benzene (26% at 28°C), Biphenyl will drop out of the organic and into the aqueous layer in the decanter.

A mass balance showed that although the OE started with 5.7 lbs of Biphenyl at the completion of the PR cycle, it contained 10.3 lbs of Biphenyl at the start of aqueous boil. Samples pulled after 18 minutes of aqueous boil indicated that approximately 3.0 lbs of Biphenyl could not be accounted for in the OE, ECD or OHT and presumably were coating the condenser tubes. A sample pulled after

shutting down the OE cycle showed that the ECD organic content had increased by 2.5 lbs of Biphenyl. This suggested that the Biphenyl must have melted from the tubes and dropped into the ECD organic.

The organic mass balance is summarized in Table 5.1. The mass balance is performed 18 minutes into the aqueous boil where interruption occurred. The Biphenyl mass balance is defined as

Biphenyl (+ or -) = BP IN OE POST H2O + BP in the ECD ORG Pre strip + BP in the ECD Aqu Pre strip + BP In the OHT before OE pre strip - BP in the OE @ 100 °C - BP in the ECD Org @ 100°C - BP in the ECD aqu @ 100°C - BP in the OHT @ 100°C

**Table 5.1**  
**Run 66 OE Organic Mass Balance**

Component	Units	OE Post H2O	ECD ORG Pre Strip	ECD AQ Pre Strip	OHT before OE Pre str	OE @100°C @AB[1]	ECD ORG @AB[1]	ECD Aqu @AB[1]	OHT ORG @AB[1]	Delta
Phenylboronic Acid	Lbs	0.000	0.000	0.034	0.000	0.000	0.000	0.000	0.000	0.03
N-Phenylformamide	Lbs	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.00
Aniline	Lbs	0.000	0.000	0.021	0.057	0.000	0.000	0.000	0.075	0.00
Phenol	Lbs	1.095	0.000	0.970	5.863	1.325	0.299	0.000	6.010	0.30
Nitrobenzene	Lbs	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.00
Nitrosobenzene	Lbs	0.000	0.000	0.000	0.151	0.000	0.000	0.000	0.000	0.15
4-Phenylphenol	Lbs	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.00
2-Phenylphenol	Lbs	0.015	0.000	0.000	0.071	0.014	0.004	0.000	0.076	-0.01
Diphenylamine	Lbs	0.680	0.000	0.005	4.185	0.479	0.256	0.000	4.279	-0.14
Biphenyl	Lbs	7.324	0.000	0.003	25.957	4.217	3.913	0.000	28.154	-3.00
o-Terphenyl	Lbs	0.026	0.000	0.000	0.053	0.027	0.005	0.000	0.059	-0.01
m-Terphenyl	Lbs	0.000	0.000	0.000	0.030	0.000	0.002	0.000	0.028	0.00
p-Terphenyl	Lbs	0.064	0.000	0.000	0.035	0.045	0.017	0.000	0.205	-0.17

1. Sample pulled approximately 18 minutes into the AB

The second OE run was initiated on October 26. Approximately 3 hours of organic reflux was used to clean the condenser tubes and the decanter before initiating the AB. The run was interrupted again approximately 51 minutes into the aqueous boil due to the high ECD vapor temperature interlock. The ECD heat transfer coefficient was running between 8 to 14 PCU/hr·ft<sup>2</sup>·°C during the organic boil and dropped almost to zero at the beginning of AB. The OE was boiled at a steam rate of 10 pph for 18 hours to allow continuation of the high boilers stripping and to maintain the ECD vapor temperature below 57°C. Several processing changes were implemented in an attempt to defoul the condenser tubes.

- The cooling fans in the cooling tower were shut down in an attempt to increase the cooling water supply temperature.
- The cooling water flow to the condenser was dropped from 40 gpm to 1.5 gpm.
- The ECD vapor outlet temperature interlock was increased from 57 to 72°C.

The increase in CW supply temperature and reduction in CW flow helped to run the condenser hot, to increase the heat transfer efficiency and to melt the high boiling organics from the condenser tubes.

The total steam stripping (approximately 24 hours at 100 pph and 36 hours at 200 pph) time was much longer than a typical run because the cycle was continued until the stripping of high boilers was

complete. The total boil up during the OE aqueous boil was approximately 10,000 lbs of steam versus the normal 2000 lbs of steam (10 hours at 200 pph).

### 5.2 Run 67

Run 67 OE cycle was completed on November 17. The OE cycle was uninterrupted and aqueous boiled for 21 hours at 200 pph. The ECD condenser was operated with warmer cooling water effluent to minimize the fouling of the condenser tubes. No fouling was noted and the final OE product was low in high boiling organics. Extensive steam stripping (21 hours) was conducted to determine the steam stripping efficiency of the high boiling organics. A graph of high boiling organics concentration vs time is summarized in Figure 5.2.1 and 5.2.2 below. A half life of Diphenylamine, Biphenyl, and 2-Phenylphenol has been summarized in figures 5.2.3, 5.2.4, 5.2.5.

Fig 5.2.1 Diphenylamine, Biphenyl, and 2-Phenylphenol Concentration vs Time into Aqueous Boil during Run 67 OE Cycle

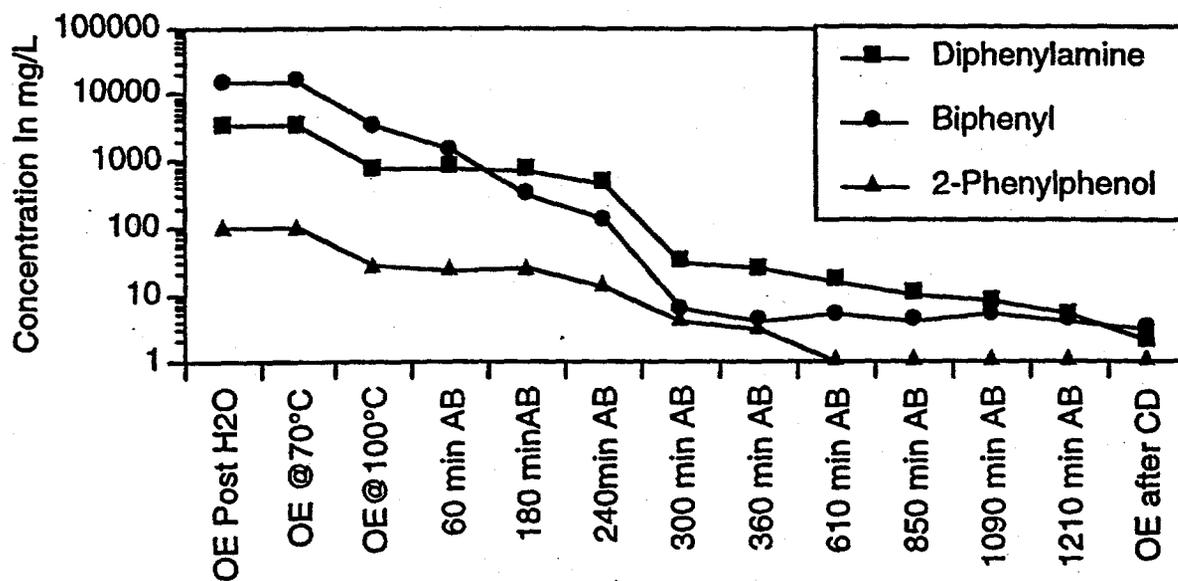


Fig 5.2.2 Phenol, O-Terphenyl, and M-Terphenyl Concentration vs Time into Aqueous Boil during Run 67

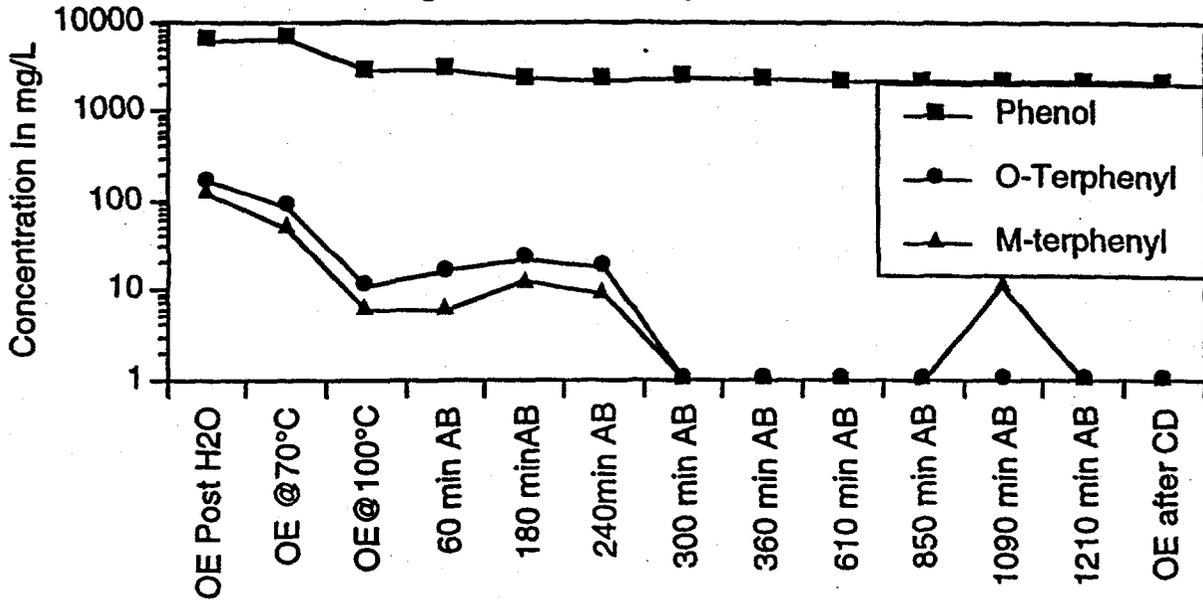


Fig 5.2.3 Ln (Diphenylamine, mg/L) vs Time (minutes) into the OE Aqueous Boil

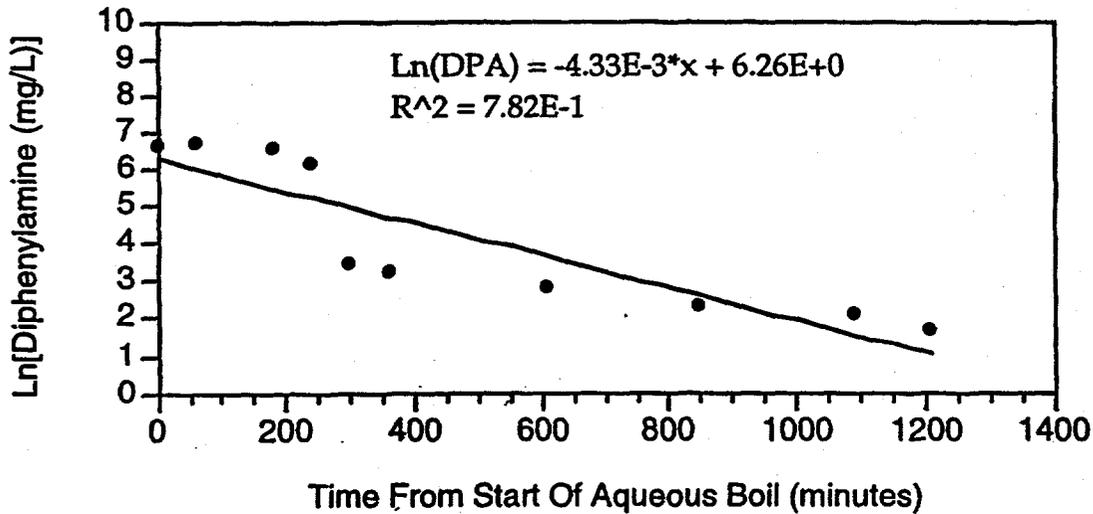


Fig 5.2.4 Ln (Biphenyl, mg/L) Vs Time (minutes) into the OE Aqueous Boil

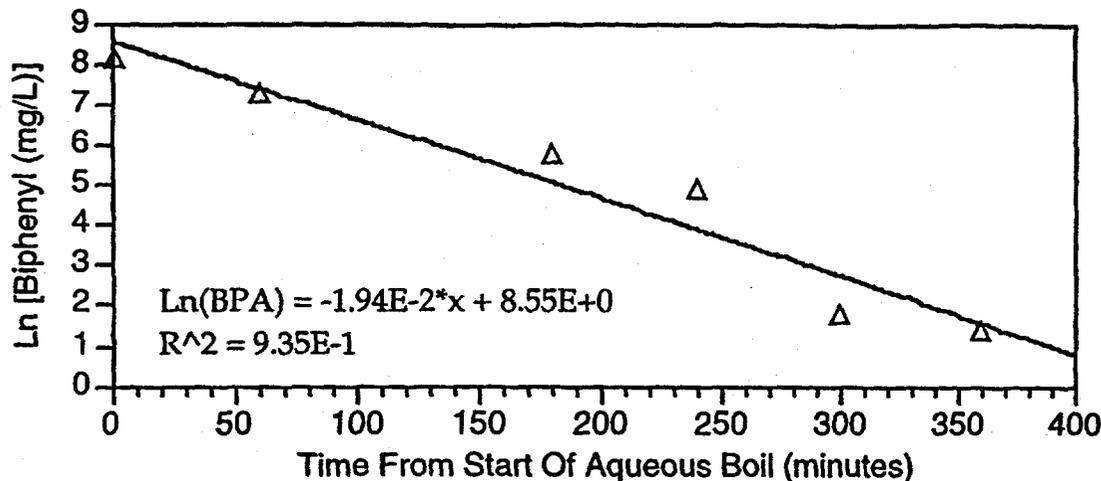
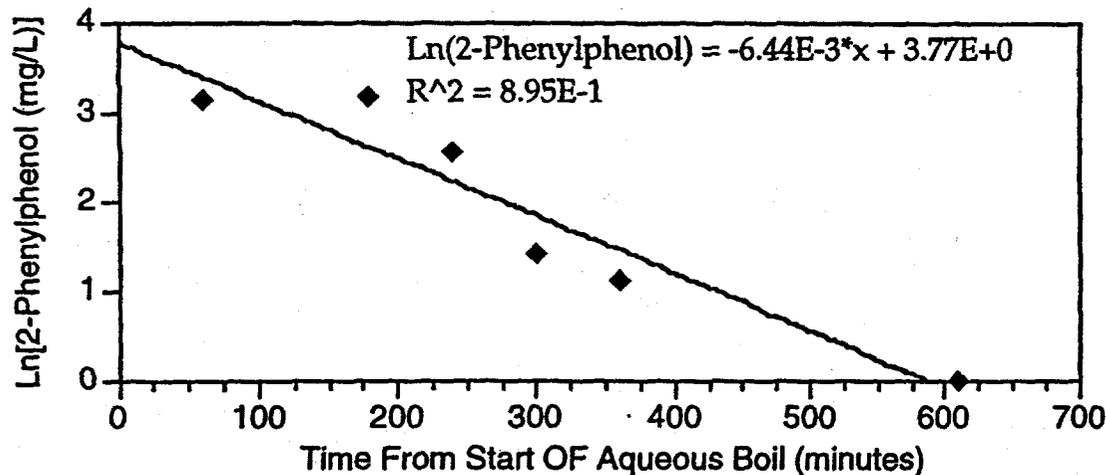


Fig 5.2.5 Ln (2-Phenylphenol, mg/L) Vs Time (minutes) into the OE Aqueous Boil



## 6. RESULTS

### 6.1 Run 66 - Reaction Kinetics

The destruction of Phenylboronic acid is the last step in the Tetraphenylborate hydrolysis. Because of the decomposed feed, very little PBA was produced during the run. The PBA concentration dropped below 53 mg/L in less than 180 minutes. The table below shows the PBA production during the feeding and the PBA concentration during the hold period.

**Table 6.1 Run 66 PBA During Feeding and Hold**

PBA During Feeding		PBA During HOLD	
Gallons Fed	PBA, ppm	Time into Hold, min	PBA, ppm
90	1794	60	0
180	2356	120	152
360	2330	180	<1
630	2070	240	<1
720	1640	300	<1

### 6.2 Run 67 - Reaction Kinetics

Because the hydrolysis of the TPB was nearly complete before feeding, very little PBA was produced during the run. The PBA concentration dropped below 53 mg/L at the end of the feeding. During the entire hold period, the PBA concentration was less than one ppm. The table below shows the PBA production during the feeding and the PBA concentration during the hold period.

**Table 6.2 Run 67 PBA During Feeding and Hold**

PBA During Feeding		PBA During HOLD	
Gallons Fed	PBA, ppm	Time into Hold, min	PBA, ppm
90	837	60	<1
180	1298	120	<1
360	980	180	<1
630	980	240	<1
720	<1	300	<1

### 6.3 High Boilers In Aqueous Product/Aromatic Carbon Removal

The Precipitate Hydrolysis product was aqueous boiled for five hours in both the runs. The final concentrations of Biphenyl and Diphenylamine are summarized in the following table. The final PHA product composition is summarized in Tables 6.3.2 and 6.3.3 for Runs 66 and 67 respectively.

**Table 6.3.1 Run 66 and 67 Aromatic Carbon Removal**

COMPONENT	RUN 66		RUN 67	
	Concentrations at the end of 5 hrs Aqueous boil		Concentrations at the end of 5 hrs Aqueous boil	
	mg/L	Lbs	mg/L	Lbs
Diphenylamine	31	0.28	22.5	0.18
Biphenyl	8	0.072	5	0.04
Calculated TAC of Final product by LC	2240	20.29	2204	17.91
Aromatic Carbon removal by LC	96.26% <sup>1</sup>	N/A	95.75% <sup>1</sup>	N/A

1. Aromatic Carbon Removal for both the runs was calculated based upon the TPB concentration 7.7 wt% before decomposition.

**Table 6.3.2**  
**Run 66 Aqueous Product Analyses**  
**(Sample ID PH-66-142A,B,C)**

<u>Component</u>	<u>Analytical</u>	<u>Units</u>
Total organic carbon	12471	ppm
Soluble copper (Cu)	1058	ppm
Total copper (Cu)	0.103	wt %
Ammonium (NH <sub>4</sub> [1+])	<1	mg/L
Sodium (Na)	7527	ppm
Potassium (K)	10318	ppm
Total wt % solids	7.3	wt %
Titanium (Ti)	133	ppm
Iron (Fe)	0.012	wt %
Boron (B)	3183	ppm
Formate	19597	ppm
Total acid	0.27	M

Component	Units	P66-142A	P66-142B	P66142C	Aver	Std Dev
Phenylboronic acid	mg/L	ND	ND	ND		
N-Phenylformamide	mg/L	84	84	86	84.67	1.15
Aniline	mg/L	33	37	40	36.67	3.51
Phenol	mg/L	2752	2772	2807	2777.00	27.84
Nitrobenzene	mg/L	ND	ND	ND		
Nitrosobenzene	mg/L	8	7	7	7.33	0.58
4-Phenylphenol	mg/L	ND	ND	7	7.00	
2-Phenylphenol	mg/L	3	3	ND	3.00	0.00
Diphenylamine	mg/L	31	27	30	29.33	2.08
Biphenyl	mg/L	10	9	8	9.00	1.00
o-Terphenyl	mg/L	ND	ND	ND		
m-Terphenyl	mg/L	ND	ND	ND		
p-Terphenyl	mg/L	ND	ND	ND		

**Table 6.3.3**  
**Run 67 Aqueous Product Analyses**  
**(Sample ID PH-67-048A,B)**

Component	Analytical	Units
Total organic carbon	12219	ppm
Soluble copper (Cu)	1139	ppm
Total copper (Cu)	1180	ppm
Ammonium (NH <sub>4</sub> {1+})	<100	mg/L
Sodium (Na)	7495	ppm
Potassium (K)	10161	ppm
Total wt % solids	7.16	wt %
Titanium (Ti)	83	ppm
Iron (Fe)	0.012	wt %
Boron (B)	3055	ppm
Formate	21284	ppm
Total acid	0.33	m
TAC (TOC-formate)	6536	ppm
TAC (from LC analysis)	2204	ppm

Component	Units	P67-048A	P66-048B	Average	Std Dev
Phenylboronic acid	MG/L	<1	<1		
N-Phenylformamide	MG/L	89	89	89	
Aniline	MG/L	<1	<1		
Phenol	MG/L	2753	2779	2766	18.38
Nitrobenzene	MG/L	<1	<1		
Nitrosobenzene	MG/L	<1	<1		
4-Phenylphenol	MG/L	<1	<1		
2-Phenylphenol	MG/L	3	3	3	0.00
Diphenylamine	MG/L	24	21	22.5	2.12
Biphenyl	MG/L	4	6	5	1.41
o-Terphenyl	MG/L	<1	<1		
n-Terphenyl	MG/L	<1	<1		
p-Terphenyl	MG/L	<1	<1		

#### 6.4 Transfer Of Product To AAHT

The Run 66 and 67 precipitate hydrolysis product was transferred to the Auxiliary Aqueous Hold Tank (AAHT) on 10/21/93 and 12/1/93 respectively. Before the Run 67 PHA was transferred to the AAHT, the AAHT was sampled. The PHA stored in the AAHT was 7 wt% total solids and 0.27 M acid. In order to bring the PHA in the AAHT up to IDMS specifications, it was decided to add water and acid to the PHA in order to bring solids down to 5.06 wt% and acid up to 0.25M. Run 67 PHA was adjusted with 60 lbs of formic acid and 930 gals of water before transferring it to the AAHT.

## 7. BENZENE PRODUCTION

The feed for both runs was decomposed feed. Because of the decomposition a very small amount of TPB solids were left in the feed tank and there were approximately 100 to 110 gallons of benzene/high boilers present in the tank. The benzene collected in both runs was mainly came from the feed tank. Very little benzene was produced by acid hydrolysis.

### 7.1 Run 66

Total benzene collected was 62.1 gallons, 51.1 gallons of benzene collected in the OE, and 11 gallons added to the RCD.

### 7.2 Run 67

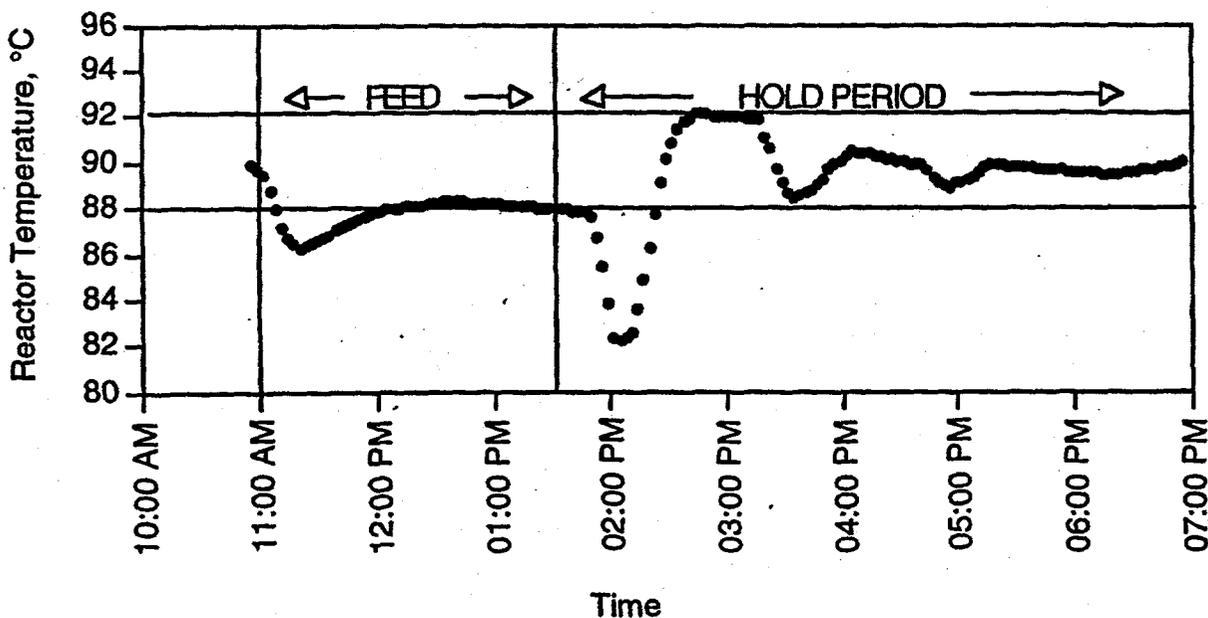
Total benzene collected was 30 gallons, 32 gallons of benzene collected in the OE, and there was a net loss of two gallons in the RCD.

## 8. TEMPERATURE CONTROL

### 8.1 Run 66

Temperature control was excellent during all periods of the run. The two periods of maximum interest were the feed period and the five hour hold period. Temperature control during the feed period was  $90^{\circ}\text{C} (\pm 2.5^{\circ}\text{C})$ . Temperature control during the five hour hold period was  $90^{\circ}\text{C} (\pm 1^{\circ}\text{C})$ . A graph of the feed and hold periods are summarized in Figure 8.1.

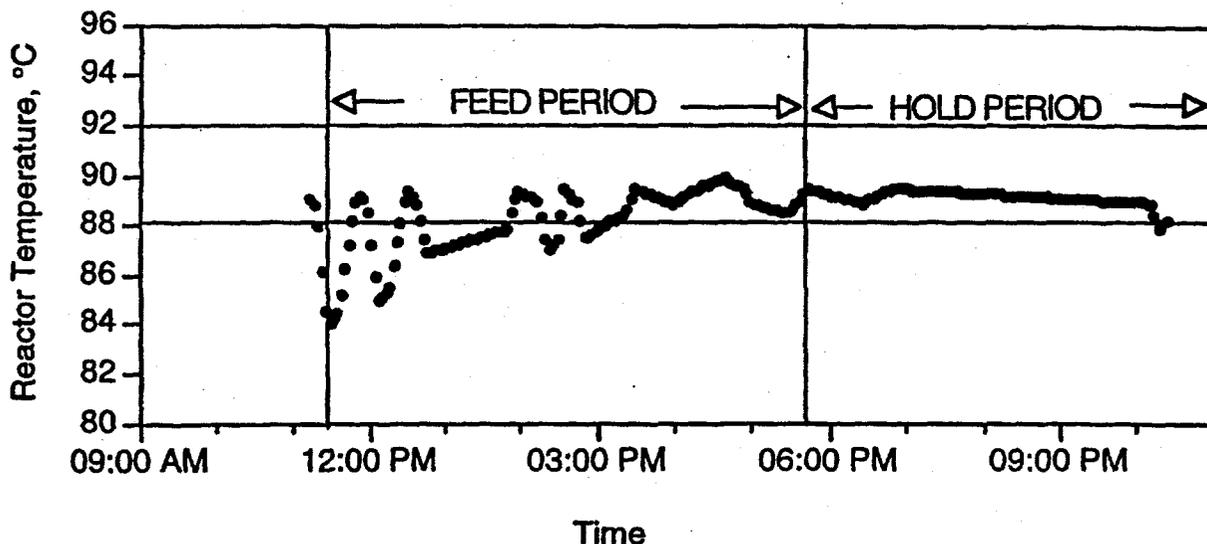
Fig 8.1 RUN 66 TEMPERATURE CONTROL DURING FEED AND HOLD PERIOD



## 8.2 RUN 67

Temperature control was good during the feeding and the five hour hold period of the run. Temperature control in the first 30 minutes of the feeding was between 84.5 to 89°C. The temperature during rest of the feeding and hold period was 90°C ( $\pm 1^\circ\text{C}$ ). A graph of the feed and hold periods are summarized in Figure 8.2.

Fig 8.2 RUN 67 TEMPERATURE CONTROL DURING FEED AND HOLD PERIOD



## 9. COOLING COIL FOULING ESTIMATES

The calculated reactor cooling coil heat transfer coefficient during cooldown was 244 (design basis = 80)  $\text{PCU}/\text{ft}^2/\text{hr}/^\circ\text{C}$  @  $55^\circ\text{C}$ . It took 90 minutes to cooldown the reactor contents at a cooling water flowrate of 20 gpm and 168 RPM agitator speed. During cooldown, cooling water flow to the reactor was only 20 gpm, due to low header pressure. This suggested that minimal high boilers deposition had occurred with the processing of decomposed feed.

The heat transfer coefficient for Run 67 was 293  $\text{PCU}/\text{hr}/\text{ft}^2/^\circ\text{C}$  at  $95^\circ\text{C}$  and 254  $\text{PCU}/\text{hr}/\text{ft}^2/^\circ\text{C}$  at  $55^\circ\text{C}$ . This suggests that minimal deposition on the PR cooling coils can be expected with the decomposed feed. The normal cooldown was initiated at 34 gpm cooling water flow and 170 RPM agitator speed.

### 10. BENZENE IN PHA

At the onset of the cooldown during Runs 66 and 67, benzene concentration in the reactor was around 25 ppm as summarized in Figures 10.1 and 10.2. The concentration had dropped to approximately 7 ppm before the PR temperature had dropped below 90°C.

Fig 10.1 Run 66 PR Benzene Concentration During and After Cooldown

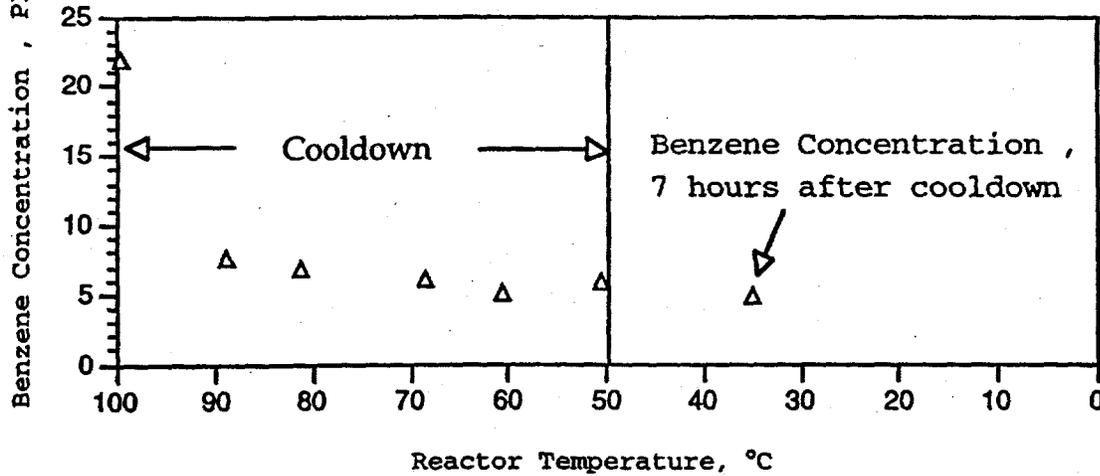
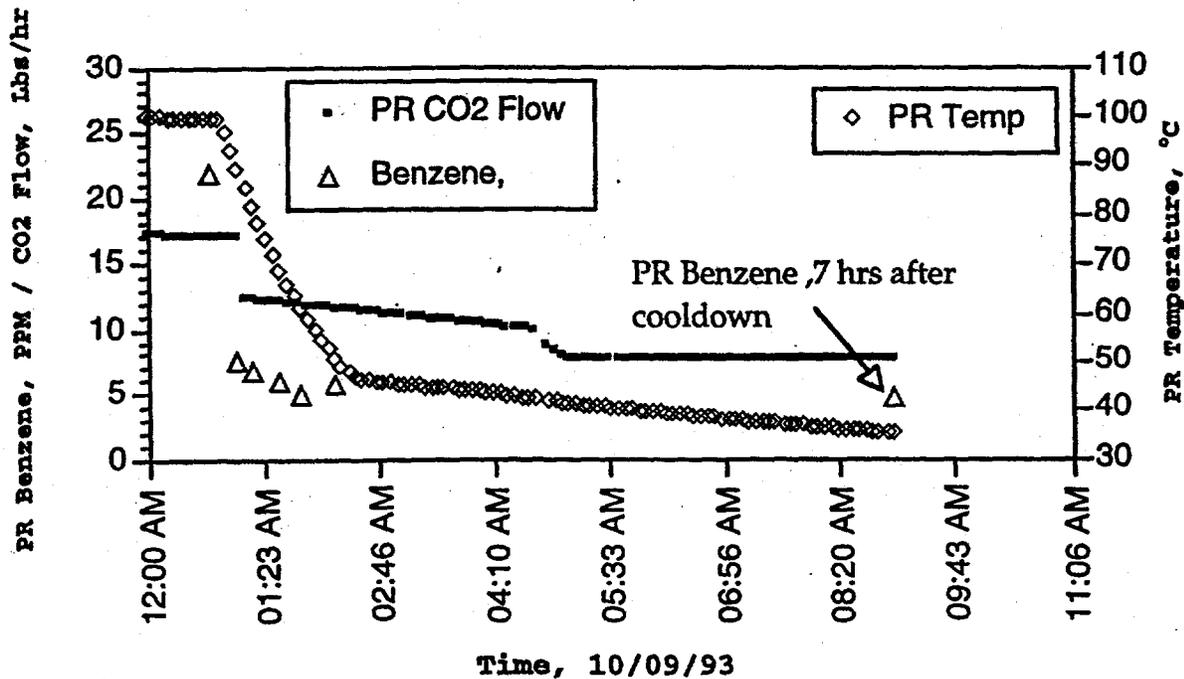


Fig 10.2 Run 67 PR Benzene Concentration during Cooldown



11. REFERENCES:

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4. PHEF Run 67 Run Plan , 682T-93-4-12, dated 10/22/93.
5. PHEF Run Details, WSRC-NB-90178.