WALK-THROUGH SURVEY OF

Gulf Oil Refinery, Petro-Chemical Division
Philadelphia, Pennsylvania

SURVEY DATE

November 20, 1975

SURVEY CONDUCTED BY

Ronald Young
Richard Hartle
Robert Rinsky

REPORT WRITTEN BY

Ronald Young
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DATE OF REPORT

February 5, 1976

Division of Surveillance, Hazard Evaluations and Field Studies
National Institute for Occupational Safety and Health
Cincinnati, Ohio

PLACE VISITED:	Gulf Oil, Petro-Chemical Division Philadelphia, Pennsylvania
DATE OF VISIT:	November 20, 1975
PERSONS MAKING VISIT:	Ronald Young Robert Rinsky Richard Hartle
PERSONS CONTACTED:	Jim DeGrafenread, Gulf Oil Regional Industrial Hygienist Dr. Carrol, Practicing M.D. Mike Dole, Director Petro-Chemical Division Frank Roan; Employee Relations
PURPOSE OF VISIT:	To ascertain the extent of benzene exposure and the feasibility of using this facility for a retrospective mortality study.
UNIONS:	None

INTRODUCTION

The Division of Surveillance, Hazard Evaluations, and Field Studies is currently investigating the hazards of benzene exposure. On November 20, 1975, Ronald Young, Robert Rinsky, and Richard Hartle conducted a walk-through survey of the Gulf Oil Refinery, Petro-Chemical Division, Philadelphia operations. In addition, the facility's records were assessed for suitability for use in a retrospective mortality study.

The presence of benzene in practically all crude oils has been recognized from almost the beginning of the petroleum industry. The amount of benzene present in most crude oil is small and its separation in a relatively pure state is ordinarily uneconomical. Benzene cannot be separated readily by simple distillation because of azatope formation with various other hydrocarbons present. Instead, a petroleum fraction which has been either catalytically reformed or thermally reformed to increase the concentration of benzene (and toluene and xylene) can be fractionally distilled to give a narrow-boiling benzene concentration cut, which in turn can be subjected to (a) extractine distillation, (b) preferential absorption on silica gel, or (c) solvent extraction to separate the aromatic hydrocarbons.

DESCRIPTION OF THE FACILITY

The entire refinery complex covers approximately 900 acres located at the Southwest side of Philadelphia. The refinery was established in the late 1920's and was adapted for exclusive use of mid-East petroleum. It has the capacity to refine 180,000 barrels of oil per day. The UDEX process of extraction was installed in 1960 with the thermal hydrodealkylation (THD) unit following in 1965. Both were constructed to increase the supply of benzene which is utilized in the production of cumene. Allied Chemicals is one of the largest purchasers of cumene from this facility. Other products from the Philadelphia refinery include propylene, elemental sulphur, and toluene.

DESCRIPTION OF THE PROCESS

Each process will be described by unit as follows:

UDEX Unit, No. 1732. (Figure 1)

The facility utilizes solvent extraction to remove aromatic hydrocarbons as the initial step in a three unit system of cumene production. A description of the process follows.

The initial phase of cumene production takes place at the UDEX unit. This unit employs an extracting process to remove toluene and benzene from reformate streams (hydrocarbons reforming) from a reforming unit.

Gulf currently licenses this process from Universal Oil Products and Udex is the trade name.

This process of extraction relies on the greater solubility of the aromatic hydrocarbons in a glycol solvent. Other non-aromatic hydrocarbons called raffinate, are not extracted and are rejected to gasoline. Originally, the unit was designed to recover benzene only; later, the unit was designed to recover both benzene and toluene.

The purpose of the UDEX process is to upgrade the quality of benzene and toluene from simple gasoline blending components, to a more valuable feedstock, called extract, for the cumene and THD units.

There are no chemical reactions involved in the UDEX process. Following extraction, benzene and toluene plus the glycol solvent are sent to a stripping tower (figure 2) where the solvent is removed and returned to the extracts. A small amount of olefins are removed in two clay towers and fractionation is all that is necessary for recovery of benzene and toluene. (Figure 3)

THD Unit, No. 1735

The second phase in the production of cumene is the conversion of toluene recovered from the UDEX unit previously mentioned. The conversion of toluene to benzene involves a process called thermal hydrodealkylation (THD). Dealkylation of toluene results in the formation of benzene. (See Figure 4)

Temperature and hydrogen are required for the reaction to occur. The reactants are maintained at 1180^{o}F for a controlled length of time with no catalyst needed. Hydrogen is introduced in a purified form to complete hydrogenation of the alkyl group following the removal of the benzene ring.

The process takes place in reactors called soakers, in which sufficient time is required for the reaction to occur. After this time allotment the material from the soakers is cooled and the reaction is stopped. Hydrogen and methane, which are formed during the reaction, are then removed. Final fractionation is accomplished in a 60 tray fractionator in which benzene is received at the upper section and is then sent to the Cumene Unit.

Cumene Unit, No. 1733 (Figure 5)

The third and final stage in the development of Cumene is the Cumene unit. This process utilized benzene from the UDEX and THD units, plus propylene. These substances are combined and preheated to 385^{o}F before entering two reactors whose purpose, theoretically, is to react one mole of benzene with one mole of propylene forming one mole of cumene. Since the feedstock of propylene is not 100% pure, unreacting saturates are recovered as LPG.

A catalyst consisting of solid phosphoric acid in pellet form is required for the reaction.

Effluent from the reactors contains unreacted benzene and propylene, cumene, and impurities (created from unreacting saturates) such as ethane, propane, and butane. Reactor effluent is sent to a flash tower for partial removal of these impurities. The stream is now fed through a recycle column, where unreacted benzene is collected and returned to the feed drum. Cumene leaves the recycle tower in a purified state and enters a series of three cumene towers. Pure cumene is collected at the top and cumene bottoms (which contain less than 5% cumene) are sent to gasoline blending.

THE SURVEY

The walk-through survey dealt mainly with the Petro-Chemical Division and the production of cumene. Following a meeting with Dr. Carrol, a walk-through of the cumene production process was made. Mike Dole, Director of the Petro-Chemical Division, assisted in the survey and explained the process.

Benzene exposure levels were furnished by Mr. DeGrafenread. A cross reference of Table I with Appendixes 1a, 1b, and 1c give concentrations at specific locations on the dates indicated. Mr. DeGrafenread also said that a peak concentration of 20 ppm of benzene had been found in the Quality Control Room, adjacent to the main control room. An employee may be exposed to these levels for short intervals, 2-3 times per shift. The refinery management is aware of the high exposure levels and is in the process of improving the condition by installing a new ventilation system.

Following the survey of the cumene manufacturing process, a tank farm was visited to view a benzene holding tank at the edge of the refinery. The harbor area was toured to view a typical barging operation.

Frank Roan, who is involved with employee relations, discussed the possibilities of a record search in order to establish a population involved with benzene exposure. Very good cooperation was experienced and it was determined that it would be possible to obtain the necessary information from the files. However, due to the small number of employees involved with the benzene unit and the other substances (cumene and toluene) they are exposed to, it is unlikely that this cohort will be chosen for study.

In an attempt to contact the local union representatives, it was discovered that the refinery is not represented by a union.

Potential Safety and Health Hazards

The major potential safety and health hazards observed during the survey were as follows:

1) Respiratory exposure to benzene vapors

2) Respiratory exposure to cumene vapors
3) Respiratory exposure to toluene
4) Fire hazards

MEDICAL, INDUSTRIAL HYGIENE AND SAFETY PROGRAM

Medical

Dr. Carrol is the occupational physician at the Philadelphia facility. Dr. Carrol gave us a brief tour of his clinic. The clinic equipment includes a spirometer and audiometric sound booth.

Dr. Carrol informed us that prior to 1966, a blood test was used to monitor employee exposure to benzene. From 1966 to the present, urinary phenals have been employed. No indication of hazardous exposure has been indicated by either type of test.

Industrial Hygiene

The industrial hygiene program at the Gulf Oil Refinery is currently conducted by Mr. Jim DeGrafenread. Monitoring of aromatic hydrocarbons is done by Mr. DeGrafenread approximately every six months. A Century Organic Vapor Analyzer is employed to measure total hydrocarbons. Charcoal tubes are used to measure benzene concentrations. Table 1 gives benzene concentrations arrived at in parts per million (ppm) by Mr. DeGrafenread on the dates indicated. By cross referencing Table 1 with the appendix as indicated on the table, sampling positions can be seen in the areas of the THD, benzene and cumene units.

No formal time table exists for visits to the facility by Mr. DeGrafenread. Surveys are established in response to any special problem. Current special surveys included asbestos, silica dust, carbon monoxide and lead.

Safety

The safety program at Gulf Oil is maintained by Mr. George Rideout, Safety Director. He is assisted by three safety inspectors whose duty consists of administering periodic programs, currently dealing with respiratory protection, confined space entry, noise and proper use of fire equipment. Safety shoes, glasses and hard hats are provided by the company.

CONCLUSIONS

From observations made and information gained during the surveys, the following conclusions are formed.

1. A retrospective mortality study on the effects of benzene would have to include a very large cohort if a rare disease such as leukemia is involved. With a latency period of only 14 years and a present total employment in the benzene area of only 22, it is doubtful that this industry alone could be used for such a study.

2. It is doubtful that employees are exposed to high levels of benzene. Operations involving benzene are contained and little manual labor is required for productivity.

FIGURE 1.

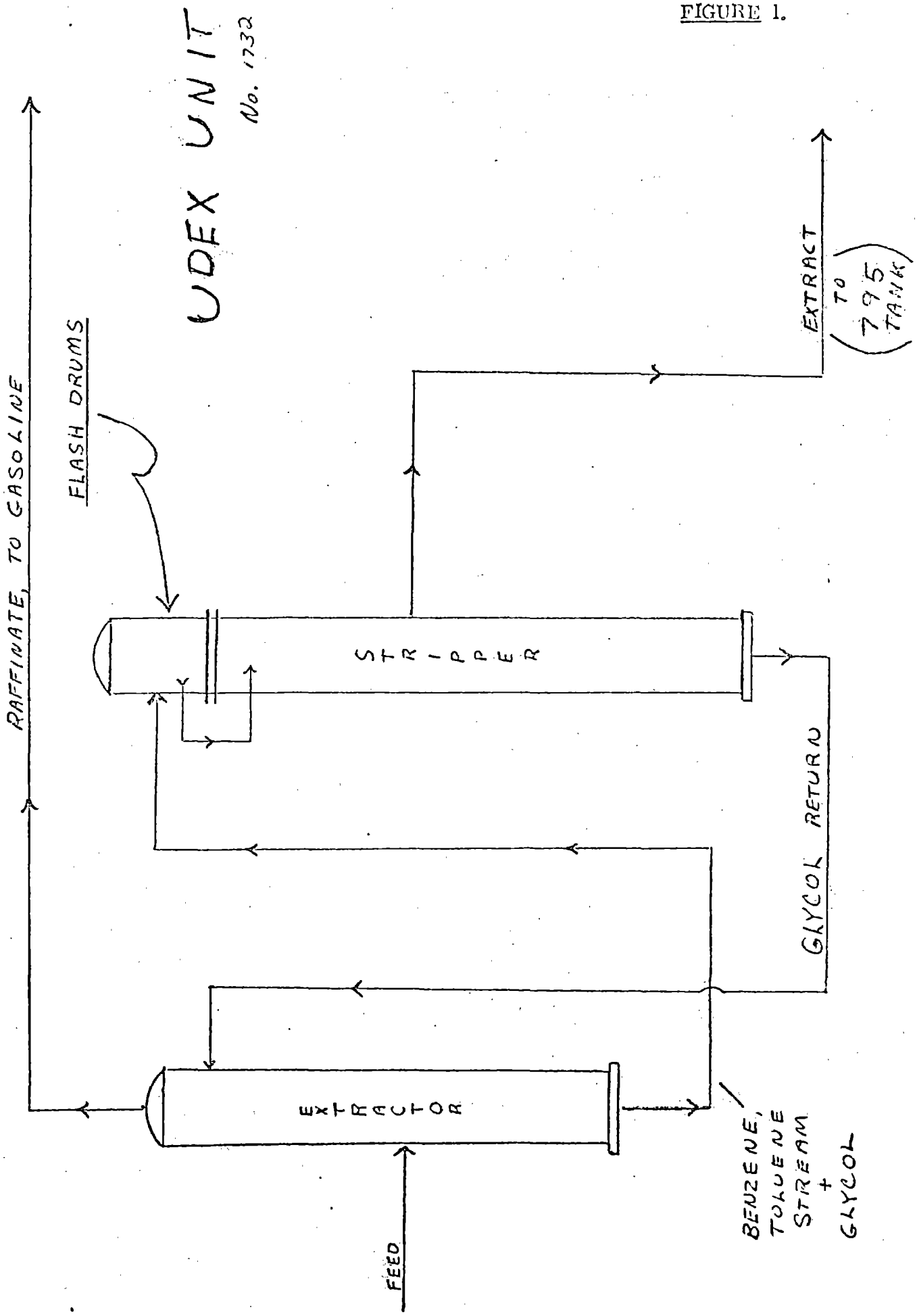

UDEX UNIT
No. 1732
RAFFINATE, TO GASOLINE
FLASH DRUMS
STRIPPER
EXTRACT
TO
795
TANK
GLYCOL RETURN
EXTRACTOR
BENZENE,
TOLUENE
STREAM
+
GLYCOL
FEED

Figure 2

Extractor on left, stripping tower on right.

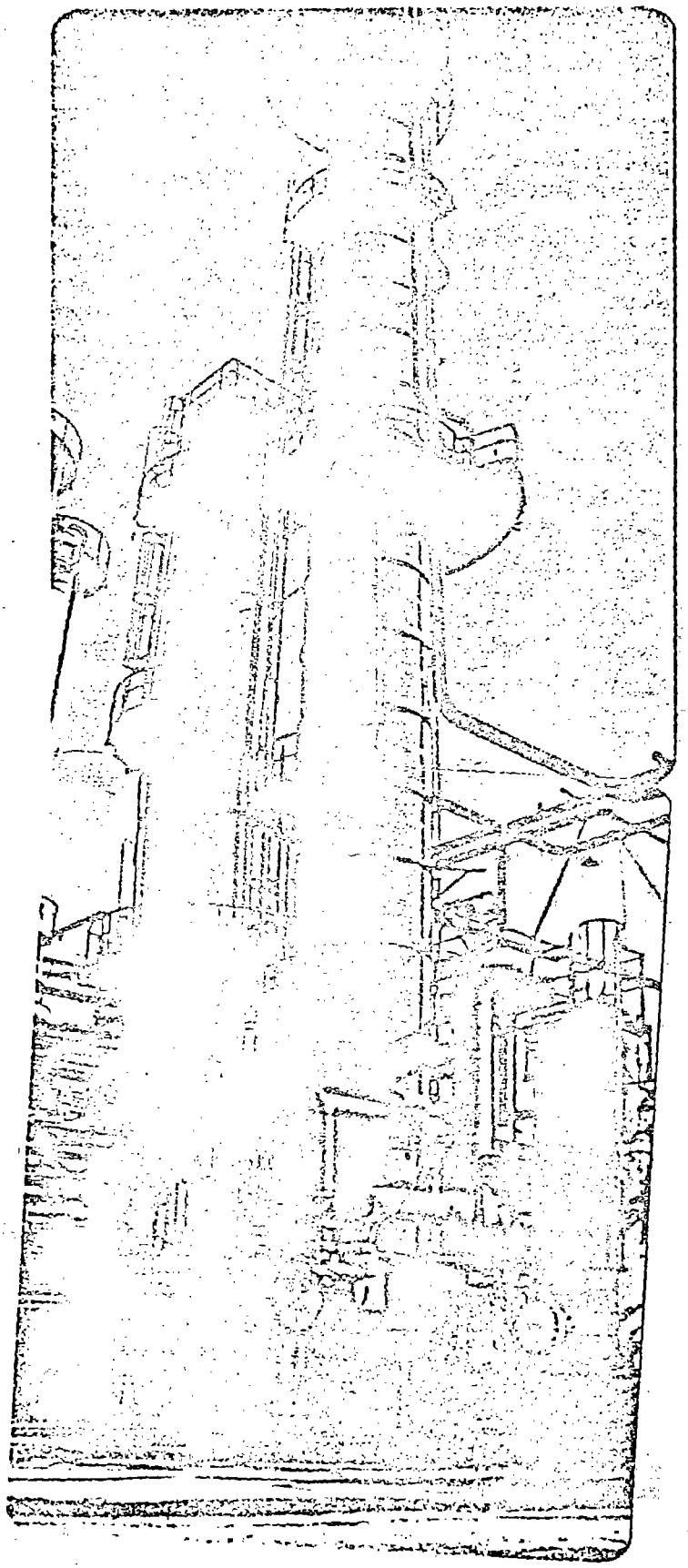
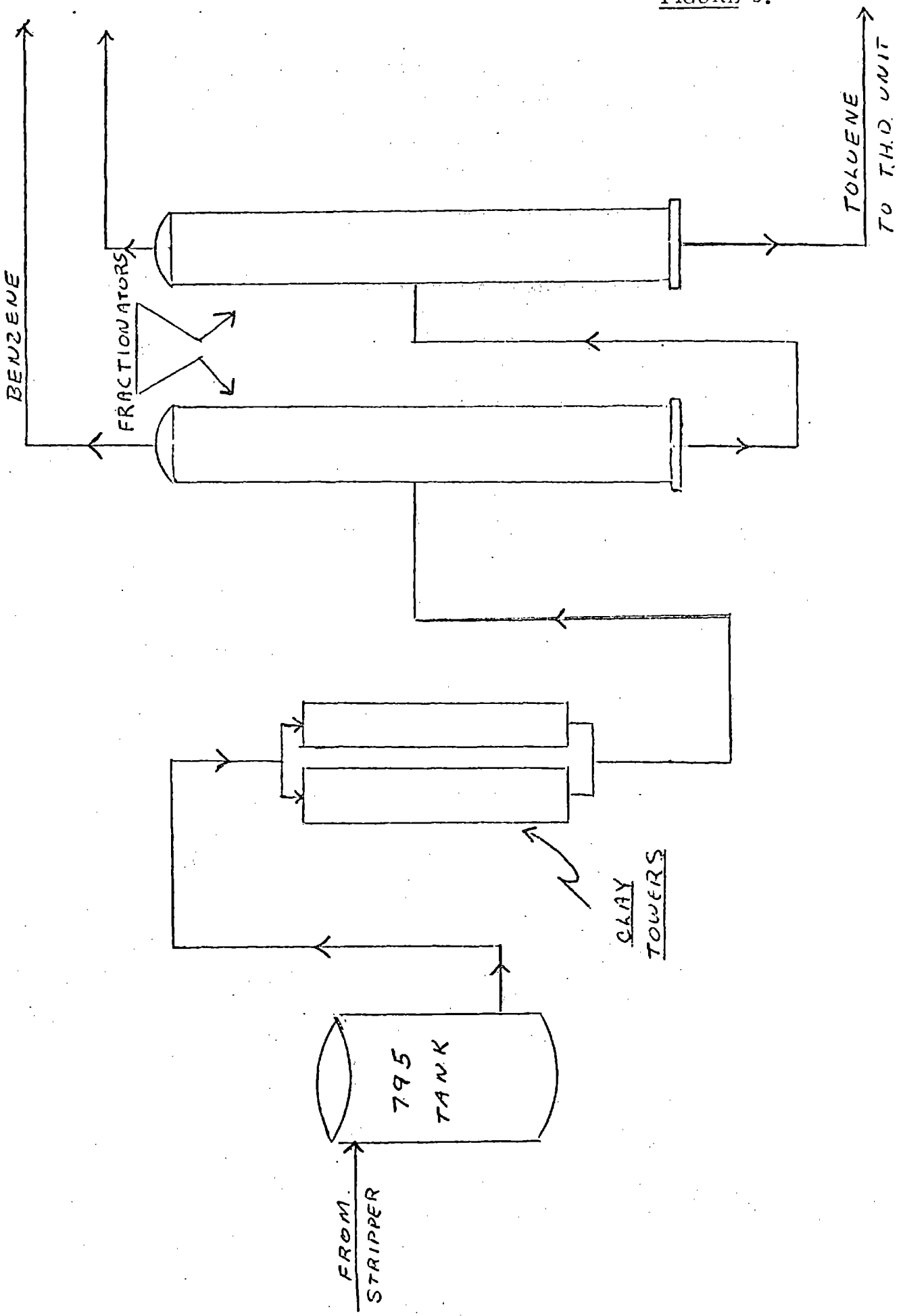


FIGURE 3.


BENZENE
FRACTIONATORS
TOLUENE
TO T.H.D. UNIT
CLAY
TOWERS
795
TANK
FROM
STRIPPER

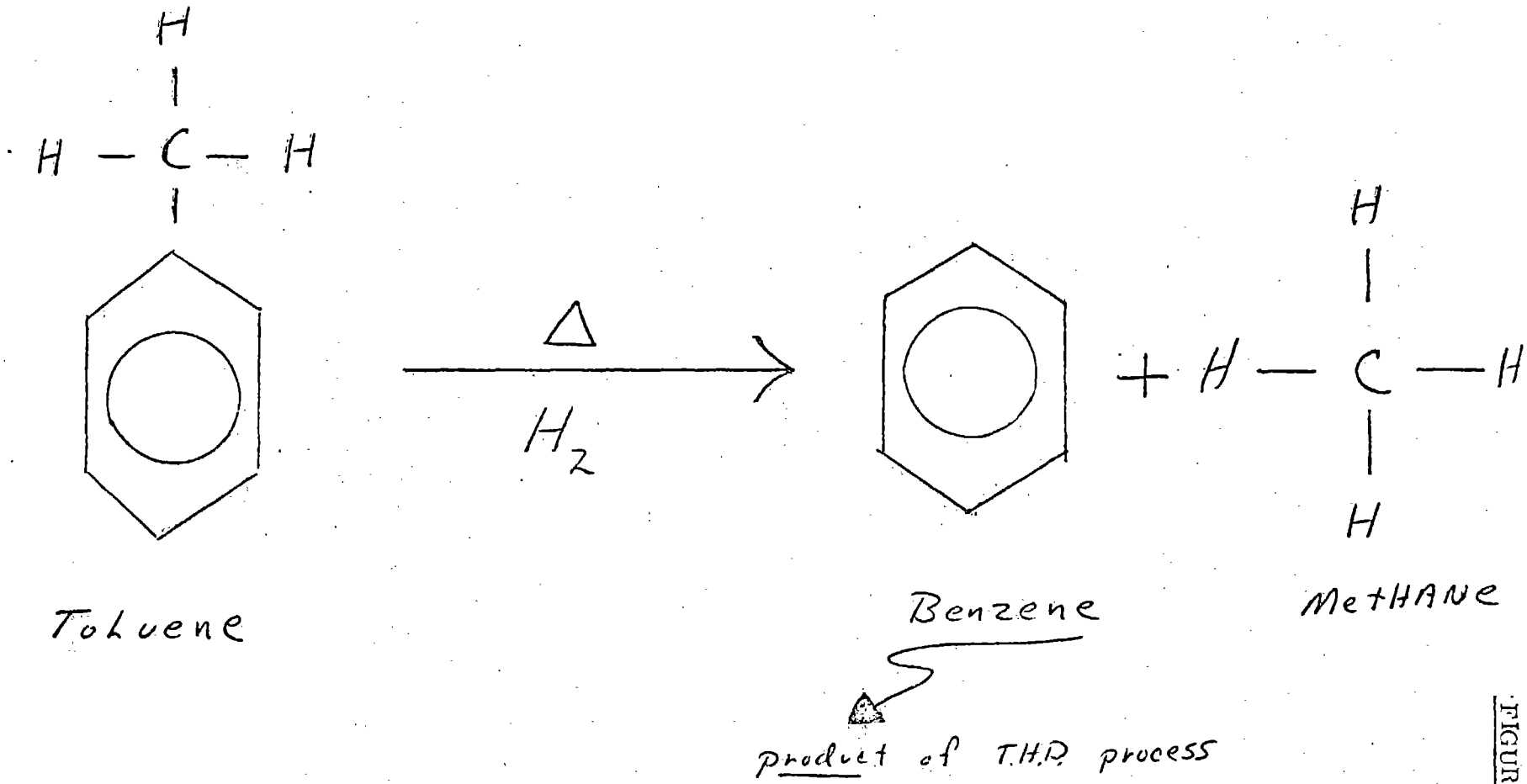

H
H — C — H
Toluene
Δ
H_2
Benzene
product of T.H.D process
+ H — C — H
H
H
Methane

FIGURE 4.

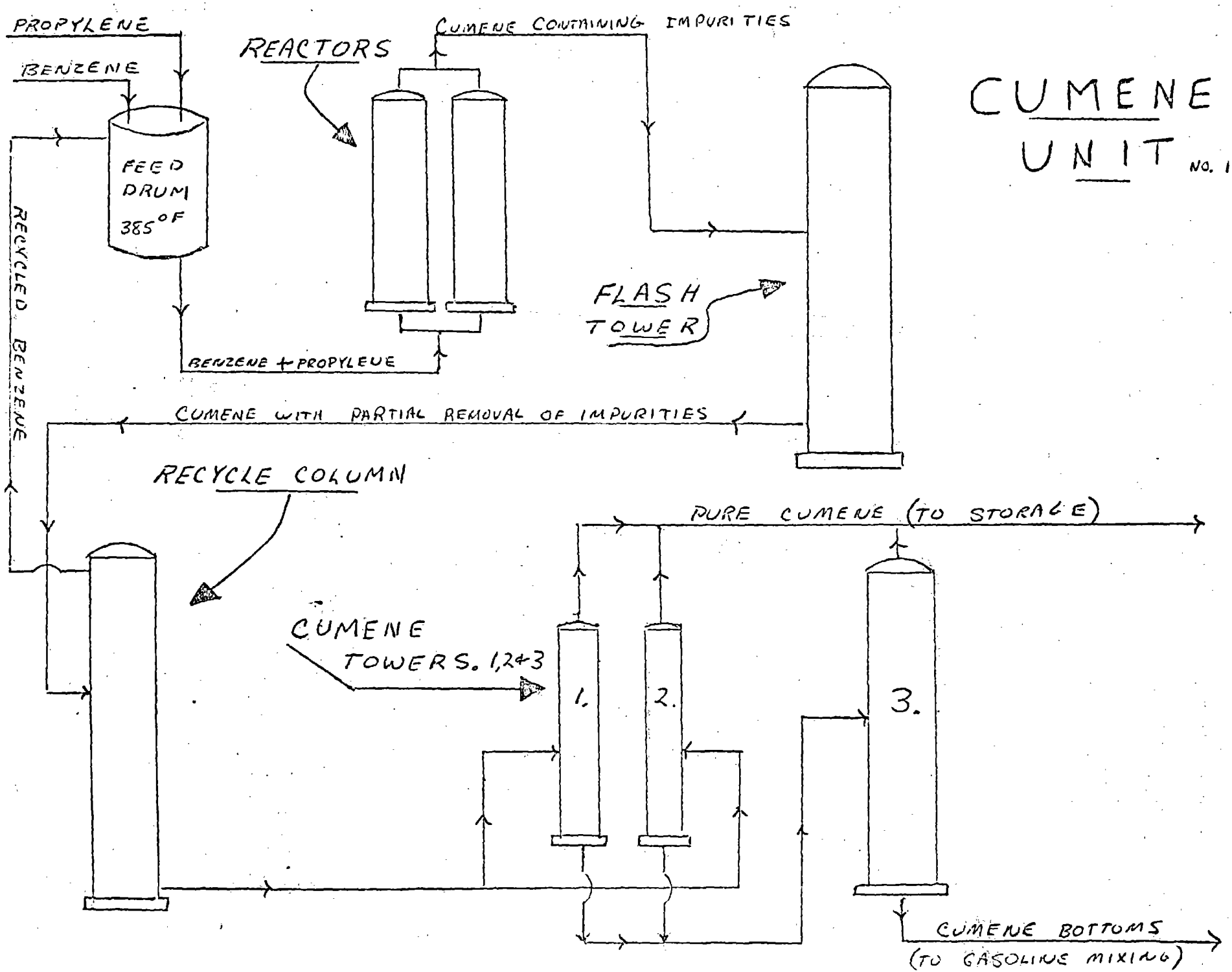

PROPYLENE
BENZENE
REACTORS
CUMENE CONTAINING IMPURITIES
CUMENE UNIT NO. 1733
FEED DRUM 385°F
RECYCLED BENZENE
FLASH TOWER
BENZENE + PROPYLENE
CUMENE WITH PARTIAL REMOVAL OF IMPURITIES
RECYCLE COLUMN
PURE CUMENE (TO STORAGE)
CUMENE TOWERS. 1,2+3
1.
2.
3.
CUMENE BOTTOMS
(TO GASOLINE MIXING)

FIGURE 5.

TABLE I

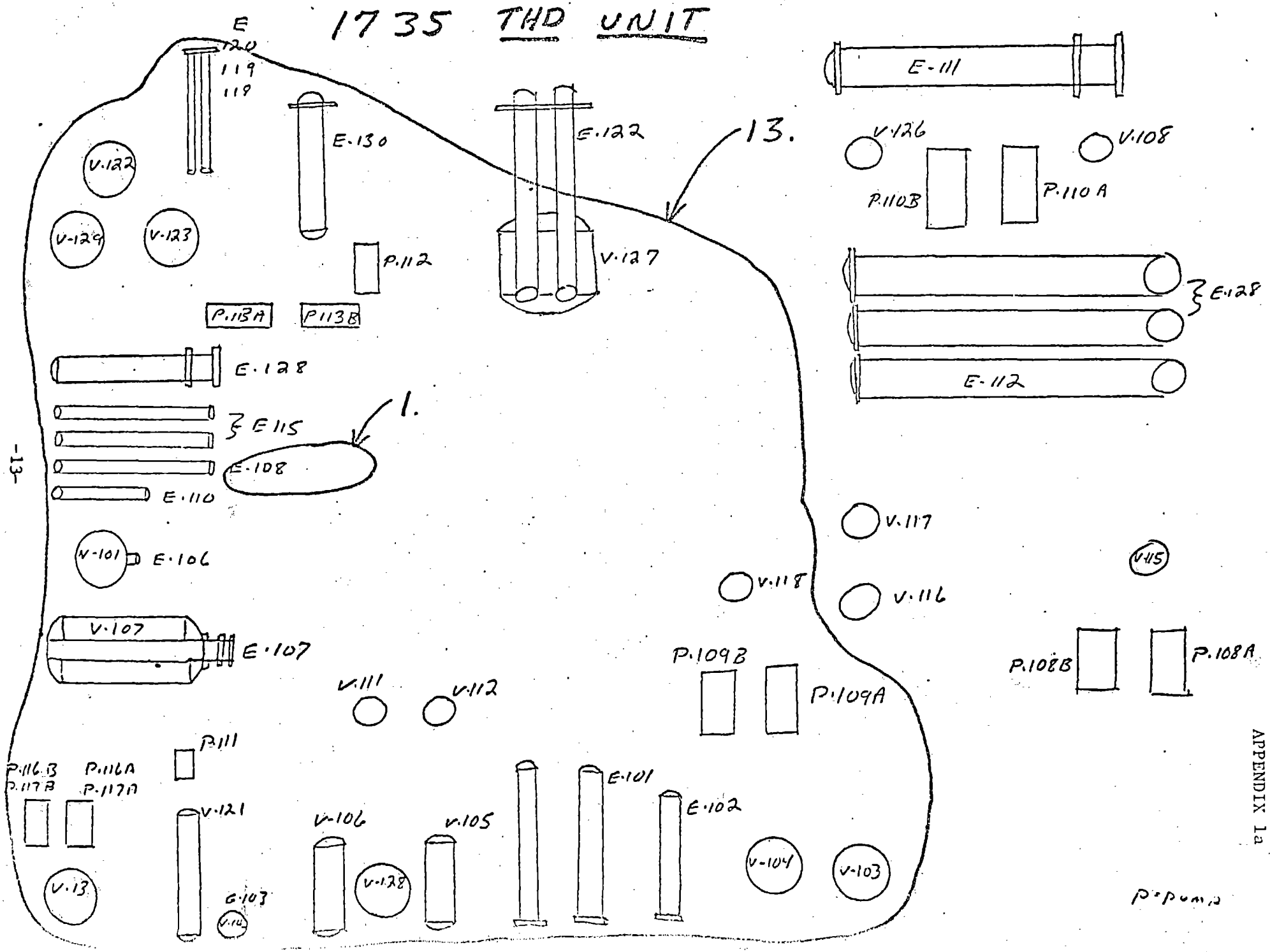
Benzene Concentrations in PPM by Date as Indicated

SAMPLE LOCATION	Appendix I.D. Number	6 - 12 - 73	6 - 13 - 73	6 - 15 - 73	6 - 21 - 73	6 - 28 - 73	11 - 6 - 73	11 - 7 - 73	2 - 20 - 74	11 - 20 - 74	7 - 17 - 75	UNKNOWN
East of E-108 Appendix 1a	1.	1	0	0		2.5				1	.4	
Outside Control Room Appendix 1b	2.	1	0	0	3	4				2	.4	
North of Benzene Tower Reboiler Appendix 1b	3.	<1								1	2	
Pump 28-B Appendix 1b	4.							4-8*	5			
Pump 22-A Appendix 1b	5.								6			
Benzene Tower Reboiler Appendix 1b	6.		5.5	1	4	6			<1	1	3	
Stripper Appendix 1b	7.								1			
Pump 1a-B Appendix 1b	8.								2			
Pumps 5A & B Appendix 1b	9.	11	1	1	14	12		3-15*	4	1	2	
Pump 8-B Appendix 1c	10.								1			
Pump 3-B Appendix 1b	11.								2			
Pump 5-B Appendix 1b	12.	10	9	9	6	4			16	<1	3	
Average HC levels THD area Appendix 1a	13.											1-
Benzene Unit Area Appendix 1b	14.							1-2*				
Pumps 1-6 Appendix 1c	15.						15-75*					

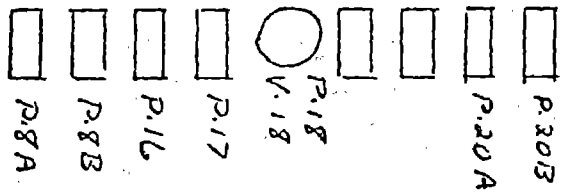
*Total HC levels

Data furnished by Gulf Oil

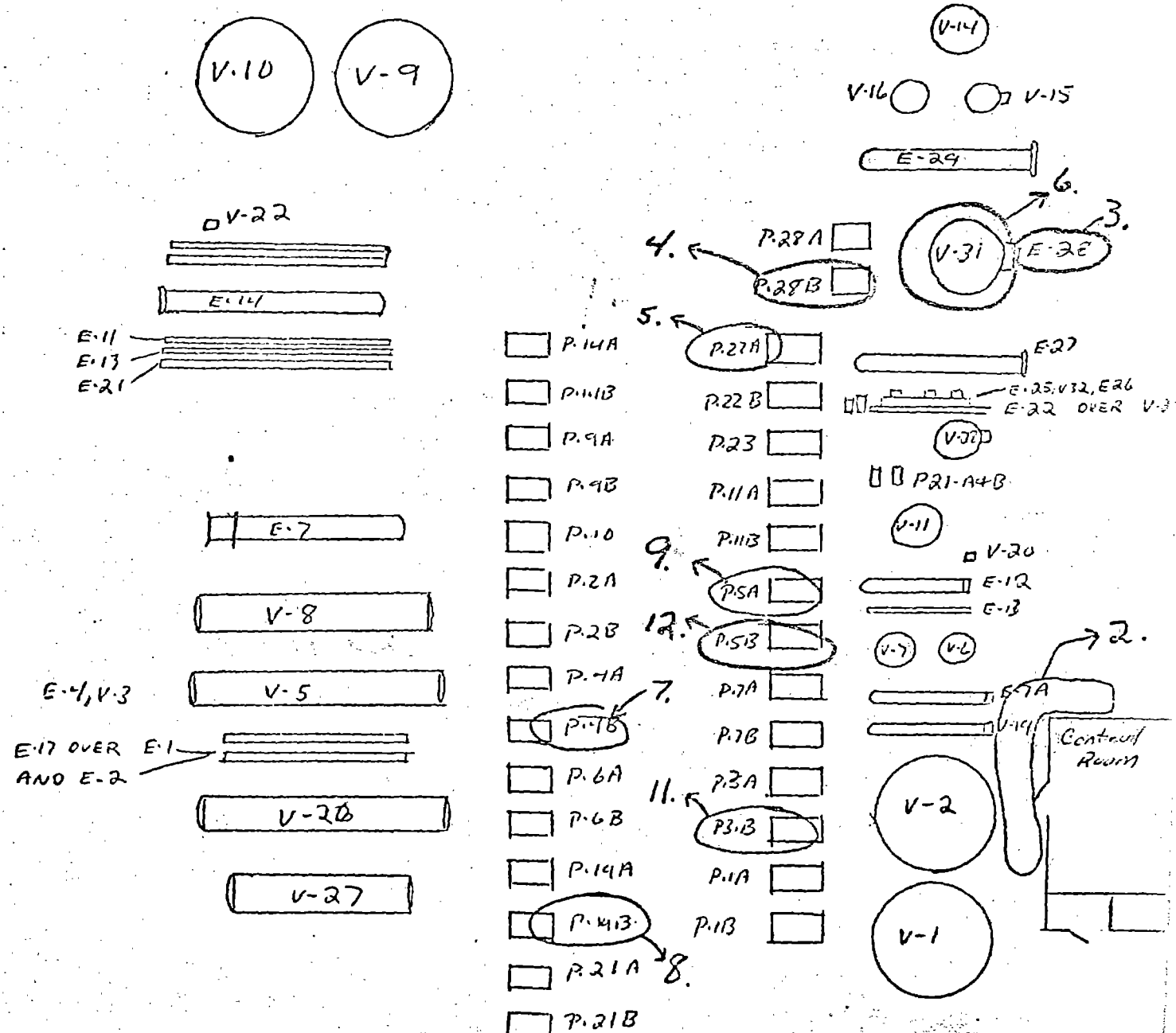
APPENDIX


1735 THD UNIT
E 120
119
119
E-130
V-122
V-124
V-123
P.112
P.113A
P113B
E-122
V-127
13.
E-111
V-126
V-108
P.110B
P.110A
E-128
E-112
E-128
E 115
E-108
1.
E-110
V-101
E-106
V-107
E-107
V-117
V-118
V-116
V-115
P.109B
P.109A
P.108B
P.108A
V-111
V-112
P.111
P.116B
P.117B
P.116A
P.117A
V-121
V-106
V-105
E-101
E-102
V-104
V-103
V-13
G-107
V-14
V-128
P-Pump

1732 BENZENE UNIT



14. AREA AVERAGE



P- PUMP

1733 CUMENE UNIT