

PHASE III SURVEY REPORT #6  
WORKER EXPOSURE TO POLYAROMATIC HYDROCARBONS  
AT SELECTED PETROLEUM REFINERY PROCESS UNITS

SURVEY LOCATION:  
KOCH REFINING COMPANY  
ROSEMOUNT, MINNESOTA

Survey Dates:  
13-15 MAY 1980

Report Date:  
OCTOBER 1980

DISCLAIMER

Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

NIOSH Project Officer: Clinton Cox  
Enviro Control, Inc., Project Officer:  
Donald W. Rumsey

## 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 polycyclic aromatic hydrocarbons (PAHs) in three different types of process units. Personal and area air samples were collected in the fluid catalytic cracker and delayed coker units 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. Thirty-two of the 33 personal and area air samples had detectable quantities of at least five PAHs or groups of PAHs with the cumulative PAH concentration for individual samples ranging from none detected for a personal sample from one of the operators at the delayed coker unit to as high as 32.6  $\mu\text{g}/\text{m}^3$  for one area location at the FCCU. The two upwind boundary samples were 0.3  $\mu\text{g}/\text{m}^3$  and none detected.

This report was submitted in fulfillment of Contract No. 210-78-0082 by Enviro Control, Inc. under the sponsorship of the National Institute for Occupational Safety and Health (NIOSH) with the financial support of the Environmental Protection Agency (EPA-IAG-DS-E773).

## CONTENTS

Abstract . . . . .	iii
I. Introduction . . . . .	1
II. Refinery Description . . . . .	4
III. Study Process Units . . . . .	8
Fluid Catalytic Cracker Unit (FCCU) . . . . .	8
Delayed Coker Unit . . . . .	13
Asphalt Processing . . . . .	19
IV. Sampling Program . . . . .	20
Protocol . . . . .	20
FCCU . . . . .	23
Delayed Coker Unit . . . . .	23
Asphalt Processing Units (Vacuum Units) . . . . .	26
V. Results and Discussion . . . . .	27
FCCU . . . . .	31
Delayed Coker Unit . . . . .	32
Asphalt Processing Units . . . . .	34
PAH Distribution . . . . .	34
Particle-Size Distribution . . . . .	35
VI. Conclusions . . . . .	36
Appendix . . . . .	39

## FIGURES

II-1. Refinery Production Area . . . . .	6
III-1. FCCU . . . . .	9
III-2. Delayed Coker Unit . . . . .	14
IV-1. Area Monitoring Device for PAHs . . . . .	21
IV-2. Personal Monitoring Device for PAHs . . . . .	21
IV-3. FCCU Area Sampling Locations . . . . .	24
IV-4. Delayed Coker Unit Area Sampling Locations . . . . .	25

CONTENTS (continued)

TABLES

V-1.	PAH Analytical Results ( $\mu\text{g}/\text{m}^3$ ) for Personal and Area Samples Collected at the FCCU . . . . .	28
V-2.	PAH Analytical Results ( $\mu\text{g}/\text{m}^3$ ) for Personal and Area Samples Collected at the Delayed Coker Unit . . . . .	29
V-3.	PAH Analytical Results ( $\mu\text{g}/\text{m}^3$ ) Area Samples Collected at the Asphalt Units and Upwind Locations . . . . .	30
V-4.	Summary of PAH Results . . . . .	31
V-5.	Personal Monitoring Results - FCCU . . . . .	31
V-6.	Personal Monitoring Results - Delayed Coker Unit . . . . .	33
V-7.	Distribution (%) of PAHs Found by Ring Number . . . . .	34
V-8.	Particle-Size Distribution (%) of Total Particulate Area Samples . . . . .	35

## 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, 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 Koch refinery at Rosemount, Minnesota was the sixth 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 Koch refinery was conducted over a period of three days, from May 13-15, 1980. The first day was devoted to an opening conference and a walkthrough 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 Executive Vice-President. All subsequent arrangements were made through the Refinery Manager.

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 Project Officer from NIOSH described the project, the status, and the specific objectives of the survey. A tentative schedule was agreed upon for the three 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 meeting, the survey team conducted a walkthrough of the four process units to be sampled. At the fluid catalytic cracker (FCC) and the delayed coker, where personal monitoring was scheduled, the Enviro industrial hygienists explained the sampling procedures to the employees.

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

## II. REFINERY DESCRIPTION

This Koch refinery is located about 20 miles south of Minneapolis, Minnesota. With its crude capacity of about 127,000 bbl/day, this refinery is classified as a "large" refinery for the purposes of the study. Since Koch Refining Company is not one of the 15 largest 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, currently spread over about 1000 acres, originated in 1955. At the time of the survey, the refinery was operating at about 90% of capacity and producing a full line of petroleum products which include:

- liquid petroleum gas (propane, butane)
- gasolines (three grades)
- Diesel fuel
- fuel oils (#1, #2, #6)
- sponge coke
- asphalt
- sulfur

Although the source varies, the crude refined here is categorized as a "heavy," "sour" (>1% sulfur by weight), naphthenic crude. Approximately 50% of the crude comes from Canada by pipeline. The rest comes from various domestic and foreign sources by pipeline and barge. Finished products are shipped by pipeline, railcars, trucks, and barges.

The major process units at the Koch refinery include:

- two crude distillation units
- two vacuum distillation units

- two delayed coker units
- hydrotreating units
- two catalytic reformers
- catalytic polymerization unit
- FCCU
- H<sub>2</sub>SO<sub>4</sub> alkylation unit
- sulfur recovery unit

There are four main control buildings for the whole production area. The delayed coker has its own, the FCCU shares one with the alkylation unit, and the asphalt processing units (vacuum units) share a control building with the crude and other adjacent units. Figure II-1 shows a rough refinery plot plan of the major production units.

There are approximately 370 hourly employees, including 120 maintenance workers, that belong to the union (Oil, Chemical, and Atomic Workers) and an additional 130 that are salaried (supervisory and administrative personnel). Most of the routine maintenance activity is performed in-house; contractors are brought in for turnarounds and other major projects. The production units operate 24 hours a day over three work shifts.

The safety and health staff at this refinery includes the Health and Safety Coordinator, a safety engineer, a fire marshal, and an occupational health nurse. All are under the direct supervision of the Industrial Relations Manager who reports to the Refinery Manager. The nurse is normally on the premises full time during the day shift, 5 days a week; during turnarounds, a nurse is on the premises at all times. Approximately 325 of the 500 employees are formally trained in first aid. The dispensary and treatment room is fully equipped to handle first aid situations and various routine examinations. All workers are given preemployment medical examinations. Employees assigned to the miscellaneous trades group are given annual physical examinations because of possible asbestos exposure. Several physicians in the area work with the refinery.

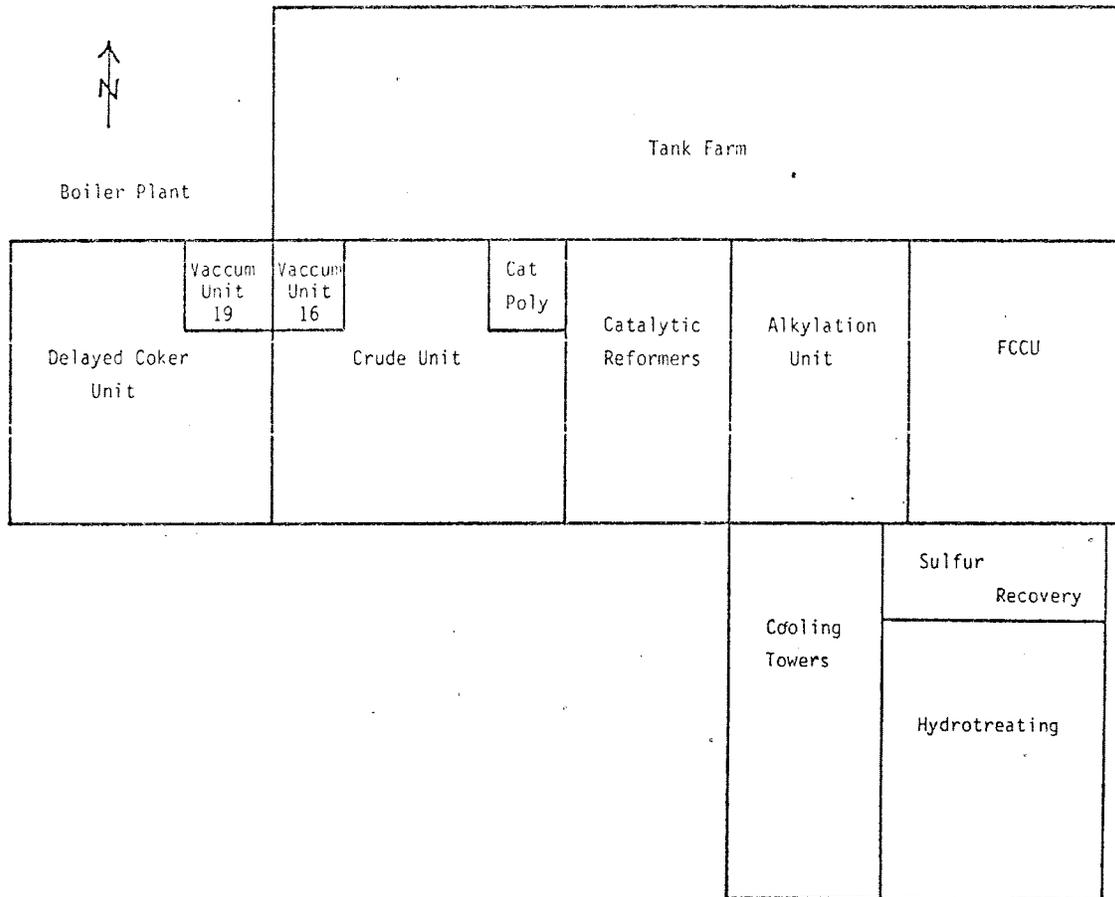


FIGURE II-1. Refinery Production Area

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 immediate production areas. Each unit operator is thoroughly trained on the unit and in the classroom on the unit equipment, operations, and associated safety hazards. 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 routine cleanup is performed by the day-shift unit operators. Any necessary equipment or structure repair is also promptly carried out by the unit operators or in-house maintenance crews.

Routine industrial hygiene sampling is not performed at this refinery. In the past, consulting firms have been used to investigate problems as they arise and have performed sampling for chromates (cooling towers), benzene, asbestos, and noise.

### III. STUDY PROCESS UNITS

#### FLUID CATALYTIC CRACKER UNIT (FCCU)

##### A. Unit and Process Description

The FCCU is located on the east side of the main production area (Figure II-1). The  $H_2SO_4$  alkylation unit is to the west, the sulfur recovery unit to the south, garage and laboratory to the east, and storage tanks to the north. The FCCU was constructed and put on stream in 1968. The CO boiler was also built in 1968. In 1974, major modifications were made to the present unit including the addition of a riser extension to increase capacity and cyclones in the reactor and regenerator. At the time of the survey, the production capacity of the unit was about 45,000 bbl/day and the FCCU was operating at about 85% of this capacity.

Figure III-1 illustrates the layout of this unit which occupies an area about 200 x 150 feet. The fractionator and side-by-side reactor/regenerator structure (R/R) are located in the center of the unit. The feed drum and furnace are just to the west of these structures; and the control building, shared by the adjacent alkylation unit, is farther west on the edge of the FCCU. The catalyst hoppers are at the south end of the unit, and the CO boiler is in the southeast corner. The whole north end of the unit is the gas recovery area, which includes the primary and secondary absorbers, stripper, and debutanizer.

Fresh feed for the FCCU consists of desulfurized atmospheric and vacuum gas oils. This feed, preheated by a gas-fired charge heater, plus slurry recycle from the fractionator are mixed with the hot catalyst in the single riser leading to the reactor. The catalytic cracking takes place in the

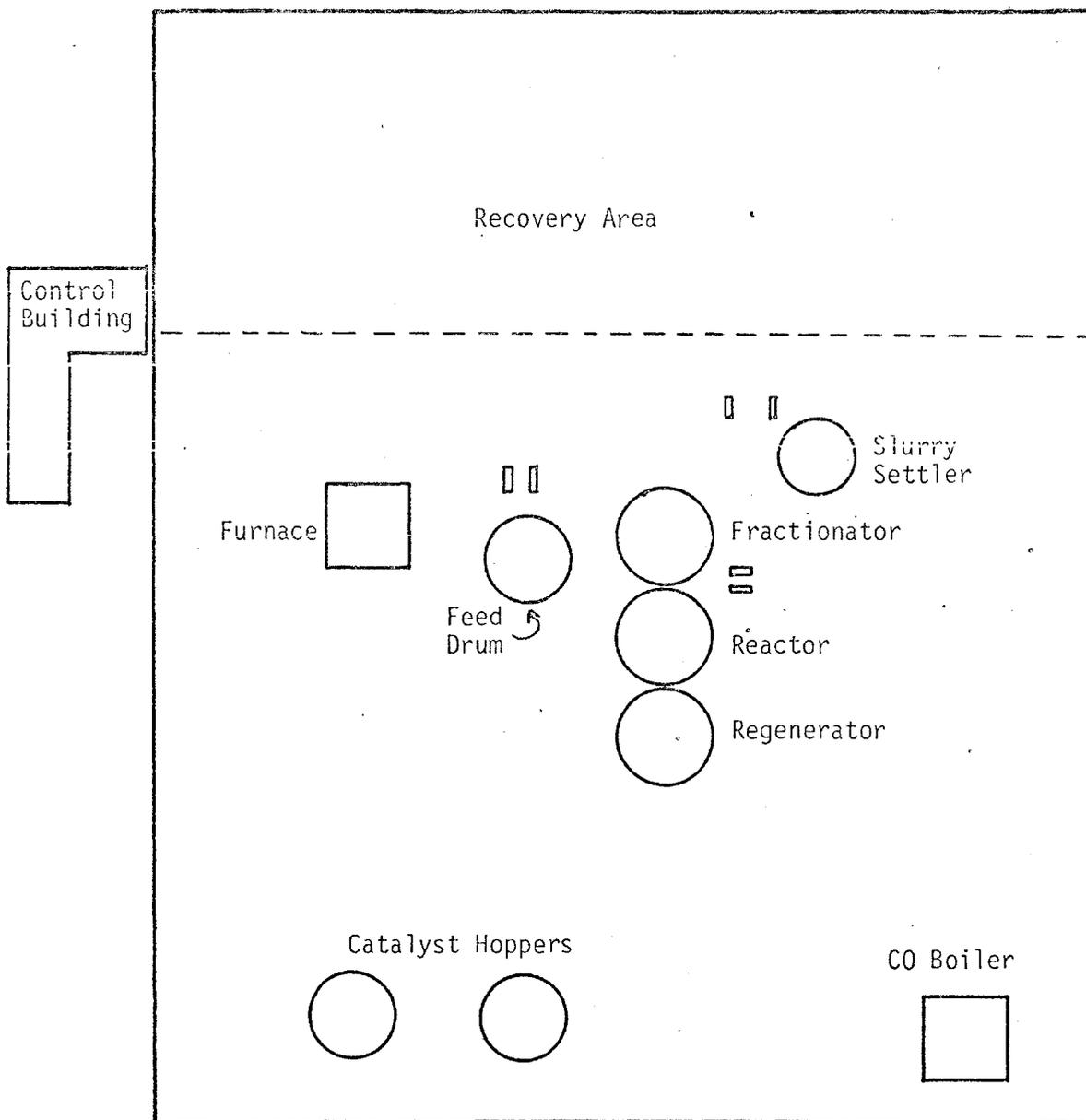


FIGURE III-1. FCCU

riser as well as in the reactor. The catalyst used at this Koch refinery is a synthetic zeolite common to other FCCUs studied in this project. The product vapors and the catalyst are separated (series of cyclones), and the hydrocarbons are taken 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 reactivated by oxidizing the accumulated carbon at a temperature above 1000°F (538°C). The regenerator has a series of cyclones which separate the catalyst fines from the flue gas. From the regenerator the flue gas goes through an orifice chamber (back-pressure stabilizer) before going on to the CO boiler. There it is burned with an auxiliary fuel before being released into the atmosphere. The regenerated catalyst is stripped with steam of any absorbed oxygen before being recirculated back to the riser.

The main products from the fractionator are:

- propane
- butane
- gasoline
- light cycle oil
- heavy cycle oil
- clarified oil (decant oil)

#### B. Work Force

There are normally four workers assigned to the FCCU full time during each shift. This includes one #1 operator and three #2 operators, including the boardman. In addition, there is a supervisor in charge of personnel, scheduling, and operations of both the FCCU and the adjacent alkylation unit. This supervisor spends about half of his time inside the joint control room and the other half split equally between the production areas of the two units. He visually inspects the units, monitors and assists the operators; and it is his overall duty to ensure smooth operations. Following is a brief description of the duties of the four full-time FCCU operators.

- e #1 Operator: This is the "master" operator on the unit who must understand the entire unit operation. He is in charge of the other operators and assigns daily work tasks. He routinely inspects the entire unit and can assist the operators in performing any of their duties. He normally spends about 60% of the shift inside the control room.
- e #2 Operator/Boardman: Spends essentially 100% of his shift inside the control building, monitoring and logging in the various meters and charts on the control board. He works closely with the #1 operator, as well as with the other outside operators.
- e #2 Operators: These two outside operators perform the routine daily tasks in the production areas under the supervision of the #1 operator. One is primarily responsible for the cat side which includes the R/R structure, fractionator, catalyst hoppers, furnace, etc.; the other is responsible for the recovery area which includes the structures in the northern part of the unit. Duties include operating and regulating valves, pumps, and compressors to direct flow of process streams; checking temperature and pressure gauges and flow meters; and checking equipment for any malfunctions. The operator in the cat side samples process streams for gasoline, light cycle oil, slurry recycle, decant oil, as well as the flue gas. He also runs tests on the boiler feedwater for chemical characteristics. Both operators perform various manual tasks to maintain process control. During an average shift, they spend about 40% of the time outside in the production area.

During both sampling shifts of the survey there was also a #1 operator trainee. This person worked very closely with the #1 operator observing and occasionally performing the various duties.

### 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 during sampling of the various streams, during maintenance and housekeeping activities, from fugitive emissions, and from the regenerator flue gas.

Liquid process stream samples are collected by the open-spigot-and-bottle method without sampling loop. The operator flushes the sample lines directly into the unit sewer system before filling the sample bottle. Product coolers (water coolers) are used to cool hot process streams before sampling. Most of the heavy-fraction process stream samples (more likely to contain the PAHs) are collected by the #2 operator assigned to the cat side. Propane and butane gas samples are collected by laboratory technicians using sample bombs.

Exposure during routine and any emergency maintenance is difficult to minimize. The ground level of the unit is mostly sand and gravel with concrete foundations around structures. The lack of a complete concrete foundation may pose a cleanup problem for major spills. The refinery has its own craft maintenance crews (e.g., pipefitters, electricians) that provide preventive and repair services. The last major turnaround of this unit was during 1978 with the next one scheduled for October of 1980.

Hard hats and safety shoes are routinely worn; eye and ear protection, and slick-suits are available. Coveralls are not provided and not normally worn. There are no routine operations that require the usage of respirators; however, NIOSH-approved air-purifying and self-contained-breathing-air (SCBA) respirators are available. The air-purifying equipment are maintained by the individual operators while the SCBA are maintained by the refinery safety department.

The areas of the unit handling heavy fraction are fairly open, minimizing potential vapor accumulation. Several of the charge, slurry recycle, and decant oil pumps are located in the same vicinity near the fractionator; the surrounding pipes and structures create a "tunnel-effect" here. This is an area where PAH concentrations might be elevated. The control house is air-conditioned and under positive pressure. A 35-foot stack provides the incoming air supply. The control building is not normally downwind of the R/R or heavy-fraction pumps.

The 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 not only removes carbon monoxide from the flue gas, but many other hydrocarbons, making the effluent suitable for discharge to the atmosphere.

#### DELAYED COKER UNIT

##### A. Unit and Process Description

The delayed coker unit is located on the west end of the main production area (Figure II-1). The boiler plant is to the north and the crude and vacuum units are to the east and northeast. The delayed coker unit is actually two identical operational units within the same physical unit. There are two pairs of 98-foot coke drums, two charge furnaces, and two fractionators. There is one coke recovery area and one control building. The total unit has a daily production capacity of about 1300 tons of sponge coke.

The unit was built in 1955-1956 with drums A and B; the other two drums were added in 1963. Drums A and B were replaced during the 1977-1978 unit turnaround. The unit is spread over an area about 200 x 200 feet (Figure III-2). The ground level of the entire unit is constructed of concrete. The control building is located in the central area of the unit and houses the locker and shower facilities in addition to the

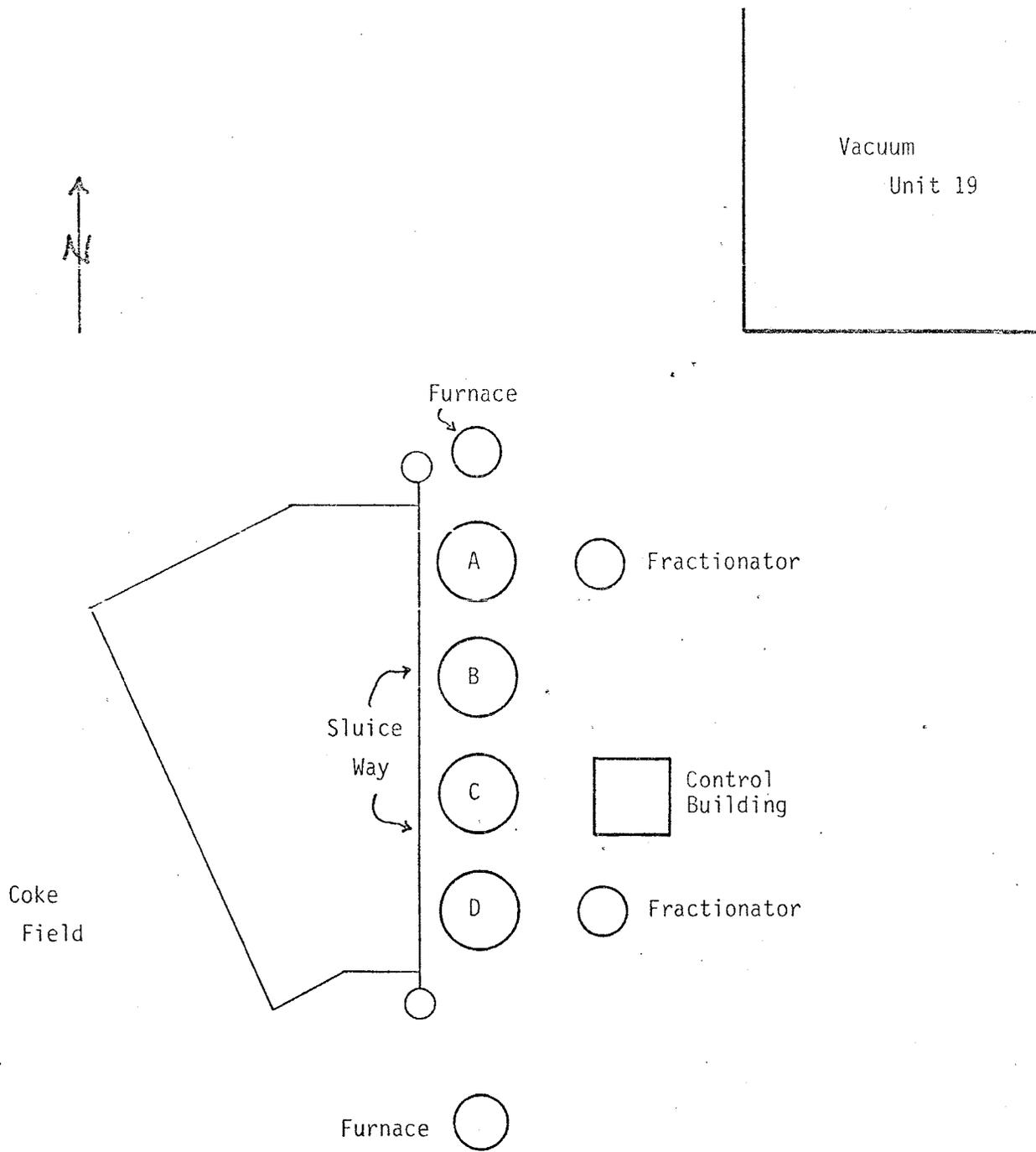


FIGURE III-2. Delayed Coker Unit

control board room. West of the control building is the coke tower (an open, multi-level structure that includes the four drums and penthouse at the top) with the sluice way and coke field farther west. The coke that has been cut is moved from the sluice way to the coke field with a drag line consisting of a cable-drawn bucket scoop. The coke is allowed to dry on the coke field and is then moved by bulldozers to the screening area where the coke is sized and loaded onto railcars and trucks by conveyor.

The two gas- and oil-fired charge furnaces are located to the north and south of the coke tower; the two fractionators are located between these furnaces and the control building. The coker gas recovery unit is to the east of the control building. The coker flare is located remotely to the south of the coker unit.

Sponge or No. 2 grade coke is the only type produced at this refinery. The charge stock is primarily residual (asphalt) from the vacuum distillation units. The charge is pumped to the fractionators where the lighter fractions are separated and processed in the vapor recovery area. The bottoms from the fractionators are then pumped to the furnaces where they are heated to a suitable reaction temperature (normally about 900°F or 482°C). The heated charge then goes to one of four coking drums where the thermal cracking process begins. There are two pairs of drums, and each drum has a 40-hour cycle (each pair has a 20-hour cycle) with coke formation lasting about 20 hours. Normally one drum is cut every 10 hours. Vapors off the top of the drum are sent to the fractionators where various products are separated and eventually recovered. Products from this unit, other than coke, include: propane, butane, gas oil, and naphtha.

Routine procedures are used at this unit for preparing each drum for cutting. Coke formation is stopped by switching the feed to the other drum of the pair. Steam followed by water is used to cool the drum; this lasts several hours. About 1 hour before cutting is scheduled, the top and bottom of the drum are opened; and the coke is cut with a high-

pressure hydraulic bit. An initial hole is bored through the coke, and then the coke is cut from the bottom up. The coke then falls down a chute into the sluice way. Drilling normally lasts from 3 to 5 hours.

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

#### B. Work Force

The work force for the delayed coker unit is divided into two groups, the operations group and the decoker (coke cutting and handling) group. Both groups work the normal 8-hour shift. The operations group is normally made up of one #1 operator, three #2 operators (including the boardman), and the unit supervisor; following is a brief description of their job activities.

- Supervisor: Has overall responsibility for both the delayed coker unit and the adjacent boiler plant. He generally spends about 75% of his shift dealing with the delayed coker unit and 25% with the boiler plant. He spends about 1-1½ hours per shift in the control room and periodically patrols the production areas, but also spends a good part of any shift in other parts of the refinery (e.g., shift supervisor's office).
- #1 Operator: Duties very similar to the #1 operator for the FCCU. He is the "master" operator and supervises the other operational personnel. He normally spends about 60% of the shift inside the control room and works closely with the boardman and other #2 operators. He normally delegates the routine outside tasks but may occasionally assist. He does perform periodic visual inspections of the production areas.

- #2 Operator/Boardman: Spends essentially 100% of his shift inside the control building, monitoring and logging in the various meters and charts on the control board. He works closely with the #1 operator, as well as with the other outside operators.
- #2 Operators: During the two sampling shifts of the survey, these two outside operators worked together to perform the routine outside tasks. This included opening and closing valves to direct charge to the various drums, depressurizing drums, steam-testing drums for leaks, testing spare pumps, draining the fire drum and clarifier, cooling the drums, and making periodic rounds to detect any equipment malfunction. They spend about 40% of their shift outside in the production area.

The decoker group is made up of the supervisor, #1 decoker (driller), and four #2 decokers. They do not work out of the main control building but a small separate building at the foot of the coke pile (coke field); most of their shift is spent outside. Following is a brief description of their job duties.

- Supervisor: Spends about 75% of his shift outside; about 90% of that time is spent in the coke-loading area. He primarily patrols the various areas monitoring workers and directing operations.
- #1 Decoker: He is the lead decoker and delegates various tasks. During the survey, he directed the deheading of the drum and then performed the drilling from the penthouse at the top of the coke tower. When cutting is not performed during a particular shift, he can assist in any of the coke handling activities.
- #2 Decokers: Normally (and during the survey), there are four #2 decokers per shift. They help dehead the top and bottom of the drum before cutting, position

the drum extender, close the drum after cutting, and clean up. While the drum is being cut, they perform the coke-handling duties. One decoker ("sauerman") is stationed in an elevated cubicle on the north end of the sluice way and operates the mechanical scoop which moves the coke to the coke field. Another decoker operates the bulldozer moving the coke from the coke field to the screening and loading area, and the other can be at the loading area. The decokers alternate what they do from shift to shift as well as during a shift.

### 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 sauerman must move the coke out of the sluice way, and the other coke handlers must move and load the coke. Basically the coke-cutting operations at this refinery were similar to those observed at other refineries; however, coke handling was more extensive after the coke was cut.

The opening of the top and bottom of the drum was done very efficiently and quickly. The three coke cutters worked as a team to complete both openings in about 30 minutes. After the bottom is dropped, a chute extender is lifted up from the floor platform to the bottom of the drum and secured with a chain mechanism ("chain fall"). This forms a closed system on this level. Once cutting starts, the cutters (except the driller) leave the coke tower to switch to coke-handling duties.

The enclosed room where the driller sits during decoking operations, which separates him from most of the dust and gases during the coke-cutting operation, had no mechanical ventilation. The whole cutting operation at this refinery is relatively clean requiring a minimum of cleanup, usually performed by hosing down the area with water.

All workers on this unit wore hard hats, safety glasses, and gloves. Neither the cutters nor the operational crew wore coveralls, but the cutters did normally change into a set of work clothes in the locker room and showered or washed up at the end of their shift. The cutters did wear rain gear or slick suits when deheading the drums. The operations crew ate in the control room while the decokers usually ate in their work building. There were no routine operations that required the use of respirators; however, NIOSH-approved air-purifying and self-contained breathing-air respirators were available.

The steam that is used to cool the drums down goes through a condensation system from which uncondensed steam and/or hydrocarbon vapors go to the coker flare. As with the FCCU, the air-conditioned control room was under positive pressure and supplied with intake air from a stack extending 35 feet above ground level.

## ASPHALT PROCESSING

### A. Unit and Process Description

The asphalt processing at this refinery consists of two vacuum distillation units; the bottoms from the fractionating towers are pumped to storage (and blending) or to the delayed coker unit as charge. The two vacuum units are adjacent to each other; vacuum unit No. 16 is in the northwest corner of the crude area, and unit No. 19 is in the northeast corner of the delayed coker area (Figure II-1). Both vacuum units are monitored from the control room located in the middle of the crude area. The asphalt production capacity of this refinery is about 35,000 bbl/day.

### B. Work Force

No workers are assigned full time to either of the vacuum units. One or more of the outside operators of the crude units spend a small part of their shift covering these units.

#### 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 Koch refinery. Sampling for airborne PAHs was conducted during the day shifts on the second and third days of the survey in the four 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- $\mu\text{m}$  pore size) and a portable MSA, Model S pump calibrated at 2.0  $\ell$ /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 33 samples were 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.

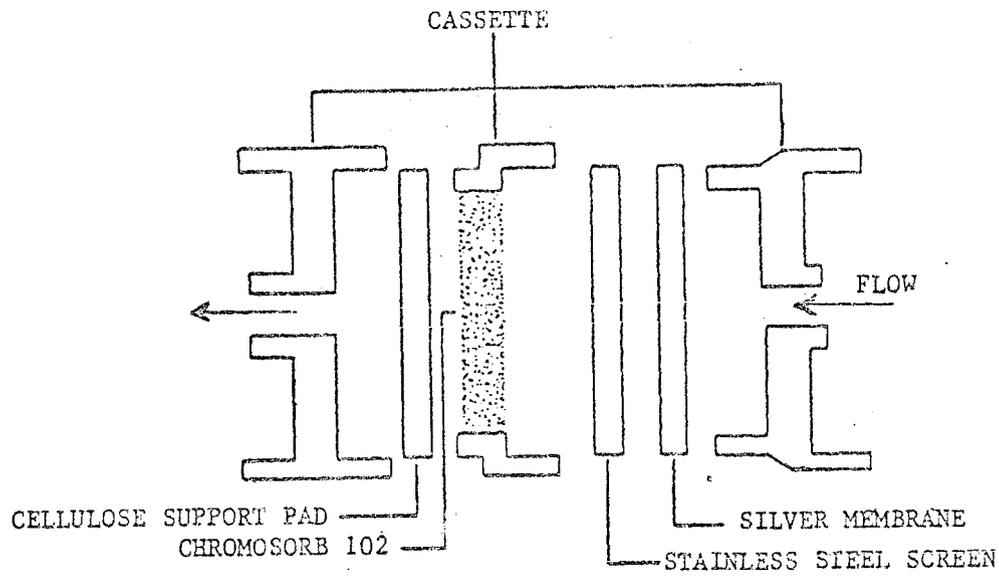


FIGURE IV-1. Area Monitoring Device for PAHs

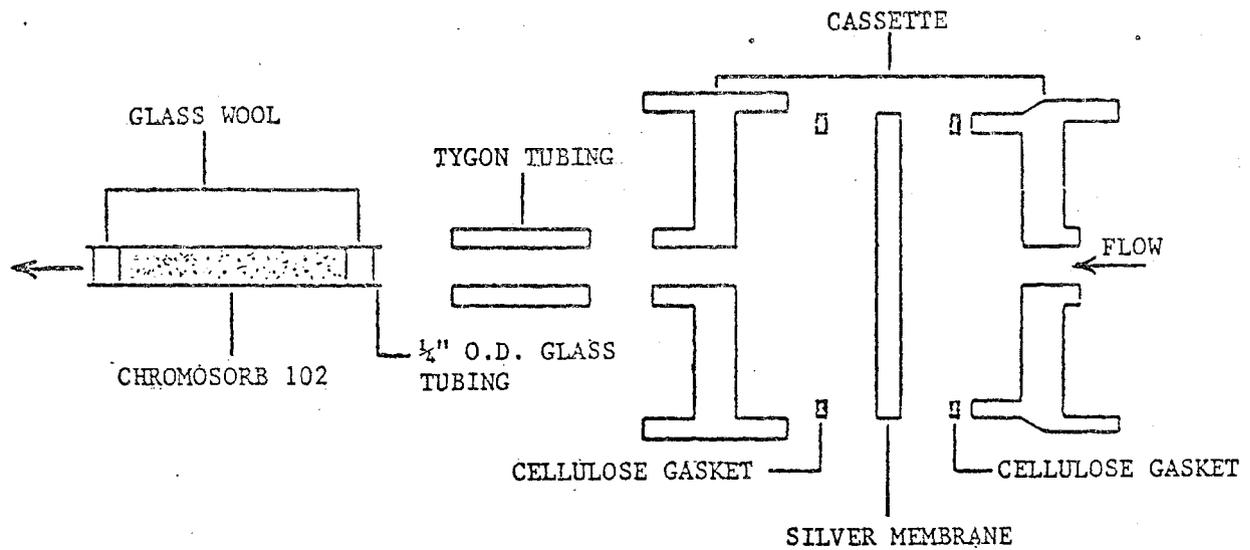


FIGURE IV-2. Personal Monitoring Device for PAHs

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

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 (May 14) was sunny with clear skies; the temperature ranged from 44°F (13°C) in the morning (0830) to about 63°F (17°C) by early afternoon (1400). The relative humidity during this period ranged from 55% to 47% with the winds generally from the north at 2-10 mph.

Skies were again clear and sunny on May 15, with the temperature ranging from 55°F (13°C) at 0900 to 68°F (20°C) at 1400. The relative humidity during this period ranged from 60% down to 32%. In the morning the winds were out of the north, northeast at 3-6 mph and shifted to the southeast at 3-12 mph by early afternoon.

## FCCU

### A. Area Sampling

Two locations in the pump areas near the fractionator and slurry settler (Figure IV-3) were selected to collect the area samples in the FCCU. Location F-1, about 4½ feet above ground on slurry pump #17P-3 was sampled on May 14, during the day shift. This electric-driven centrifugal pump returns the fractionator tower bottoms, which include spent catalyst, back to the reactor. This location was very close to the fractionator and reactor.

Location F-2 was sampled during the day shift on May 15. The sampling unit was situated about 4 feet above ground on one of the decant oil pumps (#17P-2B). This location was close to the slurry settler.

### B. Personal Sampling

The unit supervisor, #1 operator, #1 operator trainee, and two #2 operators (outside) were sampled during the day shifts on May 14 and 15.

## DELAYED COKER UNIT

### A. Area Sampling

Figure IV-4 shows the two area sampling sites selected in the delayed coker unit. Location D-1, 15 feet downwind of A drum and 25 feet west of pump #21P-1, was sampled during the day shift on May 14. Location D-2, 15 feet downwind of C drum and 25 feet west of pump #21P-33, was sampled during the day shift on May 15. The cutting operation during the first day lasted from 0900 to about 1300.

On the second day, the cutting operation was scheduled for 1400 but was slipped to 1600. As a result, the sampling period included the coke handling of the previous cut drum and the preparation for cutting, but not the actual cutting operation.

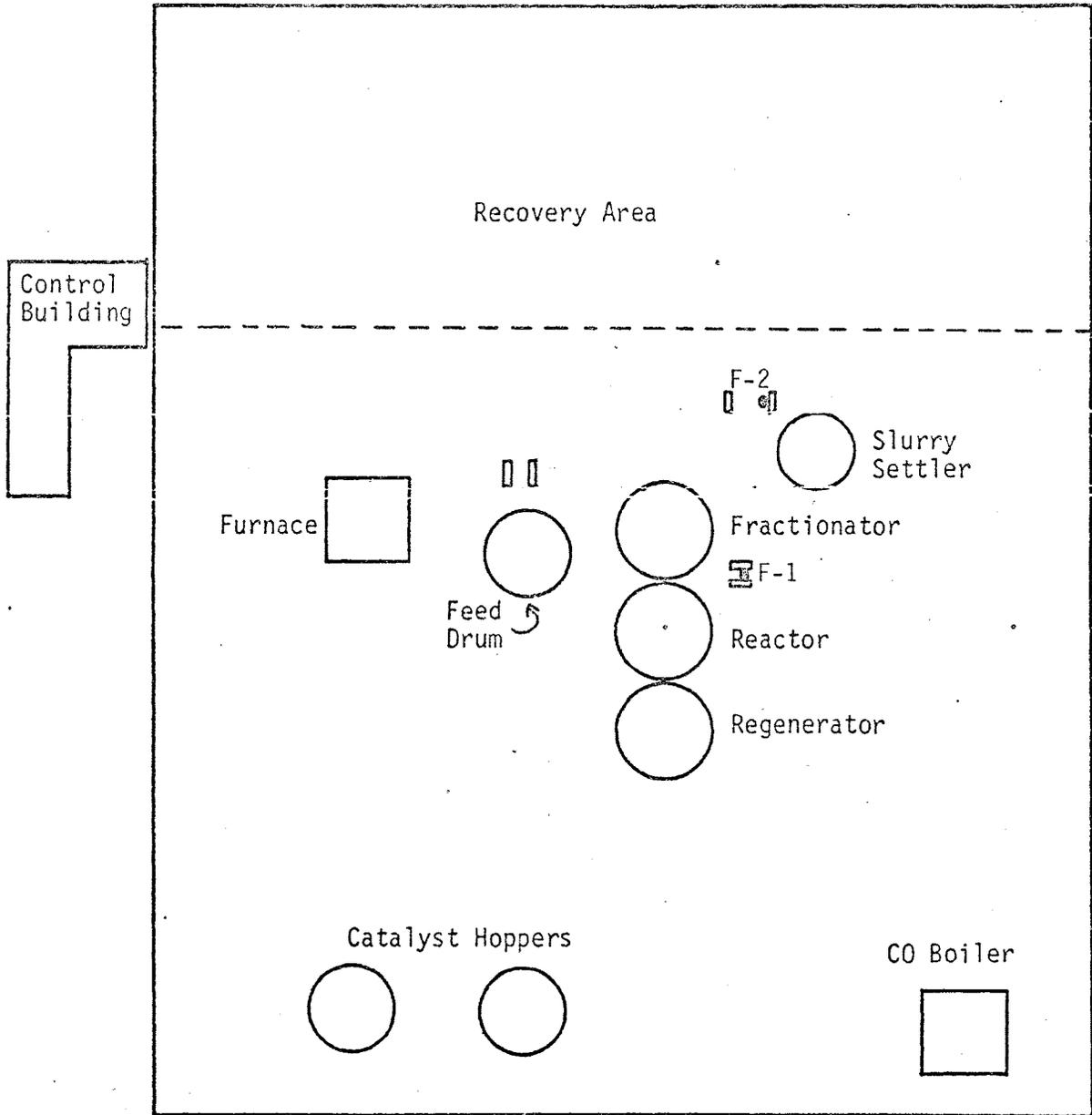
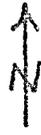


FIGURE IV-3. FCCU Area Sampling Locations

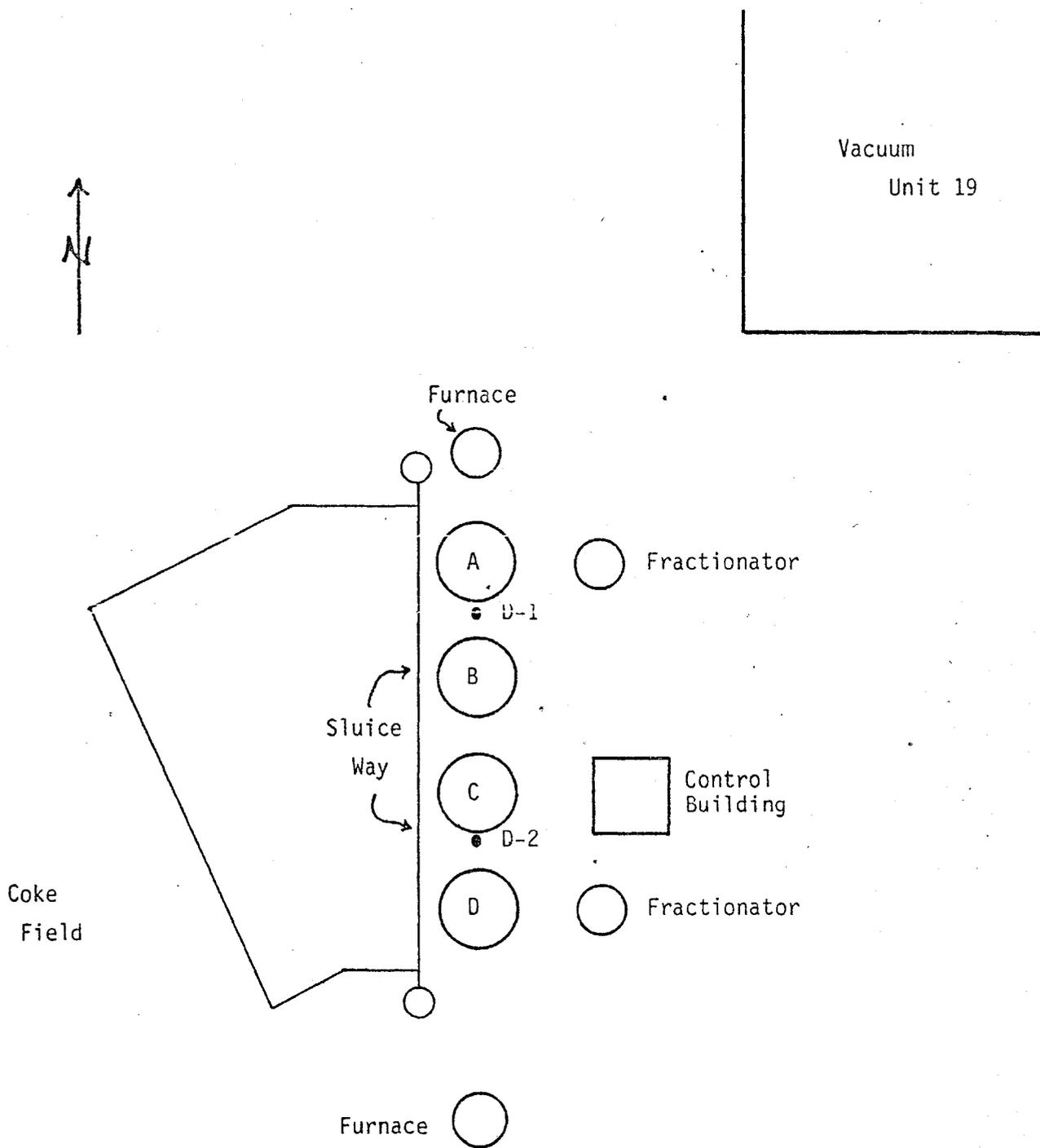


FIGURE IV-4. Delayed Coker Unit Area Sampling Locations

## B. Personal Sampling

The four operational shift workers (#1 operator, three #2 operators) and their supervisor were sampled during the day shifts on May 14 and 15.

Three coke cutters and handlers (three #2 operators) and their supervisor were also sampled during the same period.

### ASPHALT PROCESSING UNITS (VACUUM UNITS)

At both vacuum units, a single location near the asphalt pumps was sampled during both sampling shifts. At unit No. 16, the location was 4 feet above ground and 3½ feet from asphalt pump #16P-10. This electric centrifugal pump, on the north side of the unit, pumps the vacuum bottoms to the delayed coker unit.

At unit No. 19, the sampling location was about 3 feet from the base of asphalt pump No. 19P-3A above the motor shaft. This electric centrifugal pump, on the south side of unit No. 19, pumps the vacuum bottoms to asphalt storage.

## V. RESULTS AND DISCUSSION

The complete results of the area and personal PAH samples collected at this Koch refinery are presented in Tables V-1, V-2 and V-3. Of the 33 personal and area samples analyzed from the four study process units, 32 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 none detected for a personal sample from one of the operators at the delayed coker to as high as 32.6  $\mu\text{g}/\text{m}^3$  for the one area sample from the FCCU. The two upwind boundary samples collected on separate days were 0.3  $\mu\text{g}/\text{m}^3$  and none detected.

A summary of the personal and area sampling results, including the mean (arithmetic) cumulative PAH concentrations ( $\bar{X}$ ) for the three types of process units, is presented in Table V-4. On the average, the personal samples from the delayed coker were more than twice as high as those from the FCCU (8.0 versus 3.7  $\mu\text{g}/\text{m}^3$ ). The single total mass area sample analyzed from the FCCU was more than three times greater than those from the delayed coker and 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-ring and no 6- or 7-ring PAHs were found in the samples.

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

Ring No.	Sample Location:	AREA		SUPERVISOR		#1 OPERATOR		#1 OPERATOR TRAINEE		#2 OPERATOR RECOVERY		#2 OPERATOR CAT SIDE			
		F-1	F-2	5/14	5/15	5/14	5/15	5/14	5/15	5/14	5/15	5/14	5/15		
		Sample Date:	Sample Volume (L):	Sample Time:	916	b	932	1,000	921	914	906	941	882	932	900
				0740-1615		0746-1535	0731-1553	0755-1531	0755-1535	0801-1532	0749-1541	0800-1519	0802-1543	0759-1529	0758-1542
(2)	Naphthalene*	2.96		0.51	3.06	1.78	2.39	0.25	0.44	0.58	0.55	0.68	0.42		
(2)	Quinoline*	-- <sup>c</sup>		--	--	--	--	--	--	--	--	--	--	--	--
(2)	2-Methylnaphthalene	9.73		0.61	3.11	2.15	2.23	0.74	0.50	0.91	0.56	1.03	0.43		
(2)	1-Methylnaphthalene	5.93		0.45	1.88	1.11	1.40	0.46	0.30	0.65	0.33	0.64	0.29		
(2)	Acenaphthalene	0.39		--	--	--	--	--	--	--	--	--	0.01		
(2)	Acenaphthene	1.57		0.24	0.72	0.45	0.84	0.32	0.17	0.20	0.19	0.29	0.08		
(3)	Fluorene	1.32		0.15	0.30	0.21	0.23	0.19	0.09	0.04	0.12	0.14	0.02		
(3)	Phenanthrene*/Anthracene*	7.82		0.28	0.48	0.13	0.17	0.09	--	--	0.05	0.14	0.04		
(3)	Acridine	--		--	<0.01	--	--	--	--	--	--	--	--		
(3)	Carbazole	--		--	--	--	--	0.05	0.02	--	--	0.03	--		
(4)	Fluorantene	0.56		--	--	0.02	--	0.02	<0.01	--	<0.01	0.02	--		
(4)	Pyrene*	1.70		--	--	0.03	--	0.06	0.02	--	0.02	0.08	--		
(4)	Benzofluorene	--		--	--	--	--	<0.01	--	--	--	--	--		
(4)	Benz(a)anthracene*/Chrysene*/Triphenylene	0.34		--	--	--	--	0.03	--	--	--	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* <sup>d</sup>	--		--	--	--	--	--	--	--	--	--	--		
(6)	Benzo(g,h,i)perylene	--		--	--	--	--	--	--	--	--	--	--		
(7)	Coronene	--		--	--	--	--	--	--	--	--	--	--		
(6)	Dibenzpyrene* <sup>d</sup>	--		--	--	--	--	--	--	--	--	--	--		
	TOTAL	32.57		2.24	9.55	5.88	7.26	2.21	1.54	2.38	1.82	3.07	1.29		

\* Suggested as having some cancer-causing potential.

<sup>a</sup> 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.

<sup>b</sup> Sample lost during analysis.

<sup>c</sup> "--" designates compounds not detected.

<sup>d</sup> 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<sup>a</sup>

Ring No.	Sample Location: Sample Date: Sample Volume (L): Sample Time:	AREA		OPERATIONAL										DECOKERS									
		C-1	C-2	Supervisor		#1 Operator		Board Oper.		#2 Oper. (A)		#2 Oper. (B)		Supervisor		#2 Decok (A)		#2 Decok (B)		#2 Decok (C)			
		5/14	5/15	5/14	5/15	5/14	5/15	5/14	5/15	5/14	5/15	5/14	5/15	5/14	5/15	5/14	5/15	5/14	5/15	5/14	5/15	5/14	5/15
		942	866	960	868	875	902	876	916	924	907	914	899	931	b	917	910	953	953	957	854		
		0735-	0840-	0740-	0803-	0801-	0759-	0804-	0752-	0747-	0758-	0756-	0802-	0750-		0753-	0756-	0742-	0741-	0745-	0827-		
		1519	1550	1541	1524	1519	1530	1522	1530	1523	1529	1519	1527	1538		1534	1532	1540	1543	1542	1532		
(2)	Naphthalene*	0.46	3.09	0.44	0.92	0.27	0.66	1.38	1.68	1.89	1.39	-- <sup>c</sup>	0.52	2.25		2.69	4.52	0.77	10.50	3.06	8.77		
(2)	Quinoline*	--	--	--	--	--	--	--	--	--	--	--	--	--		--	--	--	--	--	--		
(2)	2-Methylnaphthalene	1.31	4.23	0.74	0.94	0.33	1.14	2.31	2.33	2.26	3.16	--	0.77	4.30		4.48	4.78	2.04	7.63	5.53	6.80		
(2)	1-Methylnaphthalene	0.70	1.88	0.56	0.67	0.25	0.81	1.50	1.76	1.43	1.33	--	0.67	3.11		2.78	2.47	1.55	4.68	4.12	5.05		
(2)	Acenaphthalene	--	0.15	--	--	--	--	--	--	0.08	--	--	--	--		0.27	0.24	--	0.25	--	--		
(2)	Acenaphthene	0.19	0.34	0.12	0.12	0.05	0.10	--	0.31	0.27	0.24	--	0.09	--		--	0.31	0.30	0.34	0.41	0.56		
(3)	Fluorene	0.41	0.65	0.14	0.13	0.04	0.11	0.28	0.21	0.27	0.20	--	0.08	0.47		0.56	0.21	0.28	0.25	0.36	0.37		
(3)	Phenanthrene*/Anthracene*	1.28	0.82	0.10	--	--	0.02	0.15	0.19	0.15	0.06	--	--	0.74		0.66	0.08	0.42	0.12	0.07	0.38		
(3)	Acridine	--	--	0.06	--	--	--	--	0.04	--	--	--	--	0.16		--	--	--	--	--	--		
(3)	Carbazole	0.27	--	--	--	--	--	--	--	--	--	--	--	0.05		--	--	--	--	--	<0.01	--	
(4)	Fluoranthene	0.20	0.06	<0.01	--	--	--	0.01	--	0.02	--	--	--	0.09		--	0.04	0.08	--	--	--		
(4)	Pyrene*	0.32	0.13	--	<0.01	<0.01	--	0.03	--	0.05	0.02	--	--	0.02		0.01	0.17	<0.01	0.03	0.05	--		
(4)	Benzofluorene	0.09	--	--	--	--	--	--	--	--	--	--	--	--		0.02	0.01	--	--	0.02	--		
(4)	Benz(a)anthracene*/ Chrysene*/Triphenylene	0.12	--	--	--	<0.01	--	--	--	0.02	--	--	--	--		0.07	0.07	--	--	0.06	--		
(5)	Benzo(e)pyrene*/ Benzo(a)pyrene*	0.03	--	--	--	--	--	--	--	--	--	--	--	--		--	0.02	--	--	0.02	--		
(5)	Perylene	--	--	--	--	--	--	--	--	--	--	--	--	--		--	<0.01	--	--	--	--		
(5)	Dibenz(a,j)acridine*	--	--	--	--	--	--	--	--	--	--	--	--	--		--	--	--	--	--	--		
(5)	Dibenz(a,i)carbazole*	--	--	--	--	--	--	--	--	--	--	--	--	--		--	--	--	--	--	--		
(6)	Indeno(1,2,3-cd)pyrene*	--	--	--	--	--	--	--	--	--	--	--	--	--		--	--	--	--	--	--		
(5)	Dibenzanthracene* <sup>d</sup>	--	--	--	--	--	--	--	--	--	--	--	--	--		--	--	--	--	--	--		
(6)	Benzo(g,h,i)perylene	--	--	--	--	--	--	--	--	--	--	--	--	--		--	--	--	--	--	--		
(7)	Coronene	--	--	--	--	--	--	--	--	--	--	--	--	--		--	--	--	--	--	--		
(6)	Dibenzpyrene* <sup>d</sup>	--	--	--	--	--	--	--	--	--	--	--	--	--		--	--	--	--	--	--		
TOTAL		5.38	11.49	2.16	2.78	0.94	2.84	5.66	6.52	6.12	6.56	0.00	2.11	11.19		11.62	13.00	5.28	23.80	13.70	21.93		

\* Suggested as having some cancer-causing potential.

<sup>a</sup> 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.

<sup>b</sup> Sample lost during analysis.

<sup>c</sup> "--" designates compounds not detected.

<sup>d</sup> 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 Locations<sup>a</sup>

Ring No.		AREA			UPWIND		
		A-1	A-2		5/14	5/15	
		Sample Date:	5/14	5/15	5/15	5/14	5/15
		Sample Volume (L):	838	909	796	660	604
Sample Time:	0825-1520	0832-1600	0825-1503	0930-1459	1010-1512		
(2)	Naphthalene*	2.68	1.39	-- <sup>b</sup>	0.20	--	
(2)	Quinoline*	--	--	--	--	--	
(2)	2-Methylnaphthalene	6.08	5.14	0.62	0.07	--	
(2)	1-Methylnaphthalene	6.32	4.28	0.34	0.07	--	
(2)	Acenaphthalene	--	--	--	--	--	
(2)	Acenaphthene	--	0.72	--	--	--	
(3)	Fluorene	1.15	0.72	0.05	<0.01	--	
(3)	Phenanthrene*/Anthracene*	0.98	0.68	0.12	--	--	
(3)	Acridine	--	0.31	0.06	--	--	
(3)	Carbazole	--	0.06	0.24	--	--	
(4)	Fluoranthene	0.04	--	0.08	--	--	
(4)	Pyrene*	0.07	<0.01	0.25	--	--	
(4)	Benzofluorene	--	--	--	--	--	
(4)	Benz(a)anthracene*/Chrysene*/Triphenylene	--	--	0.06	--	--	
(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* <sup>c</sup>	--	--	--	--	--	
(6)	Benzo(g,h,i)perylene	--	--	--	--	--	
(7)	Coronene	--	--	--	--	--	
(6)	Dibenzpyrene* <sup>c</sup>	--	--	--	--	--	
TOTAL		17.32	13.30	1.82	0.34	0.00	

\* Suggested as having some cancer-causing potential.

<sup>a</sup> 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.

<sup>b</sup> "--" designates compounds not detected.

<sup>c</sup> 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			AREA		
	No. of Samples	$\bar{X}$	No. of PAHs	No. of Samples	$\bar{X}$	No. of PAHs
FCCU	10	3.7	5-11	1	32.6	10
Coker	17	8.0	0-13	2	8.4	9-12
Asphalt	--	--	--	3	10.8	7-10
Total	27	6.4	0-13	6	13.6	7-12

FCCU

The average cumulative PAH concentration over the two shifts for the five FCCU workers sampled was 3.7  $\mu\text{g}/\text{m}^3$  with the number of individual PAHs or groups of PAHs ranging from 5 to 11. The boardman (a #2 operator) was the only regular operator not sampled over the two shifts and his exposure to PAHs is not expected to be higher than the outside operators. Table V-4 shows the mean cumulative PAH concentrations ( $\bar{X}$ ) and the number of PAHs for the FCCU supervisor and four outside operators. The #1 operator showed the highest cumulative PAH concentration (6.6  $\mu\text{g}/\text{m}^3$ ) followed closely by the supervisor (5.9  $\mu\text{g}/\text{m}^3$ ). The results for the #1 operator trainee (#1-T) and the two #2 operators were very similar at about 2  $\mu\text{g}/\text{m}^3$ . The results for the two #2 operators were very similar despite the fact that one was primarily responsible for the cat side and the other for the recovery side. No particular trends were indicated regarding the number of PAHs identified.

TABLE V-5. Personal Monitoring Results - FCCU

	No. of Samples	$\bar{X}(\mu\text{g}/\text{m}^3)$	No. of PAHs
Supervisor	2	5.9	6-7
Outside Operators	8	3.2	5-11
#1 (all areas)	2	6.6	6-8
#1-T (all areas)	2	1.9	8-11
#2 (cat area)	2	2.2	7-10
#2 (recovery area)	2	2.1	5-8
Total	10	3.7	5-11

The results of the personal monitoring were quite consistent over the two days for the FCCU workers. There was less than 30% difference between the duplicate samples collected for the #1 operator, #1 operator trainee, and #2 operator (recovery side). The results for the supervisor showed the largest variation between the 2 days; since he does split his shift between the FCCU and alkylation unit, greater variations were expected for this individual. Both day shifts during which sampling was performed were termed as routine by the workers. A statistical analysis of the data generated from this survey is not presented at this time; however, 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 pumps showed a cumulative PAH concentration of 32.6  $\mu\text{g}/\text{m}^3$ , the highest of the samples collected at this refinery; 10 PAHs were identified. The second area sample collected at this unit was lost during analysis.

#### DELAYED COKER UNIT

Table V-6 gives a summary of the personal monitoring results for the nine workers sampled at the delayed coker. These values ( $\bar{X}$ ) are again average cumulative PAH concentrations for the two sampling days. This table shows that the four decokers were exposed at much higher concentrations than the five operational workers (14.4 versus 3.6  $\mu\text{g}/\text{m}^3$ ). Also generally a larger number of PAHs were found in the decoker samples. All five of the regular operational group were sampled while four of the five regular decokers were sampled. The #1 decoker who performed the drilling the first sampling shift was not sampled due to equipment problems.

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

	No. of Samples	$\bar{X}$ ( $\mu\text{g}/\text{m}^3$ )	No. of PAHs
Operational	10	3.6	0-9
Supervisor	2	2.5	7
Boardman	2	6.1	7
#1	2	1.9	6-7
#2 (A)	2	6.3	8-9
#2 (B)	2	1.1	0-5
Decokers	7	14.4	6-13
Supervisor	1	11.2	9
#2 (A)	2	12.3	10-13
#2 (B)	2	14.5	7-8
#2 (C)	2	17.8	6-11
Total	17	8.0	0-13

The mean cumulative PAH concentration for the operational group ( $\bar{X} = 3.6 \mu\text{g}/\text{m}^3$ ) was similar to the personal samples from the FCCU ( $\bar{X} = 3.7 \mu\text{g}/\text{m}^3$ ). The fact that the boardman had the second highest PAH results of the five in this group was unexpected based on his shift being almost totally spent inside the positive-pressure control room. The one totally negative sample from one of the #2 operators sampled the first day could not be explained. The results of the personal monitoring for the operational group were generally quite consistent over the 2 days. There was less than 23% difference between the duplicate samples collected for three of the five workers.

Although the duplicate samples for the decoker group did not show this consistency, all four workers were exposed at similar cumulative PAH concentrations; the values ranged from 11.2 to 17.8  $\mu\text{g}/\text{m}^3$ , only a 37% difference from highest to lowest. As mentioned before, the actual coke cutting operation was not performed during the second sampling shift; the decokers performed mainly coke handling activities on the previously cut coke. However, all eight workers sampled during both shifts showed higher results the second day; the average cumulative PAH concentration for these eight workers was 7.3  $\mu\text{g}/\text{m}^3$  the first shift and 9.9  $\mu\text{g}/\text{m}^3$  the second shift.

The two area samples taken in the delayed coker unit showed cumulative PAH concentrations of 5.4  $\mu\text{g}/\text{m}^3$  (12 PAHs) downwind of A drum and 11.5  $\mu\text{g}/\text{m}^3$  (9 PAHs) downwind of C drum. The first sample was collected the first day during cutting operations, while the second sample was collected the second day while the drum was being prepared for cutting.

#### ASPHALT PROCESSING UNITS

The results of the two area samples collected at vacuum unit No. 16 were 17.3  $\mu\text{g}/\text{m}^3$  (7 PAHs) the first sampling shift and 13.3  $\mu\text{g}/\text{m}^3$  (9 PAHs) the second sampling shift. The result of the area sample collected at vacuum unit No. 19 the first sampling shift was 1.8  $\mu\text{g}/\text{m}^3$  (10 PAHs). The second area sample collected at this unit the second sampling day was lost during analysis.

#### 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 78% of the PAHs found were the lightermolecular weight, 2-ring compounds; at the coker this percentage was almost 92%. Naphthalene and its two methyl derivatives were the compounds found in the highest concentrations. In the FCCU area sample, there was also a considerable quantity of the 3-ring phenanthrene/anthracene group.

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

RING NO.	FCCU	DELAYED COKER	ASPHALT
2	78.4	91.7	86.9
3	17.4	7.1	12.7
4	4.2	1.2	0.4
5	0	0	0
6	0	0	0
7	0	0	0

## E. Particle-Size Distribution

Table V-8 shows the particle-size distribution of the eight total particulate samples collected alongside the PAH area samples. The sample results were consistent in that at least 99% of the particles sized were 8.3  $\mu\text{m}$  or less and all (100%) were 11.8  $\mu\text{m}$  or less. Particles less than 10  $\mu\text{m}$  are considered to be of respirable size.

TABLE V-8. Particle-Size Distribution (%)  
of Total Particulate Area Samples

PARTICLE SIZE ( $\mu\text{m}$ )	FCCU	DELAYED COKER		ASPHALT				UPWIND
	F-1	D-1	D-2	A-1	A-1	A-2	A-2	
0.4-0.7	43.5	38.4	39.2	31.9	37.4	42.4	40.7	32.9
0.7-1.0	29.1	23.8	11.3	26.4	25.8	24.8	19.6	20.7
1.0-1.5	14.4	23.5	19.9	14.0	16.7	14.7	24.3	23.4
1.5-2.1	4.1	5.6	10.3	7.3	7.6	4.6	5.4	8.9
2.1-2.9	3.4	5.3	9.0	8.9	5.7	5.2	3.8	7.2
2.9-4.2	2.7	1.7	6.3	3.8	4.1	3.3	4.1	2.6
4.2-5.9	1.0	1.0	2.0	4.5	1.6	2.9	1.0	2.3
5.9-8.3	1.0	0.3	2.0	2.2	0.9	1.6	0.3	1.0
8.3-11.8	0.7	0	0	1.0	0.3	0.7	1.0	1.0

## VI. CONCLUSIONS

The results of the personal, area, and upwind air samples from the Koch 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 2 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 schedule) that would cause one to believe that these results were not representative of these units.

The decokers at the delayed coker unit appear to be the work group exposed at the highest PAH concentrations during their work shift. It also appears that it is not the activities associated with coke cutting but coke handling that contribute more to PAH exposures. Exposures were consistently higher during the second sampling shift when only coke-handling activities were performed. The coke driller, who may have had significant exposures the first shift, was not sampled. The results for the other workers at the coke unit (the five operational workers) were comparable to those for the FCCU workers. The personal sampling data for both of these groups (delayed coker operational and FCCU) were also quite similar over the two sampling shifts (duplicate samples); while as mentioned above for the decokers, the samples were considerably higher the second shift.

It was anticipated that the personal sampling results for the delayed coker operational group would show that the outside workers were exposed

at much higher PAH concentrations than the inside worker (boardman) who spends almost 100% of his shift inside the positive-pressure control room. However, the results showed that both the variety and concentrations of PAHs to which the boardman was exposed were greater than anticipated. The results for the boardman were second only to one of the #2 operators who spends at least 40% of his shift outside in the production area. This indicates that at least this control room is not free of contaminants from the production area. It was observed that the boardman smoked during his breaks, and the final report will discuss any effects of smoking on PAH levels.

The FCCU personal samples showed that the #2 operators responsible for the recovery side and for the cat side were exposed at similar PAH concentrations. Because most of the process streams containing the heavy petroleum fractions are confined to the cat side of the unit, it was anticipated that the cat-side operator would show higher results.

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 cumulative PAH concentration of the area sample collected near the slurry recycle pumps was much higher than the mean cumulative PAH concentration for the 10 personal samples (32.6 versus 3.7  $\mu\text{g}/\text{m}^3$ ). This indicates that the slurry recycle pump area is a source of PAH emissions. In the delayed coker unit, many of the personal samples were just as high or higher than the area samples collected downwind of the coke drums. This, in addition to the PAH levels found for those workers who do not work in high PAH emission areas (control room operator and recovery-side operator), indicates 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 two asphalt processing areas were higher than expected based on Phase II area sampling. This was especially true for vacuum unit No. 16 area samples which averaged 15.3  $\mu\text{g}/\text{m}^3$  over the two shifts; the two samples were also quite consistent with less than a 24% difference between the 2 days.

As expected from Phase II results, the majority of PAHs identified during Phase III were the lighter 2- and 3-ring compounds. At least 78.4% of the PAHs in the samples from all four units were the 2-ring compounds and at least 95.8% were 2- or 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 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 almost all of the particles collected were well within the respirable-size fraction ( $<10\mu\text{m}$ ). 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 Conference

Enviro Control, Inc.

Robert Reisdorf  
John F. Rekus

Industrial Hygienist  
Industrial Hygienist

NIOSH

Clinton Cox

Project Officer

Koch Refining Company

John Ehlen  
Ray Knutson  
D. H. Sunde  
Will Dotson

Refinery Manager  
Assistant Refinery Manager  
Manager of Operations  
Health and Safety Coordinator