

PHASE III SURVEY REPORT #3

WORKER EXPOSURE TO POLYAROMATIC HYDROCARBONS
AT SELECTED PETROLEUM REFINERY PROCESS UNITS

SURVEY LOCATION:

COASTAL STATES PETROCHEMICAL COMPANY REFINERY
CORPUS CHRISTI, TEXAS

SURVEY DATES:

12-14 DECEMBER 1979

REPORT DATE:

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ABSTRACT

This industrial hygiene survey of a petroleum refinery is one of nine performed during Phase III of a National Institute for Occupational Safety and Health (NIOSH) 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 unit (FCCU) and delayed coker unit and area samples only in the two asphalt processing units. 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 32 of the personal and area air samples had detectable quantities of at least seven PAHs or groups of PAHs, with the cumulative PAH concentration for individual samples ranging from less than $0.6 \mu\text{g}/\text{m}^3$ for a personal sample from one of the operators at the FCCU to as high as $137 \mu\text{g}/\text{m}^3$ for one area location at the FCCU. The upwind boundary sample was less than $0.1 \mu\text{g}/\text{m}^3$.

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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 Phase III and Phase 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 unit (FCCU), the delayed coker, and the asphalt processing unit.
- Phase II: Refinery surveys were conducted 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 study process units.

- Phase III: The objective of this main phase of the study is to characterize worker inhalation exposure to PAHs in the 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 Phase III and the previous phases.

Phase III is currently in progress. The Coastal States refinery at Corpus Christi, Texas was the third refinery visited as part of Phase III, and this report presents the information and air-sampling data for PAHs collected during this survey.

The Phase III industrial hygiene survey of the Coastal States refinery was conducted over a period of 3 days, from December 12-14, 1979. During the first day, an opening conference and a walk-through of the study process units took place. Because of the irregularity of the coke-cutting schedule, the sampling program was carried out on four different shifts during the 3 days. Arrangements for this visit were made through the Lead Environmental Engineer and Special Projects Chemist at the refinery.

The opening conference was held with representatives from the refinery, NIOSH and Enviro (list of attendees in Appendix). The two representatives from Enviro and the Alternate Project Officer from NIOSH described the project, the status, and the specific objectives of the survey. A tentative schedule was agreed upon for the 3 days. After the meeting, the survey team conducted a walk-through of the process units to be sampled. At the FCCU and the delayed coker unit, where personal monitoring was scheduled, the Enviro industrial hygienists explained the sampling procedures to the employees. The asphalt processing at this refinery was limited to two vacuum fractionation units; there was no asphalt blowing.

Sampling at the FCCU and the No. 1 vacuum unit was carried out as scheduled during the day shifts of the second and third days. Sampling at the delayed coking and the No. 4 vacuum units was performed during the morning shift (2300-0700) of the first and second days. Problems with the coke-cutting operation prevented the sampling of a complete cutting operation the first day.

II. REFINERY DESCRIPTION

This Coastal States refinery is located in Corpus Christi, Texas on the Gulf Coast. With its crude capacity of 185,000 bbl/day, this refinery is the largest of several refineries in the city and is classified as a "large" refinery for the purposes of the study. Since the oil company that owns this refinery and two others (one in California and one in Kansas) is not one of the largest 15 companies in terms of crude capacity, the company is considered a "nonmajor" oil company. The significance of categorizing this refinery by these criteria is explained in the Phase II report.

This refinery originated in the 1940s and was purchased by Coastal States in 1962, when its capacity was 35,000 bbl/day. At the time of the survey, it was spread over 200 acres, processing over 150,000 barrels of crude a day, and producing a full line of petroleum products which includes:

- propane
- butane
- jet fuel
- gasolines
- Diesel fuel
- #2 fuel oil
- #2 (sponge) coke
- asphalt
- sulfur
- petrochemicals (e.g., benzene, xylene)

The middle eastern (e.g., Iran, Iraq) crude refined here is a high sulfur (2.15% sulfur by weight), "mixed base" (containing both paraffins and naphthenes) crude with an API Gravity Index of about 33. The crude is received by pipeline and tankers. The products are shipped by pipeline, barges, ships, and trucks.

The major process units at the Coastal States refinery include:

- three crude distillation units
- two vacuum distillation units
- FCCU
- three catalytic reformers
- HF alkylation unit
- delayed coker
- benzene, cumene unit
- hydrodealkylation unit (Hydeal)
- two light ends units (LEUs)
- sulfur unit
- hydrodesulfurization units (HDS)

These units are divided into two main production areas designated "east" and "west" and are about one-third of a mile apart. Most of the refinery's sulfur processing is performed in the "west" area. Figures II-1 and II-2 show rough refinery plot plans of each section. Most units, with the exception of the FCCU, do not have their own control building; two to four units normally share a centrally located control building.

There are approximately 400 employees, including maintenance and administrative personnel. 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 over three work shifts, 7 days a week.

The safety and health staff at this refinery includes the safety, security, and fire protection department made up of the supervisor and four fire and safety marshals; the environmental laboratory group made up of the lead environmental engineer, the special projects chemist, and four laboratory technicians; and a nurse and medic. The nurse and medic are on the premises full time during the day shift (5 days a week) and are on 24-hour call. There is also a company physician on retainer. The safety department staff as well as a number of other refinery personnel are trained in first aid and cardiopulmonary resuscitation. All of the production workers are given preplacement medical examinations and annual periodic examinations are made available. Although routine industrial hygiene sampling is not performed at this refinery, the special projects chemist is responsible for any sampling required for compliance purposes.

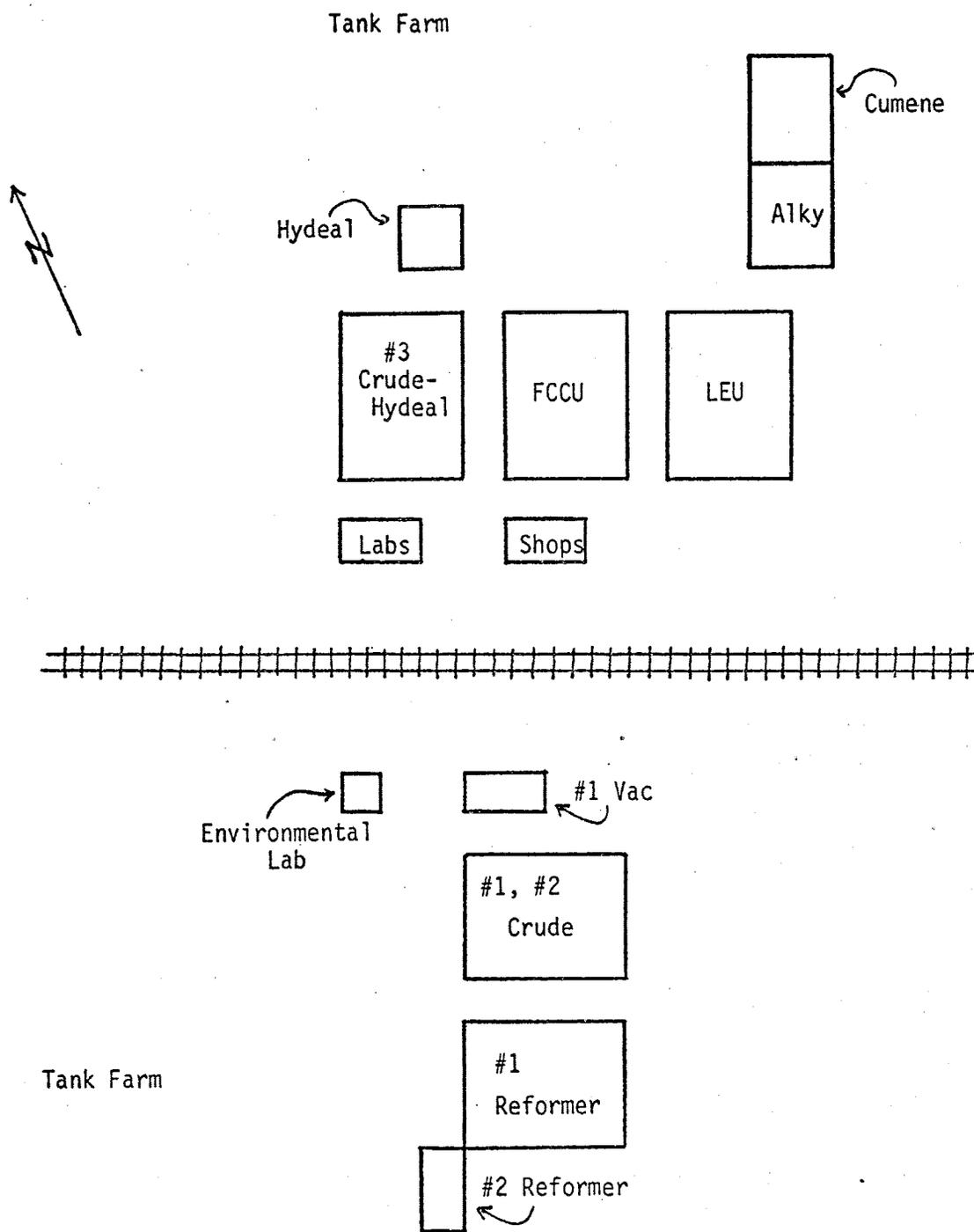


FIGURE II-1. East Production Area

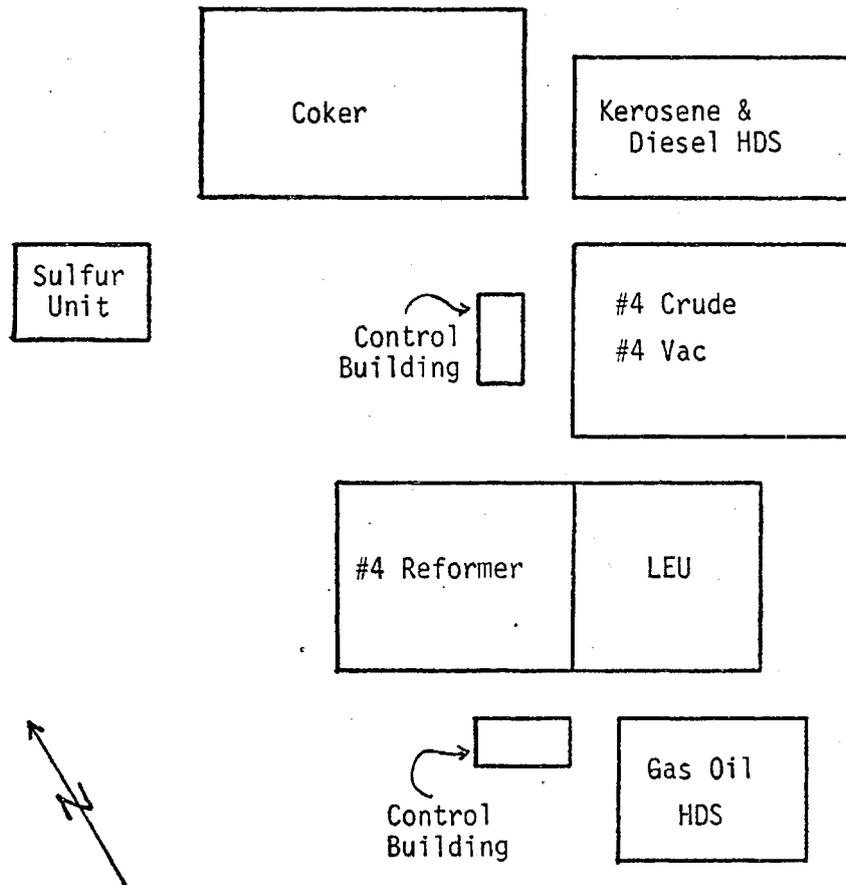


FIGURE II-2. West Production Area

As part of good industrial hygiene practice, the use of protective clothing and equipment (e.g., hard hats, safety shoes, gloves, eye protection) is emphasized. 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 extensive training session over a 3-week period which includes information on unit equipment, operations, respirator use, safety hazards, fire protection, and first aid. The practice of good personal hygiene such as the washing of hands before eating is also encouraged. Good unit housekeeping is practiced as an important means of minimizing worker exposure to potential hazards. Spills are promptly cleaned up by the unit operators, and any necessary equipment or structure repair is promptly carried out by the unit operators or in-house maintenance crews.

III. STUDY PROCESS UNITS

FLUID CATALYTIC CRACKER UNIT (FCCU)

A. Unit and Process Description

The FCCU is located in the northern section of the refinery's east production area (Figure II-1) between the light ends unit (LEU) and the No. 3 crude and No. 1 hydeal units. The present FCCU was built in 1963; there have been three major modifications, primarily to the riser, increasing the unit's capacity which is currently about 20,000 bbl/day.

Figure III-1 illustrates the layout of this unit which occupies an area about 300 x 200 feet. The stacked-type reactor/regenerator (R/R) structure is located south of the control room and north of the charge heater, CO boiler, and precipitator. The fractionator, with several heavy fraction pumps around it, is located to the west of the R/R, and the gas recovery area is located just west of the control room. The No. 2 vacuum unit, which was not in operation during the survey, is situated in the southwest corner.

Fresh feed for the FCCU consists of atmospheric and vacuum gas oil ("raw oil"). This feed is preheated by the gas-fired charge heater or goes to the raw oil drum for temporary storage. The hot charge plus slurry recycle from the fractionator are mixed with the hot catalyst in the riser leading to the reactor. The catalytic cracking takes place in the riser as well as in the reactor. The catalyst used at the Coastal States refinery is a synthetic zeolite common to other FCCUs studied in this project. The product vapors and the catalyst are separated by using a series of cyclones, and the hydrocarbons are transferred to the fractionator tower. The catalyst is stripped with steam of any remaining oil and delivered to the regenerator through the spent catalyst leg. In the regenerator, the catalyst is

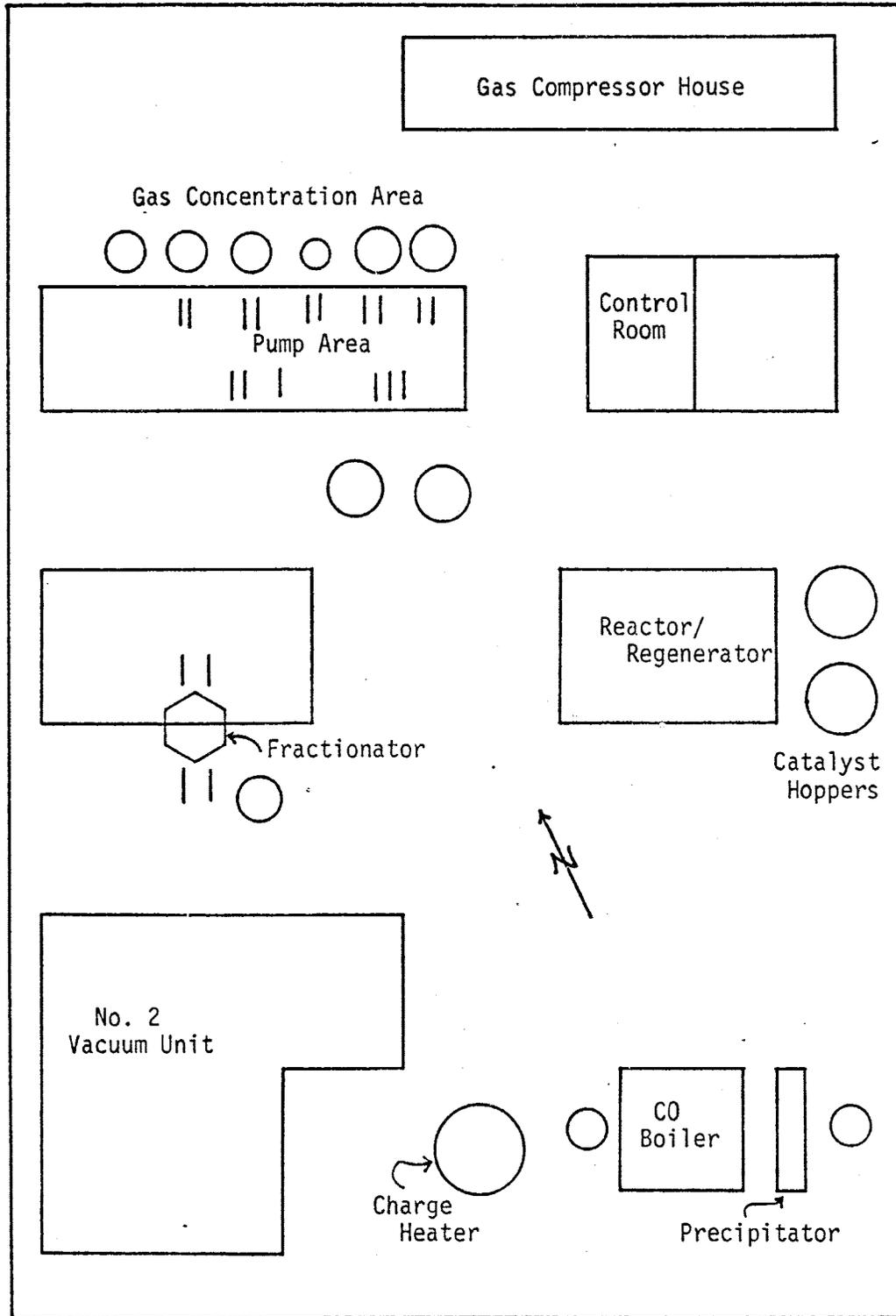


FIGURE III-1. FCCU

reactivated by oxidizing the accumulated carbon at a temperature above 1,000°F (538°C). The flue gas from the regenerator normally goes to the CO boiler where it is burned and is then passed through a precipitator to remove catalyst fines before being released into the atmosphere. The CO boiler and/or the precipitator can be bypassed under certain circumstances.

The main products from the fractionator are:

- propane
- butane
- gasoline
- light cat cycle oil
- heavy cat cycle oil
- clarified slurry

B. Work Force

There are normally four full-time workers assigned to the FCCU during each shift. In addition, there is a unit supervisor on duty during each day shift and on call 24 hours a day. Normally the unit supervisor does not spend a full shift at the FCCU; he may be at the maintenance and engineering building or at other refinery locations. Following is a brief description of the activities of the four full-time shift personnel.

- lead operator: Supervises routine unit operations, working closely with other operators as well as with the unit supervisor during the day shift. He spends about 50% of his time outside assisting and supervising other operators in all areas of the FCCU, the No. 2 vacuum unit (when in operation), and the LEU just to the east of the control building.
- operator #1 (boardman): Spends essentially 100% of his shift inside, monitoring and logging in various meters and charts on the control board. He works closely with the lead operator, as well as with other outside operators.

- operator #2 ("A" helper): Performs routine outside duties for the R/R, fractionator, gas concentration, and vacuum unit areas. Periodically he takes meter and gauge readings, makes visual inspections, gauges tanks, monitors uptake of chemical additives, keeps pumps oiled, and maintains the unit by general housekeeping. He spends about 60% of his shift outside. Although most process stream samples are collected during the morning shift (2300-0700), the day-shift operators do collect a small number of liquid and gas samples (e.g., raw oil charge, light and heavy cat gas oils).
- operator #3 ("B" helper): Performs routine outside duties for the LEU, the treating area, and the gas concentration area. Duties are similar to those of the A helper.

C. Exposure Control Measures

The exposure control measures used at this FCCU are quite typical of those observed at other FCCUs studied during this project. The primary control measure 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 during sampling of the various streams, during maintenance and housekeeping activities, from fugitive emissions, and from the regenerator flue gas.

Although most process stream samples are collected during the morning shift, some samples including heavy fraction samples (e.g., raw oil charge, clarified slurry) are also collected during the other two shifts. Sample bombs are used only for gas samples; liquid samples are collected by the spigot-and-bottle method with sampling loops that eliminate the flushing of lines. The samples are taken to the laboratory for analysis.

Exposure during routine maintenance is difficult to minimize. The ground level of the entire unit is constructed of concrete with a sewer system; this simplifies 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 in February 1977.

Hard hats, safety shoes, and rubber gloves with cotton lining are routinely worn on this unit, and eye protection is available. There are no routine operations that require the use of respirators; however, air-purifying and self-contained breathing air respirators are available.

Areas of the unit handling heavy fractions, which are more likely to contain the PAHs, are in fairly open areas, minimizing potential vapor accumulation. Several of the heavy gas oil, slurry recycle, and raw oil pumps are located close together near the fractionator tower. This is an area where PAH concentrations might be elevated. The control room, which is not under positive-pressure ventilation, is seldom downwind of the R/R or heavy fraction pumps.

Flue gas from the regenerator is burned in the CO boiler with an auxiliary fuel. The heat produced here is used to generate steam. The CO boiler removes many hydrocarbons as well as carbon monoxide from the flue gas, which then goes to an electrostatic precipitator to remove catalyst fines before the effluent is discharged through a stack into the atmosphere.

DELAYED COKER UNIT

A. Unit and Process Description

The delayed coking unit is one of about six process units located at the west production area of the refinery (Figure II-2). The coker is surrounded by the kerosene and Diesel hydrodesulfurization (HDS) unit to the east, the No. 4 crude and vacuum units to the southeast, the control building to the south, the sulfur recovery unit to the west, and the refinery boundary to the north. This coker unit has two 80-foot drums with a daily production capacity of about 450 tons of No. 2 or "sponge" coke.

The unit, built in 1972, is spread over an area of about 300 x 300 feet (Figure III-2). There are three main areas divided by two roads. The coker tower, railroad tracks and cars, water recycling, and blowdown drum are located in the north area of the unit. The coker tower is an open, multilevel structure that includes two drums, an elevator, and the penthouse at the top. Railroad cars can be positioned directly beneath the drums to provide direct loading as the coke is cut. Just to the south is the gas-fired charge furnace, the fractionating tower, and the gas-recovery area. The ground level is constructed of concrete. The air-conditioned control building is located farther south across another road. This control building is also used for the No. 4 crude and vacuum units, and the kerosene and Diesel HDS unit.

The coker charge stock comes from the vacuum units (bottoms) and storage tanks to the coker charge drum. From here the charge is pumped to the convection section of the gas-fired furnace and then to the fractionator where light and heavy ends are separated. The lighter fraction goes through a series of separators including the coker overhead receiver, primary absorber, and sponge absorber before finally going to the fuel gas plant. The bottoms from the fractionator are pumped to the radiant section of the furnace where the charge is heated further (probably to about 900°F/482°C). The hot charge goes through the switch valve on the second level of the coker tower and is directed to one of the two coke drums. Each drum has a 40-hour cycle with coke formation lasting about 20 hours. Since the drums work as a pair, cutting of one drum normally occurs every 20 hours; the average "outage" (distance from the coke to the top of the drum) is about 25 feet. Lighter vapor fractions of the thermal cracking operation are removed from the top of the drum and sent to the fractionator where various products are separated and eventually recovered. Besides coke, products from this unit include:

- fuel gas
- light gas oil
- heavy gas oil
- FCCU charge
- propane
- butane
- naphtha

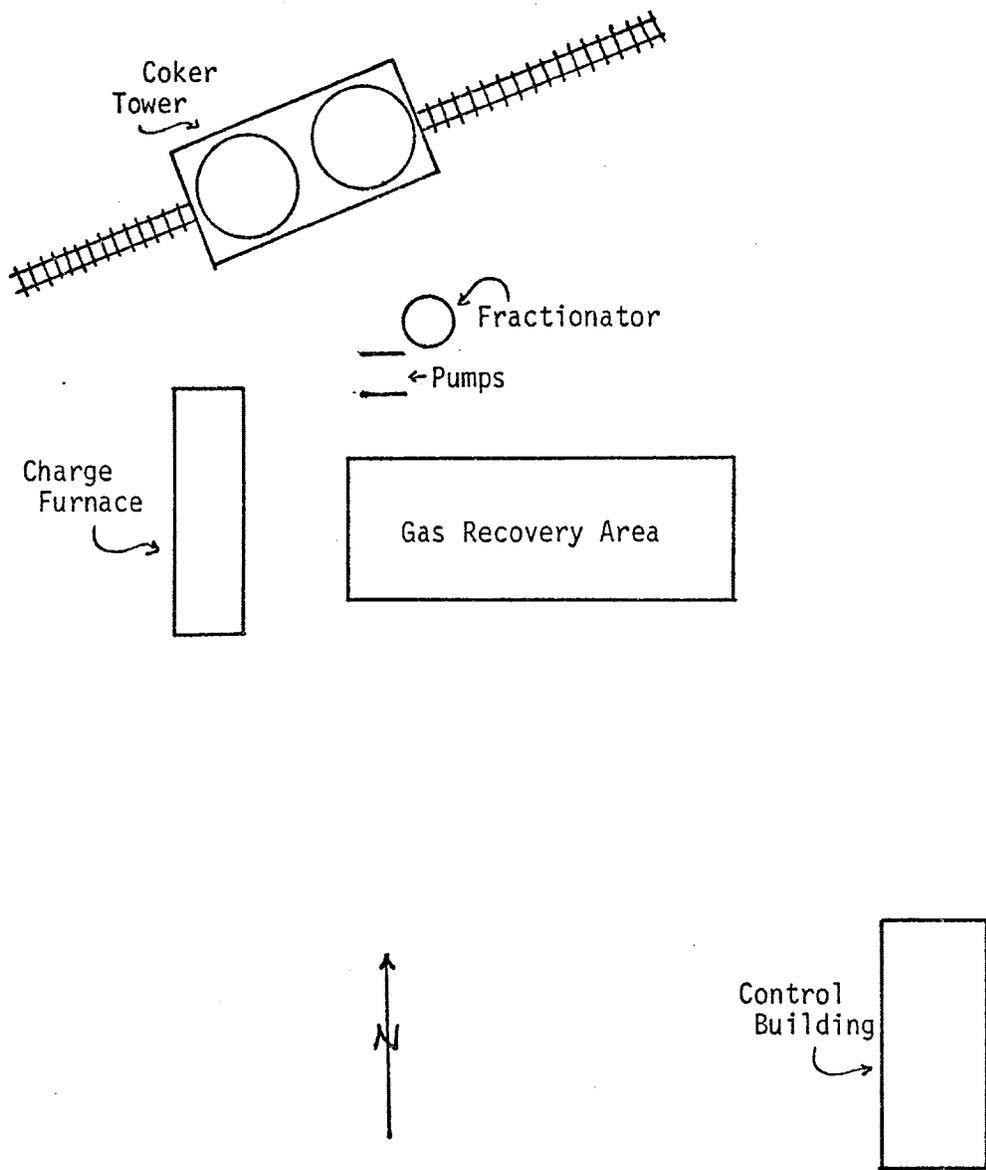


FIGURE III-2. Delayed Coker Unit

The complete cycle of each drum, from drum heating to cutting, is 40 hours. About 8 hours before the cutting operation is scheduled, coke formation is stopped by switching the feed valve to the other drum. In 30 minutes, steam is introduced into the drum to cool it. After about 5 hours, the drum is vented to the atmosphere; then water is added to further cool the drum. Eight hours after the valve is switched, the top and bottom of the drum are opened and an initial hole is bored through the coke from the top with a high-pressure hydraulic bit (>2000 psi). The bit is changed to a revolving-head type, and coke is cut from the bottom up. The coke falls directly into a railcar stationed below the drum bottom. A motorized winch is used to move the car to ensure even loading. Contractor personnel then transfer the coke from the railcars to trucks by crane.

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 charge valve is switched from the other drum. The entire cutting operation normally lasts from 4 to 6 hours.

Difficulties were encountered during both cutting shifts observed during this survey. As a result, the cutting operations lasted longer than normal. During the first cutting shift, it took well over an hour to "drop" the bottom of the drum as it was tightly adhered to the coke. During cutting, the drill bit was bent by too rapid a descent. The total cutting operation lasted about 12 hours. During the second cutting shift, the bottom of the other drum not scheduled to be cut was leaking an asphalt-like material. This had to be tightened before normal operations could be started. The bottom was dropped more easily during this second shift but the cutting operation again took longer than normal. After a total of 7 hours from the beginning of the cutters' shift, the cutting was completed.

B. Work Force

The work force for the coker unit is divided into two groups, the operations group and the coke-cutting group. During the survey, there were only two in the operations group who worked primarily on the coker unit. These

two, the boardman and the coke helper, worked the normal 8-hour shift. In addition, there was a lead operator and a unit supervisor whose responsibilities included the coker unit as well as the No. 4 crude and vacuum units, and the kerosene and Diesel HDS unit. The lead operator is a normal shift worker but the unit supervisor is on duty during the day shift and on 24-hour call. Following is a brief description of job activities of the boardman and coke helper.

- boardman: Spends essentially 100% of the shift inside, monitoring and logging in various meters and charts on the control board. Is also the boardman for other units which have their monitors in this control room. Works closely with the helpers.
- coke helper: Performs all routine outside tasks preparing for coke-cutting operation, such as switching the charge valve, opening and closing the steam and water lines, and venting the drums. Periodically performs visual inspection of entire unit, meter and gauge readings, and cleaning and oiling of pumps. Spends about 50% of his shift outside in the production area.

During the survey, the coke-cutting group consisted of a driller and two bottom cutters; occasionally there is an additional bottom cutter. This group works independently of the operations crew. They come in about 30 minutes before a drum is scheduled to be cut, work until the cutting and cleanup is finished, wash up, and leave. This usually takes 4 to 6 hours but can take much longer. Following is a brief description of work activities of the three coke cutters.

- driller: Spends about 20-30 minutes opening the top of the drum and can help with the opening of the bottom and positioning of the sleeve. Controls the drilling operation from his position in the penthouse. He usually stays there during the entire cutting operation except for breaks.

He helps to close the drum and to clean up when the operation is completed.

- bottom cutters (2): They work as a team to remove the transfer line, to open the bottom of the drum, and to position the sleeve before cutting starts. During cutting, one worker is positioned in an enclosed shelter with a window near the bottom of the drum to observe and direct the railcar loading. They both help with cleanup operations.

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 coke must be cut by the driller, the bottom cutters must clean and prepare the fittings, and at this particular unit, they must ensure the railcars are properly loaded and clean up the coke tower structure and ground area. There are several important points concerning worker exposure associated specifically with cutting the coke directly into railcars.

This method using railcars normally eliminates the necessity of the crane and any other type of loading equipment such as front-end loaders and trucks. However, this was not the case at this particular coking unit; a crane was used to transfer the coke from the railcar to trucks. The crane operator and truck drivers were not Coastal States employees. This method also requires that one of the cutters be stationed at the drum bottom area to ensure proper railcar loading. Although in an enclosed shelter, this worker is in close proximity to the falling coke, splashing water, and water mist. The coke at this point has been cooled and hydrocarbon vapor is not likely. Exposure is more likely to be dermal and to coke particulates.

The bottom of the drum normally drops off easily; however, during the survey the coke cutters had to use pneumatic hammers, sledge hammers, iron poles, and shovels to remove the bottom. The operation which normally takes 30 minutes took well over an hour. Temperature variability or inconsistent flow of the feed charge could have caused the problem. After the bottom is dropped, a metal sleeve is positioned directly under the drum. This forms a more closed system on this level where the cutters spend a good part of their time during the operation. The penthouse on the top level is a relatively enclosed one-room building (15 x 40 feet) where the driller operates the overhead drills. Natural ventilation did not appear to be good.

Direct loading of railcars normally requires considerable cleanup at the end of each cutting, as was the case at this unit. The tracks have to be cleared of the large coke chunks, and the entire ground area must be hosed down.

Clean coveralls were provided to the coke cutters daily. They also wore hard hats, eye protection, and gloves. The locker and shower room was part of the control building. During sampling shifts, the control room was downwind of the coke tower and heavy-fraction pumps.

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

ASPHALT PROCESSING

A. Unit and Process Description

The asphalt processing at this refinery consists of three vacuum distillation units; the bottoms from the fractioning towers are pumped to storage as asphalt without any further processing. The No. 1 vacuum unit is located just north of the No. 1 and No. 2 crude units in the east production area (Figure II-1). The No. 2 vacuum unit, which was not in operation during the survey, is located in the southwest corner of the FCCU (Figures II-1

and III-1). The No. 4 vacuum unit is located just east of the coker control building within the No. 4 crude unit (Figure II-2). The asphalt production capacity of this refinery is about 500 bbl/day.

B. Work Force

No workers are assigned full time to any of the vacuum units. One or more of the outside operators of nearby units spend a small part of their shift covering the vacuum units. For example, when the No. 2 vacuum unit is operating, the lead operator and the A helper of the FCCU are responsible for the vacuum unit.

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 the Coastal States refinery. Although all sampling was scheduled for the day shifts of the second and third days, the coke-cutting schedule during these days necessitated some adjustments to the original sampling plan (Figure IV-1).

FIGURE IV-1. Revised Sampling Schedule

| | 12/12 | 12/13 | | | | | | | | | | | 12/14 | | | | | | | | | | | |
|---------------------|-------|-------|------|------|------|------|------|------|------|------|------|------|-------|------|------|------|------|------|------|------|------|--|--|--|
| | 2300 | 0100 | 0300 | 0500 | 0700 | 0900 | 1100 | 1300 | 1500 | 1700 | 1900 | 2100 | 2300 | 0100 | 0300 | 0500 | 0700 | 0900 | 1100 | 1300 | 1500 | | | |
| Coker and #4 Vacuum | | | | | | | | | | | | | | | | | | | | | | | | |
| FCCU and #1 Vacuum | | | | | | | | | | | | | | | | | | | | | | | | |

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-2), was used with a portable MSA Model S pump calibrated at approximately 2 liters/minute. To investigate the influence of nonrespirable-size particles, a duplicate sampling setup was used with a cyclone preselector at each area sampling site at the FCCU, delayed coker, and vacuum units. Personal samples were collected in the FCCU and coker only. A modified sampling device (Figure IV-3) was used for the 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 at the refinery's northwest boundary (gate #10) was also collected. A total of 33 samples was collected over the 3 days.

The samples were analyzed by gas chromatography/mass spectrometry which allowed the quantitative analysis of the following 23 individual or groups of PAHs and azo-heterocyclic compounds.

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. benzo(a)fluorene/benzo(e)fluorene
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). Although specific isomers of dibenzanthracene and dibenzpyrene are not distinguishable by the analytical method, one or more of their isomers are potential carcinogens and, therefore, the designation is used. There is no definitive information to indicate that the others on this list are potentially carcinogenic. However, the analytical method allowed them to be conveniently included in the analysis, and it was felt that the identification of a large number of PAHs would be beneficial to the study.

SAMPLING CONDITIONS

Weather conditions for the first sampling shift at the delayed coker and No. 4 vacuum units (Figure IV-1) were overcast skies with periods of moderate rain. Temperatures ranged from 50°-60°F (10°-16°C) with the relative humidity ranging from 45-75%. Winds were from the north, northwest at 5-7 mph, gusting to 15 mph. Overcast skies continued during the day shift of December 13 with occasional light rain. The temperature ranged from 48°-53°F (9°-12°C); at noon the temperature was 49°F(9°C) and 93% relative humidity.

Weather conditions for the second sampling shift at the delayed coker and No. 4 vacuum units (December 13 and 14) were clear skies turning to overcast and eventually rain by 0700. Temperatures ranged from 50°-55°F (10°-13°C) with the relative humidity ranging from 70-80%. Intermittent light rain continued during the day shift. Temperatures ranged from 48°-55°F(9°-13°C); at noon the temperature was 50°F(10°C) and 97% relative humidity. Winds were generally out of the northwest at 10-15 mph.

FCCU

A. Area Sampling

Two locations very close together in the pump area near the fractionator (Figure IV-4) were selected to collect the area samples in the FCCU. Locations F-1 and F-2 were both about 3½ feet above ground level between the slurry reflux pump (P-58) and its spare (P-59). These centrifugal pumps move the bottoms from the fractionator, which include spent catalyst, to the slurry settler. The bottoms from the settler go back to the reactor. Location F-1 was sampled during the day shift on December 13 and F-2 during the day shift on December 14.

B. Personal Sampling

All four FCCU shift workers described in Chapter III were sampled during the day shifts on December 13 and 14.

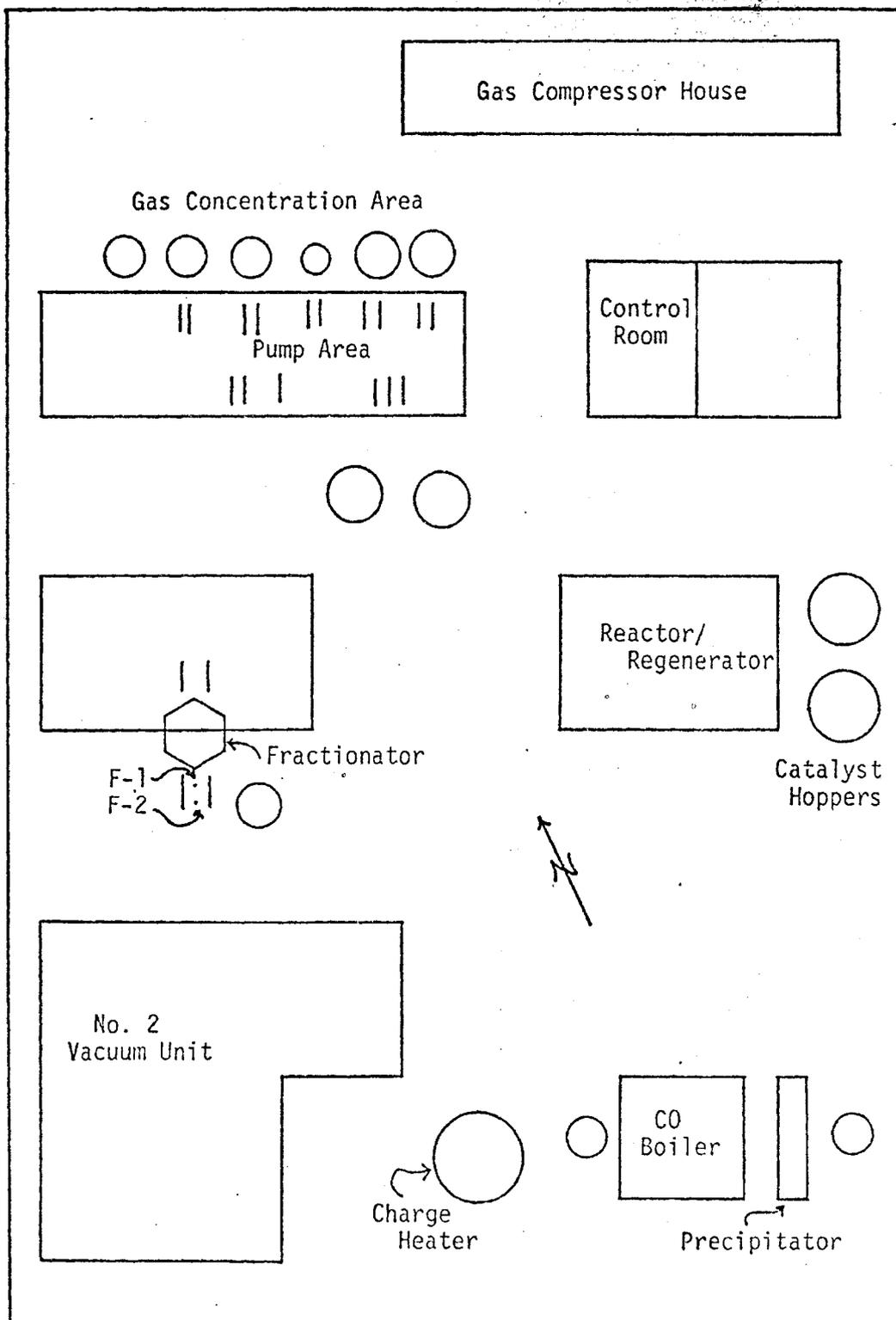


FIGURE IV-4. FCCU Area Sampling Locations

DELAYED COKER UNIT

A. Area Sampling

Figure IV-5 shows the two area sampling sites selected at the delayed coker unit. Location C-1, 15-20 yards south and downwind of the west coke drum (cut during sampling shift), was sampled from 2300 to 0700 on December 12 and 13. The sampling units were positioned about 3 feet above ground level.

Location C-2 was directly above pump P-1, a centrifugal pump, which moves the bottoms from the fractionator to the charge furnace. This location was sampled from 0030 to 0730 on December 14 while the east drum was being cut.

B. Personal Sampling

The two operational workers and the three coke cutters, described in Chapter III, were sampled during both sampling shifts (Figure IV-1). As mentioned previously, problems with the cutting operation during the first shift prevented sampling of the complete cutting operation.

ASPHALT PROCESSING UNIT

At both the No. 1 and No. 4 vacuum units, a single location near the asphalt pump was sampled during both sampling shifts. At the No. 1 vacuum unit, the location was about 6 feet downwind of the two reciprocating asphalt pumps (P-6,7) and about 5 feet above ground level. This is a fairly open area with no heavy fraction process stream equipment located upwind. The asphalt pumps move the vacuum bottoms to storage.

The sampling site at No. 4 vacuum unit was directly above the centrifugal asphalt pump and about 5 feet above ground level. This area was surrounded by the No. 4 crude unit and was not nearly as open an area as No. 1 vacuum unit.

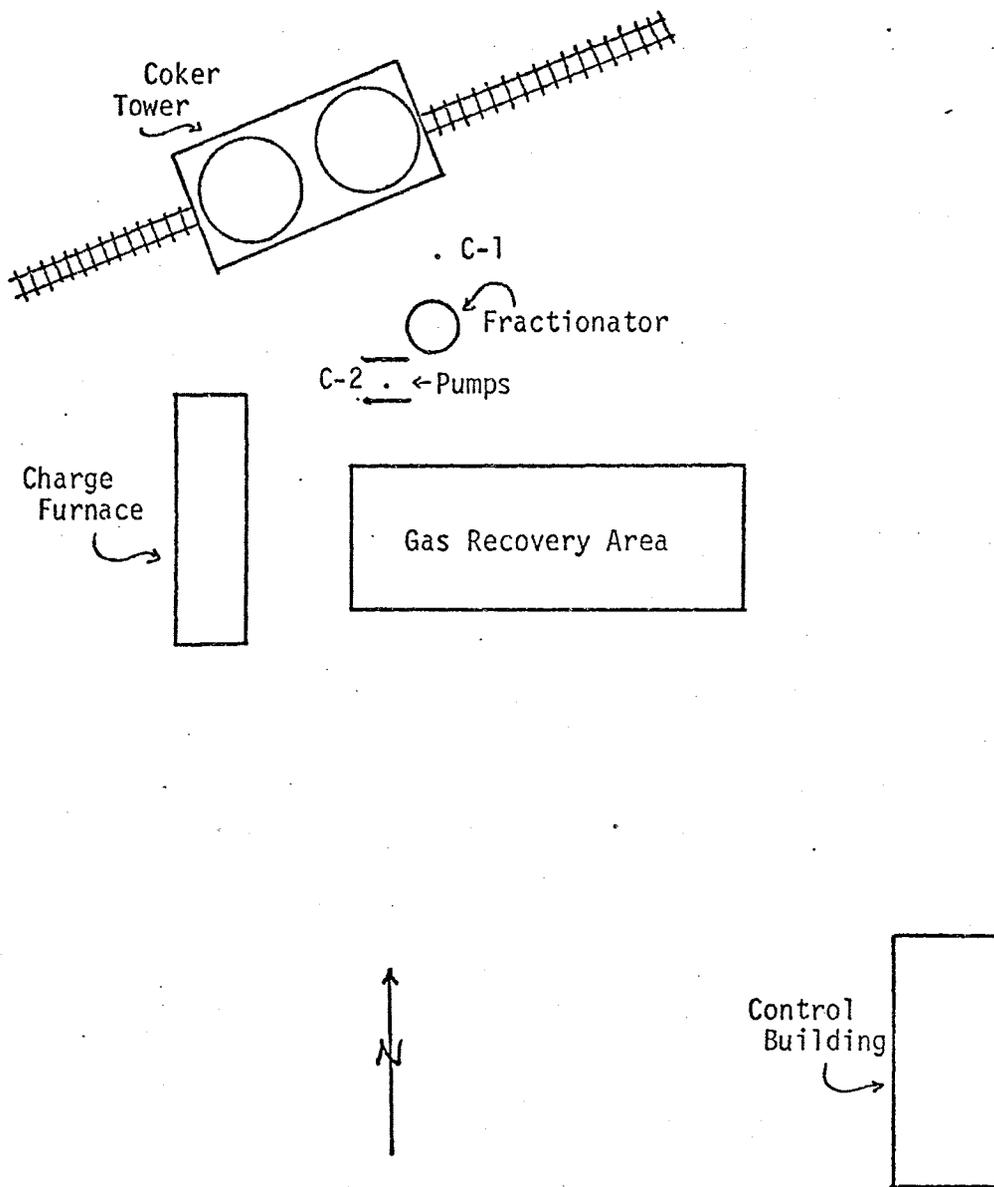


FIGURE IV-5. Delayed Coker Unit Area Sampling Locations

V. RESULTS AND DISCUSSION

The complete results of the area and personal PAH samples collected at this Coastal States refinery are presented in Tables V-1, V-2, and V-3. All 32 personal and area air samples analyzed from the four study process units had detectable quantities of at least seven of the 23 PAHs (or groups of PAHs) for which the samples were tested. The cumulative PAH concentrations for individual samples ranged from 0.6 $\mu\text{g}/\text{m}^3$ for the "B" helper at the FCCU to as high as 136.8 $\mu\text{g}/\text{m}^3$ for one area location in the FCCU. The upwind boundary sample was less than 0.1 $\mu\text{g}/\text{m}^3$.

A summary of the personal and area sampling results, including the mean (arithmetic) cumulative PAH concentrations for the three types of process units, is presented in Table V-4. On the average, the personal samples at the delayed coker were more than four times greater than those from the FCCU. The two total mass area samples collected in the FCCU were much higher than those collected in the coker and two asphalt units.

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 5-, 6-, and 7-ring PAHs were found in the majority of the samples.

TABLE V-1. PAH Analytical Results ($\mu\text{g}/\text{m}^3$) for Personal and Area Samples Collected at the FCCU^a

| Ring No. | | AREA | | | | PERSONAL | | | | | | | | |
|----------|---|--------------|-----------|-----------|-----------|-----------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-------|
| | | F-1 | | F-2 | | Lead Operator | | Boardman | | A Helper | | B Helper | | |
| | | Date: | 12/13 | 12/13 | 12/14 | 12/14 | 12/13 | 12/14 | 12/13 | 12/14 | 12/13 | 12/14 | 12/13 | 12/14 |
| | | Sample Type: | Total | Resp. | Total | Resp. | Total | Total |
| | Sample Volume (L): | 799 | 787 | 754 | 773 | 960 | 966 | 988 | 1,009 | 988 | 922 | 1,005 | 928 | |
| | Sample Time: | 0729-1459 | 0729-1459 | 0722-1503 | 0722-1502 | 0651-1452 | 0652-1456 | 0651-1453 | 0652-1456 | 0651-1453 | 0652-1457 | 0651-1452 | 0652-1455 | |
| (2) | Naphthalene* | 26.77 | 26.16 | 21.59 | 30.69 | 1.56 | 4.35 | 0.61 | 0.97 | 0.95 | 1.76 | 0.36 | 0.26 | |
| (2) | Quinoline | 4.63 | 7.93 | 1.71 | 4.23 | -- ^b | 0.23 | -- | -- | -- | 0.02 | -- | -- | |
| (2) | 2-Methylnaphthalene | 28.97 | 28.17 | 34.67 | 36.97 | 1.01 | 7.51 | 0.50 | 0.51 | 0.54 | 0.92 | 0.19 | 0.12 | |
| (2) | 1-Methylnaphthalene | 21.14 | 19.75 | 26.53 | 31.85 | 0.46 | 3.84 | 0.31 | 0.23 | 0.30 | 0.39 | 0.10 | 0.04 | |
| (2) | Acenaphthalene | 2.86 | 5.36 | 3.42 | 4.90 | 0.04 | 0.23 | -- | 0.04 | 0.04 | 0.07 | 0.01 | 0.02 | |
| (2) | Acenaphthene | 5.15 | 7.73 | 4.77 | 8.75 | 0.06 | 0.28 | 0.03 | 0.06 | 0.05 | 0.07 | 0.01 | 0.01 | |
| (3) | Fluorene | 4.08 | 6.26 | 5.12 | 7.50 | 0.12 | 0.36 | 0.10 | 0.12 | 0.12 | 0.17 | 0.06 | 0.06 | |
| (3) | Phenanthrene*/Anthracene* | 17.85 | 19.73 | 20.07 | 24.21 | 0.28 | 0.40 | 0.17 | 0.17 | 0.21 | 0.21 | 0.08 | 0.07 | |
| (3) | Acridine | 3.04 | 3.98 | 1.10 | 4.94 | 0.06 | 0.03 | -- | 0.02 | <0.01 | 0.01 | -- | <0.01 | |
| (3) | Carbazole | 0.97 | 1.25 | 1.23 | 1.67 | 0.02 | 0.02 | -- | <0.01 | -- | <0.01 | 0.03 | <0.01 | |
| (4) | Fluoranthene | 1.91 | 2.08 | 2.75 | 2.76 | 0.03 | 0.01 | -- | <0.01 | <0.01 | <0.01 | 0.03 | <0.01 | |
| (4) | Pyrene* | 4.51 | 6.03 | 4.99 | 6.11 | 0.04 | 0.03 | 0.01 | 0.02 | 0.02 | 0.01 | 0.05 | 0.02 | |
| (4) | Benzofluorene | 1.42 | 2.00 | 4.29 | 1.72 | -- | -- | -- | -- | -- | -- | 0.01 | -- | |
| (4) | Benz(a)anthracene*/Chrysene*/Triphenylene | 0.21 | 0.21 | -- | 0.44 | -- | -- | -- | -- | -- | -- | 0.02 | -- | |
| (5) | Benzo(e)pyrene*/Benzo(a)pyrene* | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | |
| (5) | Perylene | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | |
| (5) | Dibenz(a,j)acridine* | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | |
| (5) | Dibenz(a,i)carbazole* | -- | 0.14 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | |
| (6) | Indeno(1,2,3-cd)pyrene* | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | |
| (5) | Dibenzanthracene* ^c | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | |
| (6) | Benzo(g,h,i)perylene | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | |
| (7) | Coronene | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | |
| (6) | Dibenzpyrene* ^c | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | |
| TOTAL | | 123.51 | 136.78 | 132.24 | 166.64 | 3.68 | 17.29 | 1.73 | 2.14 | 2.23 | 3.63 | 0.95 | 0.60 | |

* 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 $\pm 2\%$ 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 ($\mu\text{g}/\text{m}^3$) for Personal and Area Samples Collected at the Delayed Coker Unit^a

| Ring No. | Date: Sample Type: Sample Volume (L): Sample Time: | AREA | | | | OPERATIONAL | | | | COKE CUTTERS | | | | | |
|----------|---|-------------|-----------------|-----------|-----------|-------------|-----------|-------------|-----------|--------------|-----------|-----------|-----------|-----------|-----------|
| | | C-1 | | C-2 | | Boardman | | Coke Helper | | Driller | | Cutter A | | Cutter B | |
| | | 12/12-12/13 | 12/12-12/13 | 12/14 | 12/14 | 12/12-12/13 | 12/14 | 12/12-12/13 | 12/14 | 12/13 | 12/14 | 12/13 | 12/14 | 12/13 | 12/14 |
| | | Total | Resp. | Total | Resp. | Total | Total | Total | Total | Total | Total | Total | Total | Total | Total |
| | | 891 | 821 | 680 | 680 | 905 | 898 | 929 | 778 | 647 | 875 | 608 | 886 | 642 | 867 |
| | | 2322-0711 | 2319-0715 | 0038-0713 | 0038-0713 | 2257-0634 | 0013-0737 | 2301-0630 | 0004-0637 | 0241-0758 | 0245-0952 | 0246-0750 | 0248-0952 | 0251-0804 | 0251-0952 |
| (2) | Naphthalene* | 0.99 | 1.36 | 2.40 | 1.00 | 7.09 | 3.03 | 4.29 | 6.64 | 1.89 | 8.45 | 0.30 | 0.95 | 9.82 | 2.30 |
| (2) | Quinoline | 0.27 | 0.27 | 1.11 | 0.70 | 2.01 | 0.78 | 1.49 | 1.89 | 0.23 | 0.73 | 0.14 | 0.33 | 1.39 | 0.46 |
| (2) | 2-Methylnaphthalene | 1.92 | 2.71 | 3.33 | 1.64 | 10.32 | 2.10 | 7.24 | 8.90 | 1.88 | 13.69 | 0.23 | 1.00 | 14.47 | 5.55 |
| (2) | 1-Methylnaphthalene | 0.87 | 1.75 | 1.61 | 1.21 | 7.73 | 2.38 | 4.21 | 6.39 | 0.99 | 5.14 | 0.22 | 0.64 | 8.72 | 1.88 |
| (2) | Acenaphthalene | 0.08 | -- ^b | 0.08 | 0.05 | 7.60 | 0.14 | 0.26 | 0.36 | 0.07 | 0.25 | 0.01 | 0.06 | 0.27 | 0.13 |
| (2) | Acenaphthene | 0.17 | 0.22 | 0.20 | 0.18 | 0.75 | 0.24 | 0.38 | 0.59 | 0.22 | 0.47 | 0.03 | 0.10 | 0.44 | 0.18 |
| (3) | Fluorene | 0.21 | 0.20 | 0.13 | 0.15 | 0.60 | -- | 0.30 | -- | 0.14 | 0.85 | 0.02 | 0.11 | 0.29 | 0.41 |
| (3) | Phenanthrene*/Anthracene* | 0.41 | 0.40 | 0.17 | 0.23 | 0.12 | 0.07 | 0.09 | 0.21 | 0.20 | 2.10 | 0.04 | 0.11 | 0.50 | 1.06 |
| (3) | Acridine | 0.16 | -- | 0.06 | 0.08 | 0.02 | 0.04 | 0.01 | 0.06 | 0.07 | 0.16 | -- | 0.10 | -- | -- |
| (3) | Carbazole | 0.03 | -- | 0.02 | -- | -- | -- | 0.01 | 0.01 | 0.07 | 0.08 | -- | -- | -- | 0.05 |
| (4) | Fluoranthene | 0.01 | -- | <0.01 | 0.03 | 0.03 | -- | 0.01 | -- | 0.02 | 0.12 | -- | 0.02 | 0.07 | 0.07 |
| (4) | Pyrene* | 0.03 | 0.01 | 0.02 | 0.04 | 0.04 | 0.01 | 0.02 | 0.03 | 0.02 | 0.34 | 0.02 | 0.03 | 0.09 | 0.17 |
| (4) | Benzo(a)fluorene | 0.01 | -- | -- | -- | -- | -- | -- | -- | 0.05 | 0.10 | -- | -- | -- | -- |
| (4) | Benz(a)anthracene*/Chrysene*/Triphenylene | -- | -- | 0.01 | -- | 0.01 | -- | -- | -- | 0.07 | 0.15 | -- | -- | -- | -- |
| (5) | Benzo(e)pyrene*/Benzo(a)pyrene* | -- | -- | -- | -- | -- | 0.07 | -- | 0.07 | 0.14 | 0.04 | -- | -- | -- | -- |
| (5) | Perylene | -- | -- | -- | -- | -- | 0.07 | -- | -- | 0.16 | 0.07 | -- | -- | 0.14 | -- |
| (5) | Dibenz(a,j)acridine* | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| (5) | Dibenz(a,i)carbazole* | 0.05 | -- | -- | -- | -- | -- | -- | -- | 0.13 | -- | -- | -- | -- | -- |
| (6) | Indeno(1,2,3-cd)pyrene* | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| (5) | Dibenzanthracene* ^c | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| (6) | Benzo(g,h,i)perylene | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| (7) | Coronene | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| (6) | Dibenzpyrene* ^d | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| TOTAL | | 5.21 | 6.92 | 9.14 | 5.31 | 36.32 | 8.93 | 18.31 | 25.15 | 6.35 | 32.74 | 1.01 | 3.45 | 36.20 | 12.26 |

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* 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

^b $\pm 2\%$ of actual values.

^c "--" designates compounds not detected.

^d Specific isomers not distinguishable by analytical method; reported value represents any one or combination of existing isomers.

TABLE V-3. PAH Analytical Results ($\mu\text{g}/\text{m}^3$) for Area Samples Collected at the Asphalt Units and Upwind Location^a

| Ring No. | | #1 Vacuum Unit | | | #4 Vacuum Unit | | | UPWIND |
|--------------------|---|----------------|-----------|-----------|----------------|-----------------|-----------|--------|
| | | AREA | | | | | | |
| | | A-1 | | A-2 | A-3 | | A-4 | |
| | | Date: | 12/13 | 12/13 | 12/14 | 12/12-12/13 | 12/14 | |
| Sample Type: | Total | Resp. | Total | Total | Total | Resp. | Total | |
| Sample Volume (L): | 774 | 779 | 812 | 761 | 751 | 658 | 963 | |
| Sample Time: | 0752-1515 | 0752-1515 | 0740-1522 | 2310-0637 | 0025-0700 | 0025-0658 | 0829-1614 | |
| (2) | Naphthalene* | 1.24 | 1.19 | 0.66 | 3.64 | 0.45 | 3.26 | 0.06 |
| (2) | Quinoline | 1.13 | 1.01 | 0.40 | 0.40 | -- ^b | 0.15 | -- |
| (2) | 2-Methylnaphthalene | 3.44 | 3.49 | 1.26 | 3.76 | 1.67 | 2.01 | -- |
| (2) | 1-Methylnaphthalene | 2.16 | 2.29 | 0.84 | 3.06 | 1.66 | 1.85 | -- |
| (2) | Acenaphthalene | 0.40 | 0.32 | 0.07 | 0.09 | 0.08 | 0.03 | -- |
| (2) | Acenaphthene | 0.83 | 0.79 | 0.13 | 0.18 | 0.19 | 0.08 | -- |
| (3) | Fluorene | 0.73 | 0.69 | 0.13 | 0.19 | 0.17 | 0.06 | -- |
| (3) | Phenanthrene*/Anthracene* | 2.56 | 2.14 | 0.32 | 0.37 | 0.30 | 0.14 | 0.01 |
| (3) | Acridine | 0.94 | 0.73 | 0.35 | 0.13 | 0.10 | 0.03 | -- |
| (3) | Carbazole | 0.52 | 0.44 | 0.06 | 0.13 | 0.04 | 0.07 | -- |
| (4) | Fluoranthene | 0.32 | 0.26 | -- | 0.14 | 0.03 | 0.04 | -- |
| (4) | Pyrene* | 0.45 | 0.37 | 0.17 | 0.15 | 0.04 | 0.09 | -- |
| (4) | Benzofluorene | 0.74 | 0.58 | 0.11 | 0.09 | -- | -- | -- |
| (4) | Benz(a)anthracene*/Chrysene*/Triphenylene | 0.19 | 0.22 | 0.04 | 0.10 | -- | 0.03 | -- |
| (5) | Benzo(e)pyrene*/Benzo(a)pyrene* | 0.06 | 0.05 | 0.10 | 0.14 | -- | -- | -- |
| (5) | Perylene | -- | 0.03 | 0.13 | 0.12 | -- | -- | -- |
| (5) | Dibenz(a,j)acridine* | -- | 0.07 | -- | -- | -- | -- | -- |
| (5) | Dibenz(a,i)carbazole* | -- | 0.17 | -- | 0.14 | -- | 0.19 | -- |
| (6) | Indeno(1,2,3-cd)pyrene* | -- | -- | -- | -- | -- | -- | -- |
| (5) | Dibenzanthracene* ^c | -- | -- | -- | -- | -- | -- | -- |
| (6) | Benzo(g,h,i)perylene | -- | -- | -- | -- | -- | 0.06 | -- |
| (7) | Crconene | -- | -- | -- | -- | -- | -- | -- |
| (6) | Dibenzpyrene* ^c | -- | -- | -- | -- | -- | -- | -- |
| TOTAL | | 15.71 | 14.84 | 4.77 | 12.83 | 4.73 | 8.09 | 0.07 |

* 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 $\pm 2\%$ 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-4. Summary of PAH Results

| | Personal Samples | | | Area Samples | | |
|---------|------------------|--|-------------|----------------|--|-------------|
| | No. of Samples | \bar{X} ($\mu\text{g}/\text{m}^3$) | No. of PAHs | No. of Samples | \bar{X} ($\mu\text{g}/\text{m}^3$) | No. of PAHs |
| FCCU | 8 | 4.0 | 7-12 | 2 | 129.9 | 13-14 |
| Coker | 10 | 18.1 | 11-17 | 2 | 7.2 | 13-14 |
| Asphalt | -- | -- | -- | 4 | 9.5 | 11-15 |
| Total | 18 | 11.8 | 7-17 | 8 | 39.0 | 11-15 |

FCCU

The average (arithmetic mean) cumulative PAH concentration (\bar{X}) over the two shifts for the four FCCU workers was $4.0 \mu\text{g}/\text{m}^3$ with the number of individual PAHs ranging from 7 to 12. Seven of these eight personal samples ranged from 0.6 to $3.7 \mu\text{g}/\text{m}^3$. The sample collected on the second sampling day for the lead operator was almost five times greater than the next highest personal sample (17.3 vs. $3.7 \mu\text{g}/\text{m}^3$). This single relatively high personal sample could not be explained by any specific activity or event.

Table V-5 shows that two of the three FCCU operators that spend a large portion of their shift outside the control room in the production area (lead operator and A helper) were exposed at higher concentrations than the boardman who spends almost 100% of his shift inside. These PAH concentrations reported in Table V-5 are again mean cumulative PAH values. The third outside operator (B helper) works primarily in the areas of the unit that handle the lighter fractions and consequently was exposed at PAH concentrations lower than the other two outside operators and even lower than the boardman.

TABLE V-5. Personal Monitoring Results - FCCU

| | No. of Samples | \bar{X} ($\mu\text{g}/\text{m}^3$) | No. of PAHs |
|------------------------------|----------------|--|-------------|
| Outside Operators | 6 | 4.7 | 10-12 |
| Lead Operator | 2 | 10.5 | 11-12 |
| A Helper (R/R, Fractionator) | 2 | 2.9 | 10-12 |
| B Helper (light ends) | 2 | 0.8 | 11-12 |
| Boardman (inside) | 2 | 1.9 | 7-11 |
| Total | 8 | 4.0 | 7-12 |

The results of the personal monitoring were quite consistent over the 2 days for three of the four workers. There was less than 40% difference between the duplicate samples collected for the boardman and the A and B helpers. The lead operator, as noted, was exposed at much higher concentrations during the second sampling day. Both day shifts during which sampling was performed were described as routine by the workers. The weather conditions were also fairly similar during the 2 days. A statistical analysis of the data generated from this survey 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 results of the two area samples collected without cyclones near the slurry recycle pump and the fractionator were similar ($123.5 \mu\text{g}/\text{m}^3$ and 14 PAHs identified, and $132.3 \mu\text{g}/\text{m}^3$ and 13 PAHs identified). For the duplicate sampling units with cyclones, the results were $136.8 \mu\text{g}/\text{m}^3$ (15 PAHs identified) and $166.7 \mu\text{g}/\text{m}^3$ (14 PAHs identified), respectively. The fact that both "respirable" samples were higher than the duplicate "total mass" samples could not be explained. The two area total mass samples, collected very close to each other on separate days, showed very consistent results; the cumulative PAH concentrations for these two samples were within 7% of each other.

DELAYED COKER UNIT

Table V-6 gives a summary of the personal monitoring results for the five workers sampled at the coker. These values are again average cumulative PAH concentrations for the two sampling days. Table V-6 shows that the samples for the two operational workers and two of the three cutters (driller and cutter B) yielded results that were quite similar ranging from 19.5 to 24.2 $\mu\text{g}/\text{m}^3$. The third cutter (cutter A) was exposed at much lower PAH concentrations (2.2 $\mu\text{g}/\text{m}^3$) than the other four coke workers despite the fact that both cutters A and B generally performed similar tasks. There was some problem with the sampling pump on cutter A during the first sampling shift; however, the results of the second sampling shift for this worker were also relatively low. While the average cumulative PAH exposure concentration for the driller was similar to most of the other coke workers, he was exposed to a larger number of PAHs (16-17) than the others (9-12).

TABLE V-6. Personal Monitoring Results - Delayed Coker Unit

| | No. of Samples | \bar{X} ($\mu\text{g}/\text{m}^3$) | No. of PAHs |
|-------------------------|----------------|--|-------------|
| Operational | 4 | 22.2 | 11-12 |
| Boardman | 2 | 22.6 | 11-12 |
| Coke Helper | 2 | 21.7 | 11-12 |
| Cutters | 6 | 15.6 | 9-17 |
| Driller | 2 | 19.5 | 16-17 |
| Cutter A | 2 | 2.2 | 9-11 |
| Cutter B | 2 | 24.2 | 11 |
| Operational and Cutters | 10 | 18.2 | 9-17 |

The results for the two operational workers were very similar despite the fact that the boardman spends almost 100% of his shift inside the control room while the coke helper spends about 50% of his shift outside in the production area. As mentioned previously, the control room was downwind of the coke tower, fractionator, and pumps during at least part of both sampling shifts. This could possibly explain these results.

Overall, the personal sampling results show very little consistency between the two sampling periods. This may be due to the fact that there were many difficulties during the first cutting operation which required almost double the normal working period. As a result, the full cutting operation was not sampled. The boardman and cutter B yielded much higher results the first day while the coke helper, driller, and cutter A yielded higher results the second day.

The two area samples taken in the coker unit without cyclones showed cumulative PAH concentrations of $5.2 \mu\text{g}/\text{m}^3$ (14 PAHs identified) near the cutting operation and $9.1 \mu\text{g}/\text{m}^3$ (13 PAHs identified) near the furnace charge pump. The duplicate area samples collected with cyclones showed cumulative concentrations of $6.9 \mu\text{g}/\text{m}^3$ (8 PAHs identified) and $5.3 \mu\text{g}/\text{m}^3$ (11 PAHs identified), respectively, for the same locations.

ASPHALT PROCESSING UNITS

The results of the two area samples collected without cyclones (total mass) at the No. 1 vacuum unit were $15.7 \mu\text{g}/\text{m}^3$ (15 PAHs identified) the first sampling shift and $4.8 \mu\text{g}/\text{m}^3$ (15 PAHs) the second sampling shift. During the first sampling shift, a duplicate area sample was collected with a cyclone (respirable) and the result was $14.1 \mu\text{g}/\text{m}^3$ (18 PAHs).

The results of the two area samples collected without cyclones at the No. 4 vacuum unit were $12.8 \mu\text{g}/\text{m}^3$ (17 PAHs) the first shift and $4.7 \mu\text{g}/\text{m}^3$ (11 PAHs) the second shift. During the second shift, a duplicate area sample was collected with a cyclone and the result was $8.1 \mu\text{g}/\text{m}^3$ (15 PAHs).

PAH DISTRIBUTION

Table V-7 shows the percent distribution of PAHs found at the various units by compound ring number. In all locations, as the table indicates, at least 72% of the PAHs found were the lighter molecular weight, 2-ring compounds; at the coker this percentage was over 94%. Naphthalene and its two methyl derivatives were the compounds found in the highest concentrations. In the FCCU samples, there were also considerable quantities of the 3-ring phenanthrene/anthracene group.

TABLE V-7. Distribution (%) of PAHs Found by Ring Number

| Ring No. | FCCU | Delayed Coker | Asphalt |
|----------|------|---------------|---------|
| 2 | 73.4 | 94.1 | 72.5 |
| 3 | 19.5 | 4.6 | 19.8 |
| 4 | 7.1 | 0.8 | 6.1 |
| 5 | 0 | 0.5 | 1.6 |
| 6 | 0 | 0 | 0 |
| 7 | 0 | 0 | 0 |

VI. CONCLUSIONS

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

It was anticipated that the personal sampling results would show that the outside workers at the coker and FCCU were exposed at much higher PAH concentrations than the inside workers (boardmen), who spend almost 100% of their shift inside the control rooms. However, the results showed that both the variety and concentrations of PAHs to which the boardmen were exposed were greater than anticipated. At the FCCU, the results for the boardman were comparable to those of two of the three outside operators; and at the delayed coker unit, the results for the boardman were higher than those for three of the four workers, including two of the three coke cutters, who spent all or most of their shift outside in the production area. This clearly indicates that control rooms are definitely not free of contaminants from the production areas.

The personal sampling data indicate that the workers at the delayed coker unit are exposed at much higher PAH concentrations than the workers at the FCCU. The fact that the two operational coke workers were exposed at higher PAH concentrations than the three coke cutters was unexpected.

It is not certain what effect the difficulties encountered during the coke-cutting operations, particularly the first, had on the sample results. However, the fact that the average cumulative PAH concentration for the coke workers during the first shift ($19.6 \mu\text{g}/\text{m}^3$) was similar to that for the second shift ($16.5 \mu\text{g}/\text{m}^3$) indicates that the data collected during the first cutting operation were representative.

While the personal and area sampling data for the FCCU were quite similar over the two sampling shifts, the personal sampling data at the coker for individual workers (area sampling data not comparable) varied greatly between the 2 days. This might be explained by the fact that both sampling shifts at the FCCU were considered "routine" by the employees while, as noted, the shifts at the coker were quite different.

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 would be considerably higher than the personal samples. This was the case at the FCCU as the mean cumulative PAH concentration of the two area samples collected near the slurry recycle pumps was much higher than the mean cumulative PAH concentration for the eight personal samples (127.9 vs. $4.0 \mu\text{g}/\text{m}^3$). This indicates that the slurry recycle pump area is a source of PAH emissions. In the coker unit, many of the personal samples, including those of the two operational workers, were higher than the area samples collected near the coke cutting and furnace-charge pump. This finding as well as the levels found in the control room indicate that PAHs are not restricted to the areas around major emission sources but are widespread throughout many parts of this unit.

The results of the area samples collected at the two asphalt processing areas ($\bar{X} = 9.5 \mu\text{g}/\text{m}^3$) were higher than expected based on Phase II area sampling. The results for the two asphalt units were also quite similar (10.3 vs. $8.8 \mu\text{g}/\text{m}^3$) even though No. 1 vacuum unit was in a fairly open area with no other heavy-fraction process streams nearby while No. 4 vacuum unit was surrounded by No. 4 crude unit.

The number of PAHs or groups of PAHs identified in the majority of samples collected at this refinery was greater than expected based on Phase II

area sample results. Most of the samples had detectable quantities of more than 10 PAHs. The two personal samples from the coke driller yielded 16 and 17 PAHs while up to 18 PAHs were identified in the asphaltting area samples. As expected from the Phase II results, the great proportion of the PAHs identified were the lighter 2- and 3-ring compounds.

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 makes an assessment of the actual cancer hazard of this group of compounds outside the scope of this study.

The results of the area samples collected side by side to compare the PAHs present in the total mass and respirable fraction (collected with a cyclone preselector) samples were inconclusive. In the FCCU, both area locations sampled yielded higher PAH concentrations in the respirable sample, and in both the coker and asphalt units, one of the two locations sampled showed higher concentrations in the respirable fraction sample. The small number of side-by-side samples collected and the inconsistencies at the process units make the results for this aspect of the survey inconclusive at this time.

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

Opening Conference Attendees

Enviro Control, Inc.

| | |
|-----------------|-----------------------------|
| Stan Futagaki | Senior Industrial Hygienist |
| Edward Haggerty | Industrial Hygienist |

NIOSH

| | |
|----------------|---------------------------|
| Robert Herrick | Alternate Project Officer |
|----------------|---------------------------|

Coastal States

| | |
|-------------------|--|
| Don Williams | Administrative Services Manager |
| Earl McMannis | Operations Manager |
| William L. Wilcox | West Plant Area Supervisor |
| Don Westbrook | Southside Unit Supervisor |
| Gerald Burdock | FCCU Supervisor |
| N. L. Deavers | No. 4 Crude, Coker, Vacuum Supervisor |
| E. H. Winters | Process Engineer Manager |
| L. W. Denney | Safety, Security Supervisor |
| W. E. Hobbs | West Plant Operations Manager |
| Windle Taylor | Lead Environmental Engineer |
| Anne Hubbard | Special Projects Chemist |