PHASE III SURVEY REPORT #9

WORKER EXPOSURE TO POLYAROMATIC HYDROCARBONS AT SELECTED PETROLEUM REFINERY PROCESS UNITS

SURVEY LOCATION:

TEXACO REFINERY
CASPER, WYOMING

Survey Dates:

12-14 AUGUST 1980

Report Date:

NOVEMBER 1980

DISCLAIMER

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ABSTRACT

This industrial hygiene survey of a petroleum refinery is one of nine performed during Phase III of a NIOSH-sponsored study characterizing worker exposure to polyaromatic hydrocarbons (PAHs) in three different types of process units. Personal and area air samples were collected in the fluid catalytic cracker and delayed coker (pressure coke still) units, and area samples only in the asphalt processing unit. A silver-membrane filter followed by Chromosorb 102 was used for sampling, and analysis for 23 individual or groups of PAHs was performed by gas chromatography/mass spectrometry. All 22 of the personal and area PAH air samples had detectable quantities of at least five PAHs or groups of PAHs, with the cumulative PAH concentration for individual samples ranging from 17.1 $\mu g/m^3$ for an area sample from the asphalt processing unit to as high as 1,347.2 $\mu g/m^3$ for one FCCU area location. The upwind boundary sample showed none detected.

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CONTENTS

CONTENTS (continued)

FIGURES

TABLES

I. INTRODUCTION

Enviro Control, Inc. (Enviro) is under contract to the National Institute for Occupational Safety and Health (NIOSH) to perform a study entitled, "Industrial Hygiene Characterization of Petroleum Refineries." Because petroleum refining is a complex industry involving such a large number of potentially hazardous agents, the study was structured in four progressive phases to enable the development of a meaningful yet manageable study plan. The first two phases of this study have already been completed with the information and resulting recommendations having been presented in the Phase I Report (April 1979) and the Phase II Report (November 1979). Following is a brief description of these two initial phases as well as descriptions of Phases III and IV.

- Phase I: A detailed literature search was performed including the industrial hygiene aspects and the potential occupational health problems associated with this industry. Preliminary fact-finding surveys were conducted at three refineries. This phase culminated in a preliminary study protocol which recommended the investigation of potential carcinogens in three types of refinery process units: the fluid catalytic cracker, the delayed coker, and the asphalt processing unit.

- Phase II: An attempt was made to identify specific compounds associated with some degree of cancer-causing potential in the three study process units. Area air samples were collected for a variety of compounds at three refineries, two of which were visited previously during Phase I. Results consistently showed the presence of polyaromatic hydrocarbons (PAHs) in the three study process units.

- Phase III: The objective of this main phase of the study is to characterize worker inhalation exposure to PAHs in the three study process units. Personal and area air samples will be collected in a total of nine refineries.

- Phase IV: A final report will be prepared integrating the results and information from the three previous phases.

Phase III is currently in progress. The Texaco refinery at Casper, Wyoming was the ninth refinery visited as part of Phase III, and this report presents the information and air-sampling data for PAHs collected during that survey.

The Phase III industrial hygiene survey of the Texaco refinery was conducted over a period of 3 days, August 12-14, 1980. The first day was devoted to an opening conference and a walk-through of the study process units; the personal and area air-sampling program was carried out on the second and third days. Initial contact for this visit was made through the corporate Manager of Environmental Health. All subsequent arrangements were made through the refinery Safety Supervisor.

The opening conference was held with representatives from the refinery, the refinery corporate office, and Enviro (list of attendees in Appendix). The two representatives from Enviro described the project, the status, and the specific objectives of the survey. A tentative schedule was agreed upon for the 3 days. A similar conference was held with a representative of the Oil, Chemical, and Atomic Workers International Union (OCAW) employed at the refinery. After the meetings, the survey team conducted a walk-through of the three process units to be sampled. At the fluid catalytic cracker unit (FCCU) and the delayed coker (pressure coke still), where personal monitoring was scheduled, the Enviro industrial hygienists explained the sampling procedures to the employees.

On the day shifts of the second and third days, area and personal sampling was conducted in the FCCU and the delayed coker unit. Only area samples were collected in the asphalt processing unit.

II. REFINERY DESCRIPTION

This Texaco refinery, located in Casper, Wyoming, is along the bank of the North Platte River on the eastern edge of the city. With its crude capacity of about 21,000 bbl/day, this refinery is classified as a "small" refinery for the purposes of the study. Since Texaco is one of the 15 largest companies in terms of crude capacity, the company is considered a "major" oil company. The significance of categorizing this refinery by these criteria is explained in the Phase II Report.

This refinery was originally built by Texaco in the 1920's and currently occupies over 300 acres. At the time of the survey, it was operating at close to capacity and producing a full line of petroleum products which included:

- propane
- butane
- gasoline
- Diesel oil
- kerosene
- sponge coke
- asphalt
- No. 6 fuel oil

Two types of Wyoming crude are separately refined here at different times. The primary type (about 67%) is categorized as a "light," "low-sulfur" (0.3% sulfur by weight), "mixed base" (containing both paraffins and naphthenes) crude with an API Gravity Index of 39.0. The other type of crude is a "heavy," "sour" (3.0% sulfur by weight), "mixed base" type with an API Gravity Index of 24.5. At the time of the survey, the latter type was being refined. All of the crude is received by pipeline while the products are shipped primarily by pipeline and tank truck; railcars are used to a limited extent.

The major process units at the Texaco refinery include:

- crude distillation unit (includes vacuum unit)
- hydrotreating unit
- catalytic reformer
- FCCU
- polymerization unit
- delayed coker unit (pressure coke still)

Figure II-1 shows a rough plot plan of the main production area. The FCCU and delayed coker have their own separate control rooms; the crude, hydrotreating, and catalytic reformer units share a common control room. Several tank farms are to the east, north, and west of the production area. The crude storage tanks are located to the north across the river.

There is a total of approximately 200 employees; this includes 40 supervisory and administrative and 50 maintenance workers. Most of the routine maintenance activity is performed in-house; contractors are brought in for turnarounds and other major maintenance work. The production units operate 24 hours a day, 7 days a week. There are normally four work crews that rotate on a unit (8-hour shifts).

The safety and health staff at this refinery includes the safety supervisor, an occupational nurse, and a part-time physician. The nurse is on the premises full time during the day shift 5 days a week while the physician is at the refinery 2 days a week. The dispensary and treatment room is fully equipped to handle first aid situations and various routine examinations. Almost all of the employees are trained in first aid. All of the production and maintenance workers are given preplacement medical examinations, and annual follow-ups are available.

The safety supervisor performs industrial hygiene sampling for such hazards as benzene, hydrogen sulfide, asbestos, lead, and hydrocarbons. Texaco also has a staff of corporate industrial hygienists who perform specialized periodic surveys at the various facilities. At this refinery, they have

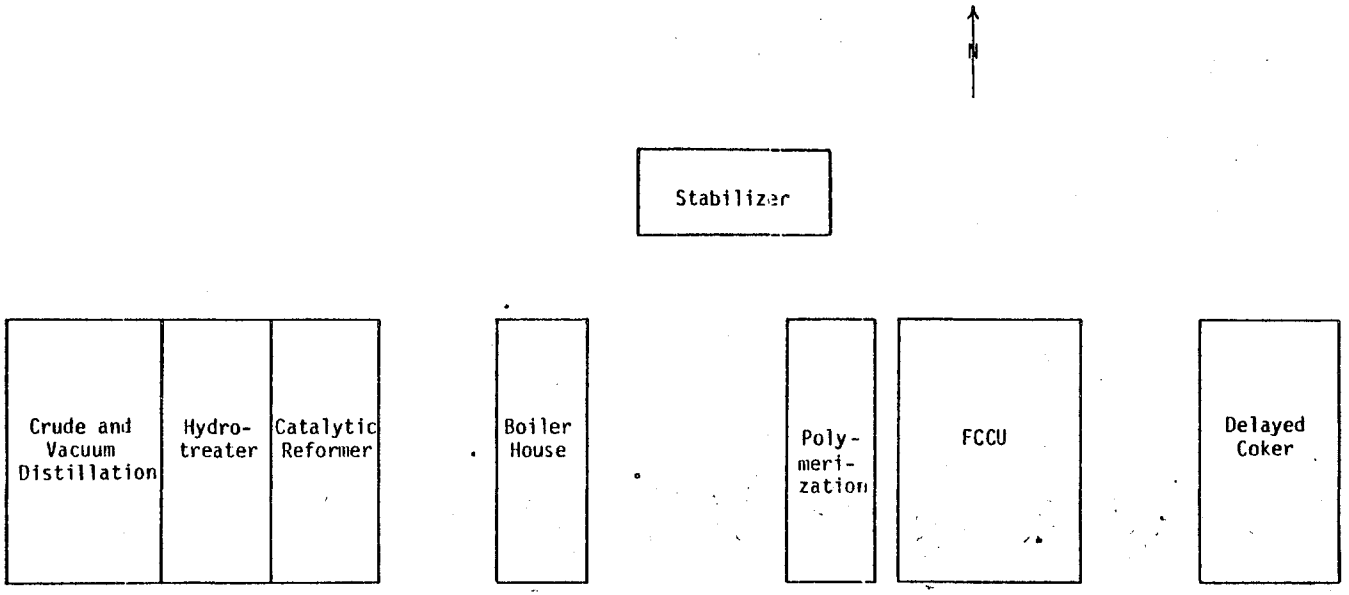

FIGURE II-1. Refinery Main Production Area

sampled for welding fumes, silica, and PAHs (benzene-soluble fraction). In the near future, the corporate industrial hygiene group will develop a specific periodic sampling program that each refinery will follow.

As part of good industrial hygiene practice, the use of protective clothing and equipment (e.g., hard hats, safety shoes) is emphasized. Special work clothes are not worn by the production workers at this refinery. Each unit has locker and wash facilities; shower facilities are located at the entrance of the refinery. While eating is allowed in most control rooms, smoking is permitted only in designated areas away from the production units. All new employees attend an intensive one-week training course which includes information on unit equipment, operations, respirator use, safety hazards, fire protection, and first aid.

III. STUDY PROCESS UNITS

FLUID CATALYTIC CRACKING UNIT (FCCU)

A. Unit and Process Description

The FCCU is located in the main production area, about 200 feet west of the delayed coker unit (Figure II-1). The present unit, including the flue gas cooler, was built in 1947; the single riser to the reactor has been replaced and enlarged several times. The current production capacity is about 7,000 bbl/day.

The unit covers an area of about 200 x 150 feet and includes three separate enclosed buildings (Figure III-1). On the west side of the unit, a long building running north to south houses the control room and the compressors. At the north end of the unit, a second building contains all of the major process stream pumps in two separate rooms. These pumps include the decant oil, slurry recycle, debutanizer, light cycle gas oil, and slurry reflux. The third building along the south border of the unit contains the bottom sections of the reactor, regenerator, flue gas cooler, and precipitator. Just to the east of this building are the two catalyst hoppers and the gas-fired furnaces. In the middle of the unit running west to east are the fractionator, slurry boiler, decant oil holding drum, absorber, and debutanizer. The ground level of the entire unit is constructed of concrete.

The fresh feed (atmospheric and vacuum gas oils) for the FCCU comes from the crude unit and is preheated to a suitable temperature by the gas-fired furnaces. This fresh feed plus slurry recycle from the fractionator are injected into the reactor where catalytic cracking is initiated as the hot oil feed contacts the catalyst. The catalyst at this refinery is an alumina-like synthetic zeolite common in other FCCUs studied in this project. The product vapors and the catalyst are separated in the

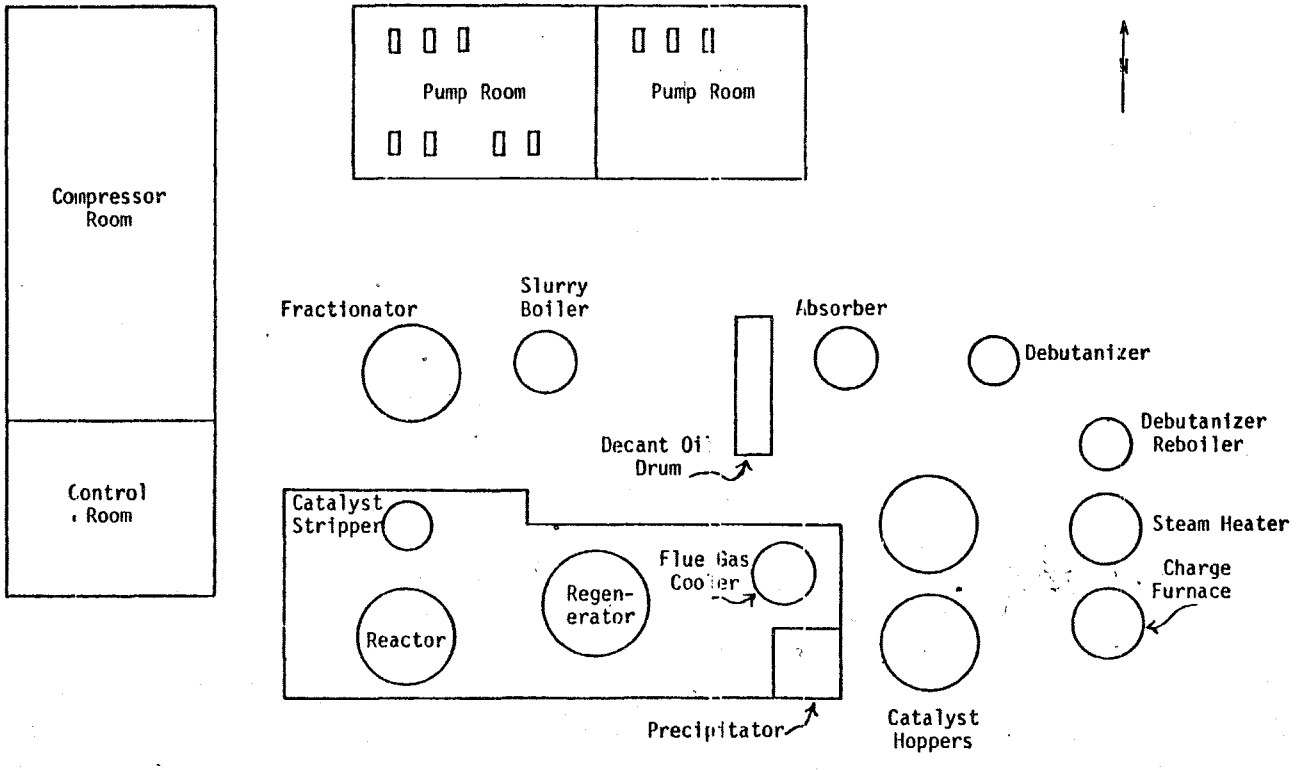

FIGURE III-1. FCCU

single feed riser line and the reactor itself. The hydrocarbons are taken to the fractionator tower where the various products are separated. The catalyst is stripped of any remaining oil with steam and delivered to the regenerator where the spent catalyst is reactivated by oxidizing the accumulated carbon at a temperature of about 1,200°F (649°C). The flue gas from the regenerator goes to the flue gas cooler and the electrostatic precipitator before being released to the atmosphere.

The main products from the fractionator are:

- butane
- propane
- gasoline
- light cycle gas oil
- decant oil
- fuel gas

B. Work Force

There are normally four workers assigned to the FCCU full time during each shift. Following is a brief description of the duties of these personnel:

- Stillman — Supervises the overall unit operations, paying particular attention to any problems such as leaks or equipment malfunctions. Works closely with the outside helper and the two control room operators. Can assist with any outside activity, including minor repairs or maintenance; however, normally spends his time outside the control room (about 60% of shift) patrolling and inspecting the various production areas. He normally spends about 15% of his shift inside the pump building.

- Helper — Primary responsibility is to assist the stillman as needed and to perform the routine outside duties. These include maintaining the numerous pumps, taking temperature and pressure readings, collecting process stream samples (normally not during the day shift), cleaning up equipment and any spills, and general unit housekeeping. Periodically, he also patrols the entire FCCU to detect any malfunctions. Spends about 70% of the shift in the production areas, including about 20% in the pump building.

- Control Room Operators (two) — These two inside boardmen spend essentially 100% of their time inside, monitoring and logging in the various meters and charts on the control boards. One is designated as the "cat controlman" and is responsible for the reactor/regenerator and related equipment; the other operator is designated the "fractionator controlman." They both work closely with the stillman.

C. Exposure Control Measures

The primary exposure control measure used at this FCCU is a closed-system process which limits exposure to products, by-products, and intermediates. Also important is a well-organized maintenance program that provides both efficient preventive and repair maintenance services. Under normal operating conditions, exposure to PAHs may occur from fugitive emissions (especially from pumps), from the regenerator flue gas, during sampling of the various streams, and during maintenance and housekeeping activities.

Enclosed buildings housing equipment are of great advantage during the winter months, reducing maintenance due to freezeups and also facilitating any work on the equipment. The major disadvantage of these buildings that do not have mechanical ventilation is that the potential for vapor (e.g., PAH) accumulation from spills and fugitive emissions greatly increases. Heavy-fraction pumps, such as those for slurry recycle and decant oil, have been associated with fugitive PAH emissions in previous surveys. It is

especially important at this unit that these pumps be maintained properly and that workers spend as little time as possible in this building. The building housing the base of the reactor, regenerator, and flue gas cooler also houses process streams containing PAHs; however, fugitive emissions are not expected to be as likely here since pumps are not involved. Increased PAH levels should not be a factor in the compressor room since heavy-fraction streams are not normally present there. The control room is not air-conditioned or under positive pressure, and is frequently downwind of the production areas. This is of particular concern since several operators spend a considerable portion of their shift there.

The regnerator flue gas first goes to a flue gas cooler and then to an electrostatic precipitator to remove catalyst fines before being discharged through a stack into the atmosphere. The recovered heat produced here is used to generate steam.

Most process stream samples are collected during the evening (1500-2300) or morning (2300-0700) shifts; no samples are normally collected during the day shift. Laboratory technicians collect gas samples (e.g., regenerator flue gas) using a rubber inner tube; the unit operators (usually the helper) collect liquid samples (e.g., naphtha, light cycle gas oil, slurry recycle, fresh feed) by the open spigot-and-bottle method without sampling loops. The samples are taken to the laboratory for analysis.

Exposure during routine maintenance is difficult to minimize, especially if it occurs in any of the enclosed buildings. There are concrete floors with effective sewer systems in the pump buildings and throughout the unit, simplifying cleanup procedures. The refinery has its own craft maintenance crews (e.g., pipefitters, electricians) that provide preventive and repair services. The last major turnaround for this unit was during September 1978.

Hard hats and safety shoes are routinely worn on these units, and eye protection is available. There are no routine operations that require the use of respirators; however, NIOSH-approved air-purifying and self-contained breathing-air respirators are available. These respirators are maintained by the foremen.

DELAYED COKER UNIT (PRESSURE COKE STILL)

A. Unit and Process Description

The delayed coker unit is referred to as a pressure coke still (PCS) at this refinery. Although it is slightly different from the other delayed coker units surveyed during this study, the thermal cracking process is essentially the same. Therefore, for the purposes of this study, this unit is considered a delayed coker unit. It is located at the east end of the production area, directly east of the FCCU (Figure II-1). This unit, built in 1946, has two pairs of 44-foot coke drums with a daily capacity of about 125 tons of sponge coke.

Figure III-2 illustrates the layout of this unit which covers an area of about 150 x 150 feet. The large brick building at the north end of the unit houses the control and locker rooms and two pump rooms. The larger of the two pump rooms is called the "hot pump room" and contains several heavy-fraction pumps including the charge pumps. Just to the south of the hot pump room are the #1 and #2 tower fractionators, the coke tower (an open, multilevel structure that includes the four coke drums), and the soaker. To the north and west of the building are the blowdown tank, lean oil cooling box, naphtha accumulator, and coke handlers' locker and wash room. The charge furnace and absorber are in the southeast corner of the unit. The ground level of the entire unit is constructed of concrete.

The coke drums are cut with a steam-driven mechanical drill; the drill shaft is housed beneath each drum below ground level. As the coke is cut, it falls onto a moving conveyor belt which loads a dump truck positioned just to the west of the charge furnace. The truck takes about 10 loads of coke per cutting to a nearby company (not Texaco) that performs a calcining

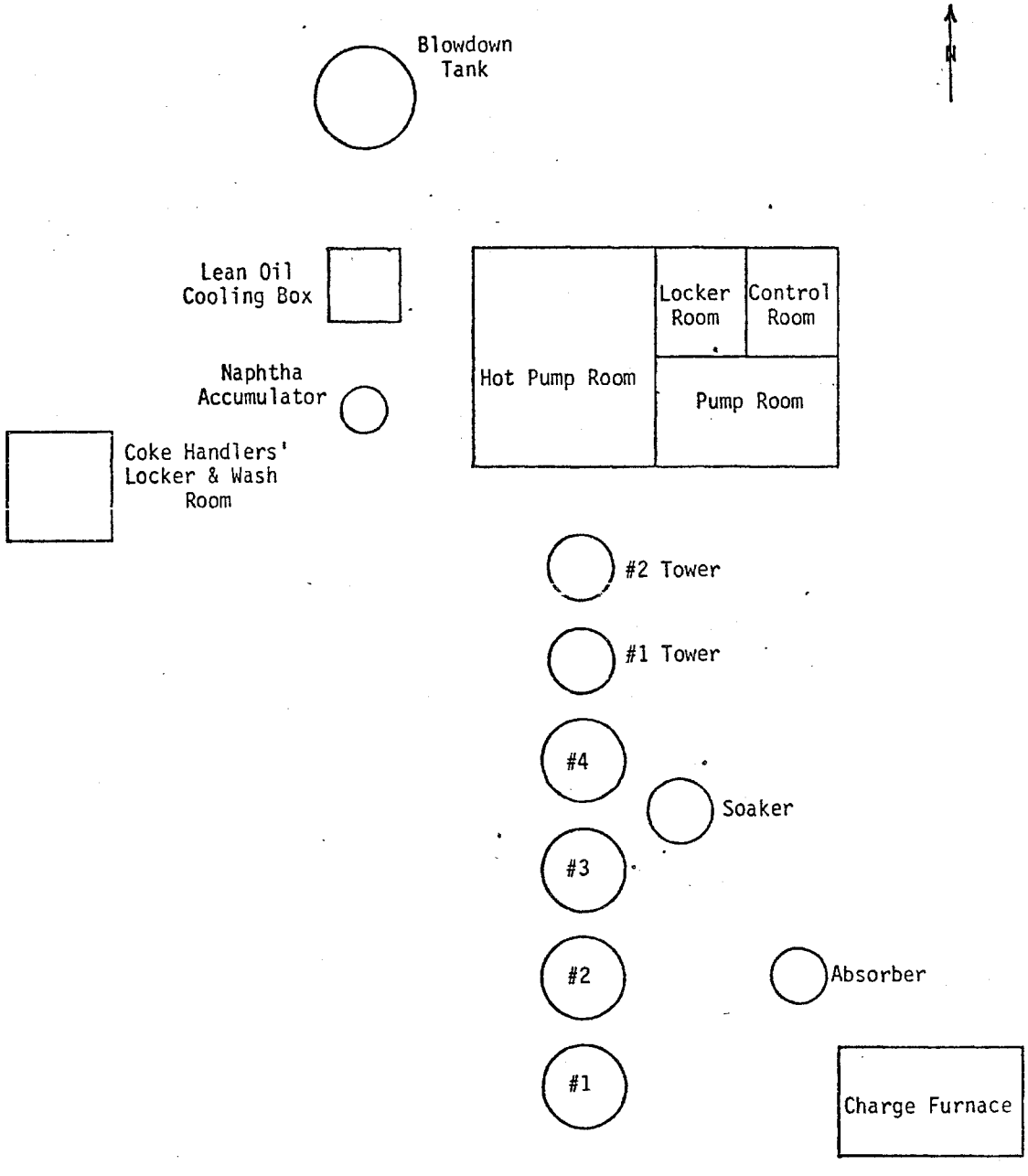

FIGURE III-2. Delayed Coker Unit (Pressure Coke Still)

operation. The company is located about 300 yards east of the unit within the refinery boundary lines.

The type of coke produced here is a #2 grade, referred to as sponge coke. The charge is a mixture mainly of vacuum residual from the crude unit with smaller amounts of light cycle gas oil and decant oil from the FCCU and recycled gas oil ("clean oil"). This mixture is pumped to the #1 tower fractionator that separates the lighter fraction from the heavy "black oil." This black oil is pumped directly to the soaker while the lighter fraction goes on to the #2 tower fractionator, where "clean oil" is separated from the naphtha and fuel gas fraction. The clean oil is pumped to the charge furnace, then to the soaker where it mixes with and heats the black oil. This heated mixture of clean and black oils is then directed to one of the four drums where the thermal cracking process begins. Each drum has a 32-hour cycle with coke formation lasting about 16 hours. Because there are four drums, one drum is cut every 8 hours. The lighter vapor fractions of the thermal cracking operation are removed from the top of the drum and recycled back to the #1 tower fractionator. The clean oil, most of which is not thermally cracked, is included in this recycled portion. Products from this unit other than sponge coke include fuel gas, propane, butane, naphtha, cycle gas oil, and cycle fuel oil.

About 6 hours before the cutting operation is scheduled, coke formation is stopped by switching the feed valve to the other drum of the pair. Immediately, steam is introduced into the charge lines to cool the drum. This lasts about an hour, and then water is added to further cool the drum (3 hours). Six hours after the feed is switched, the top and bottom of the drums are opened; and the coke is cut from the bottom with the steam-driven metal drill. The cutting operation lasts about 2 hours.

After cutting is completed, the top and bottom of the drum are replaced; the drum is pressure-tested for seal, heated, and is ready to begin coke formation when the feed is switched from the other drum.

B. Work Force

The work force for the delayed coker unit is divided into two groups, the operational group and the coke-handling group. The two-person operational group works the normal 8-hour shift; following is a brief description of their job activities.

- Stillman — Has overall responsibility for the operations of this unit, including coke cutting; works closely with the controlman and head cleaner. Normally spends from 25 to 33% of his shift in the control room; the rest of the shift he patrols the entire unit, including the various levels of the coke tower, to monitor the other operators and to detect any equipment malfunction. Other duties include opening and closing valves to direct process streams, oiling the various pumps, and occasionally collecting process stream samples (e.g., fresh feed).

- Controlman — Spends the great majority of his shift in the control room, monitoring and logging in the various meters and charts on the control board. Works closely with the stillman. He normally collects two process stream samples (i.e., naphtha, clean oil) during each shift.

The coke-handling group is normally made up of the head cleaner and still cleaner who also work the normal 8-hour shift. During the survey, there were also two trainees for the still cleaner position. Following is a brief description of the two regular coke handlers.

- Head Cleaner — Supervises the entire cutting operation. His duties include directing the positioning of the deheading platform and cutting engine, supervising the deheading operation, opening and closing various valves for water and steam lines, and performing the actual cutting. The cutting station is on the ground level about 10-15 feet from the cutting engine. After cutting is finished, he spends part of the remainder of his shift in the coke handlers' locker and wash room.

- Still Cleaner — Works under the supervision of the head cleaner. Deheads the top and bottom of the drum, positions the deheading platform and cutting engine, positions and secures the steam lines, and cleans the area of loose coke. He also operates the dump truck.

C. Control Measures

The coke-cutting operation is one of the few in a refinery that is not a closed system. Because of this, it is more difficult to minimize worker exposure during this operation. During every cutting cycle, the top and bottom of the drum must be opened manually; the deheading platform, the cutting engine, and blades must be positioned; the coke must be cut by the head cleaner; and the general area must be cleaned of loose coke. At this unit a metal drill is used to cut the coke instead of the more usual hydraulic type, and the driller (head cleaner) is positioned at ground level instead of in the penthouse located at the top of the drum. The cut coke falls directly onto a conveyor that loads a dump truck. There are several important advantages and disadvantages concerning worker exposure associated with the coke-cutting method used at this unit.

The use of the conveyor belt to move the coke directly to the dump truck eliminates the necessity of a crane or any other type of coke-handling equipment that has been associated with worker exposure to PAHs in previous surveys. The elimination of the enclosed room at the top of the drum (penthouse) is also an advantage since this room is considered a likely area for PAH accumulation. However, at this unit the driller (head cleaner) was situated within 15 feet of the bottom of the drum being cut and occasionally directly downwind of the steam and particulates being generated. The coke at this point has been cooled and hydrocarbon vapor is not likely, but exposure from dermal contact and to coke particulates is likely.

The mechanical cutting eliminates the copious amounts of water associated with hydraulic cutting and also eliminates the related water-holding and recycling structures (e.g., sluiceway, containment pit, filtering system). The disadvantage of the decreased water usage is the increased potential for

coke dust generation. However, this was not noticed during the survey; this may be due to the fact that the drums are filled with water for cooling, and the coke is sufficiently wet to suppress dust generation during cutting.

The opening of the top and bottom of the drum was done efficiently and quickly. The two cleaners normally open the top and bottom of the drum within about 45 minutes. The cutting engine is positioned directly beneath the drum and, at this point, the still cleaner must manually position the cutting blades so that they are in the correct cutting position. The still cleaner normally wears a slick suit and face shield during this operation since considerable water is still draining from the drum. Cleanup is performed at the end of each cutting operation. This consists of removing fallen coke from around the conveyor system and hosing down the entire area.

All workers at this unit wore hard hats and safety shoes. Coveralls were provided but not worn. Lockers and wash facilities were available in both the main control room (operational workers) and the separate building for the coke handlers. Shower facilities are also located near the front entrance of the refinery. There are no routine operations that require the use of respirators; however, NIOSH-approved air-purifying and self-contained breathing-air respirators are available. The operations crew ate in the control room while the coke handlers ate and rested in their separate building. Neither room was air-conditioned or under positive pressure.

Like the FCCU, the pumps are in enclosed rooms without mechanical ventilation. PAH accumulation is a possibility, especially in the larger hot pump room which contains several heavy-fraction pumps. It is important that the pumps be properly maintained to minimize fugitive emissions and that the operators spend as little time as possible in the enclosed pump rooms.

The steam that is used to cool the drums is sent through a blowdown drum before it is vented to the atmosphere. A flare is available for turnarounds or any other conditions that might require it.

ASPHALT PROCESSING UNIT (VACUUM PIPE STILL)

A. Unit and Process Description

The asphalt processing at this refinery is limited to the vacuum distillation process which is part of the crude unit; the bottoms from the fractionating tower are pumped to storage (and blending) and to the delayed coker unit as asphalt without any further processing. The atmospheric and vacuum distillation processes are located together at the west end of the production area (Figure II-1) and called the vacuum pipe still (VPS). The VPS is monitored out of the control room which is also shared with the adjacent hydrotreating and reformer units. The asphalt production capacity of this refinery is about 1,500 bbl/day.

B. Work Force

No worker is assigned full time to the vacuum section of the VPS. One or more of the outside operators spend a small part of their shift covering the equipment associated with asphalt processing.

IV. SAMPLING PROGRAM

PROTOCOL

The sampling protocol for Phase III surveys, detailed in the Phase II Report (November 1979), was followed as closely as possible during the survey of this Texaco refinery. Sampling for airborne PAHs was conducted during the day shifts on the second and third days of the survey in the three study process units. Two locations were chosen in each unit where area samples were collected. The area sampling cassette containing a silver-membrane filter followed by Chromosorb 102 (Figure IV-1) was used with a portable MSA high-flow pump. To investigate the size distribution of airborne particles in the study process units, a total particulate area air sample was collected at each sampling site for optical sizing. These samples were collected using an open-face cassette containing a mixed cellulose ester filter (0.45-μm pore size) and a portable MSA Model S pump calibrated at 2.0 ℓ/minute. A modified sampling device (Figure IV-2) was used for personal monitoring for PAHs. The Chromosorb 102 was packed in a glass tube following the cassette rather than in the cassette itself. An upwind sample was collected each sampling day at the northeast boundary of the refinery. A total of 22 samples was collected over the 2 days.

The analytical method for PAHs used in Phase III was a modification of the method used in Phase II. Gas chromatography/mass spectrometry was again used but without high-pressure liquid chromatography that is needed to resolve some of the groups of PAHs. This difference reduced the number of individual or groups of PAHs, for which the method is capable of analyzing, from 27 to the 23 listed below.

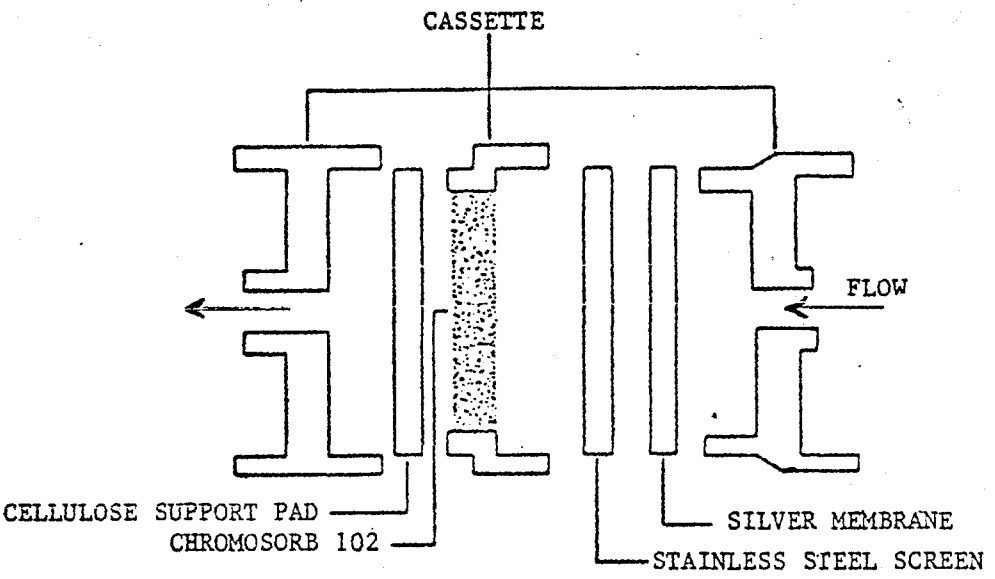

FIGURE IV-1. PAH Sampling Assembly

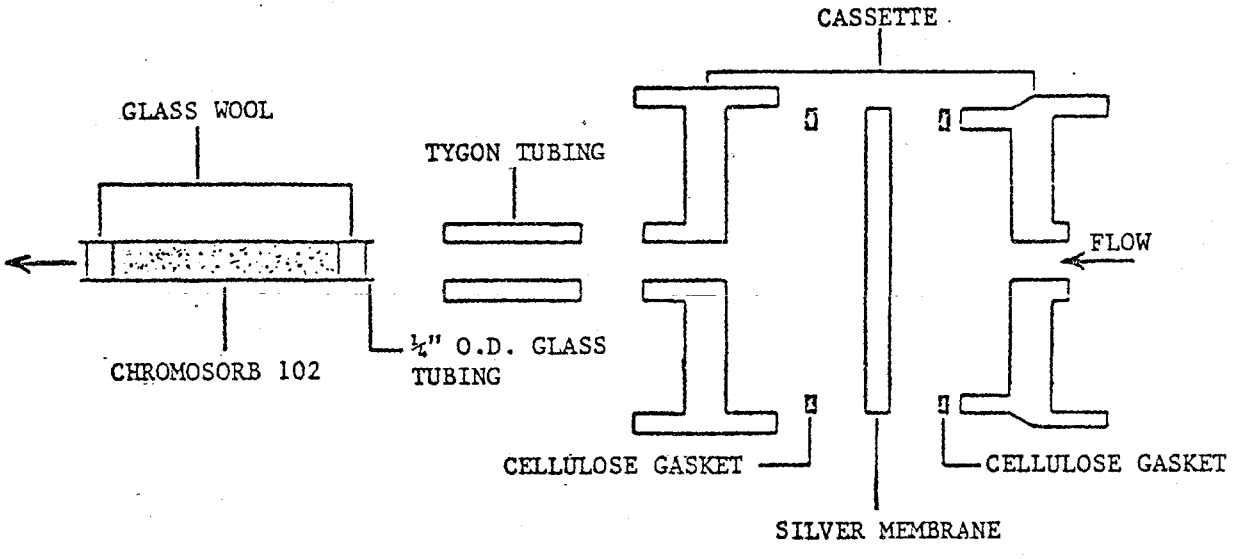

FIGURE IV-2. Personal Monitoring Device for PAHs

1. Naphthalene*
2. Quinoline*
3. 2-Methylnaphthalene
4. 1-Methylnaphthalene
5. Acenaphthalene
6. Acenaphthene
7. Fluorene
8. Phenanthrene*/Anthracene*
9. Acridine
10. Carbazole
11. Fluoranthene
12. Pyrene*
13. Benzofluorene
14. Benz(a)anthracene*/Chrysene*/ Triphenylene
15. Benzo(e)pyrene*/Benzo(a)pyrene*
16. Perylene
17. Dibenz(a,j)acridine*
18. Dibenz(a,i)carbazole*
19. Indeno(1,2,3-cd)pyrene*
20. Dibenzanthracene*
21. Benzo(g,h,i)perylene
22. Coronene
23. Dibenzpyrene*

The "*" designates those compounds considered to have some degree of cancer-causing potential (detailed discussion in Phase II Report). As with the Phase II method, the specific isomers of dibenzanthracene and dibenzpyrene are not distinguishable.

For sizing, the particulate sample is prepared for optical microscopy by rendering the mixed ester filter transparent with an immersion fluid. The prepared slide is focused in the field of the optical microscope; and particles are sized using a Porton reticle grid, which is mounted in the ocular lens so that the grid is superimposed on the field of the microscope. The reticle is calibrated at the magnification to be used by means of a stage micrometer.

B. Sampling Conditions

Weather conditions for the first sampling day (August 13) were sunny with partly cloudy skies in the early morning, turning overcast by late morning; the temperature ranged from 61°F (16°C) in the morning (0730) to about 80°F (27°C) by early afternoon (1430). The relative humidity during this period ranged from 69% down to 35%; the winds were from the northeast at 0-3 mph.

On August 14, the skies were very overcast early in the morning, clearing with sunny skies by noon. The temperature ranged from 59°F (15°C) at 0730 to 80°F (27°C) by 1415. Relative humidity ranged from 75% to 40% with the wind direction very erratic at 0-10 mph.

FCCU

A. Area Sampling

Two locations within enclosed buildings (Figure IV-3) were selected to collect the area samples in the FCCU. Location F-1 was in one of the pump rooms of the building at the north end of the unit; the sampling units were located on the slurry recycle pump which returns the fractionator tower bottoms, which include spent catalyst, back to the reactor. Several other pumps including the decant oil pump were nearby. This location was sampled on August 13 during the day shift.

Location F-2, inside the riser room at the south end of the unit, was sampled on August 14. The sampling units were located on a shelf about 6 feet from the start of the riser and about 4 feet above the floor.

B. Personal Sampling

All four full-time FCCU operators described in Chapter III were sampled during the day shifts on August 13 and 14.

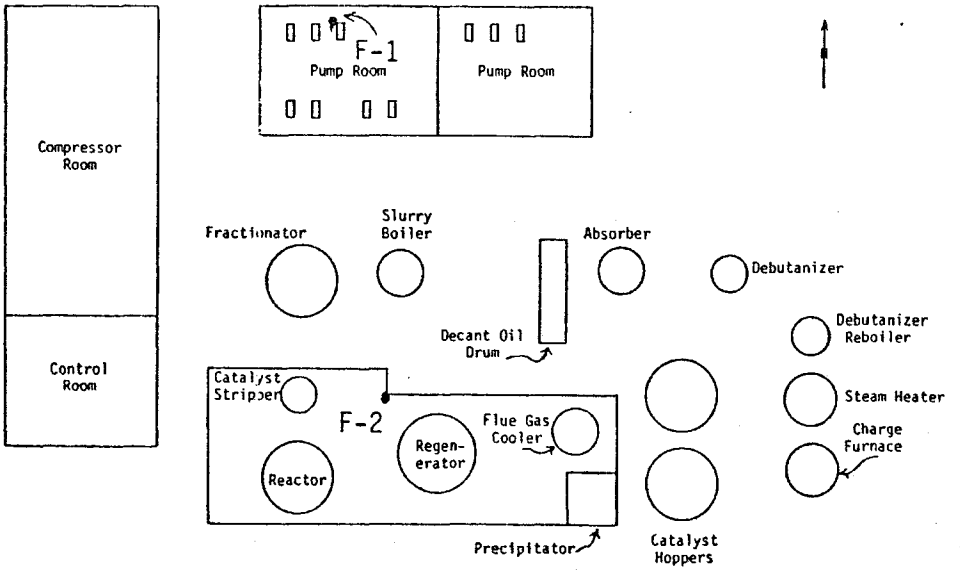

FIGURE IV-3. FCCU Sampling Locations

DELAYED COKER UNIT (PRESSURE COKE STILL)

A. Area Sampling

Figure IV-4 shows the two area sampling sites selected in the delayed coker unit. Location D-1, inside the hot pump room, was sampled during the day shift on August 13. The sampling units were positioned about 5 feet from the charge pump (#P-373) and about 4½ feet above the floor. The steam-driven reciprocating pump moves the charge to the #1 tower fractionator. Location D-2, downwind of the coke-cutting operation, was sampled during the day shift on August 14. Because of the shifting wind direction, the sampling units were shifted 1 hour after sampling was started. The locations were 5-8 yards downwind of the drum being cut (#1 drum).

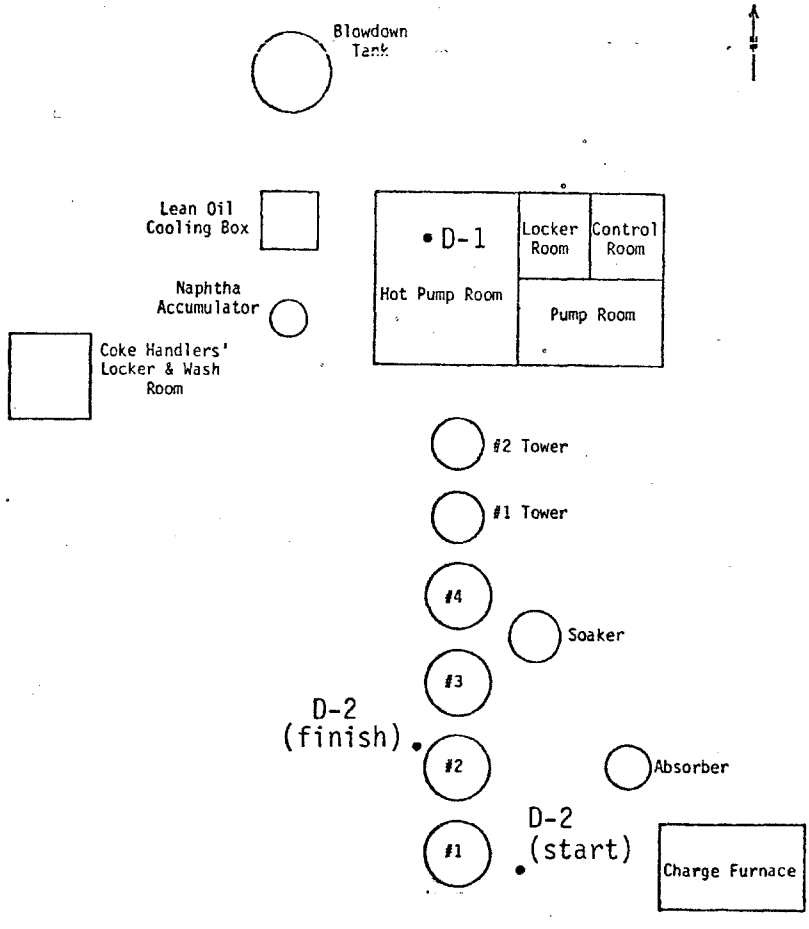

FIGURE IV-4. Delayed Coker Unit Sampling Locations

B. Personal Sampling

The two operational shift workers (stillman, controlman) and the two coke handlers (head cleaner, still cleaner) described in Chapter III were sampled during the day shifts on August 13 and 14.

ASPHALT PROCESSING UNIT (VACUUM PIPE STILL)

A single location very close to the asphalt pump was sampled during both shifts. The asphalt pump which moves the vacuum bottoms to storage is located in an enclosed pump room adjacent to the control room. The sampling units were located about 3 feet from the pump and about 6 feet above the floor.

V. RESULTS AND DISCUSSION

The complete results of the area and personal PAH samples collected at this Texaco refinery are presented in Tables V-1 and V-2. All 22 of the personal and area PAH samples analyzed from the three study process units had detectable quantities of at least 5 of the 23 PAHs (or groups of PAHs) for which the samples were tested. The cumulative PAH concentrations for individual samples ranged from 17.1 $\mu g/m^3$ for an area sample from the asphalt processing unit to as high as 1,347.2 $\mu g/m^3$ for an FCCU area sample. The upwind boundary sample showed none detected; the second upwind sample was not analyzed because of the very erratic wind direction during sampling the second shift.

A summary of the personal and area sampling results, including the mean (arithmetic) cumulative PAH concentrations ($\overline{X}$) for the three types of process units, is presented in Table V-3. On the average, personal samples from the FCCU and delayed coker were quite similar with the samples from the delayed coker showing a slightly higher mean cumulative PAH concentration (172.4 $\mu g/m^3$ vs. 157.5 $\mu g/m^3$) and number of PAHs identified (7-10 vs. 6-9). Because of one extremely high sample, the area samples from the FCCU were considerably higher than the delayed coker area samples (724.3 $\mu g/m^3$ vs. 331.0 $\mu g/m^3$); however, a larger number of PAHs were identified in the delayed coker samples (9-12 vs. 6-8). The asphalt unit area samples were much lower than those from the other two units ($\overline{X}$ = 18.1 $\mu g/m^3$, 5-7 PAHs).

The distribution of individual PAHs by ring number was consistent in all samples. The 2-ring compounds were found in the highest concentrations, and as the ring numbers increased the concentrations decreased. Only minimal amounts of the 4-ring and no 5-, 6-, or 7-ring PAHs were found in the samples.

TABLE V-1. PAH Analytical Results (μg/m³) for Personal and Area Samples Collected at the FCCU and Asphalt Processing Unit[a]

Ring No.	Sample Location:	FCCU										ASPHALT	
		AREA		Stillman		Helper		Inside Operator				AREA	
		F-1	F-2					Cat. Side		Fraction. Side		A-1	A-2
	Sample Date:	8/13	8/14	8/13	8/14	8/13	8/14	8/13	8/14	8/13	8/14	8/13	8/14
	Sample Volume (ℓ):	809	830	894	889	910	919	899	888	892	909	857	838
	Sample Time:	0725-1422	0710-1418	0703-1430	0705-1434	0700-1435	0656-1433	0709-1434	0658-1431	0707-1433	0700-1430	0650-1412	0637-1345
(2)	Naphthalene*	702.19	50.45	182.12	49.69	49.80	33.66	40.62	27.60	54.79	16.92	5.67	7.64
(2)	Quinoline*	--[b]	--	--	--	--	--	--	--	--	--	--	--
(2)	2-Methylnaphthalene	377.14	33.72	266.23	48.66	62.22	49.52	49.87	31.29	60.57	20.43	8.32	7.77
(2)	1-Methylnaphthalene	252.99	15.96	74.80	16.78	23.68	15.66	13.75	13.31	19.28	8.35	3.06	2.84
(2)	Acenaphthalene	--	--	--	--	--	--	--	--	--	--	--	--
(2)	Acenaphthene	4.32	--	3.09	0.53	0.82	0.24	0.39	--	--	--	--	0.18
(3)	Fluorene	3.23	0.48	2.98	0.70	0.68	0.56	0.32	0.50	0.91	0.43	0.02	0.20
(3)	Phenanthrene*/Anthracene*	7.17	0.84	8.15	1.21	1.61	1.09	0.88	1.34	1.60	1.12	0.03	0.35
(3)	Acridine	--	--	--	--	--	--	--	--	--	--	--	--
(3)	Carbazole	--	--	--	--	--	--	--	--	--	--	--	--
(4)	Fluoranthene	0.01	--	0.10	--	--	0.02	--	--	--	0.02	--	--
(4)	Pyrene*	0.14	0.05	0.43	--	0.04	0.09	--	0.07	0.01	0.11	--	0.05
(4)	Benzofluorene	--	--	--	--	--	--	--	--	--	--	--	--
(4)	Benz(a)anthracene*/ Chrysene*/Triphenylene	--	--	--	--	--	0.02	--	--	--	--	--	--
(5)	Benzo(e)pyrene*/ Benzo(a)pyrene*	--	--	--	--	--	--	--	--	--	--	--	--
(5)	Perylene	--	--	--	--	--	--	--	--	--	--	--	--
(5)	Dibenz(a,j)acridine*	--	--	--	--	--	--	--	--	--	--	--	--
(5)	Dibenz(a,i)carbazole*	--	--	--	--	--	--	--	--	--	--	--	--
(6)	Indeno(1,2,3-cd)pyrene*	--	--	--	--	--	--	--	--	--	--	--	--
(5)	Dibenzanthracene*[c]	--	--	--	--	--	--	--	--	--	--	--	--
(6)	Benzo(g,h,i)perylene	--	--	--	--	--	--	--	--	--	--	--	--
(7)	Coronene	--	--	--	--	--	--	--	--	--	--	--	--
(6)	Dibenzpyrene*[c]	--	--	--	--	--	--	--	--	--	--	--	--
	TOTAL	1,347.19	101.50	537.90	117.57	138.85	100.86	105.83	74.11	137.16	47.38	17.10	19.03

* Suggested as having some cancer-causing potential.
[a] Blank values have been subtracted from data. Data have not been corrected for temperature and pressure variation; maximum deviation would be within ±2% of actual values.
[b] "--" designates compounds not detected.
[c] Specific isomers not distinguishable by analytical method; reported value represents any one or combination of existing isomers.

TABLE V-2. PAH Analytical Results (μg/m³) for Area and Personal Samples Collected at Delayed Coker Unit and Upwind Location[c]

Ring No.	Sample Location:	AREA		OPERATIONAL				COKE HANDLERS				UPWIND
		D-1	D-2	Stillman		Controlman		Head Cleaner		Still Cleaner		
	Sample Date:	8/13	8/14	8/13	8/14	8/13	8/14	8/13	8/14	8/13	8/14	8/13
	Sample Volume (ℓ):	890	899	856	892	915	859	917	822	891	760	834
	Sample Time:	0718-1445	0643-1415	0704-1437	0704-1437	0707-1447	0711-1434	0659-1440	0741-1432	0702-1439	0702-1322	0733-1426
(2)	Naphthalene*	80.22	79.03	47.53	72.87	32.73	33.33	40.00	85.58	38.95	50.29	--[b]
(2)	Quinoline*	--	--	--	--	--	--	--	--	--	--	--
(2)	2-Methylnaphthalene	218.13	139.52	127.39	131.65	44.71	46.58	72.61	107.35	61.79	107.88	--
(2)	1-Methylnaphthalene	78.90	30.98	39.09	39.37	15.85	16.37	23.60	37.38	22.18	28.04	--
(2)	Acenaphthalene	--	--	--	--	--	--	--	--	--	--	--
(2)	Acenaphthene	4.79	1.70	1.80	--	0.71	--	0.98	--	1.51	1.21	--
(3)	Fluorene	4.85	2.31	1.98	2.34	0.51	0.77	0.99	2.84	1.95	1.76	--
(3)	Phenanthrene*/Anthracene*	11.86	7.83	4.17	5.27	1.31	2.28	3.75	6.20	5.07	6.03	--
(3)	Acridine	--	--	--	--	--	--	--	--	--	--	--
(3)	Carbazole	--	0.05	--	--	--	--	--	--	--	--	--
(4)	Fluoranthene	0.20	0.10	0.06	0.10	--	0.05	0.02	0.01	--	0.08	--
(4)	Pyrene*	0.72	0.59	0.21	0.30	0.01	0.18	0.20	0.33	0.27	0.50	--
(4)	Benzofluorene	--	--	--	--	--	--	--	--	--	--	--
(4)	Benz(a)anthracene*/ Chrysene*/Triphenylene	0.06	0.06	--	--	--	--	0.01	--	--	0.12	--
(5)	Benzo(e)pyrene*/ Benzo(a)pyrene*	--	0.07	--	--	--	--	--	--	--	0.11	--
(5)	Perylene	--	0.02	--	--	--	--	--	--	--	--	--
(5)	Dibenz(a,j)acridine*	--	--	--	--	--	--	--	--	--	--	--
(5)	Dibenz(a,i)carbazole*	--	--	--	--	--	--	--	--	--	--	--
(6)	Indeno(1,2,3-cd)pyrene*	--	--	--	--	--	--	--	--	--	--	--
(5)	Dibenzanthracene*[a]	--	--	--	--	--	--	--	--	--	--	--
(6)	Benzo(g,h,i)perylene	--	--	--	--	--	--	--	--	--	--	--
(7)	Coronene	--	--	--	--	--	--	--	--	--	--	--
(6)	Dibenzpyrene*[a]	--	--	--	--	--	--	--	--	--	--	--
	TOTAL	399.73	262.26	222.23	251.90	95.90	99.56	142.16	239.69	131.72	196.02	0.00

* Suggested as having some cancer-causing potential.
[a] Blank values have been subtracted from data. Data have not been corrected for temperature and pressure variation; maximum deviation would be within ±2% of actual values.
[b] "--" designates compounds not detected.
[c] Specific isomers not distinguishable by analytical method; reported value represents any one or combination of existing isomers.

TABLE V-3. Summary of PAH Results

UNITS	PERSONAL SAMPLES			AREA SAMPLES		
	No. of Samples	$\bar{X}^*$ (µg/m³)	No. of PAHs	No. of Samples	$\bar{X}$ (µg/m³)	No. of PAHs
FCCU	8	157.5	6-9	2	724.3	6-8
Delayed Coker	8	172.4	7-10	2	331.0	9-12
Asphalt (vacuum)				2	18.1	5-7
Total	16	164.95	6-10	6	357.8	5-12

* $\bar{X}$ = arithmetic mean.

FCCU

The average cumulative PAH concentration over the two shifts for the four FCCU workers was 157.5 µg/m³ with the number of individual PAHs or groups of PAHs ranging from six to nine. Table V-4 shows that the two outside operators (stillman and helper) were exposed at higher concentrations than the two inside operators (223.8 µg/m³ vs. 91.1 µg/m³). The stillman was exposed by far to the highest mean cumulative PAH concentration ($\bar{X}$ = 327.7 µg/m³) while the number of PAHs identified was similar (6-9) for all personal samples collected at this unit. As expected, the results for the two inside operators, who spend almost their entire shift within the control room, were very similar (90.0 µg/m³ and 92.3 µg/m³).

TABLE V-4. Personal Monitoring Results — FCCU

	No. of Samples	$\bar{X}$ (µg/m³)	No. of PAHs
Inside Operators	4	91.1	6-7
Cat. side	2	90.0	6
Fractionator side	2	92.3	6-7
Outside Operators	4	223.8	6-9
Stillman	2	327.7	6-8
Helper	2	119.9	7-9
Total	8	157.5	6-9

Although both day shifts during which sampling was performed were described as routine by the workers, only two of the four workers at this unit showed duplicate results within 30% of each other over the 2 sampling days. The duplicate samples for the stillman and one of the inside operators showed wide variations. The samples collected during the first sampling day for all four workers were higher than the duplicate second-day samples; no operational or environmental conditions could account for this. A statistical analysis of the data is not presented at this time; such an analysis will be included in the final summary report when data from all nine Phase III surveys are available.

The area sample (F-1) collected near the slurry recycle pump in the enclosed pump building showed a cumulative PAH concentration of 1,347.2 $\mu g/m^3$ with eight PAHs identified; this PAH concentration was the highest of the samples collected at this refinery. The result for the other area sample, collected in the riser building, was 101.5 $\mu g/m^3$ with six PAHs identified.

DELAYED COKER UNIT (PRESSURE COKE STILL)

Table V-5 gives a summary of the personal monitoring results for the four coke workers. These values are again mean cumulative PAH concentrations ($\overline{X}$) for the 2 sampling days. This table shows that the two coke handlers were exposed at slightly higher concentrations than the two operational workers; however, the stillman (an operational worker) showed the highest cumulative PAH concentration ($\overline{X}$ = 237.1 $\mu g/m^3$). He was followed by the head cleaner ($\overline{X}$ = 190.9 $\mu g/m^3$), who performs the drilling, and the still cleaner ($\overline{X}$ = 163.9 $\mu g/m^3$). As expected, the controlman who spends most of his shift in the control room showed the lowest results ($\overline{X}$ = 97.7 $\mu g/m^3$).

The results of the personal monitoring for the delayed coker workers were quite consistent over the 2 days. There was less than a 12% difference between the duplicate samples collected for both operational workers and less than a 41% difference for the two coke handlers. Both cutting shifts were considered as routine by the workers. The samples collected during the second sampling day for all four workers were higher than the duplicate

samples collected during the first shift. This could not be explained by any operational or environmental condition.

TABLE V-5. Personal Monitoring Results — Delayed Coker Unit

	No. of Samples	$\bar{X}$ (µg/m³)	No. of PAHs
Operational	4	167.4	7-8
Stillman	2	237.1	7-8
Controlman	2	97.7	7
Coke Handlers	4	177.4	7-10
Head Cleaner	2	190.9	7-9
Still Cleaner	2	163.9	7-10
Total	8	172.4	7-10

The area sample (D-1) collected near the charge pump in the enclosed hot pump building showed a cumulative PAH concentration of 399.7 µg/m³ with nine PAHs. The result for the other area sample, collected outside and downwind of the cutting operation, was 262.3 µg/m³ with 11 PAHs identified.

ASPHALT PROCESSING UNIT (VACUUM PIPE STILL)

The results of the two area samples collected in the enclosed pump room at the vacuum pipe still were 17.1 µg/m³ (five PAHs) on the first sampling shift and 19.0 µg/m³ (six PAHs) on the second sampling shift, only a 10% difference between samples.

PAH DISTRIBUTION

Table V-6 shows the percent distribution of PAHs found at the various units by the ring number of the compound. In all locations, as the table indicates, at least 96.2% of the PAHs found were the lighter molecular weight 2-ring compounds. Naphthalene and its two methyl derivatives were the compounds found in the highest concentrations. In the delayed coker samples, there was a larger percentage of the 3-ring phenanthrene/anthracene group than in the other two units.

TABLE V-6. Distribution (%) of PAHs Found by Ring Number

RING NO.	FCCU	DELAYED COKER	ASPHALT
2	98.6	96.2	98.2
3	1.3	3.6	1.7
4	<0.1	0.2	0.1
5	0	0	0
6	0	0	0
7	0	0	0

PARTICLE-SIZE DISTRIBUTION

Table V-7 shows the particle-size distribution of the six total particulate samples collected alongside the PAH area samples. The sample results were consistent in that all of the sized particles were 11.8 μm or less; at least 90% of the particles were 8.3 μm or less for all but one of the FCCU area samples. Particles less than 10 μm are considered to be of respirable size.

TABLE V-7. Particle-Size Distribution (%) of Total Particulate Area Samples

PARTICLE SIZE (μm)	FCCU		DELAYED COKER		ASPHALT	
	F-1	F-2	D-1	D-2	A-1	A-2
0.4-0.7	6.2	3.1	2.0	2.3	3.1	3.5
0.7-1.0	6.5	6.0	4.3	2.8	5.0	3.8
1.0-1.5	7.5	7.5	4.6	4.5	7.5	11.2
1.5-2.1	8.5	10.3	6.1	9.8	10.3	15.0
2.1-2.9	11.8	28.5	12.4	10.4	13.7	25.9
2.9-4.2	13.7	18.2	16.2	16.9	32.0	16.6
4.2-5.9	14.1	14.7	26.0	26.4	12.4	15.0
5.9-8.3	19.6	7.2	19.4	19.1	9.9	7.4
8.3-11.8	12.1	4.4	9.0	7.9	6.2	1.6

VI. CONCLUSIONS

The results of the personal, area, and upwind air samples from the Texaco refinery clearly indicate that workers at the FCCU and delayed coker unit of this refinery are exposed to numerous PAHs, generally at $\mu g/m^3$ concentrations. Only area samples were collected at one asphalt processing area; however, the results of these area samples indicated that worker exposure to detectable quantities of PAHs probably also exists in this area. In attempting to draw conclusions from this survey, one must keep in mind that the samples were collected over two work shifts during 2 consecutive days. The limitations of such a sampling schedule are recognized; however, there were no unusual operational or environmental conditions during the survey that would cause one to believe that these results were not representative of these units.

The personal sampling results indicate that the workers at the FCCU and delayed coker units of this refinery are exposed to the same PAHs at similar concentrations. There was a trend in the personal sampling data indicating that the outside workers were exposed at higher PAH concentrations than the inside workers. However, even those workers who spend the great majority of their shift within the control rooms were exposed at concentrations and to a variety of different PAHs greater than anticipated. At both the FCCU and delayed coker unit, the stillman was the worker exposed at the highest PAH concentrations.

Although worker exposures at the delayed coker unit were consistently higher during the second sampling shift, the results were quite similar over the 2 days. At the FCCU, worker exposure was consistently higher on the first sampling shift; the consistency between the duplicate samples was not as evident at this unit. These trends could not be explained by any operational or environmental conditions.

The purpose of the limited area sampling at the FCCU and delayed coker unit was to collect samples in areas suspected of having relatively high PAH concentrations to check suspected major PAH emission sources and to compare concentrations and PAH distributions with the personal samples. It was anticipated that the area samples, especially those area samples collected in the enclosed pump rooms, would be considerably higher than the personal samples. This was the case at one sampling location at each of the two units. At the FCCU, the sample collected near the slurry recycle pump yielded the highest cumulative PAH concentration (1,347.2 $\mu g/m^3$) of any sample collected at this refinery. This indicates that the slurry recycle pump area and the enclosed pump room are a source of PAH emissions. At the delayed coker unit, the sample collected in the enclosed pump room was considerably higher than the other sample collected downwind of the cutting operation. The facts that, in general, there was not a large difference between most of the area and personal samples and that there were relatively consistent PAH levels for all of the workers, even those who do not work in high PAH emission areas, indicate that PAHs are not restricted to the areas around major emission sources but are probably widespread throughout many areas of these units. The results of the area samples collected at the asphalt processing unit were higher than expected based on Phase II area sampling. The enclosed pump building was probably again a major contributing factor to this.

As expected from Phase II results, the great majority of PAHs identified during Phase III were the lighter 2- and 3-ring compounds. At least 96.2% of the PAHs analyzed in the samples from all three units were the 2-ring compounds, and at least 99.8% were 2- or 3-ring compounds. None of the heavier molecular weight PAHs (5-, 6-, and 7-ring compounds) were identified.

Several of the PAHs identified as being present at this refinery are associated with some degree of cancer-causing potential. However, the lack of existing definitive toxicologic and epidemiologic studies make an assessment of the actual cancer hazard of this group of compounds outside the scope of this study.

The particle-size distribution of the total particulate samples showed that 95% of the particles collected were well within the respirable-size fraction (<10 μm). These sized particles cannot be directly correlated with the PAH levels found in the area PAH samples. However, airborne PAHs are associated with particulates and the particle sizing results do indicate that the airborne particulates at the site of the area PAH samples were of respirable size.

Much of the significance of the data generated during this survey will not be evident until Phase III is completed. At that time the concentrations, PAH distributions, and general tendencies noted at this refinery will be compared for consistency with the other study refineries in the final summary report.

APPENDIX

Attendees of Opening Conferences

Enviro Control, Inc.

Stan Futagaki	Senior Industrial Hygienist
Robert Reisdorf	Industrial Hygienist

Texaco

Richard L. Masica	Plant Manager
Floyd M. Chaney	Employee Relations Supervisor
James L. Mathis	Safety Supervisor
Bill Robinson	Member of Health and Safety Committee (OCAW member)
Donald J. Slack	Corporate Industrial Hygienist (Houston)
Greg Mauldin	Corporate Industrial Hygiene Technician (Houston)