

Air



# **Benzene - Organic Chemical Manufacturing**

**Emission Test Report  
Ethylbenzene/Styrene  
Amoco Chemicals  
Company  
Texas City, Texas**

SOURCE TEST: AMOCO CHEMICALS CORPORATION  
ETHYLBENZENE/STYRENE PLANT  
TEXAS CITY, TEXAS

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**TRW**  
**ENVIRONMENTAL ENGINEERING DIVISION**

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## 1.0 INTRODUCTION

During the periods of May 7th through 11th and May 14th through 18th, 1979, personnel from TRW Environmental Engineering Division, Energy and Environmental Analysis Incorporated (EEA) and the U. S. Environmental Protection Agency's (EPA) Emission Measurement Branch (EMB) conducted tests at Amoco Chemical Company's ethylbenzene/styrene plant in Texas City, Texas.

This facility was tested in order to obtain and analyze samples to provide data in support of possible National Emission Standards for Hazardous Pollutants (Benzene) and New Source Performance Standards (Organic Chemical Manufacturing Industry).

Samples were taken from the vents to the atmosphere at the hotwell serving the ethylbenzene recycle column, the polyethylbenzene (PEB) column, and the styrene purification column, the vent recovery system serving the benzene/toluene column, and at the inlet and outlet to the superheater. Liquid samples were taken of the ethylbenzene recycle column hotwell liquid and of the benzene/toluene column vacuum equipment condensate.

The emissions analyzed were low molecular weight hydrocarbons as  $C_1 - C_6$  species, benzene, toluene, ethylbenzene and styrene. In addition, tests were performed for stationary gases, ( $CO_2$ ,  $O_2$ ,  $N_2$ ) flow, and temperature.

The purpose of testing the hotwell vents and the benzene/toluene column vent recovery system was to determine benzene concentrations and total flow at these locations. The inlet fuel gas and the outlet flue gas of the superheater were tested to determine the benzene destruction efficiency of the combustion device.

All sampling and analysis were conducted at the plant site. The exceptions to this were the liquid samples which were refrigerated

and transported to the lab in Raleigh, North Carolina for further analysis. TRW personnel performed the sampling and analysis. Plant operating data and process descriptions were obtained by personnel from EEA, Inc., Durham, North Carolina. The entire operations was supervised and audited by EPA Emission Measurement Branch personnel.

## 2.0 SUMMARY AND DISCUSSION OF RESULTS

During the testing at the ethylbenzene/styrene facility in Texas City, samples were taken at separate processes. For clarity and ease of explanation, the results and methods are presented in the following separate sections.

- Section 2.1 Benzene/Toluene Column Recovery System
- Section 2.2 Column Hot Well Vents and Liquids  
(Ethylbenzene Recycle, PEB, Styrene Purification)
- Section 2.3 Steam Superheater

The first week of testing involved sampling and analysis of the column hot well vents and the benzene/toluene column recovery system. The samples from the inlet and outlet of the steam superheater were taken during the second week of testing. The entire area was a restricted process area. The analytical trailer was set up in an approved area and monitored daily. All sampling apparatus was assembled at the trailer and transported to the sampling site at the time of each test. At the conclusion of each test the equipment and the samples were returned to the trailer.

## 2.1 BENZENE/TOLUENE COLUMN RECOVERY SYSTEM

(Figure 2.1, points 2 and 3)<sup>1</sup>

The recovered liquids from the benzene/toluene recovery system were obtained at point 2. Point 3 was a sample of the non-condensables from the recovery system to the plant fuel. Both samples were taken simultaneously.

The liquid sample at point 2 separated into a hydrocarbon and a water layer. The samples were shaken to form a single phase and then injected into the gas chromatograph. Results are shown in Table 2.1. The volumes of each layer were measured and the percent water layer is reported in Table 2.1. The liquid flow rate was determined by recording the time required to accumulate a total volume of five gallons. The total condensables recovered were directed into the five gallon container by closing off the normal recovery drain valve and shunting the flow to the container by opening the sampling valve.

Results of the analysis of point 3 samples are shown in Table 2.2. Flows at point 3 were obtained from a plant orifice which was connected to a square root differential pressure meter. The results of these flows are shown in Table 2.2. The orifice calibration sheet and example calculations are contained in the Appendices.

## 2.2 COLUMN HOT WELL VENTS

(Figure 2.1, sample points 6, 7, 8, 9)

This section includes the results of testing at the ethylbenzene column hotwell liquid (point 6) and vent to the atmosphere (point 7). Also discussed are results from the vents of the PEB hotwell (point 8)

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<sup>1</sup>The sample location numerical designations are not sequential. Potential test locations in the process were identified prior to a preliminary survey at the facility. During the initial visit, it was determined that some of the proposed locations either did not exist or could not be sampled. To maintain continuity for the overall project record, the original location designations were retained, therefore, results for test Points 1, 4, 5, and 10 do not exist.

and the styrene purification hot well (Point 9)<sup>2</sup>. The four sampling points were tested simultaneously. The results of the analyses are contained in Tables 2.3 through 2.6.

Flows were monitored at the hot well vents (Points 7, 8, and 9) before and after testing with a 4-inch vane anemometer, which was adapted to fit the two and one half inch vent pipe. The four-inch diameter was used in the calculations for total flow. Calculations and data are contained in Appendix A. Flows of the liquids were not determined.

The liquid samples were analyzed at the Raleigh, N.C. Laboratory. They were thoroughly mixed and injected into the gas chromatograph. There was no apparent water/hydrocarbon phase separation in these samples. The main constituent was water with trace amounts of hydrocarbons present. The results of the liquid samples are listed in Table 2.3.

### 2.3 STEAM SUPERHEATER (Figure 2.2)

The purpose of this third series of tests was to determine the destruction efficiency for the incineration of benzene in the process heater. The fuel input to the boiler (Point 12), and the outlet to atmosphere of the steam superheater (Point 11) were tested simultaneously and the results obtained by on-site analysis. The benzene concentration found in the first run at the outlet location was much higher than expected. Blank tests on the sampling system confirmed that residual organic contamination was present in the apparatus. The sampling procedures were changed so that glass sampling flasks were used in place of the EPA Method 110 flexible bag system. An initial run indicated that the modified procedure had eliminated the contamination. However, subsequent samples yielded results that were variable and

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<sup>2</sup>The test plan included measurement of flow and VOC concentration from the vent to atmosphere of a collector pump for the ethylbenzene recycle column and styrene purification column hot well overflows. At the time of testing, it was determined that the pumping rate from the collector was metered based on a constant level control and operates continuously. Therefore, there was theoretically no net displacement of air to the atmosphere during operation. Preliminary flow measurements confirmed that no flow to atmosphere was occurring, therefore no samples were collected for VOC and benzene determination.



inconsistent. In an attempt to clarify the results, blanks on the glass sampling system and the gas chromatograph injection system were run. A satisfactory blank of the system was not achieved. Appendix A contains the blank series that was run during testing. Gas chromatograph results reported in the following tables are uncorrected for blanks. These results are continued in Tables 2.7 and 2.8. Table 2.9 contains results of the benzene destruction efficiency and flow data.

The study of the superheater revealed problems in the testing procedures. (The sequence of problems are presented with the Superheater Study in Appendix A. The first problem in testing was the contamination of the Method 110 Sampling Apparatus. The first test run at the Superheater outlet revealed a high level of benzene ( $\sim 60$  ppm). The source of this high level was due impart to the memory effect of the sampling apparatus being previously used for testing the high levels of benzene at the hotwell vents. A blanking study of the sampling apparatus revealed the sample bags contained a 20 ppm level of benzene after being purged with nitrogen; a check of the flowmeters in the system revealed a 20 ppm benzene level of contamination. The blanking procedure was carried out on the detection instruments and a nitrogen purging of the sample loop gave benzene results of no lower than 4 ppm. An alternative to the sampling procedure was adapted since adequate cleaning of the Method 110 apparatus could not be achieved.

The sampling system was adapted in order to obtain grab samples in a glass flask. The glass sampling bomb method also encountered difficulties. The cleaning of the glass bomb with isopropyl alcohol was believed to interfere with the benzene reading due to similar retention times. The 10 cc syringe used for sample injection from the glass sample bomb was determined to be too small a volume to adequately flush a GC sample loop of 2-4 ml total volume. A blank procedure was attempted on the glass bomb sample method and the result was approximately at 2 ppm of benzene. Blanking of the sampling loop and gas chromatograph between each test run yielded results at the 1 ppm level. This consistent background of benzene was considered to be due in part to the time for an unheated sample to purge back to zero.

Ambient samples were obtained with an OVA total hydrocarbon analyzer and the result was benzene levels ranging from 5-10 ppm. The testing of the superheater was ended and hypotheses on the testing procedures were derived from subsequent lab studies and information gathered during testing. Some of the conclusions are:

1. The sampling apparatus cannot be adequately cleaned by simple purging after exposure to high level aromatics (example - benzene).
2. Glassware exposed to aromatic compounds cannot be cleaned using purging and solvent rinses alone.
3. An unheated sample loop on the gas chromatograph does not purge to zero quickly.
4. The syringe used for sample injection was too small to adequately flush and fill the G.C. sample loops.

With these testing problems in mind the preparation, sampling and analysis procedure for further testing of this type have been modified to accomodate these conclusions.

Due to the configuration of the stack and absence of adequate ports, an outlet volumetric flow rate could not be measured. Since it is necessary to calculate the benzene removal efficiency on a mass basis, a combustion calculation using the fuel and flue gas analysis was performed to calculate a combustion dilution factor for adjusting the measured inlet and outlet benzene concentrations to the same volume basis.

A carbon balance based on the combustion calculations yields significantly different exhaust gas  $\text{CO}_2$  concentrations from those directly measured. Based on this difference, it is probable that the fuel gas analyses are inaccurate. Due to the difficulty of achieving accurate results on the GC system used for  $\text{C}_1 - \text{C}_6$  analysis when  $\text{C}_1$  exceeds 5 volume %, the results for methane are probably low, and since hydrogen was determined by difference, that result is probably high.

Due to the difficulties encountered with interferences, blanking, analysis, and combustion calculations the flue gas analysis obtained at the superheater cannot be used with confidence. These sampling and analysis problems have been subsequently remedied and tests conducted after this do not contain data with these problems.

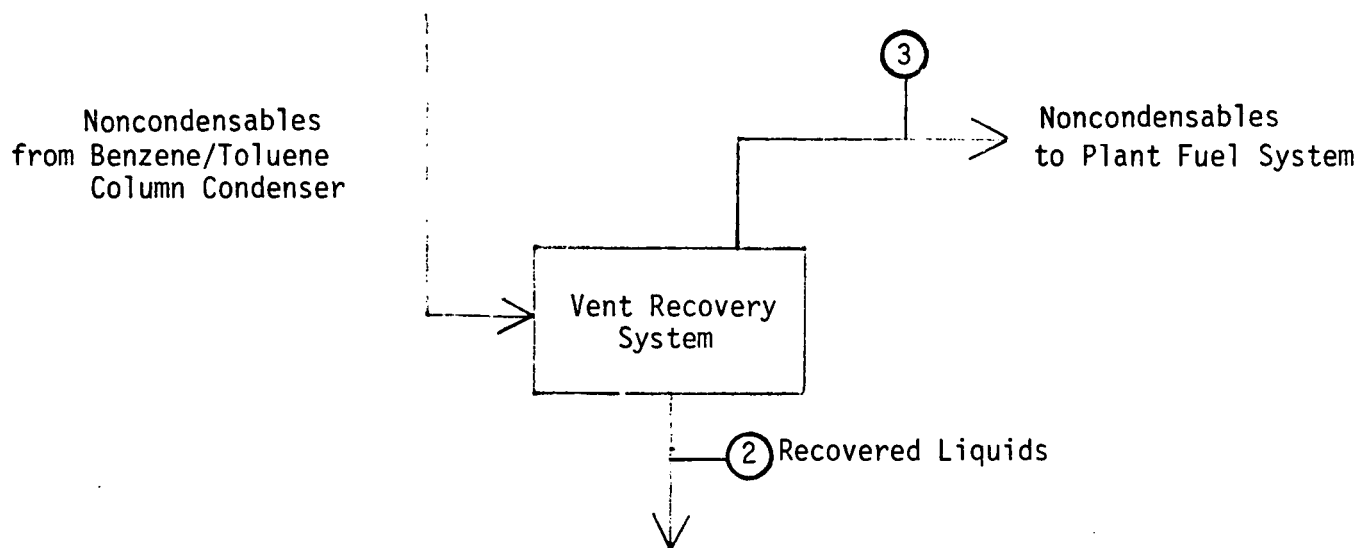


FIGURE 2-1 SAMPLE LOCATIONS - B/T COLUMN VENT RECOVERY SYSTEMS

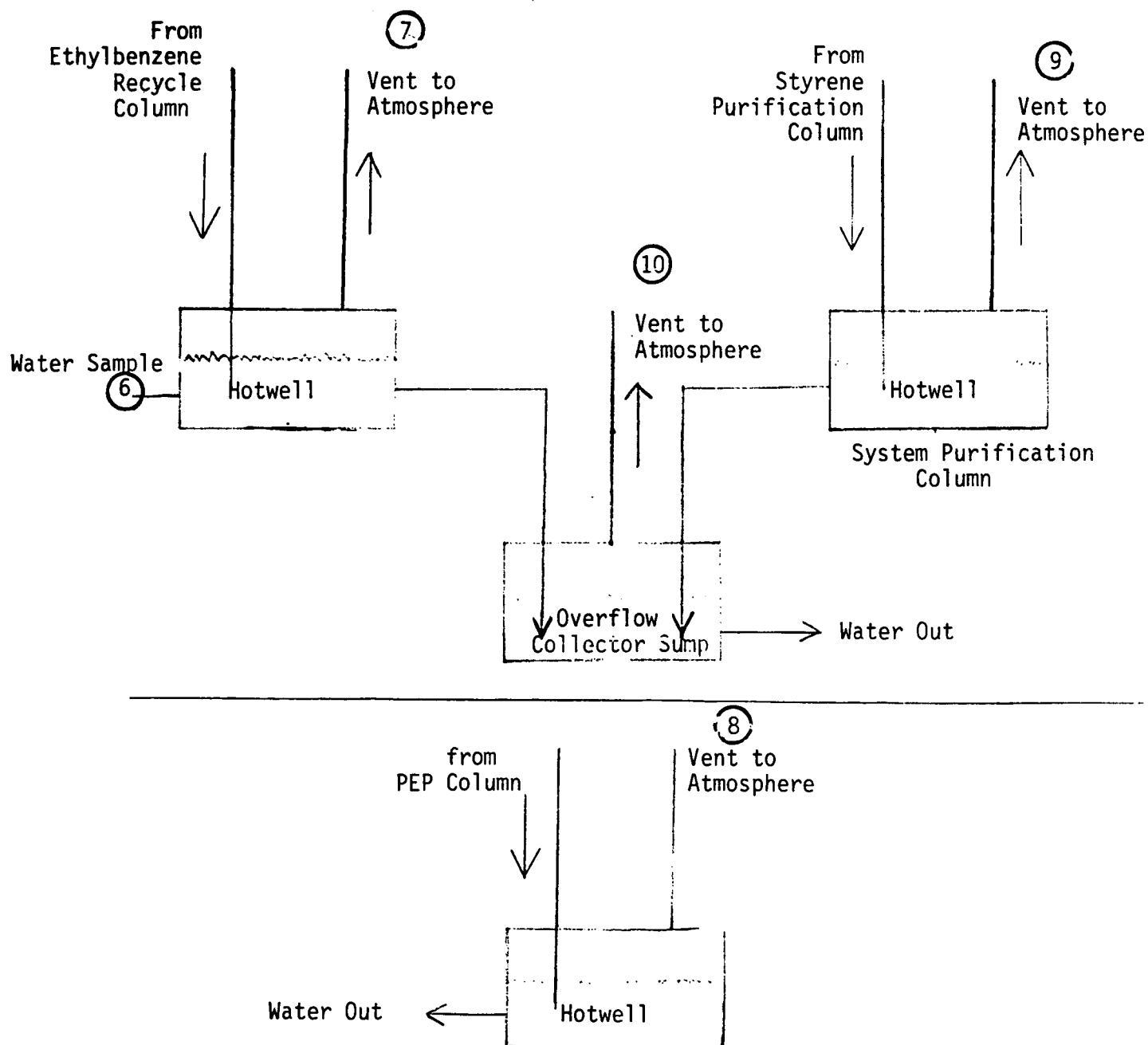


FIGURE 2.2 SAMPLE LOCATIONS - HOTWELL VENTS

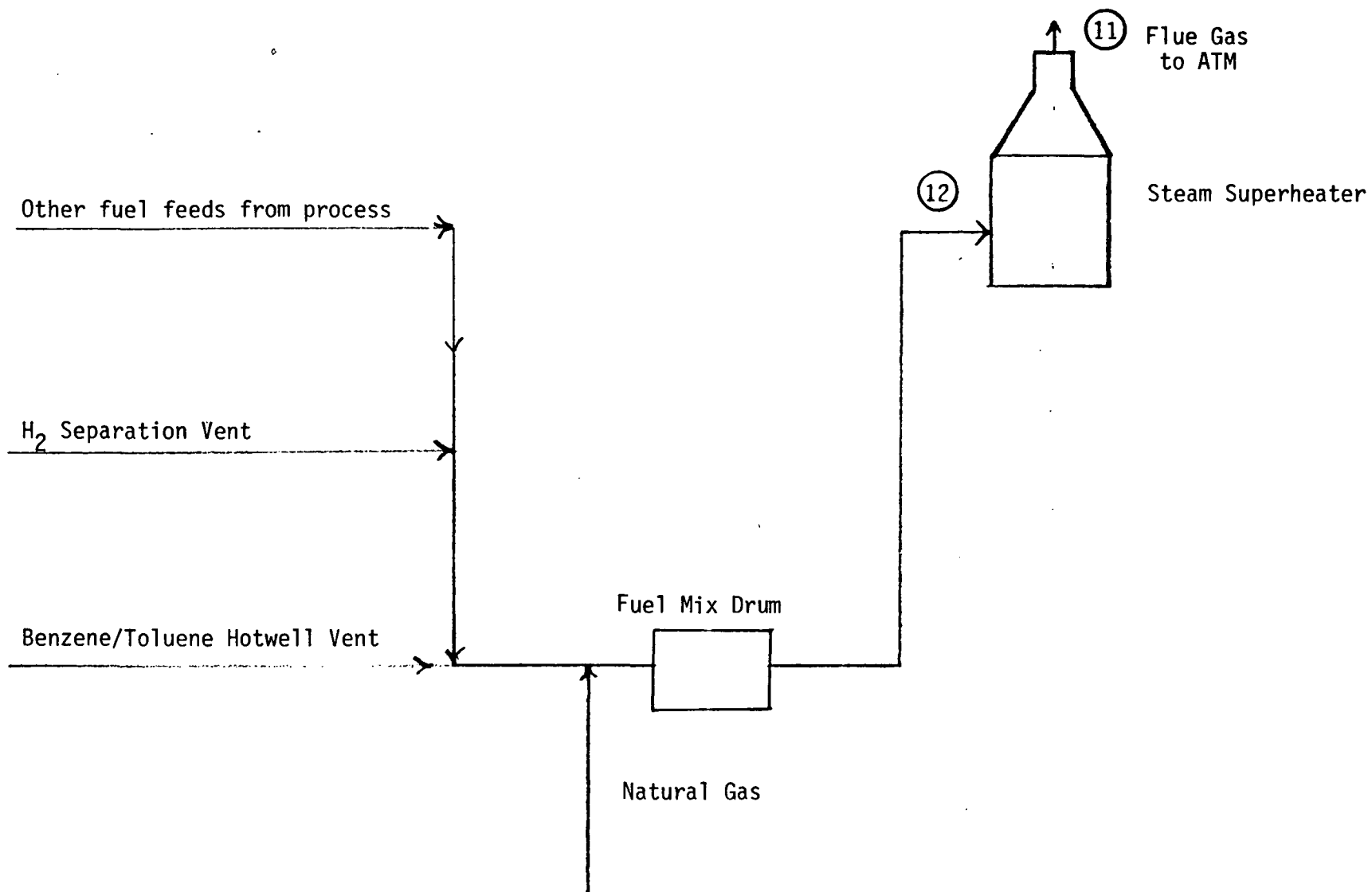


FIGURE 2.3: Steam Superheater System  
Amoco, EB/S  
Texas City, Texas

COMPOUND *	WEIGHT % (LIQUID)	VOLUME % (LIQUID)	WEIGHT (GRAM/L)	FLOW (LPM)
(RUN 2-1)				
BENZENE	59.4	59.4	522.1	
TOLUENE	26.3	26.7	231.2	
ETHYLBENZENE	9.8	10.0	86.7	
WATER	4.5	3.9	39.0	
COMPOSITE				1.04
-----				
(RUN 2-2)				
BENZENE	50.9	51.3	450.9	
TOLUENE	31.4	32.1	278.0	
ETHYLBENZENE	6.4	6.6	57.2	
WATER	11.3	10.0	100.0	
COMPOSITE				1.10
-----				
(RUN 2-3)				
BENZENE	63.5	63.4	557.3	
TOLUENE	23.3	23.6	204.4	
ETHYLBENZENE	10.6	10.7	92.8	
WATER	2.6	2.3	23.0	
COMPOSITE				1.08
-----				
(AVERAGE)				
BENZENE	57.9	58.0	510.1	
TOLUENE	27.0	27.5	237.9	
ETHYLBENZENE	8.9	9.1	78.9	
WATER	6.1	5.4	54.0	
COMPOSITE				1.07

\*Liquid sample analysis converted from vapor phase results to equivalent liquid phase concentration (see sample calculation in Appendix A.)

All values calculated from ppm as benzene.

Runs 2-4 and 2-5 were not included due to process inconsistency.

TABLE 2.1: COMPOSITION OF THE RECOVERED LIQUID STREAM AT THE BENZENE/  
TOLUENE COLUMN VENT: SAMPLE POINT 2

RUN NO.	3-1		3-2		3-3	
Species Analysis	ppmv as benzene	ppmv as species	ppmv as benzene	ppmv as species	ppmv as benzene	ppmv as species
C-1	1004.3	4268.4	970.7	4125.4	947.2	4025.7
C-2	3993.1	9064.2	3861.1	8764.1	2340.3	5312.5
C-3	1365.1	2129.5	1266.0	1975.0	1305.7	2036.8
C-4	45325.4	59376.3	40132.0	52572.9	38605.8	50573.6
C-5	4425.5	4514.0	4145.2	4228.1	3277.1	3342.6
C-6	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
BENZENE	19325.7	19325.7	17098.0	17098.0	16361.8	16361.8
TOLUENE	337.0	273.8	232.3	188.7	263.6	214.1
ETHYLBENZENE	634.9	436.5	359.0	246.8	713.2	490.3
STYRENE	135.1	82.3	69.1	113.4	170.3	103.8
<u>Total Hydrocarbons By:</u> species summation total HC analyzer	77310.5	99907.5	68133.4	89312.9	63985.0	82461.2
Inerts and Flow Data						
H <sub>2</sub> O, % by vol.	n/m		n/m		n/m	
N <sub>2</sub> , % by vol.	64.1		64.6		65.7	
O <sub>2</sub> , % by vol.	3.9		3.0		4.1	
CO <sub>2</sub> , % by vol.	12.6		13.0		12.9	
Flow rate, scfm*, dry	76.46		72.86		71.74	
Total (%)	90.4		89.5		90.9	

N.D. - NOT DETECTED

\* @ 20°C, 1atm

n/m - not measured

TABLE 2.2 POINT 3 ANALYSIS SUMMARY  
B/T COLUMN VENT



Run #	6-1	6-2	6-3
Benzene*	N.D.	443	611
Ethylbenzene	N.D.	5	29
Styrene	N.D.	N.D.	11

\*All values given in ppm as benzene (volume/volume)  
N.D. - NOT DETECTED

TABLE 2.3: COMPOSITION OF THE ETHYLBENZENE RECYCLE  
COLUMN HOT WELL WATER  
(POINT 6)

RUN NO.	7-1		7-2		7-3	
Species Analysis	ppmv as benzene	ppmv as species	ppmv as benzene	ppmv as species	ppmv as benzene	ppmv as species
C-1	0.55	2.3	2.5	10.5	2.7	11.7
C-2	N.D.	N.D.	N.D.	N.D.	3.7	8.4
C-3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
C-4	11.7	15.3	35.3	46.2	15.4	20.2
C-5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
C-6	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
BENZENE	4843.4	4843.4	4667.6	4667.6	4176.1	4176.1
TOLUENE	5778.8	4695.4	5452.6	4430.2	3881.1	4776.8
ETHYLBENZENE	6661	4579.4	6446.7	4432.1	3164.6	4603.1
STYRENE	186	113.3	180.5	110	79.7	130.8
<u>Total Hydrocarbons By:</u> species summation total HC analyzer	17481.4	14249.1	16785.2	13696.6	11323.3	13727.1
Inerts and Flow Data						
H <sub>2</sub> O, % by vol.	6.5		5.5		4.7	
N <sub>2</sub> , % by vol.	72.6		73.6		71.6	
O <sub>2</sub> , % by vol.	18.0		18.0		17.6	
CO <sub>2</sub> , % by vol.	<30 ppm		<30 ppm		<30 ppm	
Flow rate, acfm.	9.78		8.36		8.29	
Total (%)	98.5		98.4		95.2	

N.D. - Not Detected

TABLE 2.4 - POINT 7 ANALYSIS SUMMARY  
PEB COLUMN VENT

RUN NO.	8-1		8-2		8-3	
Species Analysis	ppmv as benzene	ppmv as species	ppmv as benzene	ppmv as species	ppmv as benzene	ppmv as species
C-1	948.2	4029.8	0.53	2.3	0.91	3.9
C-2	57.2	128.2	4.9	11.1	5.9	13.5
C-3	22.2	31.8	1.2	1.9	N.D.	N.D.
C-4	8.7	11.4	42.0	55.0	37.7	37.4
C-5	3.22	N.D.	N.D.	N.D.	N.D.	N.D.
C-6	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
BENZENE	325.0	325.0	1460.4	1460.4	1120.5	1120.5
TOLUENE	33.2	27.0	34.1	27.7	40.7	33.0
ETHYLBENZENE	199.0	137.4	215.3	148	986.7	678.4
STYRENE	19.7	12.0	22.9	13.9	102.7	62.6
<u>Total Hydrocarbons By:</u> species summation total HC analyzer	1614 531	4702.6	1781.3 1798	1720.3	2285.9	1966.3
Inerts and Flow Data						
H <sub>2</sub> O, % by vol.	6.5		5.5		4.7	
N <sub>2</sub> , % by vol.	74.6		80.6		77.5	
O <sub>2</sub> , % by vol.	17.2		10.3		11.2	
CO <sub>2</sub> , % by vol.	N.D.		N.D.		N.D.	
Flow rate, acfm.	35.35		38.35		8.61	
Total (%)	98.7		96.6		93.6	

N.D. - Not Detected

TABLE 2.5 - POINT 8 ANALYSIS SUMMARY - ETHYLBENZENE COLUMN VENT

RUN NO. 9	9-1		9-2		9-3	
Species Analysis	ppmv as benzene	ppmv as species	ppmv as benzene	ppmv as species	ppmv as benzene	ppmv as species
C-1	31.2	132.5	6.0	25.4	2.8	12.2
C-2	4.8	11.0	1.1	2.4	1.0	2.4
C-3	4.4	6.9	N.D.	N.D.	1.3	2.2
C-4	11.3	14.9	7.7	10.0	9.0	11.9
C-5	N.D.	N.D.	N.D.	N.D.	5.6	5.7
C-6	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
BENZENE	36.3	36.3	36.9	36.9	73.8	73.8
TOLUENE	346.3	281.4	361.8	293.9	332.4	270.0
ETHYLBENZENE	9726.4	6686.9	10364.4	7125.5	6383.2	4388.6
STYRENE	1281.7	781.0	1639.7	999.3	749.6	456.8
Total Hydrocarbons By: species summation total HC analyzer	11442.4 24339	7950.9	12417.6 23035	8493.4	7558.7	5223.7
Inerts and Flow Data						
H <sub>2</sub> O, % by vol.	6.5		5.5		4.7	
N <sub>2</sub> , % by vol.	75.6		73.6		73.6	
O <sub>2</sub> , % by vol.	15.4		16.3		15.4	
CO <sub>2</sub> , % by vol.	<30 ppm		<30 ppm		<30 ppm	
Flow rate, acfm.	8.41		8.23		3.49	
Total (%)	98.3		96.3		94.2	

N.D. - Not Detected

TABLE 2.6 - POINT 9 ANALYSIS SUMMARY - STYRENE PURIFICATION  
HOTWELL PUMP VENT

RUN NO. 11	11-1		11-2		11-3	
Species Analysis	ppmv as benzene	ppmv as species	ppmv as benzene	ppmv as species	ppmv as benzene	ppmv as species
C-1	0.12	0.5	1.2	4.9	0.23	0.97
C-2	N.D.	N.D.	4.6	10.4	N.D.	N.D.
C-3	N.D.	N.D.	51.0	79.6	N.D.	N.D.
C-4	4.2	5.5	96.5	126.5	N.D.	N.D.
C-5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
C-6	0.72	0.86	3213.7	3213.7	N.D.	N.D.
BENZENE	2.8	2.8	34.0	34.0	11.9	11.9
TOLUENE	1.6	1.3	12.2	9.9	4.6	3.5
ETHYLBENZENE	8.6	5.9	51.5	35.3	27.8	18.2
STYRENE	2.0	1.2	5.0	3.1	5.5	3.1
<u>Total Hydrocarbons By:</u> species summation total HC analyzer	20.0	18.1	3469.7	3517.4	50.0	37.67
Inerts and Flow Data						
H <sub>2</sub> O, % by vol.	4.7		4.1		3.7	
N <sub>2</sub> , % by vol.	76.7		74.2		75.5	
O <sub>2</sub> , % by vol.	8.6		8.6		8.6	
CO <sub>2</sub> , % by vol.	6.6		13.1		12.2	
Flow rate, scfm*, dry	--		--		--	
Total (%)	96.6		100.0		100.0	

N.D. - Not Detected

\* @ 200C, 1atm

TABLE 2.7 - POINT 11 ANALYSIS SUMMARY - STEAM SUPERHEATER OUTLET

RUN NO. 11	11-4		11-5		11-6	
Species Analysis	ppmv as benzene	ppmv as species	ppmv as benzene	ppmv as species	ppmv as benzene	ppmv as species
C-1	0.21	0.9	5.0	21.1	6.3	26.8
C-2	N.D.	N.D.	N.D.	N.D.	3.8	8.6
C-3	N.D.	N.D.	N.D.	N.D.	4.2	6.5
C-4	55	72.1	N.D.	N.D.	5.0	6.6
C-5	N.D.	N.D.	6.6	6.9	204.4	208.5
C-6	N.D.	N.D.	N.D.	N.D.	0.5	0.42
BENZENE	5.5	5.5	4.4	4.4	15.3	15.3
TOLUENE	3.1	2.5	1.5	1.2	1.7	1.4
ETHYLBENZENE	22.6	15.5	8.5	5.8	8.6	5.9
STYRENE	4.6	2.8	0.9	0.54	0.9	0.55
<u>Total Hydrocarbons By:</u> species summation total HC analyzer	91.0	99.3	26.9	39.9	250.7	280.57
Inerts and Flow Data						
H <sub>2</sub> O, % by vol.	5.7		4.6		3.85	
N <sub>2</sub> , % by vol.	73.8		79.8		81.3	
O <sub>2</sub> , % by vol.	8.6		8.8		7.7	
CO <sub>2</sub> , % by vol.	11.9		6.8		7.2	
Flow rate, scfm*, dry	--		--		--	
Total (%)	100.0		100.0		100.1	

N.D. - Not Detected

\* @ 200C, 1atm

TABLE 2.7 - POINT 11 ANALYSIS SUMMARY (CONTINUED)  
STEAM SUPERHEATER OUTLET

RUN NO. 11	11-7		AVERAGE			
Species Analysis	ppmv as benzene	ppmv as species	ppmv as benzene	ppmv as species	ppmv as benzene	ppmv as species
C-1	1.5	6.4	2.1	8.8		
C-2	N.D.	N.D.	4.2	9.5		
C-3	N.D.	N.D.	27.6	43.1		
C-4	N.D.	N.D.	40.2	52.7		
C-5	56.2	57.3	89.1	90.9		
C-6	N.D.	N.D.	1071.6	1071.7		
BENZENE	4.5	4.5	11.2	11.2		
TOLUENE	1.7	1.4	3.8	3.0		
ETHYLBENZENE	10.6	7.3	19.7	13.4		
STYRENE	1.2	0.73	2.9	1.7		
<u>Total Hydrocarbons By:</u> species summation total HC analyzer	75.7	77.6	1272.4	1306.0		
Inerts and Flow Data						
H <sub>2</sub> O, % by vol.	2.9		4.2			
N <sub>2</sub> , % by vol.	82.2		77.6			
O <sub>2</sub> , % by vol.	7.9		8.4			
CO <sub>2</sub> , % by vol.	7.0		9.3			
Flow rate, scfm*, dry	--		--			
Total (%)	100.0		99.5			

N.D. - Not Detected

\* @ 200C, 1atm

TABLE 2.7 - POINT 11 ANALYSIS SUMMARY (CONTINUED)  
STEAM SUPERHEATER OUTLET

RUN NO. 12	12-1		12-2		12-3	
Species Analysis	ppmv as benzene	ppmv as species	ppmv as benzene	ppmv as species	ppmv as benzene	ppmv as species
C-1	Not Run	---	13389.8	56906.8	18888.5	80276
C-2	"	---	699.0	1586.8	425.0	964.8
C-3	"	---	332.9	519.4	502.1	783.3
C-4	"	---	N.D.	N.D.	N.D.	N.D.
C-5	"	---	N.D.	N.D.	N.D.	N.D.
C-6	"	---	930.2	781.4	N.D.	N.D.
BENZENE	1165.3	1165.3	1188.6	1188.6	1183.2	1183.2
TOLUENE	434.3	352.9	310.2	252.1	594.5	483.0
ETHYLBENZENE	2770.5	1904.7	2014.5	1385.0	1143.5	786.1
STYRENE	494.4	301.3	392.8	239.4	N.D.	N.D.
<u>Total Hydrocarbons By:</u> species summation total HC analyzer	4864.5	3724.2	19258.0	62859.5	22736.8	84476.4
Inerts and Flow Data						
H <sub>2</sub> O, % by vol.	0		0		0	
N <sub>2</sub> , % by vol.	3.6		2.8		5.5	
O <sub>2</sub> , % by vol.	1.3		1.2		1.9	
CO <sub>2</sub> , % by vol.	8.6		13.8		8.7	
H <sub>2</sub> % by vol.**	86.5		82.2		83.9	
Total (%)	100.0		100.0		100.0	

N.D. - Not Detected

\*\* by difference

TABLE 2.8 - POINT 12 ANALYSIS SUMMARY - STEAM SUPERHEATER INLET



RUN NO. 12	12-4		12-5		12-6	
Species Analysis	ppmv as benzene	ppmv as species	ppmv as benzene	ppmv as species	ppmv as benzene	ppmv as species
C-1	26701.9	113483.1	14904.1	63342.5	15317.4	65098.9
C-2	14862.0	33736.7	770.8	1749.7	693.9	1575.1
C-3	12331.3	19236.8	237.7	370.9	143.4	223.8
C-4	N.D.	N.D.	41.4	54.3	25.3	33.2
C-5	N.D.	N.D.	273.2	278.6	1425.0	1453.5
C-6	972.1	816.6	N.D.	N.D.	N.D.	N.D.
BENZENE	1098.6	1098.6	989.0	989.0	1110	1110
TOLUENE	354.8	288.3	378.4	307.4	450	365.6
ETHYLBENZENE	2102.2	1444.6	989.4	680.2	905	622.2
STYRENE	385.2	234.7	177.7	108.3	155	94.5
<u>Total Hydrocarbons By:</u> species summation total HC analyzer	58808.1	170339.4	18761.7	67880.9	20225	70576.8
Inerts and Flow Data						
H <sub>2</sub> O, % by vol.	0				0	
N <sub>2</sub> , % by vol.	5.8		4.8		3.8	
O <sub>2</sub> , % by vol.	2.6		<.1		<.1	
CO <sub>2</sub> , % by vol.	8.5		7.3		7.2	
H <sub>2</sub> % by vol.**	83.1		87.8		88.9	
Total (%)	100.0		100.0		100.0	

N.D. - Not Detected

\*\* by difference

TABLE 2.8 - POINT 12 ANALYSIS SUMMARY (CONTINUED)  
STEAM SUPERHEATER INLET

RUN NO. 12	12-7		AVERAGE			
Species Analysis	ppmv as benzene	ppmv as species	ppmv as benzene	ppmv as species	ppmv as benzene	ppmv as species
C-1	15087.6	64122.3	17381.6	73871.6		
C-2	708.6	1608.5	3026.6	6870.3		
C-3	208.9	325.9	2292.7	3576.7		
C-4	32.2	42.2				
C-5	758.0	773.7				
C-6	N.D.	N.D.				
BENZENE	1524.6	1524.6	1179.9	1179.9		
TOLUENE	710.0	576.9	466.7	375.2		
ETHYLBENZENE	1482.6	1019.3	1629.7	1120.3		
STYRENE	207.9	126.7	302.2	184.2		
<u>Total Hydrocarbons By:</u> species summation total HC analyzer	20720.4	70120.1	26274.4	87178.2		
Inerts and Flow Data						
H <sub>2</sub> O, % by vol.	0		0			
N <sub>2</sub> , % by vol.	13.2		5.6			
O <sub>2</sub> , % by vol.	1.2		1.2			
CO <sub>2</sub> , % by vol.	7.1		8.7			
H <sub>2</sub> % by vol. **	78.5		84.4			
Total (%)	100		100			

N.D. - Not Detected

\*\* by difference

TABLE 2.8 - POINT 12 ANALYSIS SUMMARY (CONTINUED)  
STEAM SUPERHEATER INLET

RUN NO.	1	2	3	4	5	6	7
Stack Outlet Benzene Conc. (ppm wet)	2.8	34.0	11.9	5.5	4.4	15.3	4.5
Stack Oxygen Conc. (%v/v wet)	8.6	8.6	8.6	8.6	8.8	7.7	7.9
Stack Moisture (as analyzed in sample)	4.7	4.7	4.7	4.7	4.7	4.7	4.7
Benzene Emission (ppm @ 3% O <sub>2</sub> dry)	4.43	53.77	18.82	6.95	7.08	22.42	6.70
Fuel Inlet Benzene Conc. (ppm)	1165.3	1188.6	1183.2	1098.6	989.0	1110.0	1524.6
Dilution Factor	4.02	4.26	4.11	5.27	4.04	3.68	3.64
Benzene Removal Efficiency (%)	99.0	87.8	95.9	97.4	98.2	94.9	98.9

TABLE 2.9: SUMMARY OF RESULTS - STEAM SUPERHEATER

### 3.0 PROCESS DESCRIPTION

(to be supplied by EPA)

## 4.0 LOCATION OF SAMPLING POINTS

Sampling locations are described in separate sections for the following equipment groups:

- 4.1 Benzene/Toluene column recovery system
- 4.2 Ethylbenzene Recycle, PEB, Styrene Purification Column's hot well vents and liquids
- 4.3 Steam Superheater

The sample points are shown schematically in Section 2 and are shown specifically in Figures 4.1 through 4.3 in this section.

### 4.1 BENZENE/TOLUENE COLUMN RECOVERY SYSTEM (Figure 4.1)

Point 2 was the recovered liquids from the benzene/toluene column vacuum equipment condenser. The flow was diverted through the drain valve to a five gallon container. After the flow measurement was obtained a sample was taken at this point. The non-condensables from the final accumulator are directed to the plant fuel mix drum. Sample point 3 was located at the inlet flange tap at the flow orifice in this line.

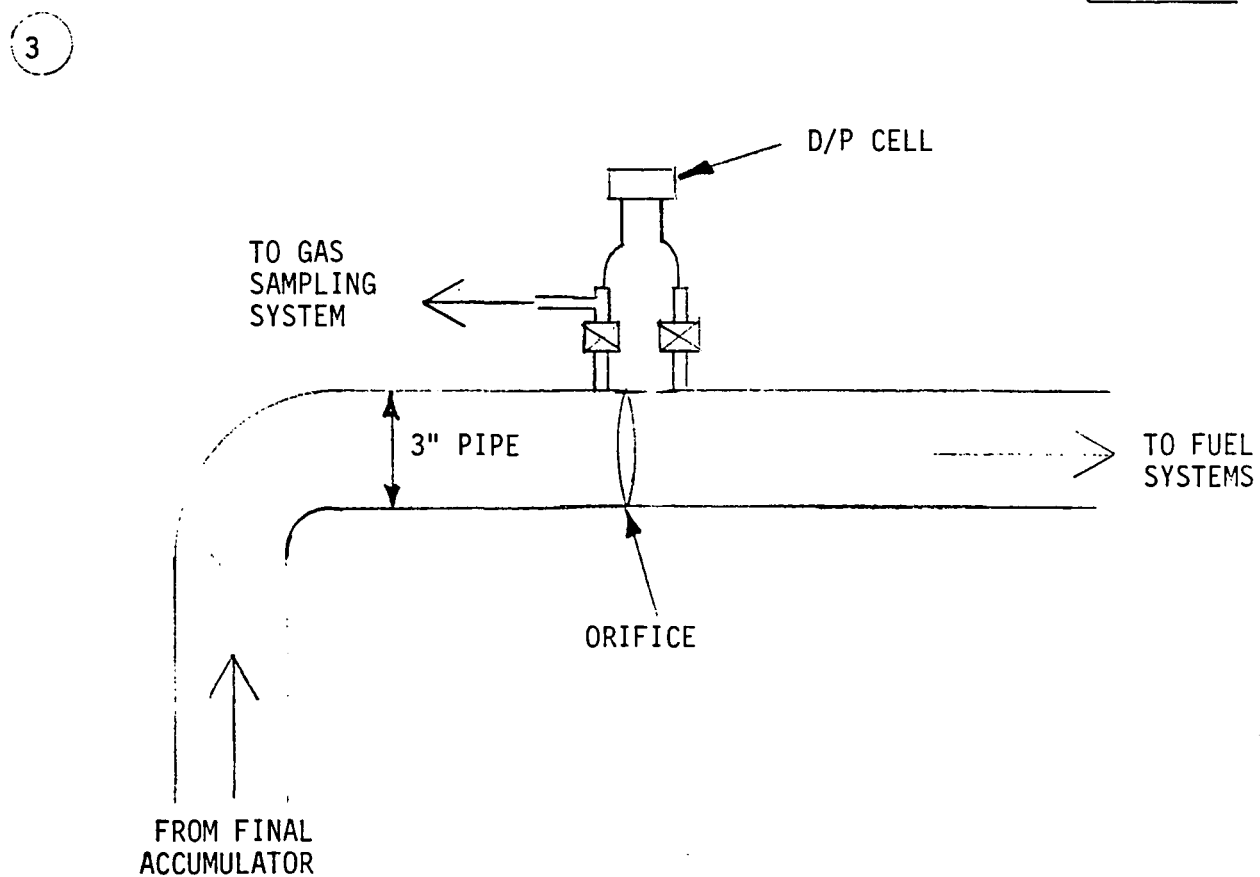
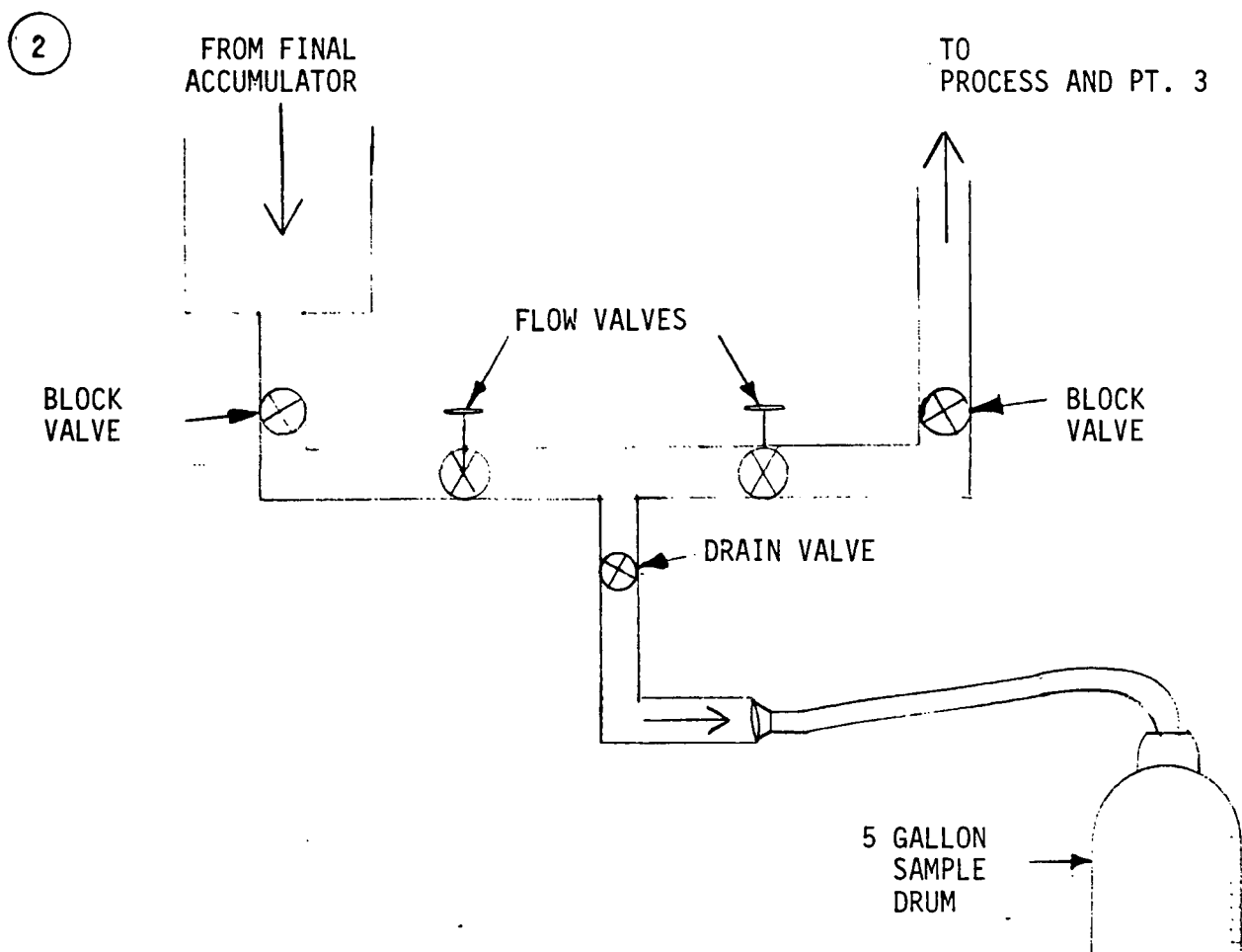
### 4.2 ETHYLBENZENE RECYCLE, PEB, STYRENE PURIFICATION COLUMN'S HOT WELL VENTS AND LIQUIDS (Figure 4.2)

Point 6 was a sample taken of the hot well liquid from the Ethylbenzene recycle column. Point 7 was taken from the gaseous vent of the same hot well. Point 8 was taken from an adapted vent at ground level from the PEB column hot well. The normal vent was blocked off to maintain flow through the adapted vent. Point 9 was taken from the vent of the styrene purification hot well liquid.

#### 4.3 STEAM SUPERHEATER (Figure 4.3)

Point 12 was the superheater inlet fuel gas and Point 11 the exhaust flue gas. The fuel sample was taken directly from the high pressure fuel stream by installing a regulator valve after a plant drain valve. The outlet was located 120' above ground level at a point 20' above the superheater.

Figure 4.1 Benzene/Toluene Column Vent (Sampling Location #2 & #3).



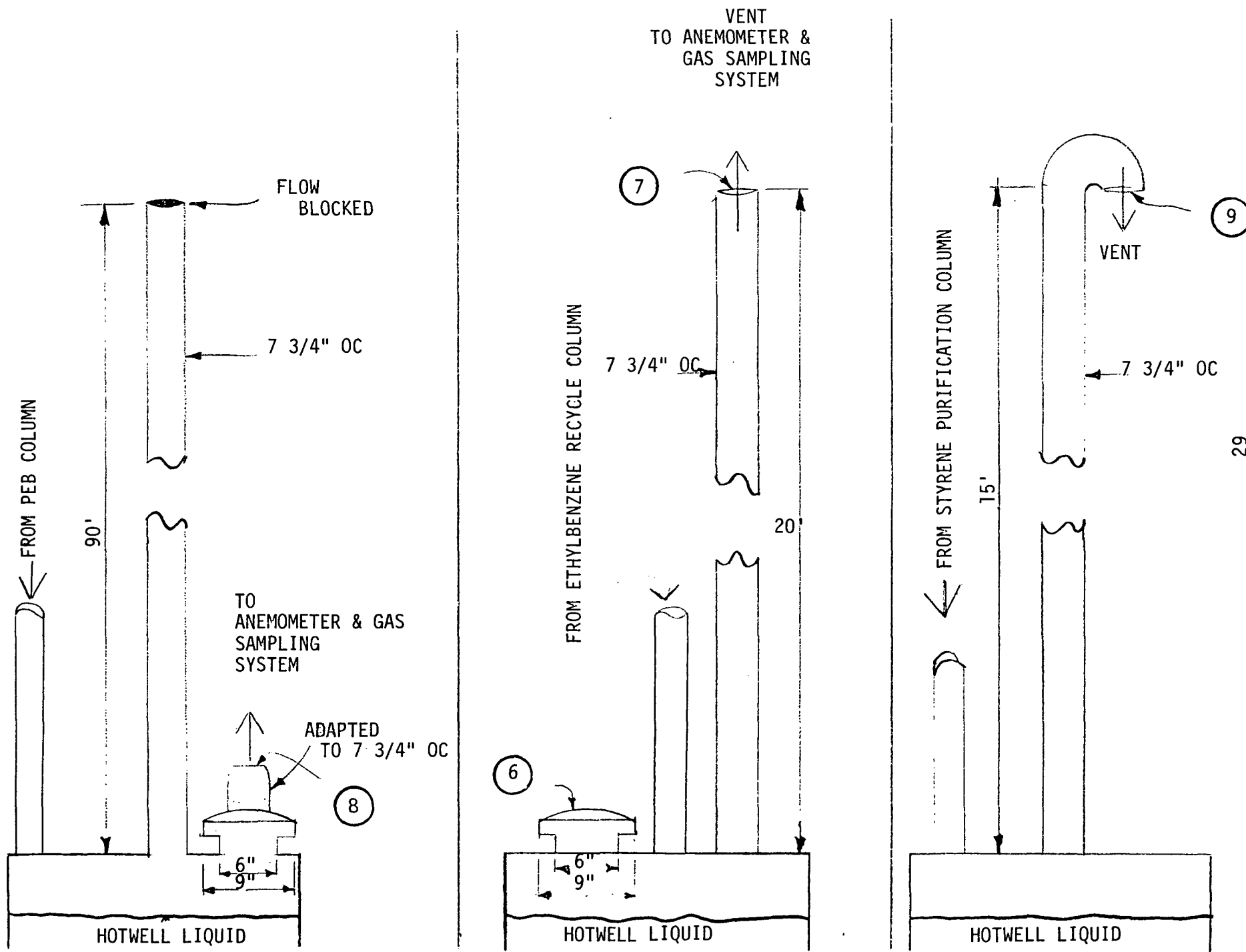
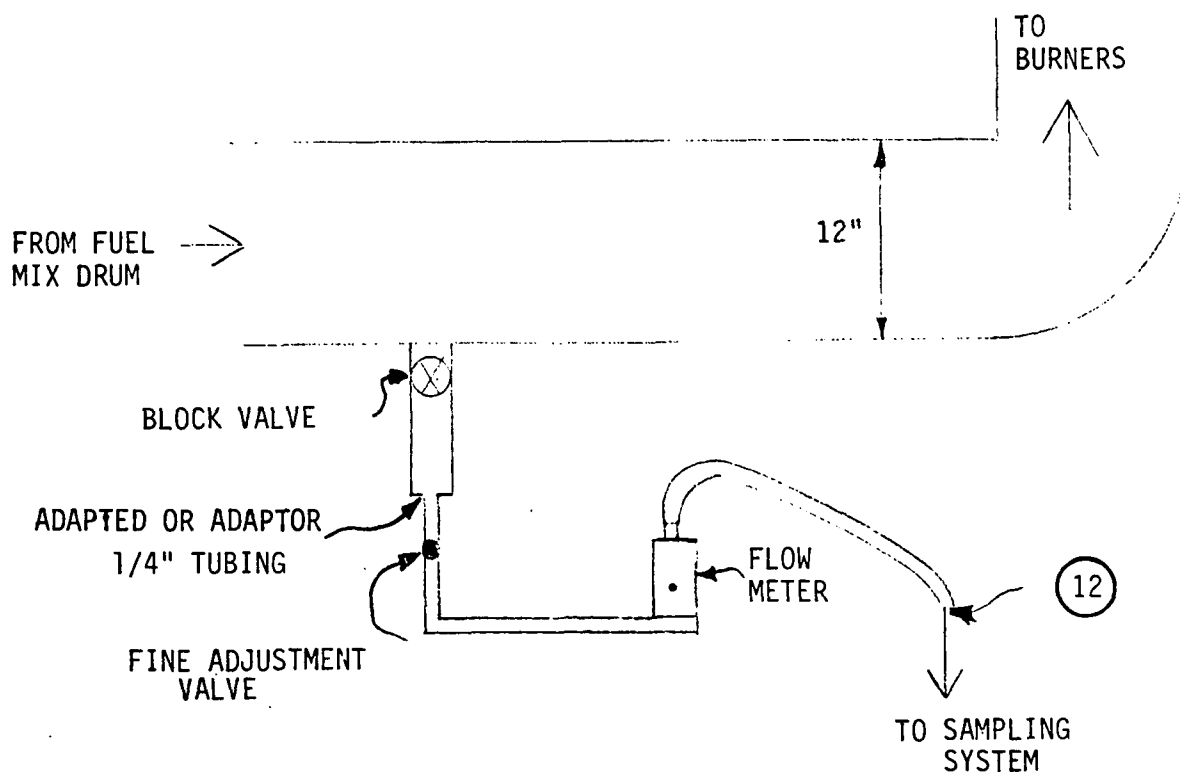
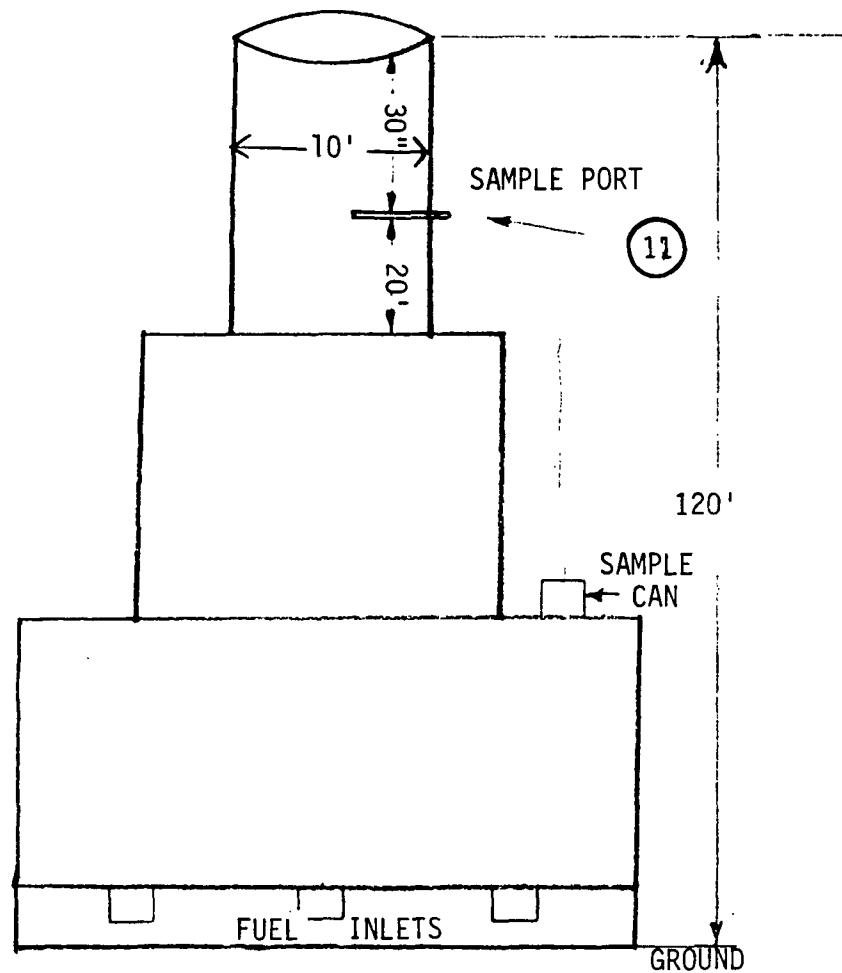


Figure 4.2: Ethylbenzene Recycle, PEB, Styrene Purification Columns (Sampling Locations 6, 7, 8, & 9).



Figure 4.3: Boiler Flue Gas Stream (Sampling Locations #11 & #12).



## 5.0 SAMPLING & ANALYSIS PROCEDURES

### 5.1 SAMPLING PROCEDURES

Figure 5.1 diagrams the sampling apparatus used during testing at Texas City. This system was chosen due to the restricted process and safety requirements of the plant. The collection system consists of a can which seals at a vacuum of 15" mercury (Hg), a bag evacuated to 29" Hg, a flowmeter for metering gas, and teflon tubing and connections which serve as a sample line.

The procedure used was to evacuate the can using the outside self-sealing valve. After a vacuum was achieved, the can vacuum was checked by placing a vacuum gauge on the outside valve and monitoring the vacuum. If the pressure did not drop more than 1" Hg, the can was considered leak-free. The second step was to evacuate the bag to 29" Hg. The same leak check was then made on the bag. The flowmeter and can were next transported to the site where the sample was to be taken. The flowmeter was plugged in and turned on at the appropriate time and the sample extracted from the stack.

For sampling Points 3 and 12, the teflon line was connected directly to the stack and purged. It was then plugged into an evacuated bag and the pressure of the stack filled the bag over a period of time. For sampling Points 7, 8, and 9, the teflon tube was inserted into the vent pipe and the evacuated can drew the sample into the can over a period of time.

For run 11-1, the evacuated can method (Figure 5.2) was used for drawing a sample into the bag. When analysis was run on the contents, it proved to be biased high, due to residual benzene being present in the flowmeter and sampling line. The system was modified to withdraw a sample through a precleaned glass bomb. The bomb (which has an inlet and outlet valve along with a septum point as shown in Figure 5.3)

was then transported to the trailer for chromatographic analysis. Figure 5.4 presents a representative gas sample run. This procedure was repeated for run 11-2 through 11-7.

## 5.2 FLOW PROCEDURES

Flows were measured on points 7, 8, and 9 by using a vane anemometer which was adapted to the pipes. The calibration data and flow measuring diagram is contained in Appendix A. Point 8 flow and sampling was done through an adapted pipe so that it could be accessible. The normal vent, which was 70' above ground level, was blocked off during flow measurement and sampling.

At point 2, the valves were controlled during sampling in order to redirect the condensate to a five gallon container. The flow was obtained by measuring the time it took to fill the container. A plant orifice was used to measure the gas flow at point 3. The results are shown in Table 2.2. An example calculation is presented in Appendix A.

The sampling point at points 11 and 12 were inaccessible to flow measurement. The destruction efficiency was determined using flow calculations as described in Section 2.

## 5.3 ANALYTICAL PROCEDURES

Analysis was performed on site on all gaseous samples. The liquid samples were refrigerated and transported to the laboratory in Raleigh for liquid gas chromatographic analysis. Three gas chromatographs were used in the analysis of the samples. The first instrument (Shimadzu Mini-1) was dual flame ionization detection (FID) equipped with two poropak Q columns. This gas chromatograph was used to determine the lower molecular weight hydrocarbons ( $C_1 - C_6$ ). The second GC was also a dual FID (Shimadzu Mini-1), which contained a 5% OV101/Bentone 34 column. The third was an AID portable thermal conductivity detector GC used for quantitative detection of stationary gases. The gas samples were transferred to the gas chromatograph through a one milliliter sample loop, this allowed consistency with the external calibration standards. Calibration standards of methane ( $C_1$ ), ethane ( $C_2$ ), propane ( $C_3$ ), butane ( $C_4$ ), pentane ( $C_5$ ) and hexane ( $C_6$ ) were used on the Poropak Q column for low molecular weight hydrocarbons. Only benzene was available as a

calibration standard on the OV-101 column. From the benzene numbers obtained in the calibrations a response factor was applied to obtain the concentrations of the individual compounds (See Appendix A).

Blanks of the system were performed and a blank series is listed in Appendix A. This is discussed in Section 2.

The analysis of the fuel gas, by GC/FID, indicated a saturation effect of the detector occurred when more than 5% total hydrocarbons were introduced. This saturation effect was remedied by diluting the fuel gas samples 100:1 before analysis. The dilutions were performed on a rotameter dilution board and the results were checked by using  $O_2$  and  $H_2$  as internal standards which were verified on the thermal conductivity detector. Since the outlet samples were of lower concentrations, they were injected directly in the GC/FID.

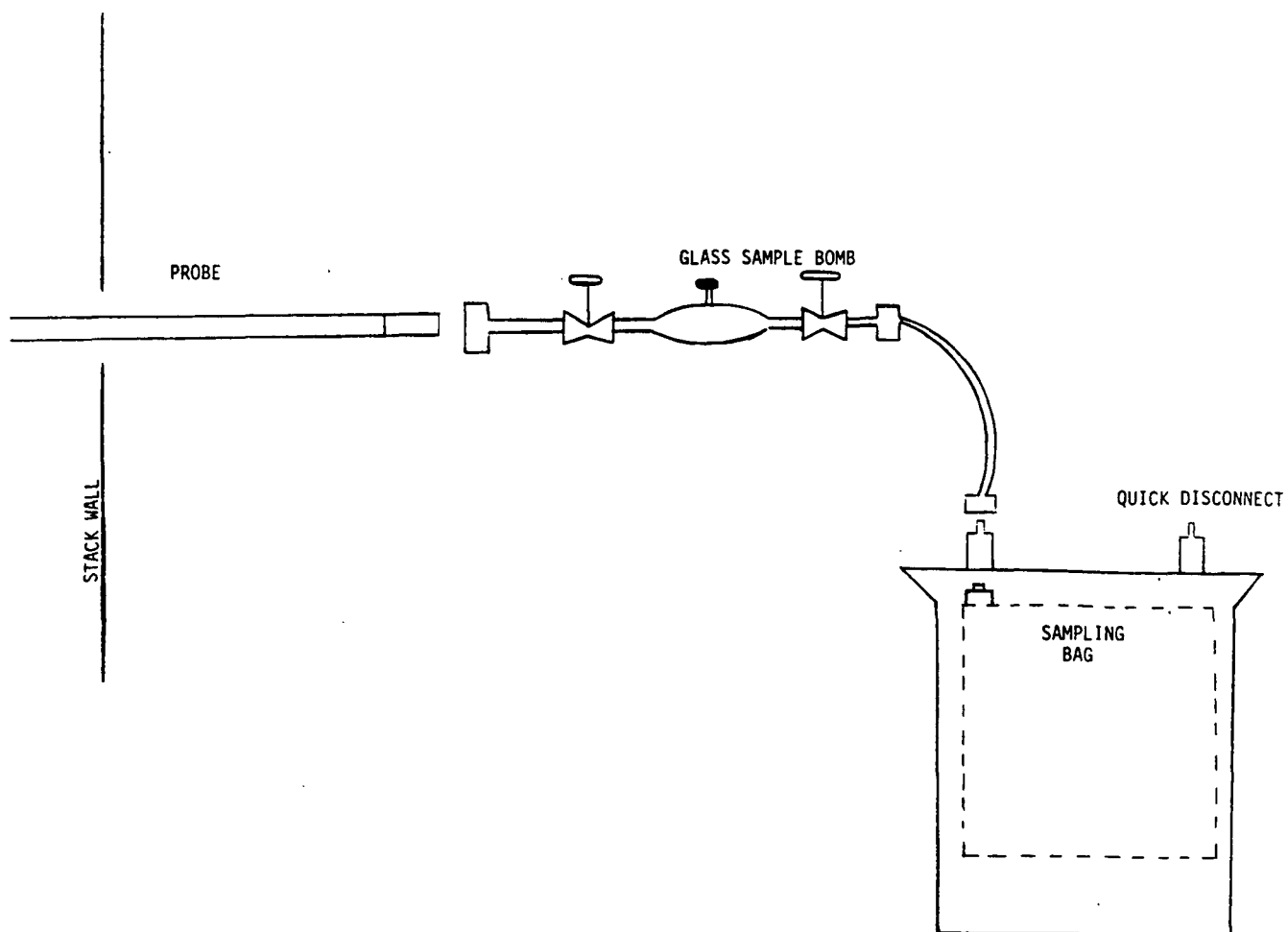


FIGURE 5.1 - Basis Sampling Apparatus

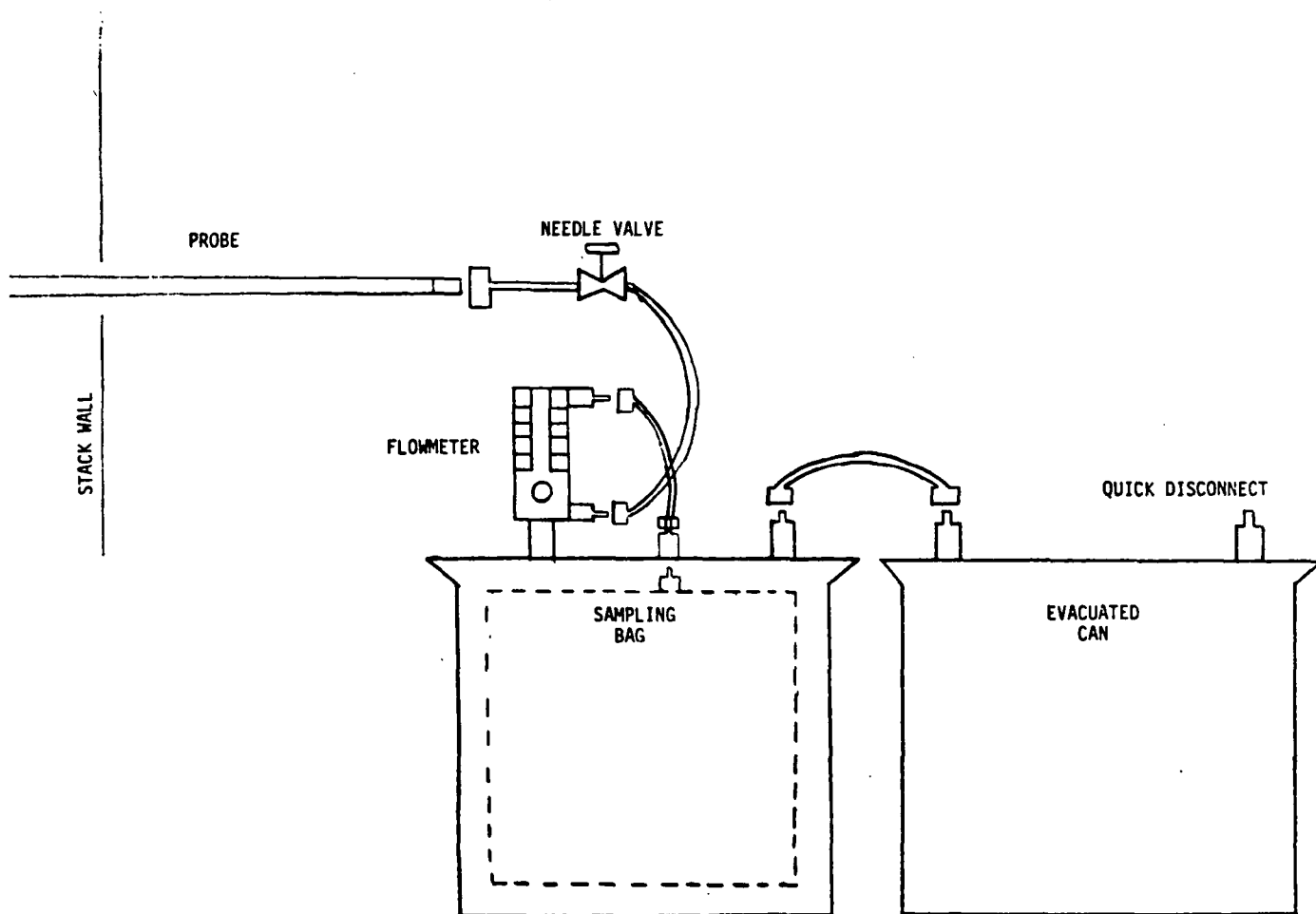


Figure 5.2. Evacuated Can Sampling Apparatus

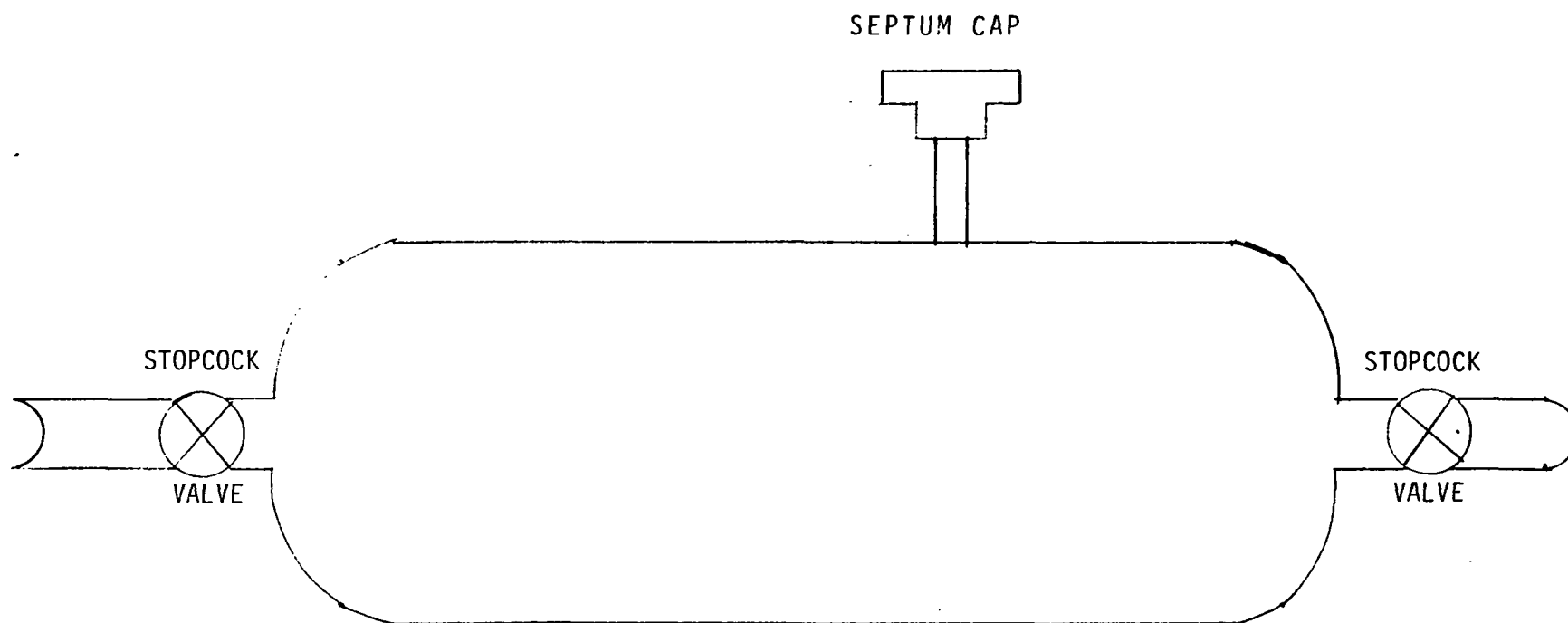


FIGURE 5.3 GLASS SAMPLING BOMB