# WASTE MANAGEMENT OPTIONS FOR
# UNITED STATES REFINERIES

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# UNITED STATES REFINERIES

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# PREFACE

A standard refinery model was developed from industrial studies. This model was then used to generate waste streams normal to such processes. The current literature was reviewed to determine what waste management options were available. These options were then analysed to determine economic viability.

I wish to express my gratitude to the individuals who assisted me in my coursework at Oklahoma State University. Special thanks are due to my family and my wife, who did without a father and a husband for so long.

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# NOMENCLATURE

| | |
|---|---|
| B | Barrels |
| BPH | Barrels Per Hour |
| BTX | Benzene, Toluene, and Xylene |
| DEA | Diethanol Amine |
| EPA | Environmental Protection Agency |
| FCCU | Fluid Catalytic Cracking Unit |
| hr | hour |
| K | Thousand |
| MEA | Monoethanolamine |
| m | minute |
| mm | million or thousand thousand |
| mmscfd | thousand thousand(million) standard cubic feet per day |
| mmscfh | million standard cubic feet per hour |
| mo | month |
| MTBE | Methyl-t-butyl Ether |
| NTE | Net Thermal Efficiency |
| ppm | parts per million |
| RCRA | Resource Conservation and Recovery Act |
| ron | research octane number |
| SCOT | Shell Claus Off-gas Treating Unit |

## NOMENCLATURE (Continued)

| | |
|---|---|
| t | ton |
| TAME | Tertiary Amyl Methyl Ether |
| TIP | Thermal Isomerization Process |
| VOC | Volatile Organic Compounds |
| # | Pounds |

# CHAPTER I

# INTRODUCTION

Petroleum refineries generate a significant number of waste streams. It was the intent of this report to determine the approximate volume and composition of those wastes, identify alternates for waste management, and economically evaluate those options. A typical U.S. refinery was compiled from industrial surveys for modeling purposes. Future new process units and designs required by current or proposed regulations were included in this evaluation. Refinery waste evaluations were also made in light of the newer requirements as specified in the new sludge listing (1), VOC(Volatile Organic Compounds) emissions, the Clean Air Act of 1990, Gasoline Vapor Pressure Reduction Requirements scheduled in 1992, new Stormwater Requirements, the Pollution Control Act of 1990 and the last portion of the land bans implemented in 1990. The economic evaluation focused on preliminary bottom line values as a guide to further evaluation. One important element of waste management which was identified was identified was waste minimization. Both are important to refinery operators for three main reasons. Waste minimization is:

(1) Required by RCRA(Resource Conservation and Recovery Act) Regulations for generators,

(2) Required by the new Clean Air and Pollution Control Acts, and

(3) Economically justifiable due to savings.

RCRA regulations specify generators shall "Have a program in place to reduce the volume and toxicity of waste generated to the extent that is economically practical.(2)" A strategy for waste management would consist of, in preferred order: (1) source reduction, (2) recycling, and (3) incineration and or treating. In general, the principle underlying the promotion of waste minimization is that it makes far more sense for a generator to not produce waste than to develop extensive treatment procedures or processes to take care of that waste so that it poses no threat to the environment. The new Clean Air and Pollution Control Acts continued this theme of encouraging generation reduction or elimination of waste rather than requiring disposal in land or air.

Additionally, waste minimization is a desirable goal which can stand on its own merits (Table I ), including savings in raw material, energy usage, and manufacturing costs. The EPA's most preferred methods of waste

## TABLE I

## WASTE MINIMIZATION INCENTIVES

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Economics

- Landfill disposal cost increases
- Costly alternative treatment technologies
- Savings in raw material and manufacturing costs

Regulations

- Certification of a waste minimization program on the hazardous waste manifest
- Biennial waste minimization program reporting
- Land disposal restrictions and bans
- Increasing permitting requirements for waste handling and treatment

Liability

- Potential reduction in generator liability for environmental problems at both on-site and off-site treatment, storage, and disposal facilities
- Potential reduction in liability for worker safety

Public Image and Environmental Concern

- Improved image in the community and from employees
- Concern for improving the environment
- Included in Right-to-Know program documentation

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minimization have been source reduction and recycling. Source reduction is the elimination of waste generation at the source, usually within a process. Recycling has some definitions and restrictions specified in 40 CFR 261. In general, a material is recycled if it is used, reused, or reclaimed (40 CFR 261.1(c)(7)) (3). A material is reclaimed if it is regenerated or additionally processed to recover a usable product (40 CFR 261.1(c)(4). A material is used or reused if it is either: (1) employed as an ingredient (including its use as an intermediate) to make a product or (2) employed in a particular function as an effective substitute for a commercial product (40 CFR 261.1 (c)(5)) (4). However a material will not satisfy this condition if distinct components of the material are recovered as separate end products. Petroleum components presented a particular problem to the determination of recycling due to the extractive nature of refining. Waste petroleum products have additional limiting requirements including halogens, lead, and other metals before non hazardous reuse can be carried out (5).

Techniques to implement the above described methods have been divided. Source reduction techniques can be either a change to the product or to the process. Product changes can include: substitution with other products that generate no hazardous by-products, reduction of the amount of product needed, and changes in the product composition makeup. Process changes are significantly more diverse, and process dependent. Items examined included raw material selection, technology improvements and good operating practices. Raw material should be evaluated to determine whether materials can be substituted to reduce waste generation. Another area reviewed was the purity of the raw materials. In many instances, waste has been generated from impurities in the feed. Purification of the raw material, either by processing or by specifications when purchasing, have been found to reduce the overall problem. Technology is improving as more effort has been devoted to improving the environment. In many cases, technology used for reduction of waste in other industries can be applied without significant changes. Specific technology evaluated to reduce waste generation should include:

(1) Equipment, piping or layout changes
(2) Additional automation
(3) Changes in operational settings to reduce margin of operator comfort
(4) Changes in catalysts. (6)

Good operating practices have represented overlooked areas of source reduction. These practices include both management and operations procedures. It is management responsibility to set policies and commit resources to waste management. Without this "good practice" little is achieved. More tangible practices should include:

(1) Waste stream segregation to reduce volume,
(2) Material handling improvements to reduce spillage, and
(3) Production scheduling to reduce inventory spoilage and loss.

Recycling techniques can be applied on or off site. It has proven easier to use or reuse a stream rather than reclaim it. Additional production of new, saleable products can impact the bottom line twice, by elimination of waste disposal costs alone with income from new sales. Reclamation to reduce or eliminate waste usually involves installation of a process or processes to perform the operation. Usual process steps involved are standard chemical engineering units such as distillation, evaporation, adsorption, filtration, separation, etc.

# CHAPTER II

## EXECUTIVE SUMMARY

Petroleum refineries generate a significant number of waste streams. These waste streams are unique due to the extractive nature of refineries. This report has determined the approximate volume and composition of those wastes, identified alternates for waste management, and estimated economic parameters for the alternatives. These alternatives have been evaluated in light of the requirements and impacts of many new regulations, such as new sludge listings, Clean Air Act of 1990, gasoline vapor pressure reduction requirements, new storm water requirements, and the Pollution Control Act.

Waste management is important for three main reasons. It is: (1) Required by RCRA Regulations for generators, (2) Required by many of the new regulations and laws, and (3) Economically justifiable due to savings in certain situations. A primary part of management, waste minimization consists of, in order of preference (1) source reductions, (2) recycling, and (3) incineration or treating. Because of numerous factors associated with refineries; such as the extractive nature of refining, the fixed nature of the available feeds, the specified nature of the products, and the age of the industry, much of the focus of refinery waste management has concentrated upon recycling, reuse, or modifications of treatment or process.

A typical refinery model was developed from industrial studies (Figure 1). This model consisted of twenty-two representative process units, for a modern, flexible refinery with the ability to comply with new regulations and produce new reformulated gasolines with additives such as MTBE(Methyl-t-butyl Ether) and TAME(Tertiary Amyl Methyl Ether). A crude feedrate of 85,000 BPD(Barrels Per Day) was determined to be the U.S. average. A modified Mississippian Era petroleum crude analysis was developed for the feedstock. The model and feedstock were then used to evaluate each process unit to determine waste streams that would be generated. Some seventy waste streams were identified, quantified, and classified. These waste streams were reduced to twenty streams which exit the refinery model as waste. These waste streams were:

| | |
|---|---|
| Brine Solution | 4,100 gallons/day |
| Coke Fines | 23 tons/yr |
| Amine Wastes | 2,500 elements/yr |
| FCC Cracker Fines | 1,300 tons/yr |
| Spent Catalysts | 660 tons/yr |

| | |
|---|---|
| HF(Hydrofluoric Acid) | |
| Carbon Filters | 100 annually |
| HF $CaF_2$/Lime Solids | 745 tons/yr |
| HF Spent Alumina | 65 tons/yr |
| Mol Sieve | 1 ton/yr |
| Filter Clays | 2 tons/yr |
| BTX Spill | as occurred, estimated at 4 occurrences/yr |
| Spent Acids | 6,000 tons/yr |
| Air Emissions Exhausts | |
| Fired Heaters | 2,257,531 tons/yr |
| Compressors | 1,152,698 tons/yr |
| Regeneration Processes | 137,904 tons/yr |
| Tail gas units | 706 tons/yr |
| $CO_2$ Units | 1,752 tons/yr |
| VOC | 85 tons/yr |
| API(American Petroleum Institute) | |
| Separator | 4,100 tons/yr |
| Air Floc | 6,300 tons/yr |
| Sludges (Biological) | 10,055 tons/yr |
| Leaded Tank Bottoms | 240 tons/yr |
| Heat Exchanger Bundles | 80 tons/yr |
| Cooling Tower Sludge | 12 tons/yr |
| Waste Waters | 770,000 tons/yr |

An industrial literary search was conducted to determine waste minimization options for each stream. These options were evaluated to determine which options appeared to have the widest applications. These options were then researched to determine the requirements for implementation. A preliminary economic estimate was made of each option. These estimates included capital costs, operating costs, and potential economic benefits. Certain options were so site specific that general cost estimates were inappropriate and therefore not made. Some estimates of breakeven distances were made in these cases.

Hopefully this collection will serve as a generator of new ideas and not as a final solution. The one concept left out of this list was the effect of good operating practices and proper regard for the operating units operations. This would result in less waste and more product than many "new processes". However to attempt to define this intangible was beyond the scope of this work.

The summary of each option and the economic estimates has been presented below. Benefits and Operational Costs were on an annual basis. Capital Costs were on a project basis.

(1) Brine Wastes

(a) Improved desalting

C(Capital Costs) - $40 K

O(Operational Costs) - $860 K

B(Benefits) - minimal impacts with
poor quantifiable results

(b) Recycling to a waterflood project
- C(Capital Costs) - $50 K
- O(Operational Costs) - $300 K
- B(Benefits) - $70 K

(c) Mineral by-product recovery
- C - $16,000 K
- O - $10 K
- B - $30 K

(2) Coke Fines

(a) Reduce generation and collect for product sale
- C - $50 K
- O - minimal
- B - $20 K

(3) Amine Wastes

(a) Change treating medium
- C- $200 K
- O - decreased
  energy 30%, neg $690 K
- B - $40 K

(b) Recycle filter wastes

C - none

O - none

B - $8 K

(4) Catalysts:

FCCU Cracker Fines and HF Spent Alumina

(a) Cement recycling

C - none

O - none

B - waste disposed of with no cost

Polymerization Catalyst

(a) Cement manufacture

C - none

O - none

B - waste disposed of with no cost

(b) Fertilizer replacement

C - none

O - minimal

B - minor revenue

FCCU Cracker Fines, HF Alumina, Mol Sieve, Spent Cobalt Molybdenum, Polymerization Catalyst

(a) Reclaiming unit

C - $20,000 K

O - $600 K

B - $760 K

Mol Sieve

(a) Reuse

C - too individualized to determine

O - too individualized to determine

B - $1 K , if need exists

(5) HF Carbon Filters

(a) Recycle for scrap

C - none

O - none

B - $1 K

(6) HF Lime Sludge

(a) Source Reductions due to high quality lime

C - none

O - 8 % increase, $2 K

B - $20 K

(b) Recycle steel manufacturing or HF acid manufacturing

C - none

O - function of distance and
location (one breakeven
estimate is 650 miles)

B - $400 K

(7) Filter Clays

(a) Thermal desorption & reuse

C - $250 K

O - $330 K

B - $150 K

(8) BTX Spills

(a) Prevention and reuse

C - $2,200 K

O - $60 K

B - clean up  $50 K
or avoidance $70 K

(9) Spent Acids

(a) Product sale

C - none

O - minimal

B - revenue of $240 K

(b) Neutralize and land dispose

C - $970 K

O - $100 K

B - minimal

(10) SOx Emissions

(a) Source reduction with new technology improvements

C - $380 K

O - $50 K

B - $300 K

(b) With new processes

C - $5,000 K

O - Improvement of $50 K

B - $1 K

(c) With fluid bed dry limestone

C - $500 K

O - $50 K

B - $20 K

(11) SOx and NOx Emissions Combined

(a) Plasma treatment

C - undeveloped

O - undeveloped

B - $1,500 K

(12) NOx Only

(a) NSCR(Nonselective Catalytic Reduction) technology

C - $755 K
O - $175 K
B - $1,400 K

(b) SCR(Selective Catalytic Reduction) technology

C - $1,500 K
O - $1,750 K
B - $950 K

(13) VOC

(a) Source reduction

Costs - too individualized to determine

(b) Bio Mass Filter

C - $251.3 K
O - $8.5 K
B - $2.0 K

(14) General Sludges Handling

(a) Segregate

Costs - too individualized
to determine

(b) Coker recycling

C - $80 K

O - minimal

B - $190 K

(c) Solvent extraction

C - $750 K

O - $230 K

B - $230 K

(d) Hot water extraction

C - $490 K

O - $120 K

B - $270 K

(15) Cooling Tower Sludge Specifically

(a) Chromium reduction

C - minimal

O - minimal

B - 70 % reduction in chromium emissions

(b) Several individual options including:

Improve Quality of Inlet Water

Reduce Water Usage with Air Exchangers

Costs - Individual Refinery Estimates

(16) Waste Water

(a) Recycle

C - $3,000 K

O - $300 K

B - $684 K

(17) Heat Exchange Source Reduction

(a) Use heat transfer fluids

C - $260 K

O - minimal

B - $30 K

(b) Improve fouling resistance measures

Costs - too individualized to determine

(18) Tank Sludge

Source reduction techniques

Costs - too individualized to determine

# CHAPTER III

# DEFINITION OF A REFINERY

## Selection of a Refinery Size

It was necessary to determine both the production size range and the type of unit processes included in the study of waste management options. The production size range was used to prepare cost estimates and determine volume amounts of waste generated. The type of unit processes available were used to determine the type and composition of wastes generated.

The OIL and GAS JOURNAL conducts an annual survey of operating U.S. refineries, listing crude processing capacity and the contained unit processes. The current survey was published in the March 26, 1990 issue of the JOURNAL (7). This survey listed the crude oil processing capacity and unit processes at all U.S. refineries. Data from the current survey was used to produce Table II and III in Appendix A. These tables were used to develop information which determined the type and size of the refinery model components.

The total crude capacity was 15,558,923 barrels per calendar day for 190 refineries (Table II in Appendix A). This was averaged to 81,889 barrels per calendar day per refinery. A calendar day is defined as the average volume per day for a year including downtime. The feedrate of crude to the refineries ranged from zero (only polishing operations) to over 400,000 barrels per calendar day. Approximately two thirds of the facilities had feedrates less than 100,000 barrels per calendar day. Therefore the average of 85,000 barrels per calendar day appeared to reflect the industry most common facility and was used for the study refinery total crude capacity.

## Selection of Charge Unit Processes

Specific charge unit processes listed by plant (presented in Table II) were summarized in Table IV by size, type, and average. Each unit was described as it related to the typical U.S. refinery process (Figure 1).

Vacuum distillation is the separation of reduced crude into constituent fractions under reduced pressure or vacuum. This unit process has been performed in a refinery because of the tendency of higher boiling materials to participate in rearrangement, condensation, or decomposition at temperatures above approximately 660 F (often referred to as the cracking temperature). The aim

# TABLE IV

## CHARGE UNIT PROCESSES IN BARRELS PER CALENDAR DAY

| PRODUCTION UNIT PROCESSES | TOTAL IN BBL/CD | AVERAGE BBL/CD FOR ALL REFINERIES | NUMBER OF UNITS BY TYPE | AVERAGE BBL/CD BY UNIT TYPE | PERCENTAGE OF U.S. REFINERIES WITH UNIT | PERCENTAGE BY TYPE OF UNITS |
|---|---|---|---|---|---|---|
| VACUUM DISTILLATION | | | | | | |
| | 7132525 | 37540 | 158 | 45143 | 83.16% | 100.00% |
| THERMAL OPERATIONS | | | | | | |
| GAS/OIL CRACKING | 144000 | 758 | 2 | 72000 | 1.05% | 2.63% |
| THERM CRACKING | 34600 | 182 | 4 | 8650 | 2.11% | 5.26% |
| VISBRAKING | 154800 | 815 | 12 | 12900 | 6.32% | 15.79% |
| COKING(FLUID) | 247600 | 1303 | 9 | 27511 | 4.74% | 11.84% |
| COKING(DEDAYED) | 1290700 | 6793 | 45 | 28682 | 23.68% | 59.21% |
| OTHER | 100700 | 530 | 4 | 25175 | 2.11% | 5.26% |
| ALL | 1972400 | 10381 | 76 | 25953 | 40.00% | 100.00% |
| CAT CRACKING | | | | | | |
| FLUID TOTAL | 5186200 | 27296 | 114 | 45493 | 60.00% | 92.68% |
| FLUID RECYCLE | 276565 | 1456 | 57 | 4852 | 30.00% | 46.34% |
| OTHER TOTAL | 217900 | 1147 | 9 | 24211 | 4.74% | 7.32% |
| OTHER RECYCLE | 11300 | 59 | 5 | 2260 | 2.63% | 4.07% |
| ALL | 5404100 | 28443 | 123 | 43936 | 64.74% | 100.00% |

## TABLE IV (Continued)

| PRODUCTION UNIT PROCESSES | TOTAL IN BBL/CD | AVERAGE BBL/CD FOR ALL REFINERIES | NUMBER OF UNITS BY TYPE | AVERAGE BBL/CD BY UNIT TYPE | PERCENTAGE OF U.S. REFINERIES WITH UNIT | PERCENTAGE BY TYPE OF UNITS |
|---|---|---|---|---|---|---|
| REFORMING | | | | | | |
| CONVEN. CAT. | 47350 | 249 | 9 | 5261 | 4.74% | 5.36% |
| BIMETAL. CAT. | 220320 | 1160 | 108 | 2040 | 56.84% | 64.29% |
| CYCLIC CONVEN | 424000 | 2232 | 10 | 42400 | 5.26% | 5.95% |
| CYCLIC BIMET. | 606600 | 3193 | 19 | 31926 | 10.00% | 11.31% |
| OTHER CONVEN. | 461700 | 2430 | 14 | 32979 | 7.37% | 8.33% |
| OTHER BIMET. | 188500 | 992 | 8 | 23563 | 4.21% | 4.76% |
| ALL | 3930470 | 20687 | 168 | 23396 | 88.42% | 100.00% |
| HYDROCRACKING | | | | | | |
| DISTILLATE | 826500 | 4350 | 34 | 24309 | 17.89% | 68.00% |
| RESIDUAL | 157000 | 826 | 6 | 26167 | 3.16% | 12.00% |
| LUBE-OIL | 35000 | 184 | 2 | 17500 | 1.05% | 4.00% |
| OTHER | 181190 | 954 | 8 | 22649 | 4.21% | 16.00% |
| ALL | 1242690 | 6540 | 50 | 24854 | 26.32% | 100.00% |
| HYDROREFINING | | | | | | |
| RESIDUAL | 343000 | 1805 | 6 | 57167 | 3.16% | 8.33% |
| HEAVY GAS/OIL | 570600 | 3003 | 16 | 35663 | 8.42% | 22.22% |
| CAT CRACKER | 1001500 | 5271 | 25 | 40060 | 13.16% | 34.72% |
| MIDDLE DIST. | 421400 | 2218 | 19 | 22179 | 10.00% | 26.39% |
| OTHER | 74500 | 392 | 6 | 12417 | 3.16% | 8.33% |

TABLE IV (Continued)

| PRODUCTION UNIT PROCESSES | TOTAL IN BBL/CD | AVERAGE BBL/CD FOR ALL REFINERIES | NUMBER OF UNITS BY TYPE | AVERAGE BBL/CD BY UNIT TYPE | PERCENTAGE OF U.S. REFINERIES WITH UNIT | PERCENTAGE BY TYPE OF UNITS |
|---|---|---|---|---|---|---|
| ALL | 2411000 | 12689 | 72 | 33486 | 37.89% | 100.00% |
| REFORMING | | | | | | |
| PRETREATING | 3266900 | 17194 | 111 | 29432 | 58.42% | 38.14% |
| NAPHTHA | 728050 | 3832 | 37 | 19677 | 19.47% | 12.71% |
| OLEFIN | 177500 | 934 | 13 | 13654 | 6.84% | 4.47% |
| STRAIGHT RUN | 1433400 | 7544 | 53 | 27045 | 27.89% | 18.21% |
| DISTILLATE | 1064900 | 5605 | 36 | 29581 | 18.95% | 12.37% |
| LUBE OIL | 223700 | 1177 | 20 | 11185 | 10.53% | 6.87% |
| OTHER | 358850 | 1889 | 21 | | | 7.22% |
| ALL | 7245300 | 38133 | 291 | 24898 | 153.16% | 100.00% |

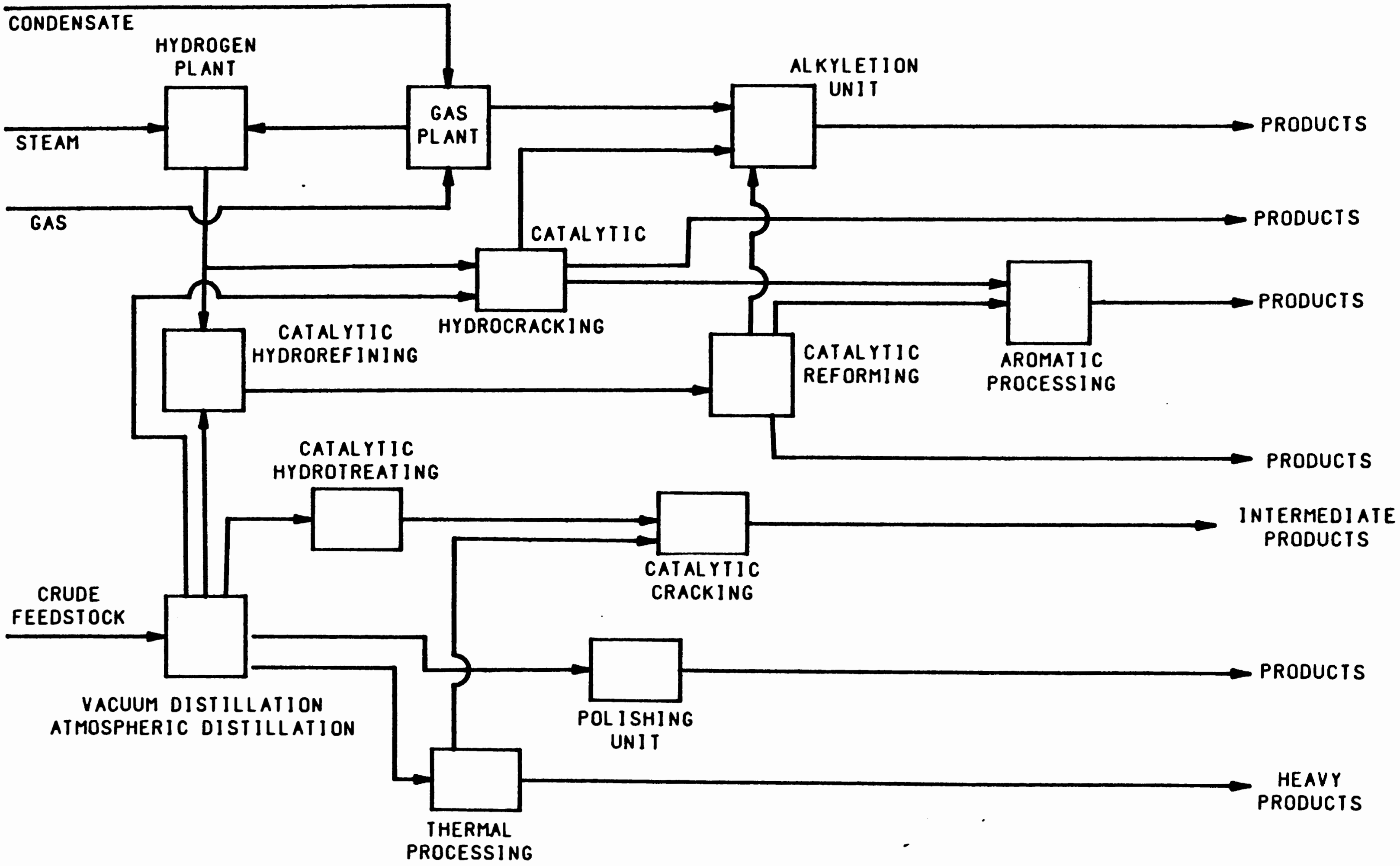


Figure 1 Simple Refinery Concept

of vacuum distillation was not the isolation of individual compounds, but the separation into several broad fractions based on boiling ranges. This type of preliminary processing was very common (Table IV) with eighty-three percent of U.S. refineries having had such a unit. The average size of those refineries with vacuum distillation processes was 45,143 barrels per calendar day (7). The size used in the study model refinery was 45,000 barrels per calendar day. This was consistent with refinery operations and a 85,000 BPD feedrate.

Thermal operations are the group of refinery processes that crack (by using high temperatures without the present of catalyst material) heavy molecular portions of crude oil into smaller molecules and leave behind a carbonaceous solid. Thermal cracked gasoline contained large quantities of mono-olefins and di-olefins. Thermal operations were fairly common in most refineries, occurring in some form in forty percent of all U.S. refineries (7). Several different thermal operation methods of processes were employed including (7):

| | Process Name | Process Description |
|---|---|---|
| (1) | Gas-oil cracking | a visbreaking process for gas oil production |

| | | |
|---|---|---|
| (2) | Thermal cracking | thermal decomposition without coking |
| (3) | Visbreaking | mild thermal cracking for fuel oil generation |
| (4) | Fluid Coking | Older style of cokers |
| (5) | Delayed Coking | current type of cokers, coking being the cracking of petroleum fractions and leaving behind a high BTU solid fuel called coke |
| (6) | Proprietary Processes | Limited in scope and usage to usually one user |

The most common thermal process was delayed coking, which was used in approximately twenty five percent of all U.S. refineries (Table IV). Delayed coking has produced transportation fuels from reduced, heavy high-sulphur crudes, or processed vacuum residues(bottom of the barrel). Delayed coking got its name from the process of delaying the deposit of unwanted coke in the heater. This was achieved by rapid temperature increase above the cracking zone until the mixture was delivered to an insulated surge drum downstream of the heater. Many units were coupled with downstream vapor recovery units for production of light fuels, fuel gas, and sulfur compounds.

New refinery design has added hydrodesulfurization units upstream of the coker and vacuum units. This has resulted in cleaner coke and reduced metals carryover. The delayed coker used in the refinery study model utilized this arraignment of a hydrodesulfurization unit upstream of the coker and vacuum units with a charge capacity of 28,000 crude barrels per calendar day.

Catalytic cracking is basically the same as thermal cracking, in which larger molecular components are cracked or broken into smaller, higher-octane, hydrocarbon products but with the use of catalyst. A catalytic cracked gasoline is higher in octane number and consists mostly of isoparaffins and aromatics which are more stable than the larger, straight chain paraffins. In general, catalytic cracking has been used to convert the high boiling crude fractions into high-quality gasoline. Catalytic cracking processes were divided by type into fluid-bed, fixed-bed, and moving bed units. Almost all units, ninety-three percent (Table IV) of the straight through units, in operation utilized the fluid-bed process. The fluid catalytic cracking unit (FCCU) consisted of two large vessels. In the first, the separator, hot catalysts were mixed with a liquid petroleum feedstock. The liquid was vaporized and cracked as it rose in the riser pipes. At the tip, the vapor was removed for distillation and separation into petroleum products. The catalyst was coated with coke in the risers. This coating occurred as the reaction took place in the risers. The reaction left a residue of heavy petroleum material that was subjected to a higher temperature. This coated catalyst was transferred to a second large vessel for regeneration. Regeneration was achieved by pumping air in to burn off the coke. Waste heat units were used to recover energy from the flue gas of the regenerator. The remaining flue gas was then taken to a process that removed particular carryover before emission to the atmosphere. FCCU units were in over sixty percent of U.S. refineries (Table IV). The study refinery included a FCCU unit rated for 45,000 barrels per calendar day.

Catalytic reforming is the conversion of low-octane gasolines into high-octane reformates on the order of 90-95 ron (research octane number). Catalytic reforming has been conducted in the presence of hydrogen over a hydrogenation-dehydrogenation catalyst. The catalyst was usually supported on alumina or silica-alumina. In general sulphur and organic nitrogen compounds were removed before processing. Reforming was divided into types based on the type of catalyst and the type of regenerative process employed. The catalyst used was determined by the naphtha composition of the feed and the amount of sulphur poisons. Bimetallic catalysts contained precisely controlled metal and acid functions which were more sensitive to sulphur feed levels than conventional all platinum catalysts. The catalysts have been regenerated by:

(1) Semiregenerative - shutdown of the reforming unit at specified intervals for regeneration in situ.
(2) Cyclic - continual regeneration in situ of any one of several reactors that are isolated for regeneration and returned to service.
(3) Other processes - including continuous catalyst replacement of moving bed systems.

Almost ninety percent (Table IV) of U.S. refineries included reforming units. The most common units used a bimetallic catalyst with semiregenerative processes or TIP (Thermal Isomerization Process) units. The average size unit, which the study used in the refinery model, was approximately 20,000 barrels per calendar day.

Catalytic hydrocracking included processes in which fifty percent or more of the feedstock was reduced in molecular size. This means that fifty percent of the molecules that make up the feedstock were broken into smaller molecules. Hydrocracking is a very versatile process. Most petroleum fractions could be processed from naphtha to the bottom of the barrel nondistillables. Hydrocracking is carried out over a fixed catalyst bed in a hydrogen atmosphere. This is an exothermic reaction with heat removal at various stages. Hydrocracking of all types of feedstocks was not as popular, twenty six percent of U.S. refineries (Table IV), as other types of refinery processing and the units were small. Therefore hydrocracker units were not included in the study refinery model (but it has been included in Figure 1 to show its relative usage).

Catalytic hydrorefining included processes in which ten percent or less of the feedstock has been reduced in molecular size. This means approximately ten percent of the feed molecules had reduced to compounds containing smaller molecules. The process upgraded low-quality, high-sulphur petroleum fractions into reformer feed or other naphtha-type materials with lower sulphur content. The basic processes consisted of initially heating the feedstock and then passing the feedstock with hydrogen through a reactor containing a metal oxide catalyst. The treated oil was cooled and separated from the excess hydrogen. Downstream a stripping tower was used to remove the hydrogen sulfide formed by the hydrogenation reaction.

The catalyst was regenerated or replaced in a batch type operation. The catalyst usually has contaminating metals, nitrogen compounds, oxygen compounds, and sulphur contained or trapped within as a result of the process. Hydrorefining has been used in approximately forty percent (Table IV) of U.S. refineries, particularly as a cat-cracker feed pretreatment or as a desulfurization unit. The study refinery contained a hydrorefining unit for desulfurization.

The final crude charging type process group evaluated was catalytic hydrotreating. Catalytic hydrotreating is defined as processes which cause essentially no reduction in molecular size to the feed. Most refineries have had one or more of these processes depending upon the feedstock and product mix. These units were included in the refinery model. The most common hydrotreating process usage was as a sulfur reduction unit, pretreating the FCCU feedstock for sulphur-containing materials. This occurred in over half of the U.S. refineries (Table IV). Typically improvements due to this process have been shown in Table V on the following page (8). For instance the sulphur percentage was reduced from 1.3 weight percent to 0.04 while cracking conversion was increased from fifty nine to eighty three percent (8).

TABLE V

Fluid Catalytic Cracking Unit Feed

Hydrotreating Effects

| Value | Untreated Feed | Mildly Desulfurized | Severely Hydrotreated |
|---|---|---|---|
| API | 18.4 | 22.3 | 26.3 |
| Sulphur wt% | 1.3 | 0.21 | 0.04 |
| Nitrogen wt% | 0.43 | 0.32 | 0.05 |
| Hydrogen wt% | 11.42 | 12.07 | 12.74 |
| Conversion LV% | 59.0 | 66.1 | 82.5 |
| Gasoline LV% | 41.1 | 46.0 | 55.6 |
| Coke st% | 8.8 | 6.1 | 5.6 |
| UOP K Factor | 11.28 | 11.48 | 11.67 |

(LV% is Liquid Volumetric Percent)

(Source 8)

## Selection of Production Finishing Units

In addition to crude charge processes, most U.S. refineries included various product polishing or finishing units (see Table VI). Polishing units process feedstock that already has had some processing performed upon it as opposed to either the feedstock or a fraction thereof. The most significant of these were discussed below and included in this study's refinery model.

Hydrogen plants were required by refineries where the reforming units did not produce enough hydrogen for hydroprocesses. Hydrogen was used in many processes to provide material for hydrogenation. The majority of U.S. refineries used the steam methane reforming process (7). This has been a reliable process where the continuous catalytic formation of carbon monoxide and hydrogen from methane and steam takes place. The carbon monoxide further reacted with steam and produced carbon dioxide which was removed by amine washing. The resultant hydrogen was high purity, greater than ninety-nine percent. The amount of hydrogen required varied depending upon feedstock. The study refinery included a 47 mmscfd(million standard cubic feed per day) plant.

Alkylation units were employed in approximately one half of all U.S. refineries. These units were equally divided between sulfuric acid ($H_2SO_4$) and hydrofluoric acid (HF) units. In general, alkylation units catalytically combined light olefins (usually propylene and butylenes) with tertiary carbon atoms (usually isobutane) which produced a branched chain paraffin fuel. Composition of

# TABLE VI

## PRODUCTION POLISHING UNIT PROCESSES IN BARRELS PER CALENDAR DAY

| PRODUCTION UNIT PROCESSES | TOTAL IN BBL/CD | AVERAGE BBL/CD FOR ALL REFINERIES | NUMBER OF UNITS BY TYPE | AVERAGE BBL/CD BY UNIT TYPE | PERCENTAGE OF U.S. REFINERIES WITH UNIT | PERCENTAGE BY TYPE OF UNITS |
|---|---|---|---|---|---|---|
| ASPHALT | 760654 | 4003 | 81 | 9391 | 42.63% | 100.00% |
| ALKYLATION/POLYMERIZATION | | | | | | |
| SULFURIC | 499600 | | 50 | 9992 | 26.32% | 36.76% |
| HYDROFLUORIC | 528800 | | 61 | 8669 | 32.11% | 44.85% |
| POLYMERIZATION | 106775 | | 25 | 4271 | 13.16% | 18.38% |
| ALL | 1135175 | 5975 | 136 | 8347 | 71.58% | 100.00% |
| LUBES | 240350 | 1265 | 34 | 7069 | 17.89% | 100.00% |
| AROMATICS | | | | | | |
| BTX | 267120 | | 32 | 8348 | 16.84% | 28.57% |
| HYDRODEALKYLA. | 32805 | | 9 | 3645 | 4.74% | 8.04% |
| CYCLOHEXANE | 87100 | | 6 | 14517 | 3.16% | 5.36% |
| BUTANE FEED | 69000 | | 17 | 4059 | 8.95% | 15.18% |

## TABLE VI (Continued)

| PRODUCTION UNIT PROCESSES | TOTAL IN BBL/CD | AVERAGE BBL/CD FOR ALL REFINERIES | NUMBER OF UNITS BY TYPE | AVERAGE BBL/CD BY UNIT TYPE | PERCENTAGE OF U.S. REFINERIES WITH UNIT | PERCENTAGE BY TYPE OF UNITS |
|---|---|---|---|---|---|---|
| PENTANE FEED | 62900 | | 6 | 10483 | 3.16% | 5.36% |
| HEXANE PLUS | 335200 | | 42 | 7981 | 22.11% | 37.50% |
| ALL | 785915 | 4136 | 112 | 7017 | 58.95% | 100.00% |
| HYDROGEN (IN MMCF, MILLION CUBIC FEET) | | | | | | |
| STEAM METHANE | 2036 | | 44 | 46 | 23.16% | 83.02% |
| STEAM NAPHTHA | 148 | | 2 | 74 | 1.05% | 3.77% |
| OXIDATION | 111 | | 2 | 56 | 1.05% | 3.77% |
| CRYOGENIC | 95 | | 2 | 48 | 1.05% | 3.77% |
| OTHER | 99 | | 3 | 33 | 1.58% | 5.66% |
| ADD | 2489 | 13 | 53 | 47 | 27.89% | 100.00% |
| COKE | 74393 | 392 | 54 | 1378 | 28.42% | 100.00% |

NOTE THERE ARE 190 TOTAL U. S
(Source 7)

the finished products were generally estimated from pilot plant studies. Oxynates, water, and alcohols were considered poisons to the process. The basic process consisted of pretreatment to dry the feed and remove the poisons. Fixed bed reaction included recycle of isobutane, followed by the settled separation of the acid, and fractionation of the products into fuels as needed by the marketplace. The HF acid process required regeneration. In HF units, defluorination was required due to combined fluoride carryover. The study refinery model included a 9,000 barrels per calendar day HF alkylation unit.

Aromatics processing units were included in the majority of U.S. refineries. Three of the most common types were included in the study refinery model. They were TIP units, BTX (benzene, toluene, and xylenes) complexes, and hydrodealkylation units. TIP units were used to convert low octane pentanes and hexanes into the higher octane isomers. The first step was to separate by shape-selective adsorption, the normal paraffins from the feedstock and reactor effluent while the isomers were allowed to pass through. The normal paraffins were desorbed with hydrogen and passed to the isomerization reactor in a vapor form. Catalyst and molecular sieves were regenerated with oxygen in a batch operation approximately every seven years. TIP units were the simplist units in the refinery that increase octane numbers approximately twenty ron. The survey (Table VI) indicated over one third of U.S. refineries have TIP units (types 4, 5, and 6 of Aromatics) .

BTX complexes have been defined as an integrated aromatics complex of six processing units which can produce benzene, toluene, p-xylene, and o-xylene from naphtha feedstocks. The six processes are catalytic reforming, aromatics extraction, p-xylene recovery, xylene isomerization, dealkylation, and transalkylation. A simplified diagram was shown in Figure 2. These BTX units were present in seventeen percent of 190 total U.S. refineries (Table VI).

In the last significant unit, five percent of the total 190 refineries, was a hydrodealkylation unit for converting alkylbenzenes and alkylnaphthalenes into benzene and naphthalene (7). Side chains and nonaromatics in the feed were converted to light straight chain paraffins, usually methane. Fresh feedstock was combined with recycle and hydrogen, heated and charged to a catalytic reactor. A separation and fractionation unit followed. There were six refineries in the U.S. which also have a cyclohexane production unit downstream of the benzene unit (7).

Polishing units for certain saleable products were included. Typical examples were asphalt units (Forty three percent of U.S. refineries, Table IV), and coke units (Twenty eight percent of U.S. refineries, Table VI). Both

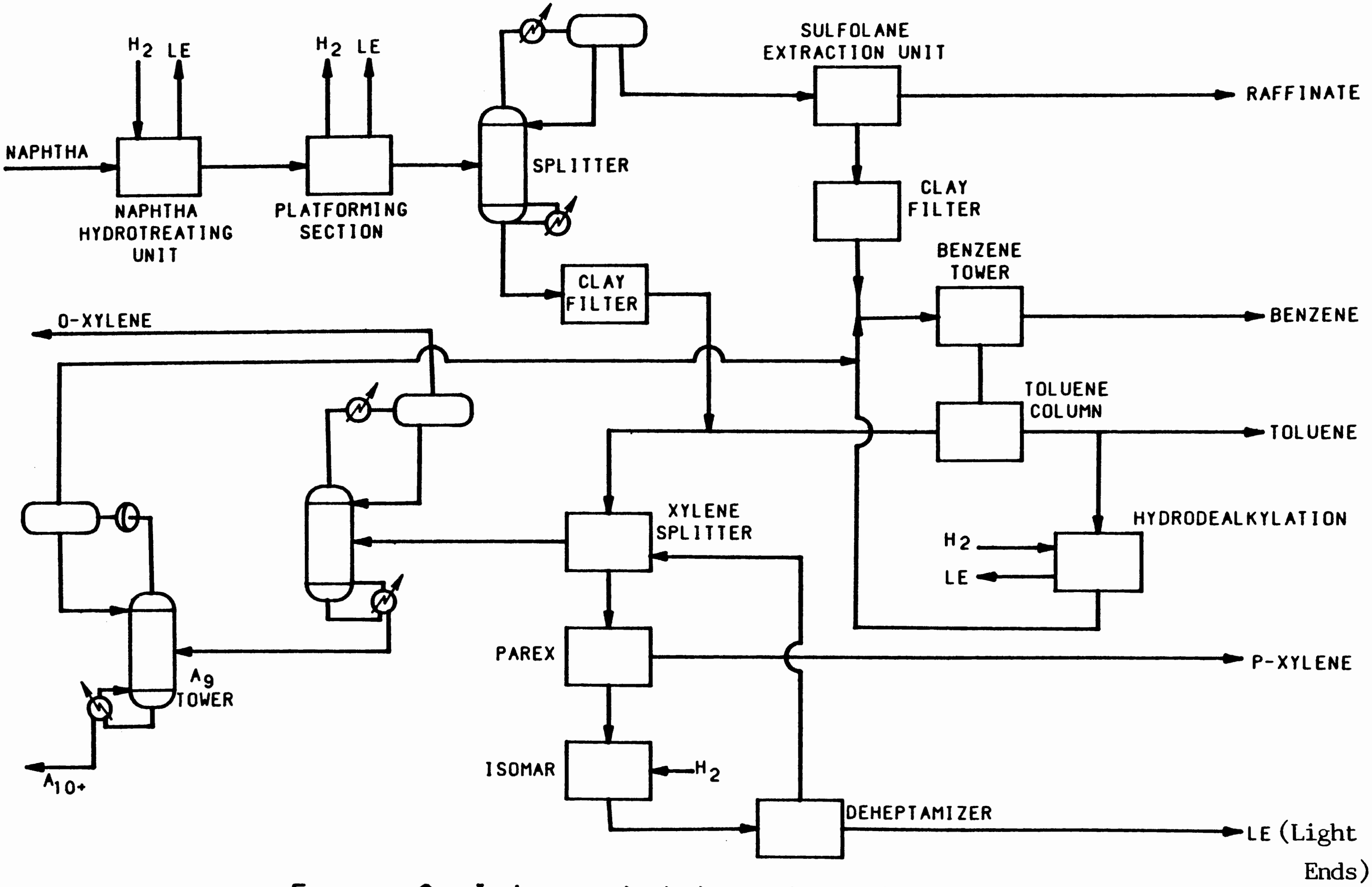


Figure 2 Intergrated Aromatics Complex

(Source 10)

were included in the study refinery. In addition, with the new emphasis in refinery operations on reduction of the gasoline pool vapor pressure and oxynate additives, the study refinery included modified FCCU operations, MTBE, and TAME units.

The study refinery model compiled as described above represented a moderate-sized, independent, modern refinery with significant product flexibility, futuristic oxynate capacity, and meeting new EPA vapor pressure rules.

## Selection of Auxiliary Unit Processes

There were various supporting process units which were required for ensuring refinery operations. These systems interacted with the main process units throughout the refinery. Included in the study refinery model were the following auxiliary processes:

- steam boiler processes - at various pressure levels
- cooling water - recirculating process water
- electricity - purchased
- fuel gas - both internally generated and externally purchased
- amine plant - MEA (Monoethanolamine)
- sulphur plant - Claus units
- tail gas cleanup - SCOT (Shell Claus Off-gas Treating) unit

# CHAPTER IV

## INITIAL DEFINITION OF WASTE STREAMS

A series of figures detailing the refinery units would aid in understanding the complexity of the main process units and the beginning of waste stream identification. The overall view of the main processes was shown in Figures 3 and 3a. Starting with the crude oil inlet line, new undiscussed boxes or processes were added, for example storage and desalter units. Storage was required for proper smooth, continuous operation of the refinery and to cope with upset conditions. Typically storage was based upon each refineries crude sources, their mode of delivery, and the location of the refinery. Therefore an average value would not be of value. Ninety days storage has been used, 7.65 mm(million) barrels, in the model refinery. This resulted in sixteen, half million barrel tanks for crude storage. These were floating roof storage tanks (Figure 4). Storage created several waste streams on both a routine and non-routine basis, such as oil-water emulsions, sludges, vapor emissions, and possible maintenance waste when cleaning the tank. Desalting of crude petroleum was required due to contamination by

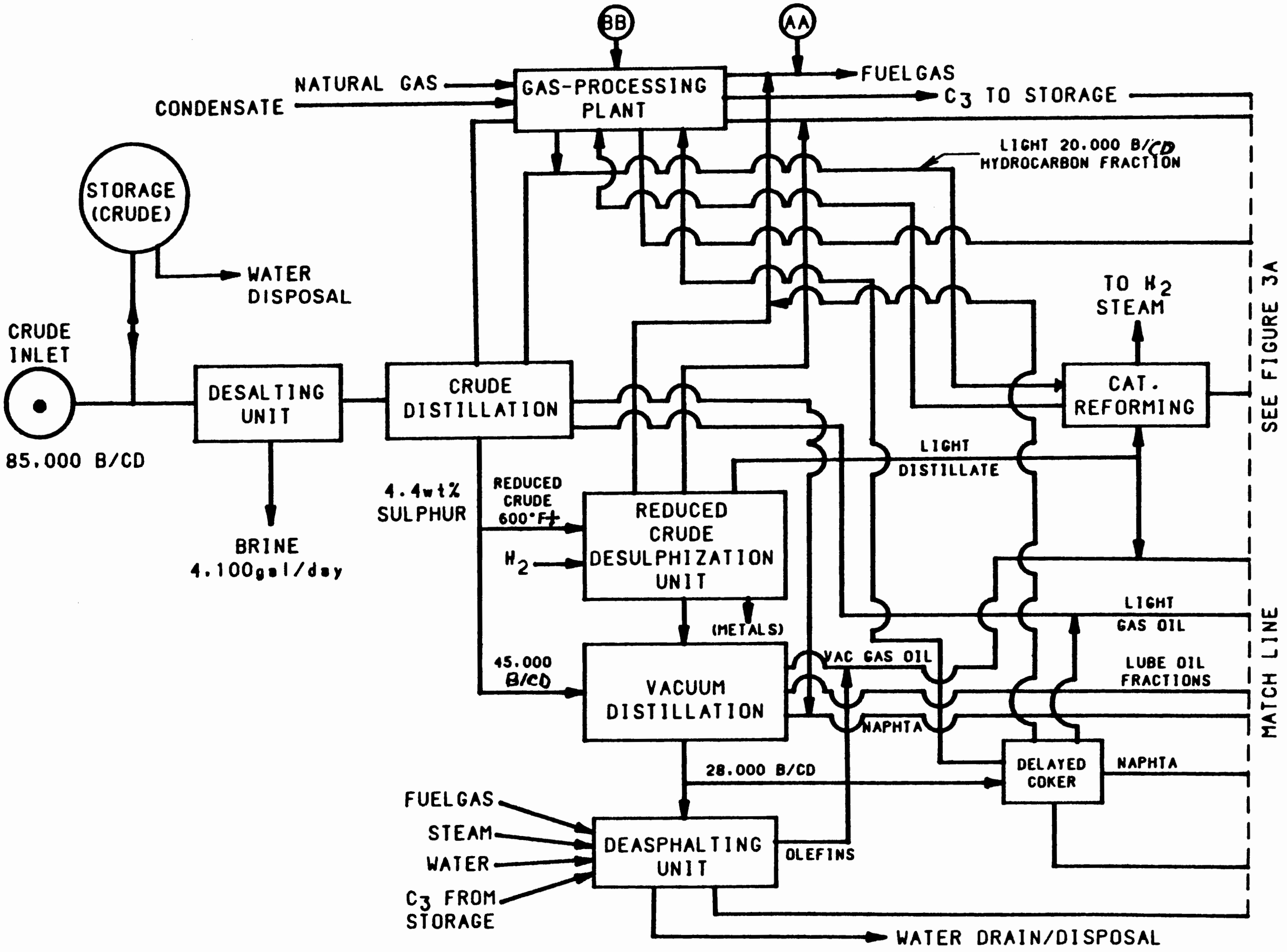


Figure 3 Overall View Of Study Refining Model

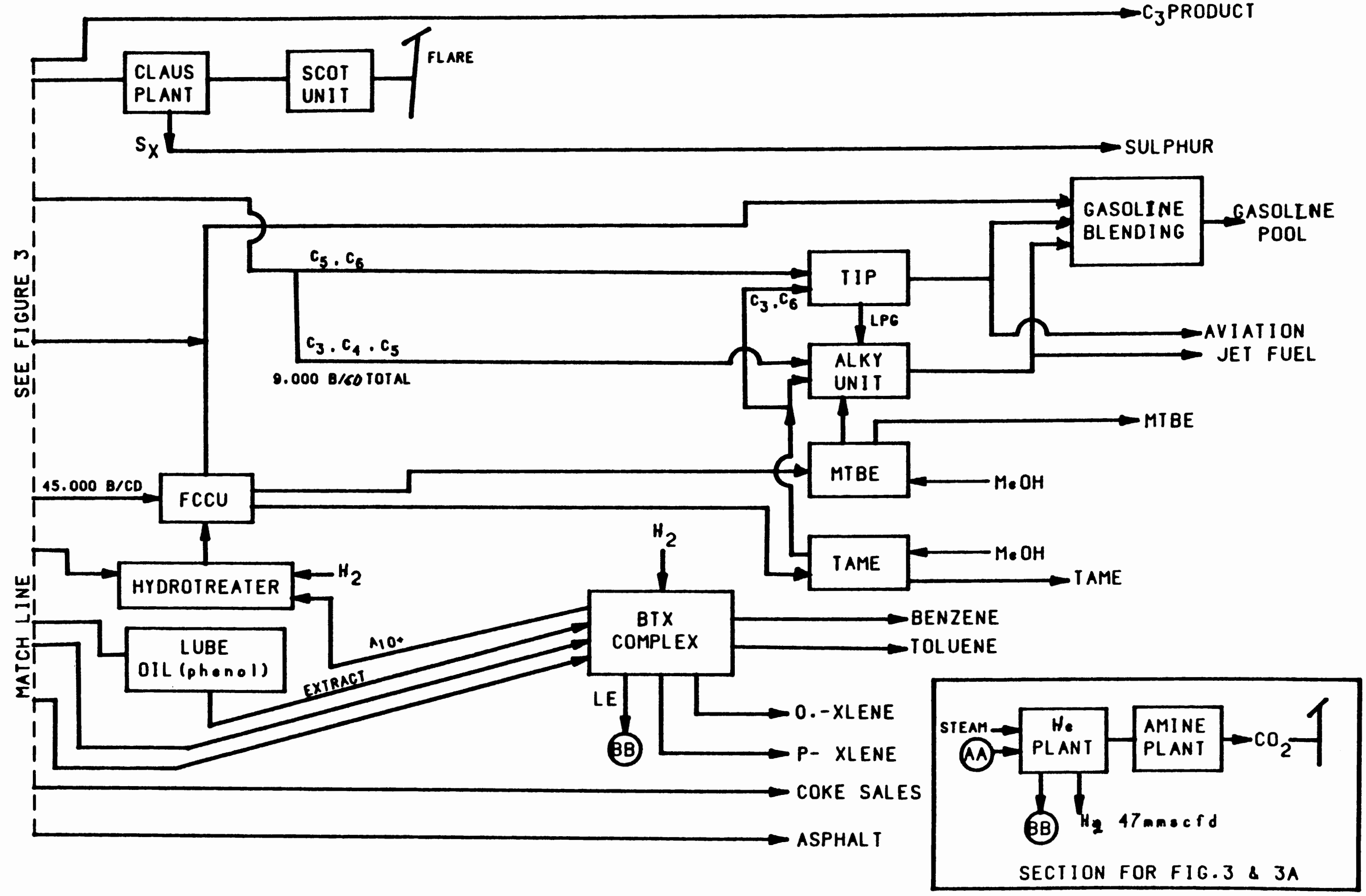


Figure 3A Overall View Of Study Refining Model (cont.)

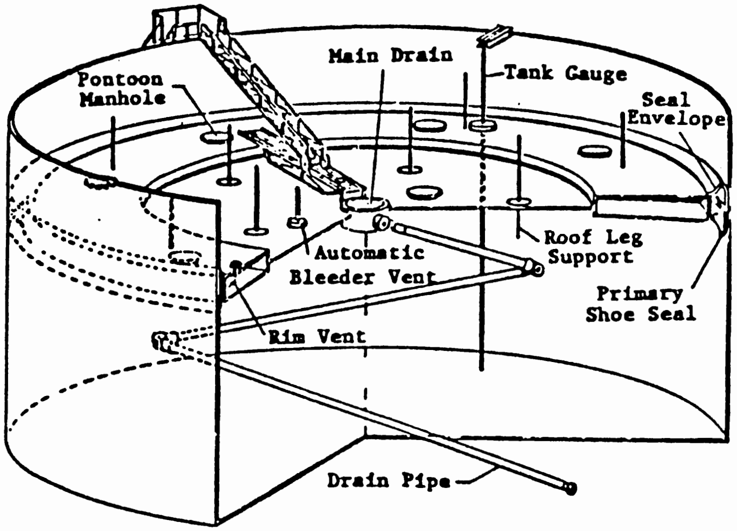


Figure 4. Floating Roof Storage Tank

(Source 12)

saltwater. The source of the salt water was either from underground storage or poor wellhead separation or mixing during transportation. Specific desalting units were designed based upon the type of salt dispersion and the type of crude oil. In general, heating with hot water injection followed by emulsion breaking additives, if needed, allowed the brine to settle out (Figure 5). This is a more detailed process flow diagram of the Figure 3 box labeled "Desalting Unit" and would be part of the box labeled "Vacuum Distillation Atmospheric Distillation" in Figure 1. The brine that settled out was a waste stream. The waste contained chemical additives if used in the processing. The steam system, with its own peculiar wastes, has been discussed later as part of the steam system.

The crude distillation system (Figure 6) consisted of a collection of towers with fired heaters (or pipe stills). This system was part of the "Vacuum Distillation Atmospheric Distillation" unit in Figure 1. Waste steams were generated on a routine basis from the fired heaters exhaust, the water draw-off, the exhaust of the non-condensables gas compressor (to help maintain a vacuum), and the water plus non-condensables stream. In general, neither the towers nor the fired heaters would have any routine maintenance performed on them. The heat exchanger bundles required cleaning at intervals determined by

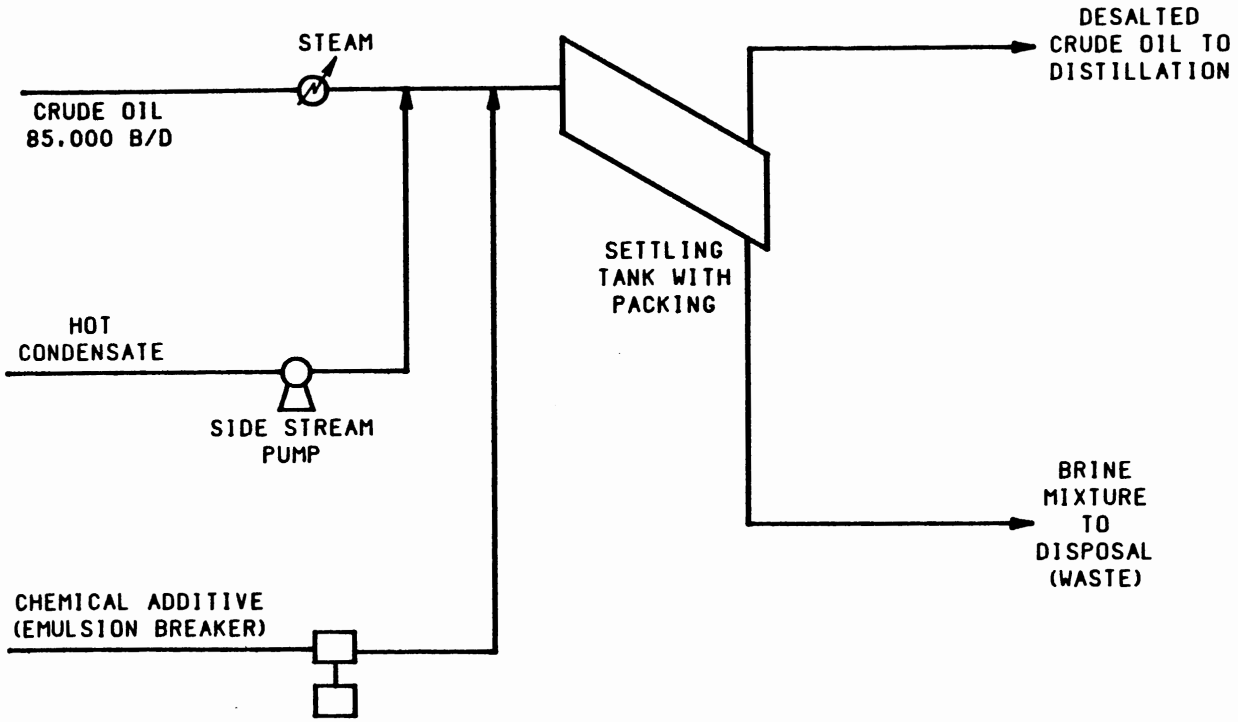


Figure 5 Desalting Process Flow Deagram

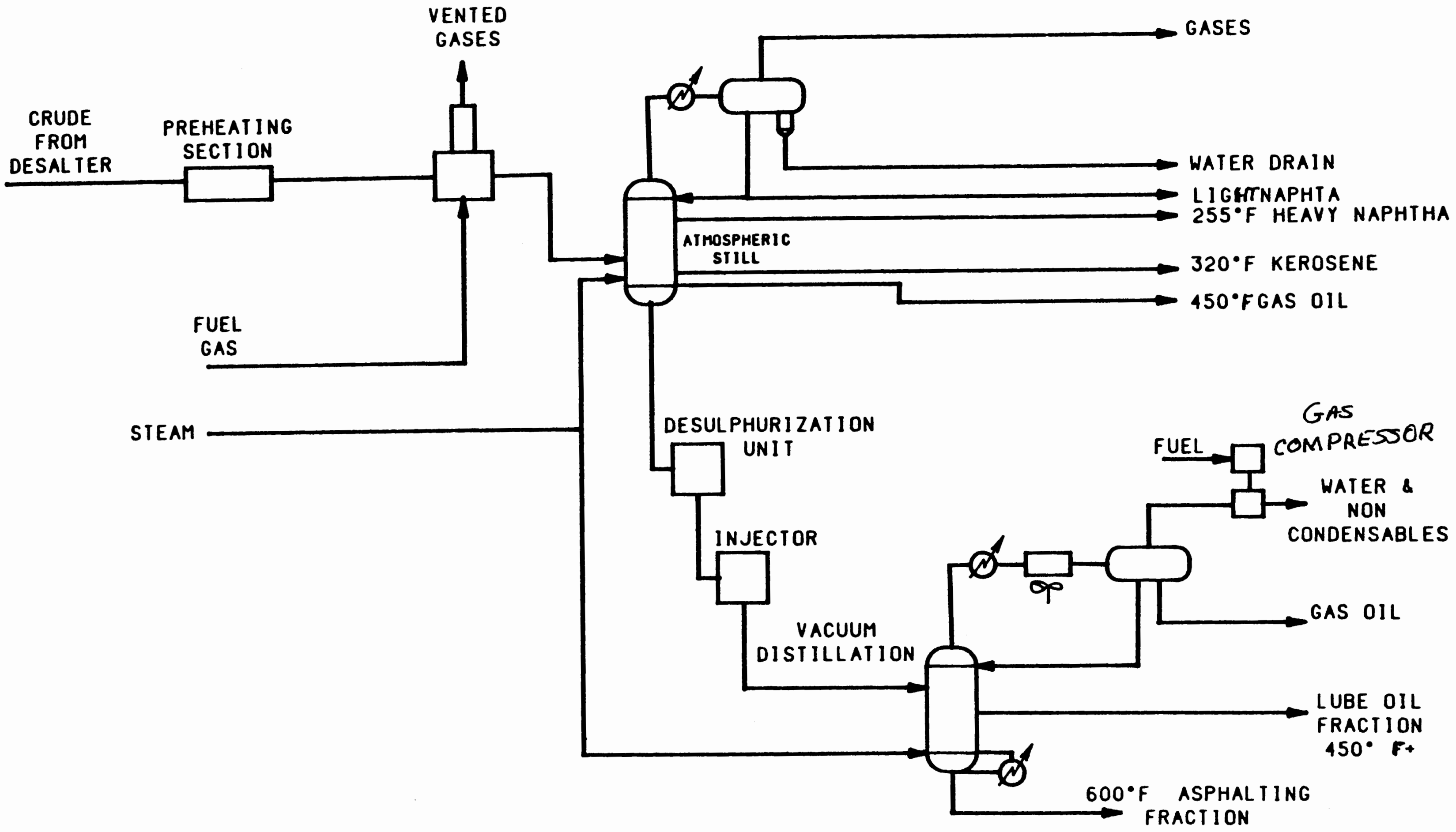


Figure 6 Crude Distillation Unit Process Flow Diagram

the fouling, which generated waste sludge that consisted of the foulant plus the cleaning agent.

Starting with the heavier fractions, the deasphalting unit (Figure 7) used propane solvent to strip out the asphalt which created an olefin liquid product for cracking and an asphalt product for sale. Routine wastes from this unit consisted of water wash disposal, fuel exhaust from fired heaters and recompressors, and lube oil drains. Non-routine wastes again included heat exchanger bundle washings. In addition, due to the number of pumps, seal failure and the associated pump washing (maintenance procedures) contributed to normal non-routine waste streams.

The delayed coker unit (Figure 8) has the wastes generated from leaking pump seals, burned fuel gas exhaust, and heat exchanger bundle cleaning. Additionally, the coke product as it is mechanically handled ( e.g. conveyors), presented a potential spill or waste generation possibility due to the presence of small chips or "fines". The coker unit was part of the box labeled "Thermal Processing" in Figure 1.

The FCCU is a continuous system (Figure 9) with continuous waste generation. The largest waste streams were catalyst fines and flue gas exhaust. Non routine wastes associated with exchanger cleanings, leaking pumps, and gas powered compressors were present.

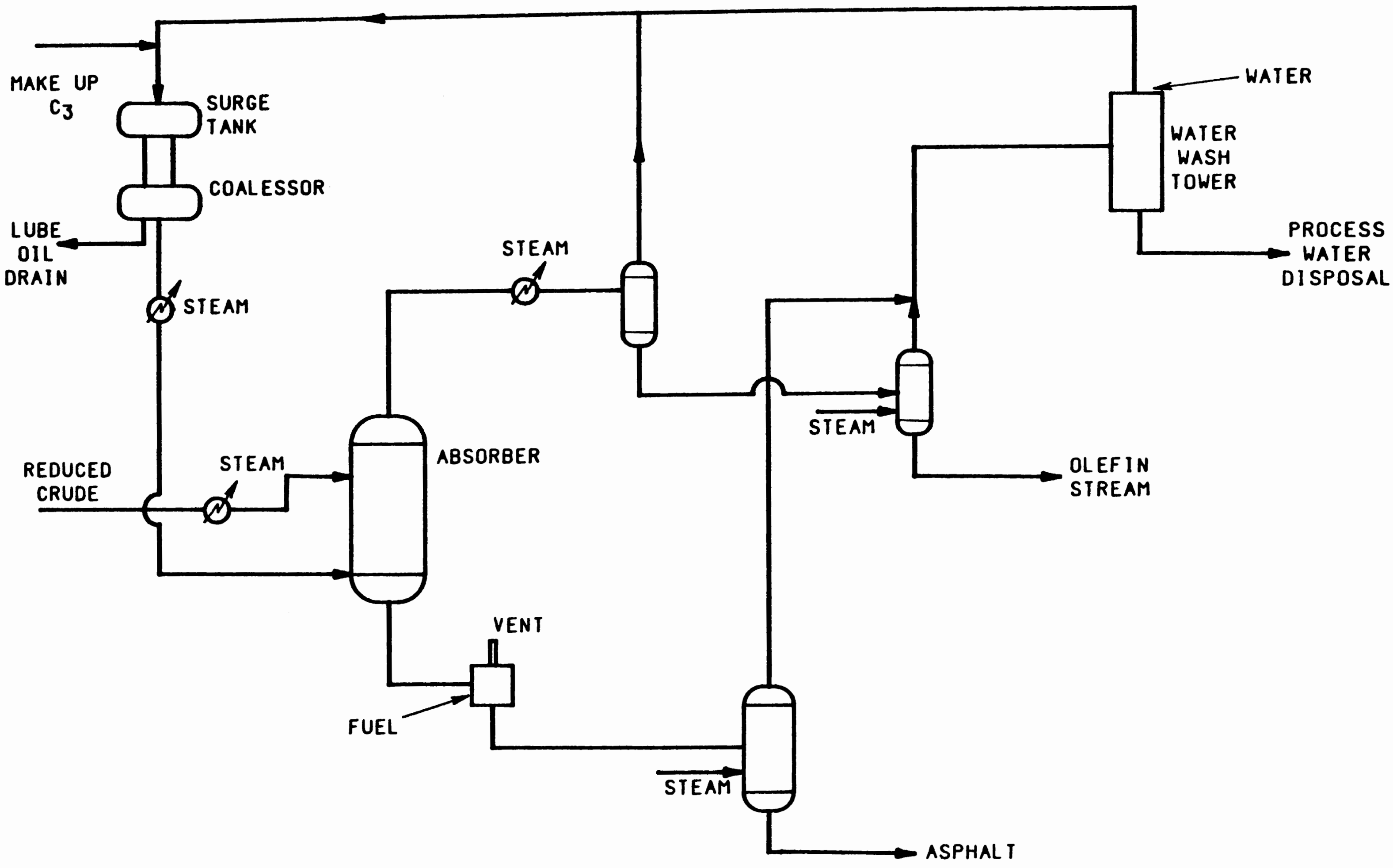


Figure 7 Deasphalting Process Flow Diagram

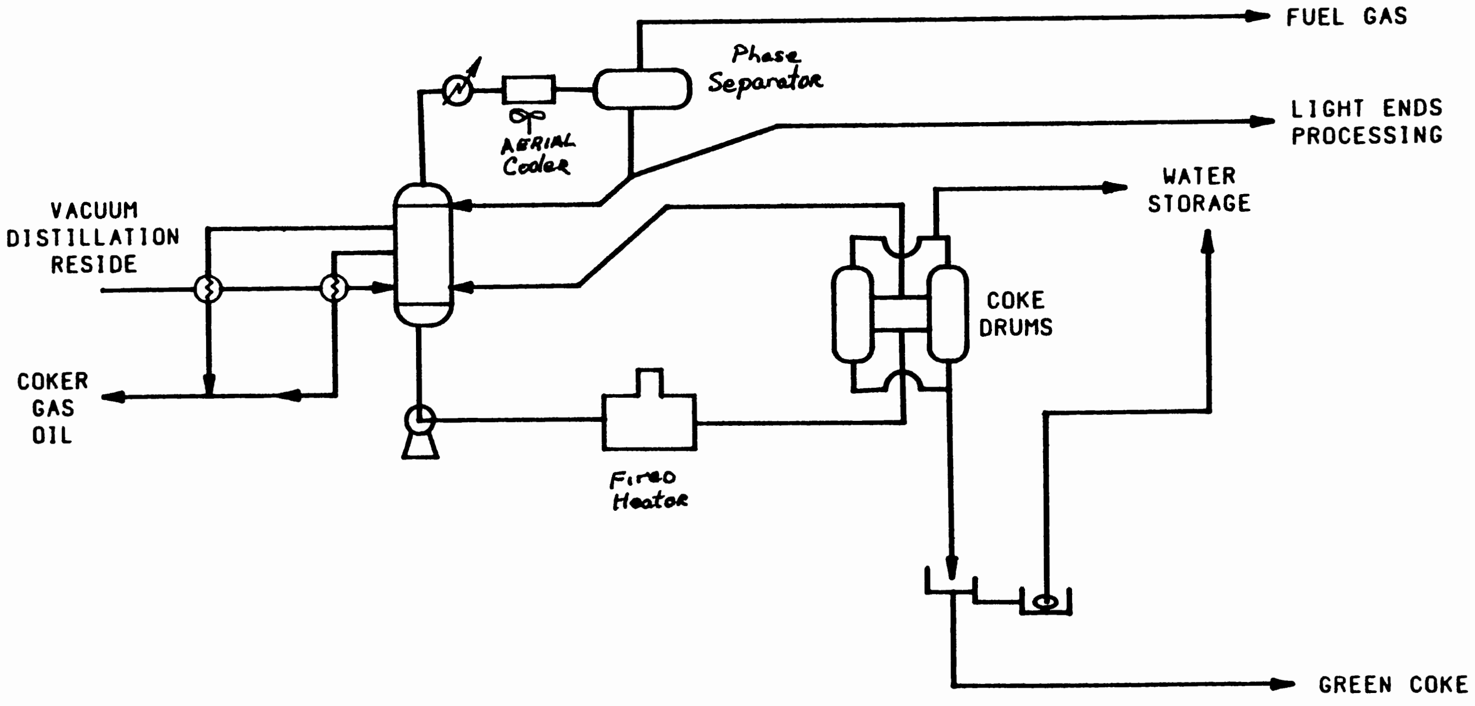


Figure 8 Delayed Coker Process Flow Diagram

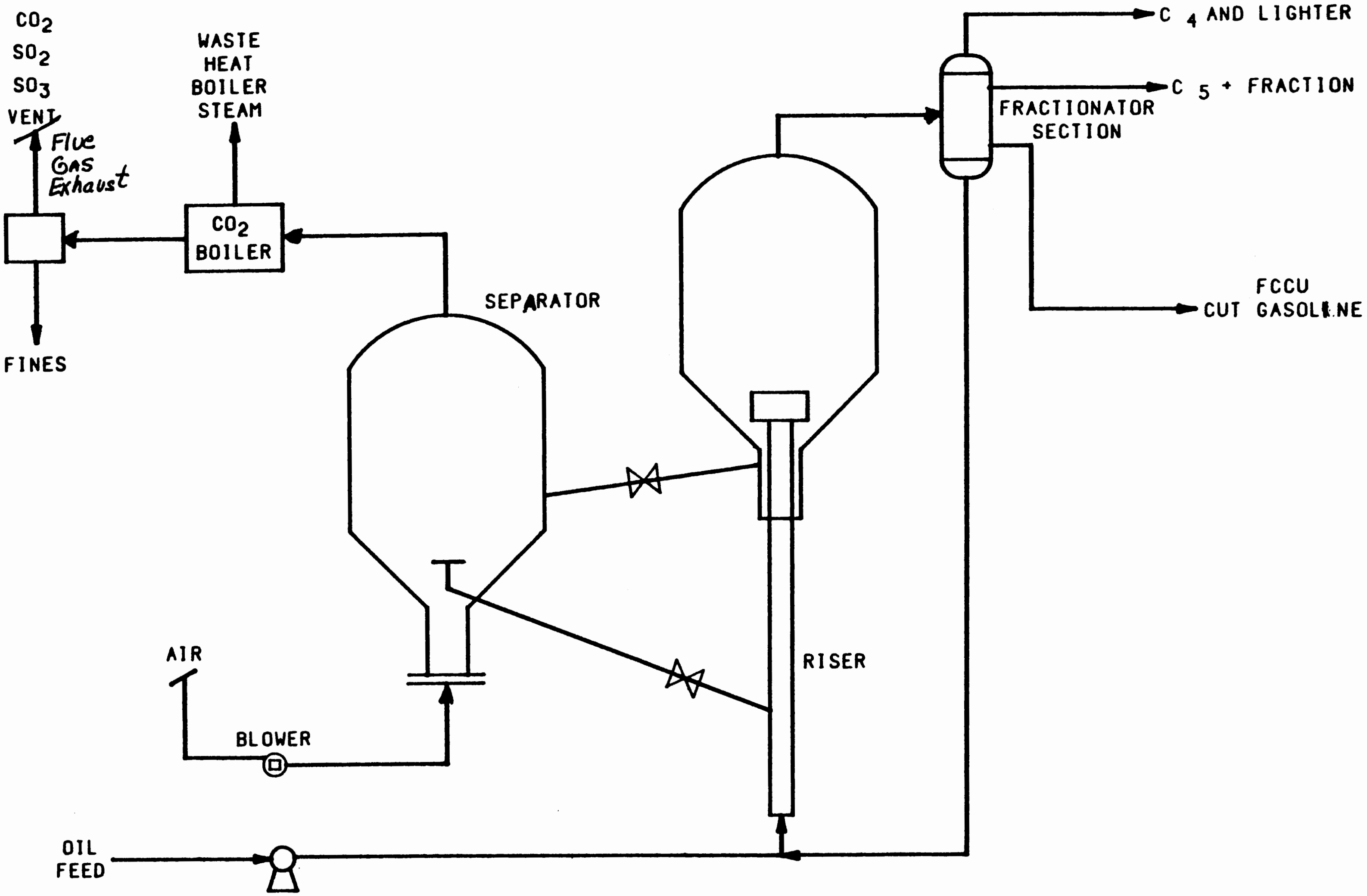


Figure 9 Fluidized Catalytic Unit Process Flow Diagram

The reforming unit (Figure 10) was the only unit which required hydrogen and is an exporter of hydrogen. The unit operated in a batch mode with in situ regeneration of the platinum catalyst. The regeneration consisted of two steps: first a carbon burn off, followed by a chloride activity adjustment. Routine operating wastes consisted of fuel exhaust from the compressor and fired heater. Non-routine waste generated by the unit consisted of pump seal losses and heat exchange bundle cleanings.

The atmospheric distillation vacuum reside's sulphur content was reduced and the molecular structure reformed in size by a catalytic hydroreforming unit called a hydrodesulfurization unit. This unit (Figure 11) used a cobalt-molybdenum metal catalyst to demetalize and desulfurize the crude reside. The reactions were exothermic with the metals deposited on the catalysts as metal sulfides and the sulphur was removed as hydrogen sulfide in a conventional amine unit. Ammonia by-products were produced by oxygen or nitrogen compounds in the incoming reside. These were produced in the catalysts and exhausted with the waste water. The waste streams generated were small (the hydrogen sulfide stream was not considered waste at this point). The fired heater generated fuel exhaust. The reactors operated in batch operation mode and the catalysts were replaced at exhaustion. Amine degradation and removal required

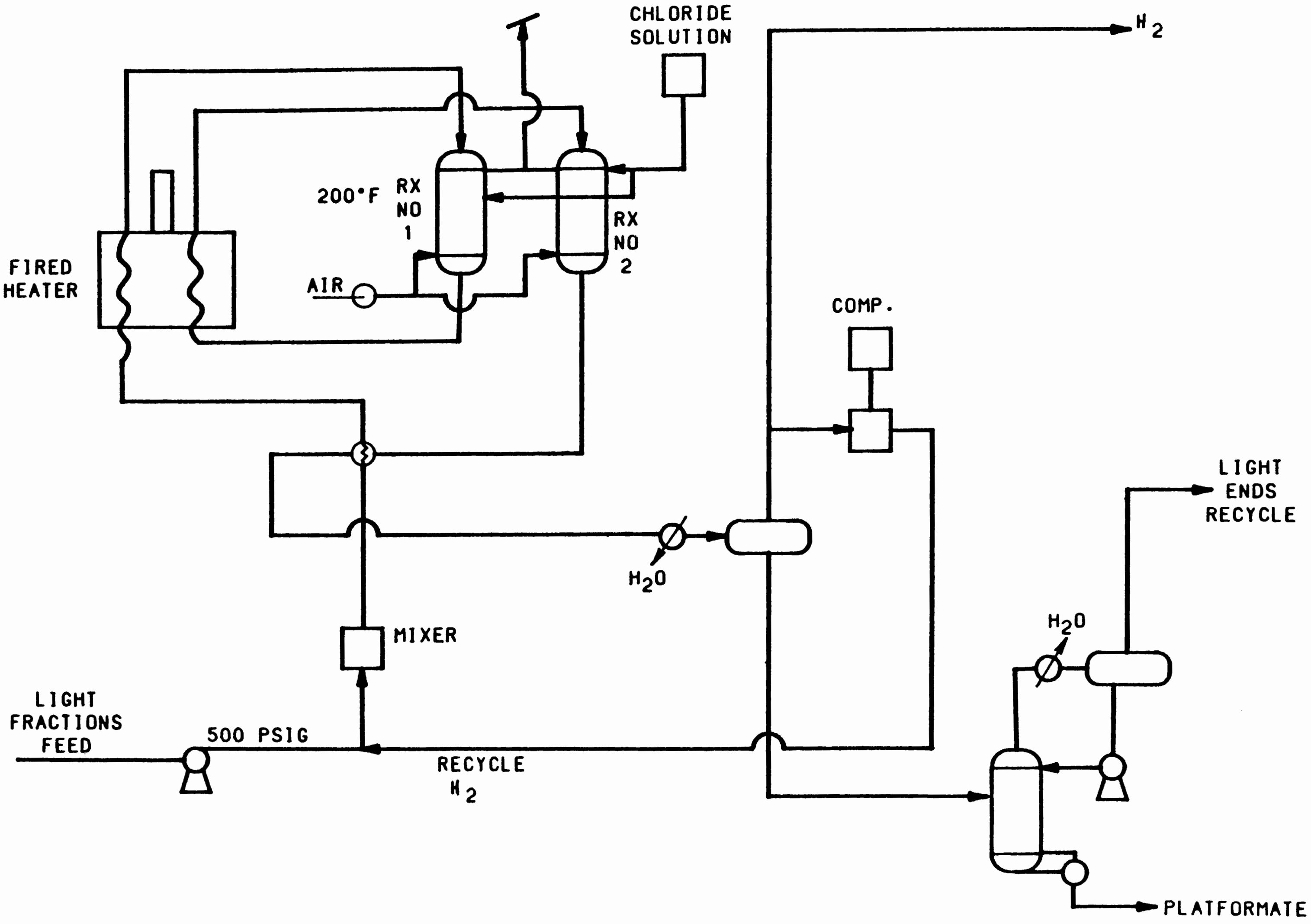


Figure 10 Catalytic Reforming Unit Process Flow Diagram

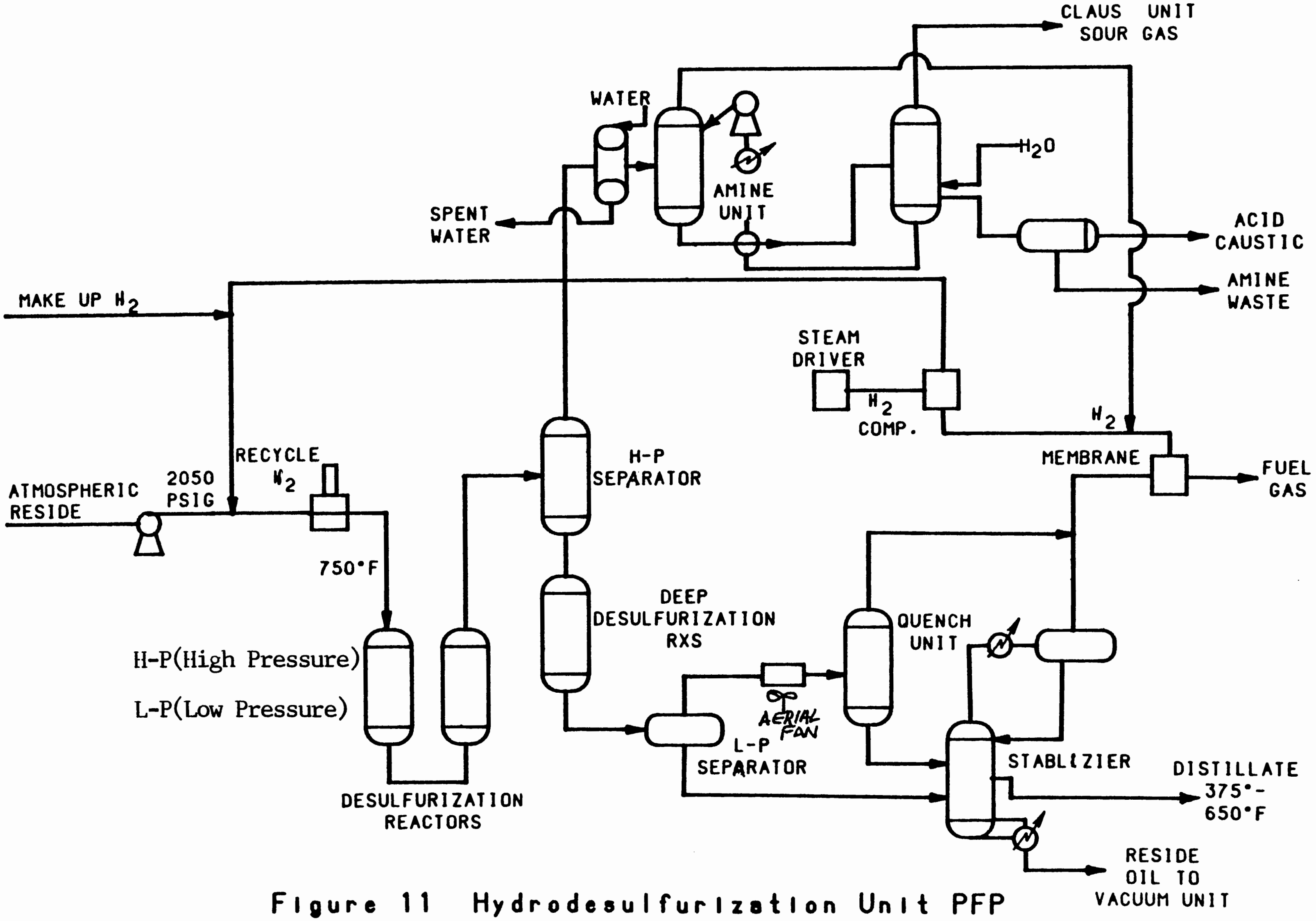


Figure 11 Hydrodesulfurization Unit PFP

disposal of the cracked amine by-products. Non-routine wastes associated with leaking pumps, fired heater exhausts, and heat exchangers cleanings were present.

In addition to the crude units wastes discussed above, the polishing units created wastes also. Most of these units have associated storage and product spills (ie waste). Where it was inappropriate to simply clean up the spill and mix the spill into the remaining product, the product spill was identified as a separate waste, otherwise no discussion of product handling was included.

The hydrogen plant was a 47 mmscfd steam methane reforming process (Figure 12). Waste streams continuously generated from this unit were amine wastes, $CO_2$ vent gas, and combustion fuel from the furnace exhaust. Non-routine wastes associated with leaking pumps, heat exchanger cleanings, and towers were also generated. Regeneration of the furnace tubes generated coke/coking burned products. This occurred on a batch basis as needed.

The alkylation unit in this refinery was an HF unit (Figure 13). The HF unit created hazardous and undesirable fluoride materials as a result of upset conditions, therefore the alkylation unit had its own waste treatment system before these wastes discharged into the refinery waste system. The wastes treated were vented gases, acid regeneration bottoms, and alumina treating solids, as

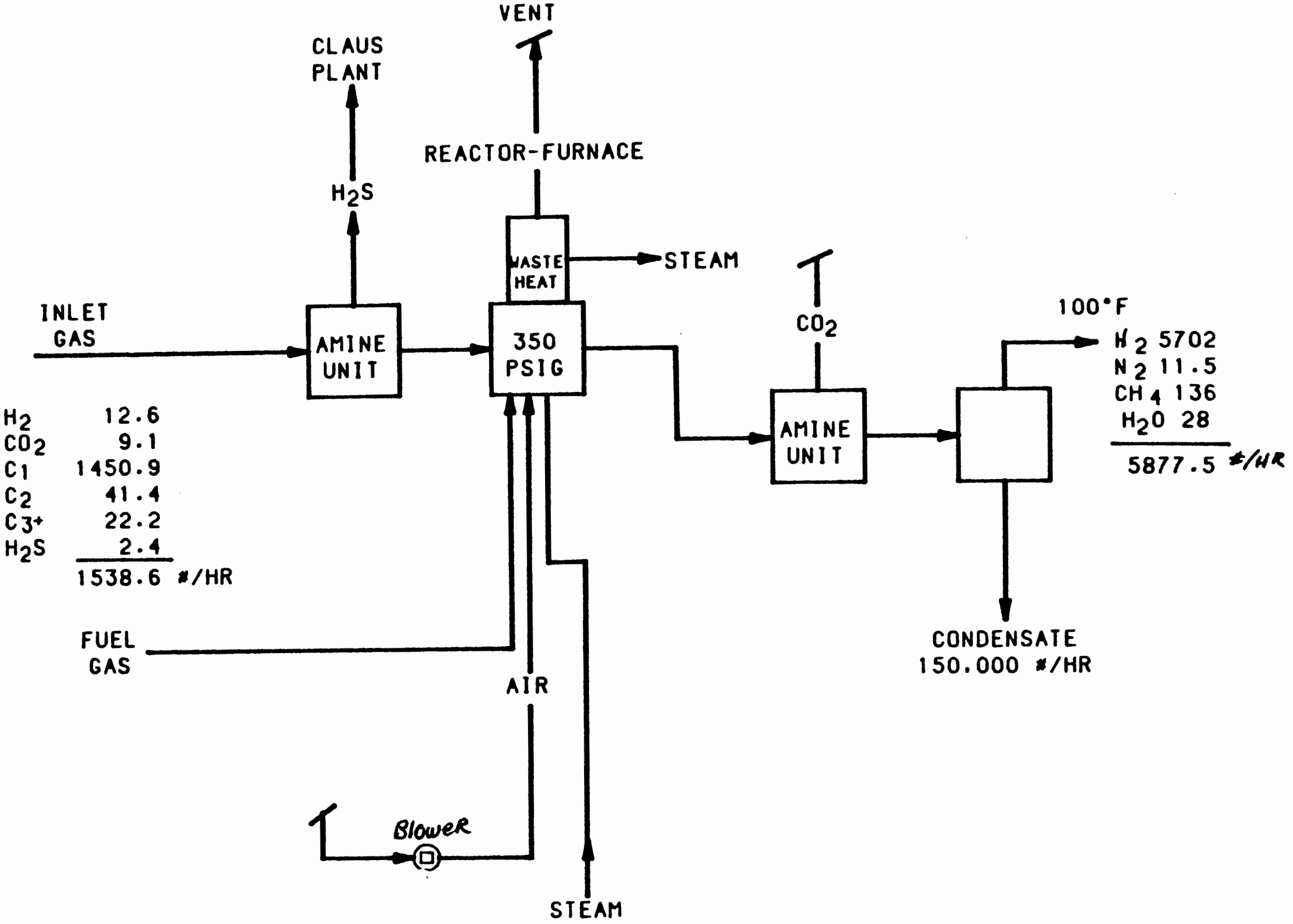


Figure 12 Hydrogen Generation Plant

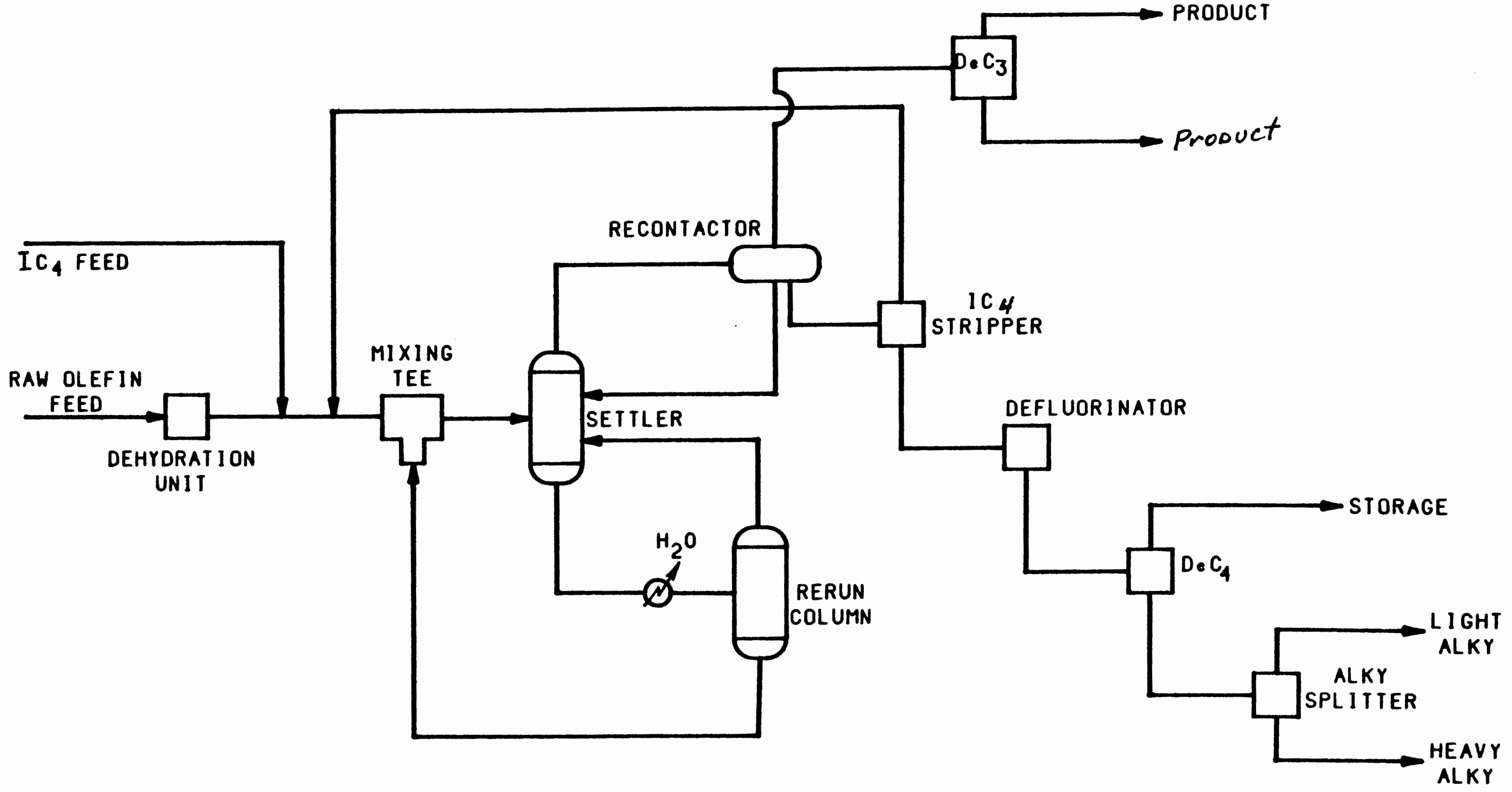


Figure 13 Alkylation Unit Process Flow Diagram

well as wastes from relief valves, pump vents, acid sewers, and storm sewers in the area. The non-routine waste of heat exchanger bundle washings was also addressed. Exhausts for several fired heaters, occurred on a routine basis and was reviewed later with other air emissions below.

The TIP unit (Figure 14) is one of the more simpler units in the refinery. The reaction took place in the vapor phase which was usually a cleaner process. The only routine wastes created were caused by periodic burn, as in situ catalyst regeneration, and molecular sieve or catalyst replacement (approximately every seven years). The regeneration process consisted of burning the coating coke off the molecular sieve material. Non-routine wastes associated with heat exchanger cleanings and leaking pumps were also generated.

The BTX or aromatics complex (Figure 2) was a large grouping of towers, reactors, exchangers, and filters. Wastes were generated on a non-routine basis, such as clay filter replacement. The products were considered waste if spilled and therefore included with waste streams below.

The lube unit (Figure 15) was a phenol (or carbolic acid) process which removed aromatic compounds from the lubricating fractions(usually considered the $C_{25}$ to $C_{45}$ cut). Because phenol is toxic, this units gas vents, relief valves, pump vents, acid sewers, and storm sewers

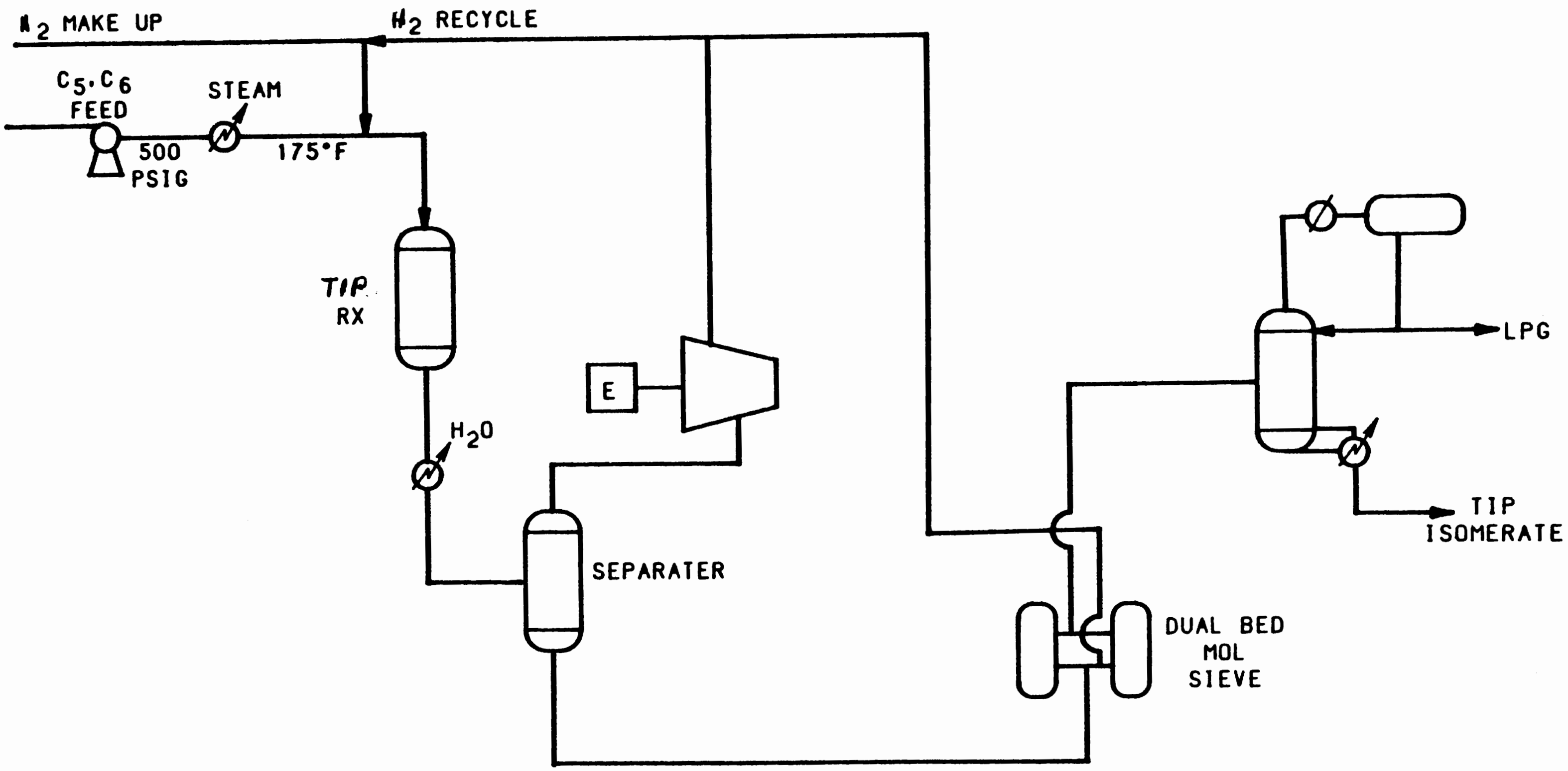


Figure 14 Thermal Isomerization Process

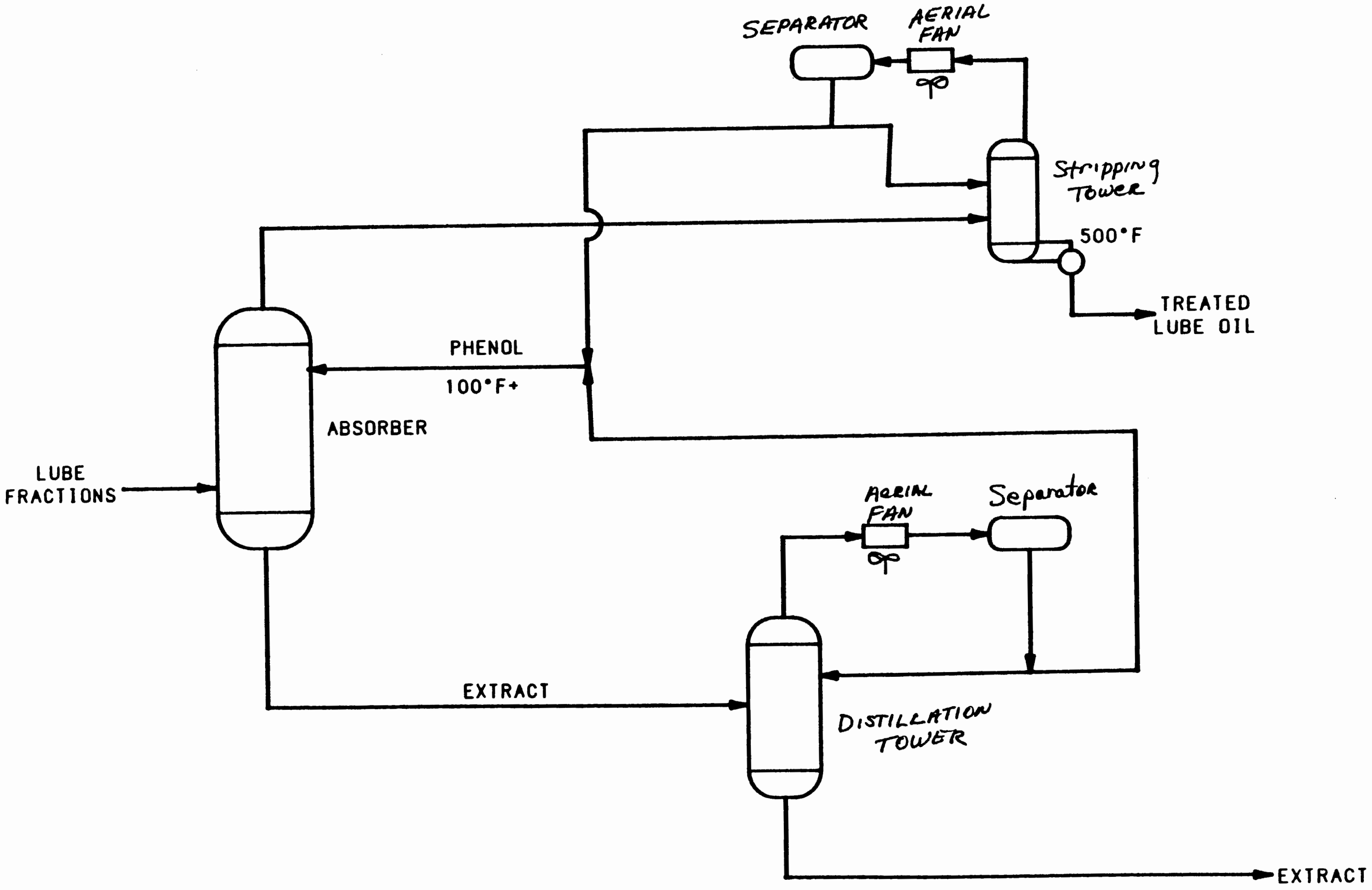


Figure 15 Lube Oil Solvent Process Flow Diagram

were treated in the process unit area separately from other units waste streams. The non-routine washings of exchangers and pumps were also be wastes.

The MTBE and TAME units (Figure 16 and 17) had special problems in addition to the waste problems previously encountered. Both required methanol as a feedstock. Methanol required special drains, collection points, and sumps. Additionally MTBE and TAME are extremely soluble in water (MTBE solubility is approximately 43,000 ppm vs 65 ppm benzene), therefore double lined pipe drains and other soil protection precautions were observed in the development of waste handling (9).

Auxiliary systems generated wastes also. These systems and the wastes generated will be discussed below.

Claus units are (Figure 18) common for conversion of sour (Hydrogen Sulfide) gases into liquid sulphur. Before SOx emission standards, a common recovery was approximately 90%. Due to current air standards, 95%+ must be achieved and tail gas unit processing has been required to recover upwards of 99.5% or higher. The study reactor type used in the refinery model was a straight through Claus unit with three reactor beds. A tail gas unit developed by Shell (SCOT) (Figure 19) was used to reduce emissions to approximately 250 ppm sulphur. Wastes generated by the Claus/SCOT unit were amine by-products and SOx emissions

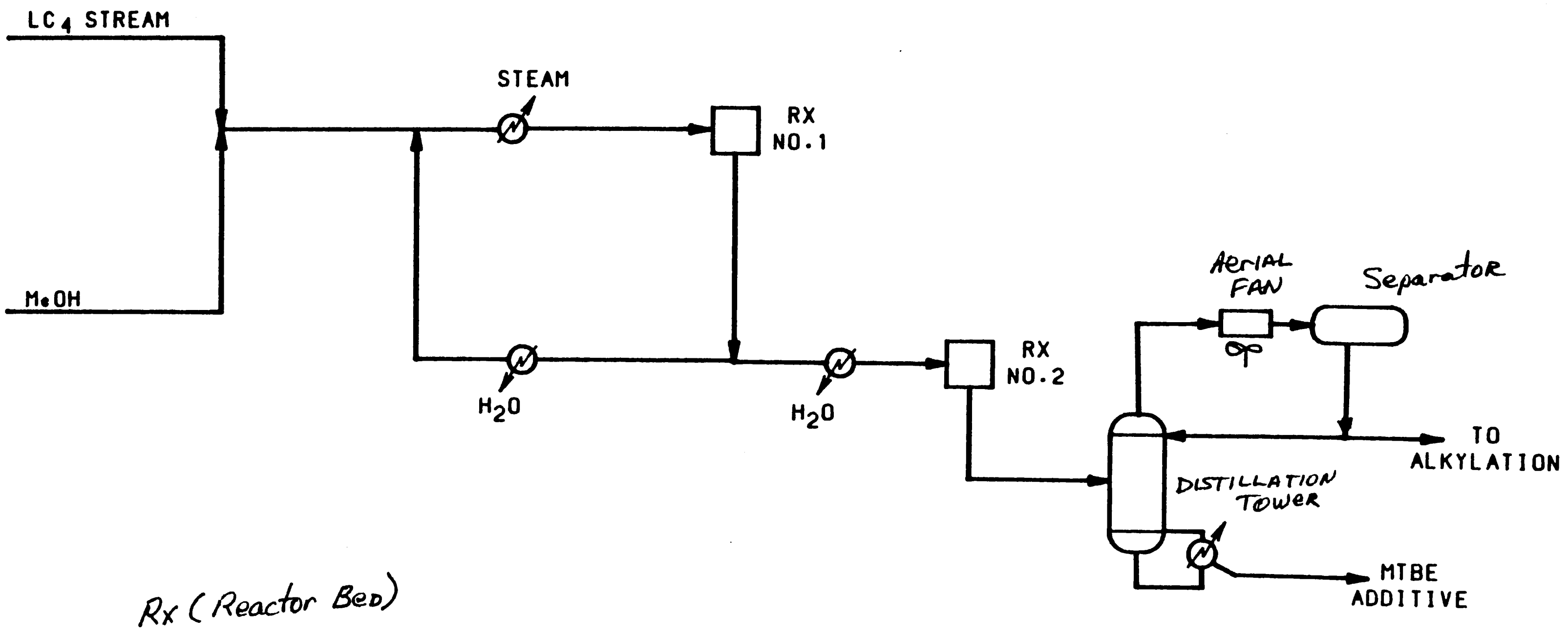
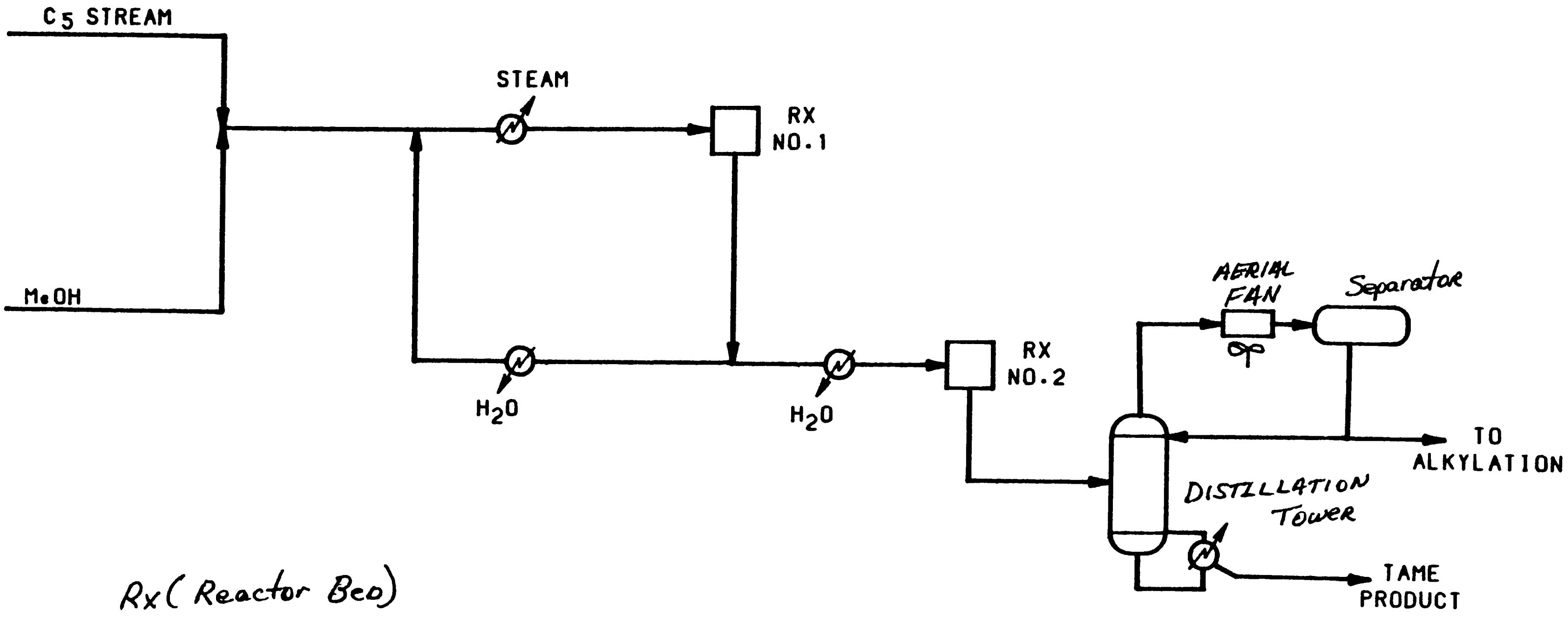


Figure 16 MTBE Process Flow Diagram



Rx( Reactor Bed)

Figure 17 TAME Process Flow Diagram

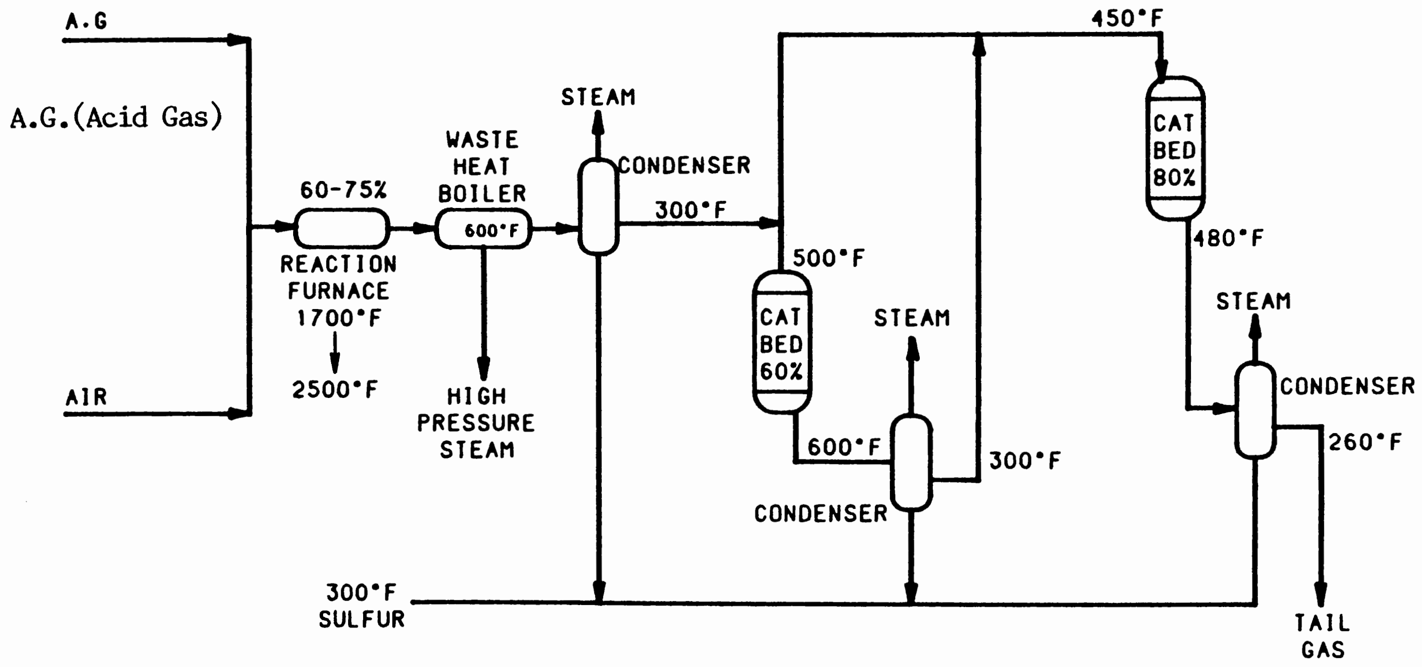


Figure 18 Claus Unit Process Flow Diagram

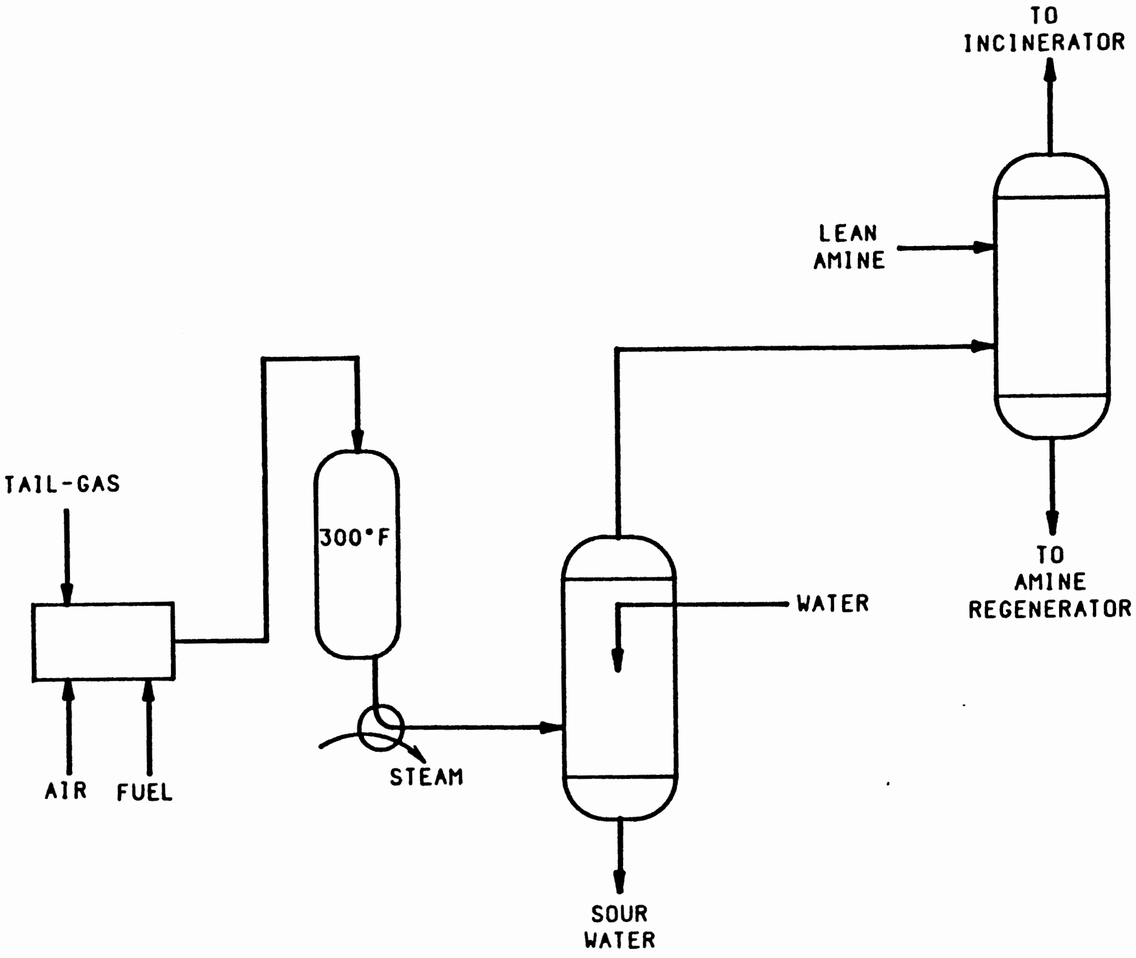


Figure 19 Scot Unit Process Flow Diagram

gas. Non-routine heat exchanger bundle cleanings and leaking pump losses will be generated.

Cooling water systems are generally recycled, closed systems. To maintain these water systems required chemical controls. One such chemical was chlorine, used to control bacterial growth. To maintain the proper level of chemicals within a closed system required blowdown. Blowdown was a routinely generated waste, which consisted of water, dirt, any cross tube leakage contamination and concentrated chemicals which were added. Sludge from silt and dust would build up in the basin of the cooling tower and required disposal of. The chemicals contained in the blowdown were dependent upon the initial quality of water used for the makeup stream. Non-routine wastes were generated as exchangers were cleaned and as tower (cooling) replacement parts were required. These replacement parts were usually wooden and were not considered as a waste within this refinery model.

The steam system was another water system which was chemically treated for corrosion and bacterial growth. This system also had make up and blowdown requirements. In addition steam was vented to the atmosphere at various points all over the refinery. This mostly water vapor venting was not considered waste within this refinery model. With this system, non-routine wastes were generated by heat exchanger cleanings.

Process water is defined as water that has been drained from refinery units that were in contact with the process (usually hydrocarbon fractions) streams. Unless special note has been taken (e.g. methanol) these streams were collected and treated as one waste in one large water treating unit for the entire refinery model. Most of this water originated from steam injected into the processes as required and later condensed and removed.

Electricity, air(instrument), and fuel systems were considered non waste generating streams.

Finally, there were wastes generated from the refinery which were generic to the facility as a whole. An example would be the fugitive VOC (volatile organic compounds) emissions. These losses would be lost through piping flanges, valve stems, and packing glans. This group of generic wastes were included in the study refinery model for evaluation. They include:

VOC emissions
Rain/Storm Water Sewers and Runoff
Process Equipment and Area Sewers
API Separator
Slop Oil and Water Separator
Air Flotation Systems
Biological Treatment Systems
Product Storage Systems

Table VII was a summary of the waste streams identified in this chapter. This was an initial identification which has been expanded in later discussions after compositions of the inlet streams was developed.

## TABLE VII

## INITIAL IDENTIFICATION OF WASTE STREAMS

| REFINERY SYSTEM | FEEDS | PRODUCTS | WASTES | ROUTINE | NONROUTINE |
|---|---|---|---|---|---|
| Storage | | | | | |
| | Crude Oil | Crude Oil | | | |
| | | | oil-water emulsions | x | |
| | | | sludges | x | |
| | | | tank bottoms | | x |
| | | | vapor emissions | x | |
| Desalter | | | | | |
| | Crude Oil W/ brine | Crude Oil | | | |
| | | | brine | x | |
| | | | chemical additives | | |
| Crude Distillation | | | | | |
| | Crude Oil | Gases | | | |
| | Fuel Gas | Light Naphtha | | | |
| | Steam | Heavy Naphtha | | | |
| | Fuel Oil | Kerosene | | | |
| | | Gas Oil | | | |
| | | Lube Fractions | | | |
| | | Asphalt | | | |
| | | | burned fuel exhaust | x | |
| | | | water draw from separators | x | |

Nonroutine indicates generation at greater than annually intervals or in accidental mode

## TABLE VII (Continued)

| REFINERY SYSTEM | FEEDS | PRODUCTS | WASTES | ROUTINE | NONROUTINE |
|---|---|---|---|---|---|
| | | | water plus air plus non-condensables | x | |
| | | | heat exchange washings | | x |
| | | | pump drains and seals | | x |
| Deasphalting | | | | | |
| | Reduced Crude | Asphalt | | | |
| | Fuel Gas | Resins | | | |
| | | Deasphalted Oil | | | |
| | | Heavy Resid | | x | |
| | | | burned fuel exhaust | x | |
| | | | water wash disposal | x | |
| | | | gas comp exhaust | x | |
| | | | lube oil drain | x | |
| | | | pump drains and seals | | x |
| | | | spilled product | | x |
| | | | heat exchange washings | | x |

TABLE VII (Continued)

| REFINERY SYSTEM | FEEDS | PRODUCTS | WASTES | ROUTINE | NONROUTINE |
|---|---|---|---|---|---|
| Delayed Coker | | | | | |
| | Vacuum Residue | Coke | | | |
| | Water Storage | Fuel Gas | | | |
| | | C3-Naptha Fraction | | | |
| | | Gas Oils | | | |
| | | | coke fines | x | |
| | | | burned fuel exhaust | x | |
| | | | pump drains and seals | | x |
| | | | heat exchange washings | | x |
| FCCU unit | | | | | |
| | Gas Oils | Gasolene | | | |
| | | C5 plus | | | |
| | | C4 and lighter | | | |
| | | | catalyst fines | x | |
| | | | burned fuel exhaust | x | |
| | | | pump drains and seals | | x |
| | | | heat exchange washings | | x |

## TABLE VII (Continued)

| REFINERY SYSTEM | FEEDS | PRODUCTS | WASTES | ROUTINE | NONROUTINE |
|---|---|---|---|---|---|
| Catalyst Reforming | Light H-C Fraction | Platformate<br>Light Ends<br>Hydrogen | | | |
| | | | batch regeneration | x | |
| | | | burned fuel exhaust | x | |
| | | | pump drains and seals | | x |
| | | | heat exchange washings | | x |
| Catalytic Hydroreforming (Hydrodesulfurization) | Atmosphere Residue | Residue to Vacuum<br>375 F + distillate<br>Fuel Gas<br>Sour Gas | | | |
| | | | amine by-products | x | |
| | | | catalysts | x | |
| | | | replacement | x | |
| | | | burned fuel exhaust | x | |
| | | | pump drains and seals | | x |
| | | | heat exchange washings | | x |

## TABLE VII (Continued)

| REFINERY SYSTEM | FEEDS | PRODUCTS | WASTES | ROUTINE | NONROUTINE |
|---|---|---|---|---|---|
| Hydrogen Plant | Inlet Gas<br>Fuel Gas<br>Steam<br>Air | Light Condensate<br>H2S to Claus Unit | | | |
| | | | furnace exhaust | x | |
| | | | amine wastes | x | |
| | | | CO2 vent | x | |
| | | | pump drains and seals | | x |
| | | | heat exchange washings | | x |
| | | | regeneration waste | x | |
| Alkylation | iso-Butane<br>Butane<br>C5+ fraction | Alkylate | | | |
| | | | vent gases | x | |
| | | | relief valve | | x |
| | | | pump vents | | x |
| | | | acid sewers | | x |
| | | | storm sewers | | x |
| | | | acid regeneration bottoms | x | |
| | | | alumina treating solids | x | |
| | | | burned fuel exhaust | x | |
| | | | pump washings | | x |
| | | | heat exchange washings | | x |

## TABLE VII (Continued)

| REFINERY SYSTEM | FEEDS | PRODUCTS | WASTES | ROUTINE | NONROUTINE |
|---|---|---|---|---|---|
| TIP Unit | | | | | |
| | Pentanes<br>Hexanes | Isomate | | | |
| | | | regeneration gases | x | |
| | | | replacement mol sieve | x | |
| | | | replaced catalyst | | x |
| | | | burned fuel exhaust | x | |
| | | | pump washings | | x |
| | | | heat exchange washings | | x |
| | | | tower washings | | x |
| | | | fired heaters tube cleanings | | x |
| Aromatics BTX Complex | | | | | |
| | Naphtha | Benzene<br>Toluene<br>o-xylene<br>p-xylene | | | |
| | | | benzene waste | | x |
| | | | toluene waste | | x |
| | | | o-xylene waste | | x |
| | | | p-xylene waste | | x |
| | | | clay filter waste | | x |
| | | | burned fuel exhaust | x | |
| | | | pump washings | | x |
| | | | heat exchange washings | | x |

TABLE VII (Continued)

| REFINERY SYSTEM | FEEDS | PRODUCTS | WASTES | ROUTINE | NONROUTINE |
|---|---|---|---|---|---|
| Lube Unit | | | | | |
| | Lube Fraction | Lube Oil | | | |
| | | Aromatics | | | |
| | | | Phenol(carbolic acid) | x | |
| | | | gas vents | x | |
| | | | relief valves | | x |
| | | | pump vents/drains | x | |
| | | | acid sewers | x | |
| | | | storm sewers | | x |
| | | | burned fuel exhaust | x | |
| | | | pump washings | | x |
| | | | heat exchange washings | | x |
| MTBE Unit | | | | | |
| | iso-Butane | MTBE | | | |
| | Methanol | iso-Butane | | | |
| | | Butanes | | | |
| | | Butenes | | | |
| | | | MTBE waste | | x |
| | | | Meoh waste | | x |
| | | | drains | | x |
| | | | pump vents | | x |
| | | | relief valves | | x |

## TABLE VII (Continued)

| REFINERY SYSTEM | FEEDS | PRODUCTS | WASTES | ROUTINE | NONROUTINE |
|---|---|---|---|---|---|
| | | | storm sewers | | x |
| | | | pump washings | | x |
| | | | heat exchange washings | | x |
| | | | catalyst waste | x | |
| TAME Unit | | | | | |
| | iso-Pentane<br>Methanol | TAME<br>Pentanes | | | |
| | | | TAME waste | | x |
| | | | Meoh waste | | x |
| | | | drains | | x |
| | | | pump vents | | x |
| | | | relief valves | | x |
| | | | storm sewers | | x |
| | | | pump washings | | x |
| | | | heat exchange washings | | x |
| | | | catalyst waste | x | |

## TABLE VII (Continued)

| REFINERY SYSTEM | FEEDS | PRODUCTS | WASTES | ROUTINE | NONROUTINE |
|---|---|---|---|---|---|
| Claus/SCOT units | $H_2S$ | $SO_x$ | | | |
| | $H_2O$ | $S_x$ | | | |
| | | | amine by-products | x | |
| | | | $SO_x$ emissions | x | |
| | | | storm sewers | | x |
| | | | pump washings | | x |
| | | | heat exchange washings | | x |
| Cooling Water | Cold Water | Hot Water | | | |
| | | | cooling tower sludge | x | |
| | | | blowdown | x | |
| | | | heat exchange washings | | x |
| | | | tower wood replacement | | x |
| | | | mist/spray | x | |

## TABLE VII (Continued)

| REFINERY SYSTEM | FEEDS | PRODUCTS | WASTES | ROUTINE | NONROUTINE |
|---|---|---|---|---|---|
| Steam | Water/ condensate | Steam | blowdown | x | |
| | | | heat exchange washings | | x |
| | | | vents | x | |
| | | | deaerator | x | |
| Process Water | Steam Condensate | | water plus solutes | x | |
| VOC | | | VOC | x | |
| Rain/storm Sewers | | | water plus | | x |
| Process Area Sewers | | | water plus | | x |
| API Separator | | | sludge | x | |
| | | | oil | x | |
| | | | water | x | |

TABLE VII (Continued)

| REFINERY SYSTEM | FEEDS | PRODUCTS | WASTES | ROUTINE | NONROUTINE |
|---|---|---|---|---|---|
| Slop Oil/Water Separator | | | sludge | x | |
| | | | oil | x | |
| | | | water | x | |
| Air Flotation Systems | | | Float | x | |
| | | | oil/water | x | |
| Biological Treatment System | | | biosludge | x | |
| | | | water | x | |
| | | | scum off top | x | |
| Product Storage | | | sludge | | x |
| | | | water | | x |
| | | | oil | | x |

# CHAPTER V

# DEFINITION OF THE REFINERY CRUDE AND OTHER INLET COMPOSITIONS

All of the raw inlet streams to the refinery model were defined in terms of their compositions, temperature, pressure, and other physical values. The inlet streams were defined in order of the crude feedstock followed by the remaining streams in heaviest to lightest density order.

## Definition of a Crude Feedstock

Petroleum crude is a complex mixture of hydrocarbons plus organic compounds containing sulphur, oxygen, and nitrogen, and metallic compounds of vanadium, nickel, iron, and copper. There were estimates that over 700 different hydrocarbon compounds were included in crude oil (11). Therefore a precise component analysis was not used for this study but a more generic analysis was defined. This analysis was defined in a similar manner to the way the industry currently defines feedstock.

A modified Mississippian Era Petroleum was used with properties shown in Table VIII (10). This would be a very common feedstock for a Mid America located refinery.

## TABLE VIII
## CRUDE FEEDSTOCK PHYSICAL PROPERTIES

| | |
|---|---|
| Specific Gravity | 0.945 |
| API Gravity | 18.3 |
| Carbon Residue, wt/wt % | 12.43 |
| Sulphur, wt/wt % | 4.3 |
| Asphaltenes, wt/wt % | 15.5 |
| resins | 31.2 |
| oils | 4.3 |
| Aromatics wt % | |
| benzene | 0.07 |
| toluene | 0.58 |
| ethylbenzene | 0.22 |
| o-xylene | 0.30 |
| m-xylene | 0.64 |
| p-xylene | 0.17 |
| n-propylebenzene | 0.08 |
| isopropylbenzene | 0.17 |

TABLE VIII (Continued)

| | |
|---|---|
| tetrahydronaphthalene | 0.06 |
| naphthalene | 0.08 |
| Lube Fractions | |
| mono-naphthenes | 5.0 |
| di-naphthenes | 4.0 |
| tri-naphthenes | 1.0 |
| Inorganic Chlorides | |
| Oxygen Compounds | 5.0 |
| Nitrogen Compounds | 0.5 |
| Porphyrins complexes | 135 ppm |
| Metal Compounds, ppm | |
| Cu | 12 |
| Ca | 2.5 |
| Mg | 2.5 |
| Ba | 0.1 |
| Sr | 0.1 |
| Zn | 1.0 |
| Hg | 0.1 |
| Ce | 0.6 |
| B | 0.1 |
| Al | 1.0 |
| Ga | 0.1 |
| Ti | 0.4 |
| Zr | 0.4 |

TABLE VIII (Continued)

| | |
|---|---|
| Si | 0.5 |
| Sn | 0.3 |
| Pb | 1.0 |
| V | 1500 |
| Fe | 120 |
| Ni | 120 |

(Source 10)

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## Definition of Inlet Brine

The inlet brine was a simple brine suspension with inorganic water soluble chloride and sulfate salts of sodium, potassium, magnesium, and calcium present in percentages large enough to require a sulfonate emulsion breaker. The chemical was added to the crude before the desalter and to the fresh water (condensate) prior to mixing. The salt concentration of the inlet crude was 80 pounds per 1000 barrels of crude (0.228 mg/l).

## Definition of the Cooling Water System

The cooling water system consisted of a 30,000 gpm open recirculating system. The temperature drop through the cooling tower was twenty degrees F. The evaporation loss was assumed to be two percent of circulation or 600 gpm (12). Therefore make up water consisting of 600 gpm plus blowdown was treated and added to the system. Three treatment chemicals were added to the water: for pH control, for algae control, and a corrosion inhibitor. Windage loss from the cooling tower was assumed to be 0.3 % (12). The concentration of compounds in the circulation system is usually reported in terms of concentration cycles and refers to the number of times the compounds in the makeup water are concentrated in the blowdown water. The recommended value of concentration cycles for these systems is three (12). While the concentration cycle value was unitless, the actual compound readings were given in grains per gallon or parts per million. Maintaining the concentration cycles at three for the refinery model, the blowdown rate was one percent of the total system. Reduced for windage losses the blowdown was 0.7 % or 210 gpm. Therefore, total makeup was 810 gpm. The treatment for blowdown water was discussed in more detail as a generated waste later in this report.

## Definition of Steam System

The steam system consisted of a 250,000 pound per hour boiler system. The maximum level of solids in the recirculating water was 2000 ppm. The solids content of the makeup water was assumed to be 100 ppm after treatment by precipitation softening. Steam loss usage rate was set at twenty percent (12). The feed makeup rate was calculated at be 50,000 pounds per hour. Therefore to control solids, blowdown was set at 2,500 pounds per hour. This was based upon the makeup of 50,000 pounds per hour makeup rate, the 100 ppm makeup solids content and the requirement to hold a level of solids in the recirculating water of 2000 ppm (50,000 x 100 / 2000). The precipitation softening was with lime and soda ash at an elevated temperature. The softening process added a waste stream of $CaCO_3$ and $Mg(OH)_2$ sludge to be processed. The standard spray type deaerator used in conjunction with steam stripping stripped the water of $CO_2$ and dissolved oxygen. Internal boiler water treatment consisted of (1) oxygen scavenger, (2) scale control, and (3) pH control. The oxygen scavenger used was sodium sulfite. The resultant $Na_2SO_4$ increased the blowdown solids in the sludge. The scale control consisted of precipitating scale forming ions as calcium hydroxyapatite or serpentine. PH control consisted of adding soda ash ($Na_2CO_3$) to control pH to approximately 10-11.

## Definition of Condensate

Condensate raw products was added to the gas plant at a rate of 5000 bpd. The composition was shown in Table IX.

TABLE IX

RAW CONDENSATE FEEDSTOCK

| compound | mol. percent |
|---|---|
| ethane | 0.11 |
| propane | 52.00 |
| i-butane | 12.76 |
| n-butane | 17.49 |
| i-pentane | 5.65 |
| n-pentane | 10.19 |
| hexane plus | 1.80 |
| TOTAL | 100.00 |

## Definition of Natural Gas

Natural gas feedstock plus internally generated gas streams were processed in a industrial standard gas plant. The natural gas plant employed a turboexpander for medium cryogenic recovery and recovered 95% of the propane and 65% of the ethane from the inlet stream. The inlet natural gas feedstock composition was shown in Table X, which represents a typical East Texas gas. A raw product mix was produced and sent to the light fractionation tower system.

## Definition of Fuel Gas

The fuel gas composition was assumed constant and available as needed. The composition used was shown in Table XI, based upon heating value gas.

Table X

NATURAL GAS PLANT FEEDSTOCK

| component | mol. percent |
|---|---|
| nitrogen | 3.02 |
| carbon dioxide | 1.42 |
| hydrogen sulfide | 1.65 |

TABLE X (Continued)

| | |
|---|---|
| methane | 66.54 |
| ethane | 13.72 |
| propane | 7.21 |
| i-butane | 0.91 |
| n-butane | 2.63 |
| i-pentane | 2.65 |
| n-pentane | 0.95 |
| hexane plus | 1.25 |
| TOTAL | 100.00 |
| PRESSURE, PSIG | 325 |
| TEMPERATURE, F | 70 |
| FLOWRATE, MMSCFD | 90 |

## TABLE XI

## FUEL GAS COMPOSITIONS

| component | mol. percent |
|---|---|
| carbon dioxide | 0.03 |
| methane | 93.79 |
| ethane | 0.96 |
| TOTAL | 100.00 |

# CHAPTER VI

# FINAL DEFINITION AND CHARACTERIZATION OF WASTE STREAMS

The waste streams from the refinery can now be characterized by their hazardous listing, the frequency and amount generated, the physical phase they exist in, the current disposition, and the major constitutes contained within.

## Storage

The waste streams generated by crude storage included oil-water emulsions, oily sludges, maintenance scale material from the bottoms, and vapor losses through the seals of the floating roof. The composition of the liquid and solids wastes generated by storage was largely mixtures of water, hydrocarbon components, and dirt or silt. Benzene and metals may be present. Volumes present depended upon the amount of water delivered with the crude, mode of delivery, and the general condition of the storage vessels. The model refinery had a ratio of one fourth gallon of water per barrel inlet or 21,250 gallons of water and emulsion per day delivered through both a truck and pipeline delivery system. Vapor emissions from storage were a result of the light petroleum components vaporizing and escaping through the relief vent or around the floating roof seal. The tanks were at approximately atmospheric pressure with temperatures as high as 100 degrees F (ambient). The vapor pressure of hydrocarbons under these conditions indicated the major constituents of the releases were methane through butanes plus benzene. The amount of volume of emission was determined per the EPA's recommended vapor emission and included with VOC emissions (13).

## Desalter

The brine waste stream consisted of salts, water, and sulfonate additives to break emulsions. The mixture was not a listed waste and would not fail any characteristic test based on a comparison of 40 CFR Section 261, therefore it was not a EPA hazardous waste. The flowrate was determined from the amount of salt present. At eighty tons per 1000 barrels, the model refinery would have 6,800 pounds per day of salt. With a 20 percent by weight brine solution, the waste contained 34,000 pounds per day of water (approximately 4,100 gallons). This non-listed waste could not be readily used within the refinery. Currently, land application is extensively used for disposal.

## Crude Distillation

The burned fuel exhaust consisted of burned hydrocarbons and water vapor from a fifty mmbtu/hr fired heater. This exhaust was combined with the exhaust from all other fuel exhaust sources in the refinery and treated as if from only one fired source. These exhaust calculations from all sources are in Appendix B and are discussed later.

Crude unit water draw off would consist of oily contaminated water. This stream was small, approximately seven bph, and intermediate in flow. The water came from condensed steam plus additional water vapor carried in by the crude stream. This flow was segregated from rain or storm runoff or open drain water and collected for further treatment with similar streams. This stream was not considered to be EPA hazardous waste.

The vapor stream removed from the vacuum distillation tower consisted of water vapor, air, and trace quantities of hydrocarbons. This stream was removed to help maintain a vacuum pressure condition in the fractionator. The stream was not considered hazardous per EPA regulations.

Heat exchanger bundle cleanings were discussed as a group later. Pump pad, seal leaks, and pump washings in this unit went to the open drain system. An open drain system is defined as a pipe system that is open to the atmosphere at the entrance and or exit ends. Vapors generated from these openings were added to the VOC's totals. The liquid exited the open drain system and was sent to an oil-water separator.

## Deasphalting Unit

The unit sent wash water to the closed drain system. The closed drain system consisted of a piping system, without exposure to the atmosphere, to the oil-water separator. As there was no significant additional contamination at this point, the stream consisted of water with trace quantities of oil. The fired heater and gas compressor fuel exhaust were combined with others and discussed later.

The compressor lubrication oil was collected at low points in the system and disposed of in the closed drain. Some lubrication oil was mixed with the processing streams and left the process as olefin intermediate product.

The pump pad washings and seal leaks went to the open drain for further processing. The heat exchanger cleanings have been discussed later.

The asphalt product from this unit was in its final form with no further treatment needed. As such spills of the product were considered waste. Of course with this product spills, the usual method of disposal was to use the spill on a road or other surface as a covering. The material was non-hazardous and beneficial usage was obtained.

## Delayed Coker

Coke fines are composed of coke or solid carbon and are not hazardous. They were usually lost by wind action or rain action carrying the fines off-site. The amount created was dependent upon the process used to generate the coke and the physical equipment used to transport the coke to a staging or finishing area. The model refinery had 1150 tons of coke per year feed, of which two percent was usually resultant as fines (14).

The fuel exhaust and heat exchange wastes were discussed later. The pump associated wastes were sent to the open drain. These pump wastes were not hazardous.

## FCCU

Catalyst fines were separated from the regeneration exhaust gases and disposed of. These fines consisted of spent replacement catalyst, contaminated catalyst, and catalyst dust. The amount of catalyst disposed was approximately 130 thousand tons per year (15). The usual disposal method was by land disposal.

The exhaust gas from the FCCU section was slightly different from the burned fuel exhausts previously generated by other units. This exhaust was created by burning coking hydrocarbons off the catalyst. The mixture was a much heavier "fuel" than the normal fuel gas used in fired heaters or compressors. The gas contained greater amounts of CO than other exhaust streams.

The pump associated wastes were sent to the open drain system. These wastes were neither hazardous or large in volumes.

## Catalyst Reforming Unit

The routine batch regeneration of the two reactors created a gaseous exhaust and a spent chloride solution. The gaseous exhaust was similar to exhaust created by the coker unit. The spent chloride solution was sent to the closed drain system. The amount was determined by the volume of the vessels, in this case approximately 4,000 gallons per year.

The associated pump wastes was sent to the open drain for further treatment . The remaining wastes were consolidated and discussed later.

## Hydrodesulfurization Unit

The type of amine unit wastes that were generated were determined by the type of amine employed. MEA resulted in the following wastes; spent reclaimer bottoms, spent water wash, and disposable sock type filter elements. The reclaimer bottoms consisted of MEA, water, thiosulfate, and small traces of caustic soda, formic acid, and acetic acid (12). This mixture was non-hazardous. The flowrate was usually very small, approximately eight barrels per day. Usual disposal was to the open drain. The water wash used was to remove carbonyl sulfide, hydrogen cyanide, and carbon disulfide. Therefore these compounds appeared in the spent wash water. The flowrate was approximately 2,000 pounds per hour, which flowed to the closed drain system. The filter elements removed suspended solids, such as iron sulfide, iron oxide, sand, pipeline dust, mill scale, and trace quantities of magnesium, calcium, and silicate carbonates or sulfates. Particles above 1.5 microns were removed. Changeout of filter elements resulted in approximately one thousand of the filter elements annually. The current disposal method was to a landfill. The elements were hazardous per EPA CFR 40 based on actual laboratory tests (16).

The cobalt-molybdenum metal catalysts contaminated with metal sulfides were replaced with new catalyst material. The spent catalysts were hazardous. The volume was based upon the size of the reactors or approximately 250 barrels per reactor. The changeout occurred as activity tests indicated degradation in the catalyst. In the study refinery model, API studies were used to estimate the amount at 660 tons per year (14).

The pump associated wastes were routed to the open drains. All other wastes were consolidated and discussed later.

## Hydrogen Plant

The "normal" furnace exhaust was similar to ordinary fired heaters. The exhaust during regeneration periods was similar to burned coke exhaust. The normal exhaust was discussed below with the other fired heaters. The regeneration exhaust was heavier with more CO and combined with the coke exhaust discussion.

There were two amine units within the hydrogen plant, each generated approximately the same quantity and composition of wastes as the amine unit in the catalytic hydroreforming unit. The second amine unit generated a vent stream to the atmosphere, it consisted of carbon dioxide and water vapor. The stream had a flowrate of approximately four hundred pounds per hour. The stream was continuous. The pump associated wastes were sent to the open drain system. Other wastes were discussed as a group later.

## Alkylation Unit

The alkylation unit had several unique wastes due to the HF employed in the process. The acid vent gases and relief valves gases were contacted with KOH before the gases were released to the refinery flare system. The KOH was regenerated in a batch process by using lime. The lime generated $CaF_2$ and KOH. The sediment was directed to a neutralizing basin. The neutralizing basin also collected pump vent and acid sewer fluids. These fluids were treated by converting the fluoride into $CaF_2$. Then the treated liquids were released into the normal refinery sewer system. The neutralizing basins had odoriferous gases which are trapped in carbon filters. The carbon filters must be disposed of as a waste. The treated gas was then released to the atmosphere. The last liquid waste was the liquid hydrocarbon acid process wastes rejected by the acid regeneration column. Two types of wastes were generated, an acid-water phase and a polymer mixture formed by side reactions. The two wastes were separated by settling. The acid water phase was sent to the neutralizing basin for treatment. The polymer mixture was washed to remove the HF and then incinerated. As these wastes were handled internally, no additional discussion was needed.

Solid wastes were also generated by the alkylation process. The $CaF_2$ and unreacted lime were generated in the neutralizing basin. This material was removed on a batch basis from the basin. As the sludge was inert, it had been sent to a landfill. When LPG products are produced by the unit, the products must be defluorinated before usage. This was done over an activated alumina. This alumina was "used up" and was usually continuously replaced with new. The spent alumina was inert and has been successfully landfilled.

## TIP Unit

The TIP unit regeneration created a waste similar to other coke regeneration wastes. The coke burn exhaust was released to the atmosphere and was included in the other heavy burns. Exhausted mol sieve was removed and replaced on an as needed basis. Typical runs of five years were common. The amount of sieve material was approximately 10,000 pounds per event. Currently, this material was stored, Typical wastes associated with pumps and exchangers was sent to the open drain.

## BTX Complex

Hazardous waste material created during this process included clay filter media. This material must be disposed of considering land bans. At this time, most firms are ultimately incinerating such waste. Product spills also generated hazardous waste. These wastes were also incinerated. Relatively small quantities of hazardous material were generated by this complex.

## Lube Unit

A neutralizing process was used with the carbolic acid unit and other streams before releasing them to the normal refinery drains/vents. The amount of spent acid generated was 6,000 tons/year (15). These acids were treated, neutralized, and then disposed of by land farm.

## MTBE/TAME Unit

Wastes from these units cannot be sent to the refinery open drain or to the refinery biological treatment units due to the methanol contamination. All streams were sent to the methanol still for separation into methanol and water streams. The water was distilled into disulfides and other by-products which were usually lost with the oxygenate product. The only waste sent off site was four pounds per hour of waste water with trace quantities of methanol per unit (16). The percent methanol used in the feedstock to the unit was by law defined as hazardous (17).

## Claus/SCOT Unit

The Claus unit would have pure liquid sulphur as a product. Spilled product, plus other pump leaks, catalyst waste, and flange/piping spills were all recycled back into the liquid storage tank thereby creating no waste. The SCOT unit would have the same amine wastes as described with other amine units previously noted and at similar flowrates.

## Cooling Water and Steam Systems

The blowdown from the cooling system had been previously calculated as 210 gpm. The additives included in the water were also defined as trisodium phosphate, chlorine(in amounts of approximately 1 ppm free), and buffered chromate (present at 600 ppm). Normally this stream would be discharged under a NPDES permit. However as the more stringent regulations were implemented, the stream required pretreatment due to chromium (limit 5 mg/l) (18). Therefore additional options for processing this stream prior to discharge were explored.

The cooling tower collected silt and dust in the basin during normal operations. Each year the basin was cleaned, producing approximately twelve tons per year of sludge.

Steam systems have blowdown to be disposed of. Steam systems also have internal treatment processes that generated impurities in the blowdown (12). Internal treatment systems consisted of conditioning agents and chemicals added to the boiler water to scavenge oxygen, control scale, condition sludge, control pH and foaming, and mitigate corrosion. External systems were not be included. In general the blowdown contained the same residual level as the steam system. The amount of blowdown was determined by the amount of solids added per day. A typical amount of solids was 1000 pounds per day based upon 10,000,000 pounds per day of feedwater to the model refinery system (12). Therefore the levels in the boilers were at 1000 ppmw and the amount of blowdown was 1,000,000 pounds per day or 1000 pounds of solids.

This stream of blowdown included: (1) sodium sulfite residual of 10 ppmw used as an oxygen scavenger; (2) 10 ppmw of sodium sulfate present as a result of oxygen removal; (3) soda ash($Na_2CO_3$) residual of 10 ppmw, used to generate sludge to control scale; (4) starch residue of 1 ppm, used to condition the sludge; (5) and ammonia residue of 5 ppm used to mitigate corrosion (19). This stream was sent to the water system for further treatment.

## Process Water and Process Area Sewers

These streams were waters which have come into contact with hydrocarbon liquids. These were sent to the oil water separator for disposal. The volume of liquid handled by the oil water separator was estimated at 22,000 tons per year. This was based upon API Studies of similar refineries (14). The major constituents were water and hydrocarbon (oils). Based on EPA studies (18), approximately 97 % of this steam should be water and the rest oil.

## Rain/Storm Water Sewers

This water discharge has not been regulated. This will change as of October 1992, when a permit will be required (20).

The runoff stream will pick up petroleum fractions, soils, and other water soluble chemicals. An analysis of these pollutants will have to be made and a pretreatment system may be needed depending upon the types and amount of pollutants carried by the rainwater. In the refinery model, this processing would take place in the water system. The amount of water handled was a function of location. The model refinery treated 724,838 tons per year. This was based upon 40 inches of rain per year on a one fourth square mile site (Appendix C).

## Water Treatment System

The water treatment system (or wastewater treatment system) received wastewaters from throughout the refinery and processed these wastewaters to meet pertaining environmental regulations before the waters were discharged offsite. Treatment required removal of oils, suspended solids, reduction of biochemical and chemical oxygen demand, and removal of toxic contaminants. A standard water processing system (19), along with the input waste streams generated by the model refinery was shown in Figure 20. The treatment system was divided into foul, or oily, process streams and relatively oil free streams. The oil-free streams were separated in the absence of

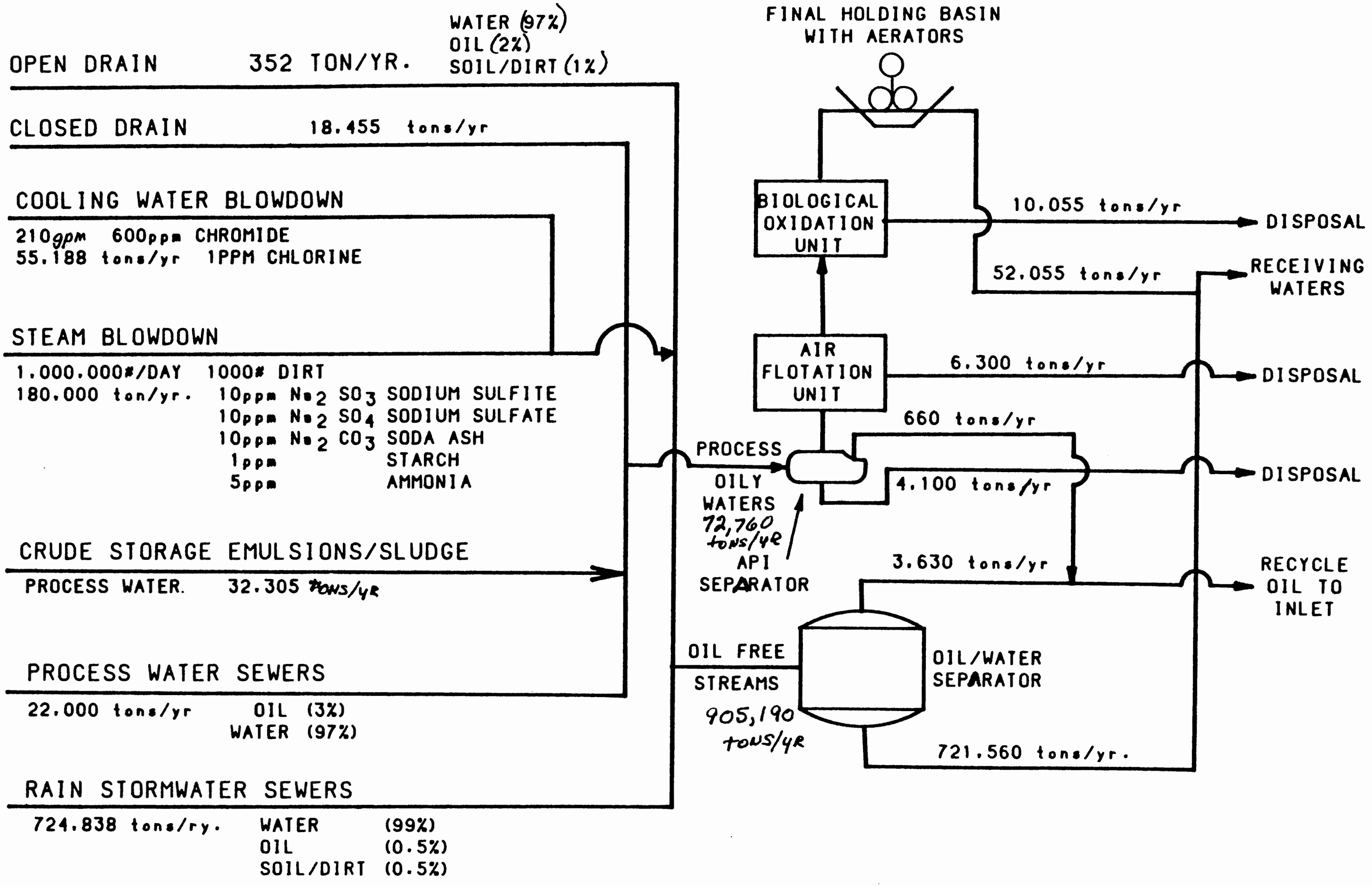


Figure 20 Water Treatment System

contamination by emulsion chemicals into oil and water streams. The oil stream was recycled into the inlet crude processing unit. This amount was estimated by material balance at 3,630 tons per year. The waters were sent to receiving waters offsite. The fouled waters were treated in a series of units (19). The first unit was an API separator. This is a corrugated plate interceptor where oil can be skimmed from water. Solid waste was settled out at a rate of 4,100 tons per year. This was a listed hazardous waste which must be disposed of per RCRA regulations, currently stabilized and stored. The separated oil was recycled back to the inlet processing units. The remaining wastewater was conditioned with pH and flocculates before being sent to the air flotation unit. This unit depended on the use of very fine air bubbles to increase the rate of rise of the larger agglomerations caused by the coagulants so they could be floated to the surface and removed. The surface material removed was a listed hazardous waste and must be disposed of per RCRA regulations, currently stabilization and storage. The remaining waste water was then treated in a biological treatment unit. This unit was designed to allow for the biodegradation of certain hydrocarbons (Table XII). The process usually occurred in two stages, first carbonaceous and second nitrogenous. The sludge from this process was usually land farmed after testing to ensure an acceptable heavy metal content. The final treatment unit before discharge was an aeration basin to improve odor, and to reduce oxygen demand and oil content. This unit acted as a polishing unit. It also served to help lower effluent toxicity. The basin served as an emergency water source for fire fighting. The water, after treatment, was then discharged to receiving waters.

TABLE XII

REFINERY WASTEWATER CHARACTERISTICS

OF TYPICAL HYDROCARBON INFLUENTS

| | MG/L |
|---|---|
| BOD | 100-450 |
| COD | 150-1750 |
| SUSPENDED SOLIDS | 20-400 |
| PH | 6.5-9.5 |
| PHENOLS | 5-100 |
| SULFIDES | 1-40 |
| OIL | 20-150 |
| AMMONIA | 10-200 |
| PHOSPHATE | 20-100 |
| TEMP. F | 50-140 |
| CHLORIDES | 200-1000 |
| TOTAL HEAVY METALS | 0.2-1. |

## Product Storage Systems (leaded)

Products were stored in metal tanks prior to blending or distribution to customers. Most storage tank waste was similar to that of crude storage. The one exception were tanks which contained petroleum products that had been amended with lead additives. These additives were phased out and the amount of this type of waste was significantly reduced. However, the bottoms from these existing tanks were listed as hazardous and for the average refinery consisted of 240 tons per year (14). VOC emissions from these storage units were included with other VOC emissions discussed below.

## Heat Exchanger Bundle Cleaning Solutions

These wastes were hazardous by listing. They consisted of the cleaning solutions and dissolved or removed scale from the cleaning of heat exchanger bundles. The average refinery generated eighty tons per year (18). Currently this solution was dewatered and the residue stabilized for storage.

## VOC Emissions

VOC emissions were generated by the refinery literally all over. The prime points of emission included crude oil floating roof storage, product storage, open drain systems, refinery piping, open wastewater treatment systems, and associated vessels. VOC's were estimated by EPA to be 170,000 pounds per year (21) and were displayed by group in Table XIII.

TABLE XIII

VOC CONTRIBUTIONS BY GROUP

| Unit | Uncontrolled Emissions (mmg/year) |
|---|---|
| Group A Units | |
| Crude Distillation, FCCU | 30.8 |
| Group B | |
| Treating Processes, Lube Oil Processes, Alkylation, Catalytic Polymerization, Isomerization, Thermal Cracking /Coking, Solvent Extraction, Hydrocracking | 14.6 |

TABLE XIII (Continued)

| | |
|---|---|
| Group C | |
| Hydrotreating, Hydrorefining, Light Ends/LPG, Catalytic Reforming, Vacuum Distillation, Hydrogen Manufacturer | 9.3 |
| Group D | |
| Oil- Water Separator, Storage Tanks | 11.0 |
| Group E | |
| DAF | 12.0 |

## Fuel Exhaust

Burned exhaust gases cane from three basic sources: fired heaters/boilers, compressors, and regeneration burns. Additional emissions were generated by the SCOT units. The fired heaters or boilers totaled approximately 644 mmbtu per hour heat duty for the refinery model. This resulted in 11.033 mcfh of exhaust (Appendix B). The components of that exhaust were shown in Table XIV. Emission data for compressor prime drivers was quite extensive due to permitting requirements. A standard separative unit was used in the model. Emissions totaled 254,460 tons per year (Appendix B). The regeneration burns consisted of

# TABLE XIV

## EMISSIONS PER COMPOUND
## FOR TOTAL FIRED HEATER EXHAUST

| | #/HOUR | TONS/YEAR |
|---|---|---|
| Nitrogen | 287170 | NC |
| Oxygen | 15178 | NC |
| Carbon Dioxide | 104373 | NC |
| Carbon Monoxide | 414 | 22317 |
| Nitrous Oxides | 13814 | 1256 |
| Water | 94469 | 229387 |
| Hydrocarbon | 0 | 1500 |
| TOTAL | 515418 | 254460 |

NC (Not Calculated)

controlled burning of coked materials from catalyst or tube surfaces. A series of burn measurements conducted by the author in conjunction with contracts for process development were used to simulate all burns (22). The total amount of burn was 8,832 hours per year for all pieces of equipment. This resulted in 137,904 tons per year of NOx. The SCOT units generated additional waste emissions including sulphur compounds. These emissions totaled 705.7 tons per year of SOx.

A summary of the detailed descriptions of this chapter has been compiled in Table XV below. This summary of the model refinery waste streams included each of the process unit wastes identified in the model. Hazardous listings were defined by 40 CFR Section 261.

## TABLE XV

## SUMMARY OF THE DETAILED DESCRIPTIONS OF THE REFINERY'S WASTE STREAMS

| WASTE | HAZARDOUS LISTING | FLOWRATE | PHASE | MAJOR CONSTITUENTS | OCCURENCES PER YEAR | CURRENT DISPOSAL |
|---|---|---|---|---|---|---|
| CRUDE STORAGE OIL-WATER EMULSIONS | NONE | 21250 GPD<br>32305 T/YR | LIQ. | OIL<br>WATER<br>DIRT<br>SCALE | BATCHED AS NEEDED | API SEPARATOR |
| CRUDE STORAGE EMULSION SLUDGE | NONE | 10 % OF TOTAL EMULSIONS | LIQ. | OIL<br>WATER<br>DIRT | BATCHED AS NEEDED | API SEPARATOR |
| CRUDE STORAGE TANK BOTTOMS | NONE | 1 % OF TOTAL EMULSIONS | LIQ. | OIL<br>WATER<br>DIRT<br>METALS | BATCHED AS NEEDED | API SEPARATOR |
| CRUDE STORAGE VAPOR EMISSIONS | AIR EMISSION | INCLUDED IN VOC | GAS | C1 +<br>BENZENE | CONTINUOUS | TO ATMOSPHERE |
| BRINE WITH ADDITIVES | NONE | 4,100 GPD | LIQ. | WATER<br>NaCL<br>SULFONATE<br>ADDITIVES | CONTINUOUS | LAND FARM |

TABLE XV (Continued)

| WASTE | HAZARDOUS LISTING | FLOWRATE | PHASE | MAJOR CONSTITUENTS | OCCURENCES PER YEAR | CURRENT DISPOSAL |
|---|---|---|---|---|---|---|
| DEASPHALTER WATER WASH | NONE | 1250#/HR | LIQ. | OILY WATER | CONTINUOUS | CLOSED DRAIN |
| DEASPHALTER LUBE OIL | NONE | 1 BARREL/ MONTH | LIQ. | LUBE FRACTIONS | CONTINUOUS | CLOSED DRAIN |
| ASPHALTS SPILLS | NONE | ESTIMATED SMALL | SOLID | ASPHALT | INFREQUENT | USED AS ROAD MATERIAL |
| COKE FINES | NONE | 23 T/YR | SOLID | CARBON | CONTINUOUS | ATMOSPHERE OR TO SOIL |
| FCCU CATALYST FINES | NONE | 130,000 T/YR | SOLID | NICKLE & RARE METALS | CONTINUOUS | LAND DISPOSAL |
| CATALYST UNITS AMINE RECLAIMER LIQUIDS | NONE | 4 B/D | LIQ. | WATER<br>MEA BY-PRODUCTS | CONTINUOUS | OPEN DRAIN |
| AMINE WATER WASH | NONE | 1,000#/HR | LIQ. | WATER | CONTINUOUS | CLOSED DRAIN |
| AMINE FILTER ELEMENTS | HAZ. | 500 PER YEAR | SOLID | SCREEN<br>IRON SULFIDE<br>IRON OXIDE | | |

TABLE XV (Continued)

| WASTE | HAZARDOUS LISTING | FLOWRATE | PHASE | MAJOR CONSTITUENTS | OCCURENCES PER YEAR | CURRENT DISPOSAL |
|---|---|---|---|---|---|---|
| | | | | SAND<br>SCALE<br>DUST<br>MAGNESIUM CARBONATE/SULFATES<br>CALCIUM CARBONATE/SULFATES<br>SILICATE CARTONATE/SULFATES | FOUR TIMES PER YEAR | LANDFILL |
| HYDRODESULFURIZATION SPENT CATAYST | HAZ. | 660 T/YR | SOLID | COBALT-MOLYBDENUM METAL SULFIDES | ONE BATCH PER 15 MONTHS | LANDFILL |
| HYDRODESULFURIZATION UNIT AMINE RECLAIMER LIQUIDS | NONE | 8 B/D | LIQ. | WATER<br>MEA | CONTINUOUS | OPEN DRAIN |
| AMINE WATER WASH | NONE | 2,000#/HR | LIQ. | WATER | CONTINUOUS | CLOSED DRAIN |
| AMINE FILTER ELEMENTS | HAZ. | 1000 PER YEAR | SOLID | SCREEN<br>IRON SULFIDE<br>IRON OXIDE | | |
| | | | | SAND<br>SCALE<br>DUST<br>MAGNESIUM CARBONATE/SULFATES<br>CALCIUM CARBONATE/SULFATES<br>SILICATE CARTONATE/SULFATES | FOUR TIMES PER YEAR | LANDFILL |

TABLE XV (Continued)

| WASTE | HAZARDOUS LISTING | FLOWRATE | PHASE | MAJOR CONSTITUENTS | OCCURENCES PER YEAR | CURRENT DISPOSAL |
|---|---|---|---|---|---|---|
| AMINE CO2 VENT | NONE | 400 #/HR | GAS | CO2<br>WATER | CONTINUOUS | ATMOSPHERE |
| HF CARBON FILTERS | NONE | 100 PER YEAR | SOLID | ACTIVATED CARBON | FOUR CHANGES PER YEAR | LANDFARM |
| HF CaF2/ LIME SLUDGE | NONE | 170#/HR | SOLID | CaF2<br>LIME<br>WATER | 12 BATCHES PER YEAR | LANDFILL |
| HF SPENT ALUMINA MATERIAL | NONE | 15#/HR | SOLID | ALUMINA | CONTINUOUS | LANDFILL |
| MOL SIEVE | NONE | 10000 #/BATCH | SOLID | MOL SIEVE | BATCH EVERY FIVE YEARS | LANDFILL |
| BTX FILTER CLAYS | HAZ. | 1000 PER OCCURANCE | SOLID | CLAY<br>BTX | ONCE PER QUARTER | INCINERATION |
| BTX SPILLS | HAZ. | 10 CU. YDS. PER SPILL | SOLID | BTX<br>SOIL | ESTIMATED ONCE PER YEAR | TREATMENT<br>LANDFILL |
| SPENT ACIDS | HAZ. | 6000 | LIQ. | CARBOLIC ACID | CONTINUOUS | TREATMENT |

TABLE XV (Continued)

| WASTE | HAZARDOUS LISTING | FLOWRATE | PHASE | MAJOR CONSTITUENTS | OCCURENCES PER YEAR | CURRENT DISPOSAL |
|---|---|---|---|---|---|---|
| | | TONS/YR | | ACIDS | | LANDFARMING |
| BTX UNIT | | | | | | |
| AMINE RECLAIMER LIQUIDS | NONE | 4 B/D | LIQ. | WATER<br>MEA | CONTINUOUS | OPEN DRAIN |
| AMINE WATER WASH | NONE | 1,000#/HR | LIQ. | WATER | CONTINUOUS | CLOSED DRAIN |
| AMINE FILTER ELEMENTS | HAZ. | 500 PER YEAR | SOLID | SCREEN<br>IRON SULFIDE<br>IRON OXIDE<br>SAND<br>SCALE<br>DUST<br>MAGNESIUM CARBONATE/SULFATES<br>CALCIUM CARBONATE/SULFATES<br>SILICATE CARTONATE/SULFATES | FOUR TIMES PER YEAR | LANDFILL |
| PROCESS WATER/ PROCESS AREA SEWERS | NONE | 2100 TONS/YR | LIQ. | OIL<br>WATER<br>DIRT<br>PHENOLS | CONTINUOUS | OIL\WATER SEPARATOR |
| COOLING WATER | | | | | | |

## TABLE XV (Continued)

| WASTE | HAZARDOUS LISTING | FLOWRATE | PHASE | MAJOR CONSTITUENTS | OCCURENCES PER YEAR | CURRENT DISPOSAL |
|---|---|---|---|---|---|---|
| BLOWDOWN | NONE | 210 GPM | LIQ. | CHROMATE<br>CHLORIDE<br>WATER | CONTINUOUS | WATER SYSTEM |
| COOLING WATER SLUDGE | NONE | 12 T/YR | LIQ. | WATER<br>SILT | CONTINUOUS GENERATION WITH BATCH REMOVAL | LANDFILL |
| TREATED WASTE WATER DISCHARGE | NONE | 721560 T/YR | LIQ. | WATER | CONTINUOUS | WATERS OF THE U.S. |
| HEAT EXCHANGER BUNDLES | HAZ. | 80 T/YR | LIQ. | DIRT<br>SCALE<br>WATER | AS NEEDED | OFF-SITE DISPOSAL |
| CRUDE UNIT PROCESS DRAW OFF | NONE | 7 B/HR | LIQ. | OIL<br>WATER | INTERMITTENT | WATER SYSTEM |
| DESALTER WATER WASH | NONE | 1 B/MONTH | LIQ. | OIL<br>WATER | CONTINUOUS | OIL-WATER SEPARATOR |
| HYDROGEN UNIT AMINE WATER WASH | NONE | 1,000#/HR | LIQ. | WATER | CONTINUOUS | CLOSED DRAIN |
| AMINE FILTER | | | | | | |

## TABLE XV (Continued)

| WASTE | HAZARDOUS LISTING | FLOWRATE | PHASE | MAJOR CONSTITUENTS | OCCURENCES PER YEAR | CURRENT DISPOSAL |
|---|---|---|---|---|---|---|
| ELEMENTS | HAZ. | 500 PER YEAR | SOLID | SCREEN<br>IRON SULFIDE<br>IRON OXIDE<br>SAND<br>SCALE<br>DUST<br>MAGNESIUM CARBONATE/SULFATES<br>CALCIUM CARBONATE/SULFATES<br>SILICATE CARTONATE/SULFATES | FOUR TIMES PER YEAR | LANDFILL |
| ALKYLATION UNIT NEUTRALIZED WATER | NONE | 200 #/HR | LIQ. | WATER<br>SALTS | BATCH | WATER SYSTEM |
| REFORMING UNIT CHLORIDE SOLUTION | NONE | 4000 GALLONS/YR | LIQ. | CHLORIDE<br>WATER | BATCH ONCE PER YEAR | WATER SYSTEM |
| MTBE/TAME | NONE | 8 #/YR | LIQ. | MeOH<br>WATER | CONTINUOUS | ON SITE TREATMENT |
| CRUDE UNIT PUMPS | NONE | EST 50 B/YR | LIQ. | WATER<br>OIL | ESTIMATED AT 12 PER YEAR | WATER SYSTEM |
| DEASPHALTER UNIT PUMPS | NONE | EST 50 B/YR | LIQ. | WATER<br>OIL | ESTIMATED AT 12 PER YEAR | WATER SYSTEM |
| COKER PUMPS | NONE | EST 50 B/YR | LIQ. | WATER<br>OIL | ESTIMATED AT 12 PER YEAR | WATER SYSTEM |

## TABLE XV (Continued)

| WASTE | HAZARDOUS LISTING | FLOWRATE | PHASE | MAJOR CONSTITUENTS | OCCURENCES PER YEAR | CURRENT DISPOSAL |
|---|---|---|---|---|---|---|
| FCCU PUMPS | NONE | EST 50 B/YR | LIQ. | WATER<br>OIL | ESTIMATED AT 12 PER YEAR | WATER SYSTEM |
| CATALYST REFORMER PUMPS | NONE | EST 50 B/YR | LIQ. | WATER<br>OIL | ESTIMATED AT 12 PER YEAR | WATER SYSTEM |
| AMINE RECLAIMER PUMPS | NONE | EST 50 B/YR | LIQ. | WATER<br>OIL<br>THIRSULFATE<br>SODIUM SALT<br>CAUSTIC SODA<br>FORMIC ACID<br>ACETIC ACID | ESTIMATED AT 12 PER YEAR | WATER SYSTEM |
| AMINE RECLAIMER LIQUIDS | NONE | EST 50 B/YR | LIQ. | WATER<br>OIL | ESTIMATED AT 12 PER YEAR | WATER SYSTEM |
| HYDRODESULFURIZATION PUMPS | NONE | EST 50 B/YR | LIQ. | WATER<br>OIL | ESTIMATED AT 12 PER YEAR | WATER SYSTEM |
| HYDROGEN PUMPS | NONE | EST 50 B/YR | LIQ. | WATER<br>OIL | ESTIMATED AT 12 PER YEAR | WATER SYSTEM |
| HYDROGEN AMINE RECLAIMER LIQUIDS | NONE | EST 50 B/YR | LIQ. | WATER<br>OIL<br>THIRSULFATE<br>SODIUM SALT | ESTIMATED AT 12 PER YEAR | WATER SYSTEM |

TABLE XV (Continued)

| WASTE | HAZARDOUS LISTING | FLOWRATE | PHASE | MAJOR CONSTITUENTS | OCCURENCES PER YEAR | CURRENT DISPOSAL |
|---|---|---|---|---|---|---|
| | | | | CAUSTIC SODA<br>FORMIC ACID<br>ACETIC ACID | | |
| TIP UNIT PUMPS | NONE | EST 50 B/YR | LIQ. | WATER<br>OIL | ESTIMATED AT 12 PER YEAR | WATER SYSTEM |
| TIP UNIT CATALYST EXHAUST | HAS. | EST 2000 # ANNUALLY | SOLID | MOL SIEVE | ONCE PER 5 YEARS | STORAGE |
| BTX PUMPS | HAZ. | EST 50 B/YR | LIQ. | WATER<br>OIL | ESTIMATED AT 12 PER YEAR | WATER SYSTEM |
| PRODUCT STORAGE | HAZ. | 240 TONS/YR | LIQ. | LEAD ADDITIVES<br>WATER<br>OIL | ONCE PER YEAR | STORAGE |
| VOC EMISSIONS CRUDE STORAGE | NONE | TO BE DETERMINED | GAS | C1+<br>BENZENE | CONTINUOUS | ATMOSPHERE |
| OPEN DRAIN | NONE | TO BE DETERMINED | GAS | C1+<br>BENZENE | CONTINUOUS | ATMOSPHERE |
| REFINERY PIPING, VALVING, AND VESSELS | NONE | TO BE DETERMINED | GAS | C1+<br>BENZENE | CONTINUOUS | ATMOSPHERE |

TABLE XV (Continued)

| WASTE | HAZARDOUS LISTING | FLOWRATE | PHASE | MAJOR CONSTITUENTS | OCCURENCES PER YEAR | CURRENT DISPOSAL |
|---|---|---|---|---|---|---|
| BURNED FUEL EXHAUST SOURCES(DISPOSAL TO ATMOSPHERE) | | | | | | |
| CRUDE UNIT 50 MMBTU/HR | | | | | | |
| DEASPHALTER UNIT 35 MMBTU/HR | | | | | | |
| DEASPHALTER GAS COMPRESSOR 60 MMBTU/HR | | | | | | |
| DELAYED COKER 40 MMBTU/HR | | | | | | |
| CATALYST REFORMING 25 MMBTY/HR | | | | | | |
| HYDRODESULPHURIZATION 15 MMBTU/HR | | | | | | |
| HYDROGEN PLANT FURNACE 15 MMBTU/HR | | | | | | |
| FCCU UNIT EXHAUST | | | | | | |
| CATALYST REFORMER BATCH REGENERATION | | | | | | |
| REFINERY FLARE SYSTEM | | | | | | |
| ALKEYLATION POLYMER BURN REGENERATION | | | | | | |
| TIP UNIT REGENERATION | | | | | | |
| STEAM BOILER 40+ MMBTU/HR | | | | | | |

Table XV presented over seventy streams which had been identified as outputs from the model refinery. These streams included air, water, and solid waste streams. Quantities were estimated for each stream. The number of times a waste stream was generated annually was also developed. Current disposal practices were also defined. This listing can now be used to determine overall waste requirements for the model refinery.

## CHAPTER VII

# IDENTIFICATION AND ECONOMIC EVALUATION OF MINIMIZATION OPTIONS FOR EACH WASTE STREAM

The waste streams generated by the refinery and identified in Table XV were combined and summarized. Waste options were investigated for these collected waste streams. There were twenty streams identified (Table XVI). As explained above, these streams were the collected result of the previously defined refinery wastes(Table XV). For example, Brine Solution(Table XVI) had a volume of 6,734 t/yr. This was a result of Table XV item "BRINE WITH ADDITIVES" with a flowrate of 4,100 gpd. This 4,100 gpd of a nine pound per gallon solution for 365 days was 6,734 tons per year. A second example of this development of these streams was the second entry "Coke Fines" (Table XVI) and "COKE FINES" (Table XV). The value, 23 t/yr, was the same. A final example was the third item of "Amine Filter Elements" (Table XVI) of 2,500 elements per year. This value was derived from Table XV "AMINE FILTER ELEMENTS" (page 112) of 500 /yr from the FCCU unit, "AMINE FILTER ELEMENTS" (page 113) of 1000/yr from the

Hydrodesulfurization unit, "AMINE FILTER ELEMENTS (page 115) of 500/yr from the BTX unit, and "AMINE FILTER ELEMENTS (page 115) of 500/yr from the Hydrogen unit. Each of these streams was evaluated in regards to the waste management options which were introduced in Chapter I. They were, in order of preference:

(1) Source Reduction
(2) Recycling
(3) Incineration and or treating

These areas were uniquely evaluated as they applied to the generated wastes of the model refinery. Because of the extractive nature of the refineries, the fixed nature of the raw feedstocks, the specified nature of the products, the type of processes involved, and the maturity of the industry, much of the waste minimization concentrated on recycling , reuse, or modified treating.

TABLE XVI

REFINERY WASTE STREAMS SUMMARIZED

| No | Stream | RCRA Rating | Volume |
|---|---|---|---|
| 1 | Brine Solution | non-haz. | 6,734 t/yr |
| 2 | Coke Fines | non-haz. | 23 t/yr |
| 3 | Amine Filter Units | non-haz. | 2,500 Unit Elements/yr |

TABLE XVI (Continued)

| | | | |
|---|---|---|---|
| 4 | FCCU Cracker Fines | non-haz. | 1,300 t/yr |
| 5 | Spent Cobalt-Molybdenum Catalyst | haz. | 660 t/yr |
| 6 | HF Carbon Filters | non-haz. | 100 /yr |
| 7 | HF $CaF_2$/ Lime Solid | non-haz. | 744.6 t/yr |
| 8 | HF Spent Alumina | non-haz. | 65.7 t/yr |
| 9 | Mol Sieve | haz. | 1 t/yr |
| 10 | Filter Clays | haz. | 2 t/yr |
| 11 | BTX Spills | haz. | 0.5 t/yr |
| 12 | Spent Acids | haz. | 6,000 t/yr |
| 13 | Air Emission Exhausts(NOx, Sox, N, O,$CO_2$, CO, HC, $H_2O$) | | |
| | Fired Heater | | 2,257,531 t/yr |
| | Compressors | | 1,152,698 t/yr |
| | Regeneration Burns | | 137,904 t/yr |
| | VOC | | 85 t/yr |
| | SCOT Off-Gas | | 706 t/yr |
| | $CO_2$ Venting | | 1,752 t/yr |
| 14 | API Separator | haz. | 4,100 t/yr |
| 15 | Air Floc | haz. | 6,300 t/yr |
| 16 | Sludge (Bio) | non-haz. | 10,055 t/yr |
| 17 | Leaded Tank Bottoms | haz. | 240 t/yr |
| 18 | Heat Exchanger Bundle | haz. | 80 t/yr |
| 19 | Cooling Tower Sludge | haz. | 12 t/yr |
| 20 | Wastewater | non-haz. | 770,000 t/yr |

Minimization options were developed for the waste streams (Table XVII). The numerical values under each category were the results of API studies to determine the current waste management practices utilized by U.S. Refineries (14). Wastes without values indicated waste streams not identified by the API studies.

These options were developed from the following various petroleum refinery's efforts to date; related and unrelated technologies of other industries; and application of efforts developed in field usage. Hopefully this collection will serve as a generator of new and additional ideals, not as a final solution. A summary of the options, economics, and streams discussed was included in Table XVIII.

## ECONOMIC EVALUATIONS AND CALCULATIONS

The economic evaluations and calculations developed for usage with this document were presented to aid the reader in determining whether to pursue individual options for more details and greater information. The costs presented were to be used by individual refinery locations as specific economic values. Specific economic values require significant time and professional expertise, as well as individual location and economic inputs. These were beyond the scope of this work and cost required.

## TABLE XVII

## WASTE MINIMIZATION OPTIONS INCLUDING CURRENT REFINERY WASTE MINIMIZATION EFFORTS

| STREAM | SOURCE REDUCTION | RECYCLING | INCINERATION OR TREATMENT | SECURE LAND DISPOSAL |
|---|---|---|---|---|
| BRINE SOLUTION | IMPROVED BRINE DESALTING | SECONDARY RECOVERY | MINERAL BY-PRODUCT RECOVERY | - |
| COKE FINES | REDUCE GENERATION | CAPTURE AND SELL<br>79 % | INCINERATION | -<br>21 % |
| AMINE WASTES | CHANGE TREATING MEDIUM | RECYCLE FOR METAL ELEMENTS<br>40 % | -<br>56 % | -<br>4 % |
| FCCU CRACKER FINES | - | RECYCLE TO CEMENT | RECLAIM CATALYST | - |
| SPENT COBALT MOLYBDENIUM OR POLYMERIZATION CATALYST | - | A. RECYCLE TO CEMENT<br>B. SELL AS FERTILIZER<br>13 % | RECLAIM CATALYST<br>68 % | -<br>19 % |
| HF SPENT ALUMINA | - | SELL AS ALUMINA FEED | RECLAIM CATALYST | - |

TABLE XVII (Continued)

| STREAM | SOURCE REDUCTION | RECYCLING | INCINERATION OR TREATMENT | SECURE LAND DISPOSAL |
|---|---|---|---|---|
| MOL SIEVE | - | SELL AS ALUMINA FEED | RECLAIM CATALYST | - |
| HF CARBON FILTERS | - | RECYCLE FOR ENERGY AND ELEMENTS | - | - |
| HF CaF2 LIME SOLID | IMPROVE LIME QUALITY | A. SEND TO STEEL MANUF.<br>B. SEND TO HF MANUF. | SOLVENT AND METALS EXTRACTION | - |
| | | 76 % | 20 % | 4 % |
| FILTER CLAYS | - | THERMAL DESORPTION TO REMOVE AND STRIP IMPURITIES | | |
| CO2 VENT | PART OF AIR EMISSIONS OPTIONS | PART OF AIR EMISSIONS OPTIONS | PART OF AIR EMISSIONS OPTIONS | PART OF AIR EMISSIONS OPTIONS |
| BTX SPILLS | SPILL CONTAINMENT AND ELIMINATION | | | |
| | | 4 % | 84 % | 12% |
| SPENT ACIDS | | SELL AS PRODUCT | NEUTRALIZE | |

## TABLE XVII (Continued)

| STREAM | SOURCE REDUCTION | RECYCLING | INCINERATION OR TREATMENT | SECURE LAND DISPOSAL |
|---|---|---|---|---|
| AIR EMISSIONS | SOx TAIL GAS UNITS | - | A. SOX FLUID BED<br>B. NSCR NOX REMOVAL<br>C. SCR NOX REMOVAL | - |
| VOC | VALVE AND PIPING REDUCTIONS | - | BIOFILTRATION | - |
| API SEPARATOR | SEGREGATE<br>21 % | RECYCLE TO COKER FEEDSTOCK | A. SOLVENT EXTRACTION<br>B. HOT WATER EXTRACTION 56% | -<br>23% |
| AIR FLOC | | RECYCLE TO COKER FEEDSTOCK<br>14 % | A. SOLVENT EXTRACTION<br>B. HOT WATER EXTRACTION 77% | -<br>9 % |
| BIOSLUDGE | | RECYCLE TO COKER FEEDSTOCK<br>4 % | A. SOLVENT EXTRACTION<br>B. HOT WATER EXTRACTION 61% | -<br>35 % |
| WASTEWATER DISCHARGE | | RECYCLE WATER | | |

## TABLE XVII (Continued)

| STREAM | SOURCE REDUCTION | RECYCLING | INCINERATION OR TREATMENT | SECURE LAND DISPOSAL |
|---|---|---|---|---|
| COOLING TOWER SLUDGE | A. REDUCE WATER USAGE<br>B. IMPROVE RAW WATER<br>C. CHANGE INHIBITORS | RECYCLE TO COKER | A. SOLVENT EXTRACTION<br>B. HOT WATER EXTRACTION | - |
| HEAT EXCHANGER BUNDLE SLUDGE | A. REPLACE WATER<br>B. IMPROVE FOULING RESISTANCE | - | - | - |
| LEADED TANK BOTTOMS | A. INSTALLATION OF MIXERS<br>B. IN LINE BLENDERS<br>C. SCHEDULE RUNS | RECYCLE TO COKER | | |
| | | 2 % | 69 % | 29% |

# TABLE XVIII

# FINAL SUMMARY OF WASTE OPTIONS AND ESTIMATED ECONOMIC IMPACT

---

(1) Brine Wastes

- (a) Improved desalting
  - C(Capital Costs) - $40 K
  - O(Operational Costs) - $860 K
  - B(Benefits) - minimal impacts with poor quantifiable results
- (b) Recycling to a waterflood project
  - C(Capital Costs) - $50 K
  - O(Operational Costs) - $300 K
  - B(Benefits) - $70 K
- (c) Mineral by-product recovery
  - C - $16,000 K
  - O - $10 K
  - B - $30 K

(2) Coke Fines

- (a) Reduce generation and collect for product sale
  - C - $50 K
  - O - minimal
  - B - $20 K

TABLE XVIII (Continued)

(3) Amine Wastes

- (a) Change treating medium
  - C- $200 K
  - O - decreased
    - energy 30%, neg $690 K
  - B - $40 K
- (b) Recycle filter wastes
  - C - none
  - O - none
  - B - $8 K

(4) Catalysts:

FCCU Cracker Fines and HF Spent Alumina

- (a) Cement recycling
  - C - none
  - O - none
  - B - waste disposed of with no cost

Polymerization Catalyst

- (a) Cement manufacture
  - C - none
  - O - none
  - B - waste disposed of with no cost

TABLE XVIII (Continued)

(b) Fertilizer replacement

C - none

O - minimal

B - minor revenue

FCCU Cracker Fines, HF Alumina, Mol Sieve, Spent Cobalt Molybdenum, Polymerization Catalyst

(a) Reclaiming unit

C - $20,000 K

O - $600 K

B - $760 K

Mol Sieve

(a) Reuse

C - too individualized to determine

O - too individualized to determine

B - $1 K , if need exists

(5) HF Carbon Filters

(a) Recycle for scrap

C - none

O - none

B - $1 K

TABLE XVIII (Continued)

(6) HF Lime Sludge

- (a) Source Reductions due to high quality lime
  - C - none
  - O - 8 % increase, $2 K
  - B - $20 K
- (b) Recycle steel manufacturing or HF acid manufacturing
  - C - none
  - O - function of distance and location (one breakeven estimate is 650 miles)
  - B - $400 K

(7) Filter Clays

- (a) Thermal desorption & reuse
  - C - $250 K
  - O - $330 K
  - B - $150 K

(8) BTX Spills

- (a) Prevention and reuse
  - C - $2,200 K

TABLE XVIII (Continued)

O - $60 K
B - clean up $50 K
or avoidance $70 K

(9) Spent Acids

- (a) Product sale
  - C - none
  - O - minimal
  - B - revenue of $240 K
- (b) Neutralize and land dispose
  - C - $970 K
  - O - $100 K
  - B - minimal

(10) SOx Emissions

- (a) Source reduction with new technology improvements
  - C - $380 K
  - O - $50 K
  - B - $300 K
- (b) With new processes
  - C - $5,000 K
  - O - Improvement of $50 K
  - B - $1 K

TABLE XVIII (Continued)

(c) With fluid bed dry limestone

C - $500 K

O - $50 K

B - $20 K

(11) SOx and NOx Emissions Combined

(a) Plasma treatment

C - undeveloped

O - undeveloped

B - $1,500 K

(12) NOx Only

(a) NSCR(Nonselective Catalytic Reduction) technology

C - $755 K

O - $175 K

B - $1,400 K

(b) SCR(Selective Catalytic Reduction) technology

C - $1,500 K

O - $1,750 K

B - $950 K

TABLE XVIII (Continued)

(13) VOC

(a) Source reduction

Costs - too individualized to determine

(b) Bio Mass Filter

C - $251.3 K
O - $8.5 K
B - $2.0 K

(14) General Sludges Handling

(a) Segregate

Costs - too individualized to determine

(b) Coker recycling

C - $80 K
O - minimal
B - $190 K

(c) Solvent extraction

C - $750 K
O - $230 K
B - $230 K

TABLE XVIII (Continued)

(d) Hot water extraction

C - $490 K

O - $120 K

B - $270 K

(15) Cooling Tower Sludge Specifically

(a) Chromium reduction

C - minimal

O - minimal

B - 70 % reduction in chromium emissions

(b) Several individual options including:

Improve Quality of Inlet Water

Reduce Water Usage with Air Exchangers

Costs - Individual Refinery Estimates

(16) Waste Water

(a) Recycle

C - $3,000 K

O - $300 K

B - $684 K

TABLE XVIII (Continued)

(17) Heat Exchange Source Reduction

- (a) Use heat transfer fluids
  - C - $260 K
  - O - minimal
  - B - $30 K
- (b) Improve fouling resistance measures
  - Costs - too individualized to determine

(18) Tank Sludge

- Source reduction techniques
  - Costs - too individualized to determine

---

Because of the relative accuracy of the numbers, rounding of results to one significant number was reported for values below $100,000 and to two numbers above $100,000. Values below $1,000 and above $100 were reported as $1 K.

If location of the refinery was deemed to be more important to the costs than the actual valuation of the economic components, then no cost estimates were presented. In those cases, a determination by individual refineries was required. In retrospect, location of a specific location for the refinery model would have allowed many more economic evaluations to be made. However due to the diversity of these sites, no general location would serve the overall intent of this work.

The economic calculations were based upon differential estimates. That is the difference in costs due to the change, not the actual total costs.

### Capital

In general, all economic evaluations of equipment were based upon mid 1990 dollars. Dollar values were changed to this time frame based upon Nelson-Farrar Cost Indexes and the equation:

Mid 1990 $ = Original Cost(Year1) x (Mid 1990
Factor) x (1/Year1 Factor)

For example:

Given: 1980 Original Cost $100
mid 1990 Factor 1000
1980 Factor 500

Then: Mid 1990 Cost would be $200
($100 * (1000/500))

If specific cost estimates were not available in the literature, then more general estimates were utilized. Many of these costs were based upon confidential, professional work the author was performing in the period January 1990, to July 1991. This body of work included significant quantities of commercial cost estimation of refinery work. These estimates were based upon actual solicitations for purchase of material and equipment or installation of same. These estimates were guaranteed to be within ten percent of actual, finished cost. While this body of work as a whole is confidential, specific cost values for specific items of work or equipment were generalized for refinery work or modifications or additions. In addition commercial programs, PEPCOST and PEPCOST II were utilized for parts of these cost evaluations.

Therefore this body of work has been generalized into various categories for use within this work. This generalization reduced the overall accuracy of the total estimates. In comparison of the generalized values with the original work, an estimate of accuracy of 40% or + 20% would appear reasonable. These generalizations are listed below:

| | Mid 1990 $ (in thousands) |
|---|---|
| Tower; absorber, stripper, or distillation with associated vessels, coolers, exchangers, and pumps | $1,000 |
| One refinery unit; 5-10 towers, 1-3 reactors, associated items | $130,000 |
| One refinery unit stream detail with concrete curbing and surfacing | $8,000 |
| One alkylate battery limits unit | $9,000 |
| One fired heater; with burned regeneration process | $25,000 |
| One compressor Installation maximum of one thousand horsepower | $500 |
| One fired heater; standard burners | $100 |
| Crude handling units in $/Barrel | 0.128 |
| One closed reactor (100,000 gpd) | $10,000 |
| One filter unit using charcoal | $50 |
| One exchanger steel or admiralty tubes | $20 |

| | | |
|---|---|---|
| Storage vessel, atmospheric | small | $5 |
| | 500-1000 barrels | $15 |
| | 1000-5000 barrels | $50 |
| Electric driver with centrifugal pump | | |
| vertical or | small | $5 |
| horizontal | medium | $25 |
| | large | $75 |
| One water treatment unit | | $1,000 |

<u>Operations Costs</u>

These costs were based on the individual costs listed below and a markup factor of 100% for externally provided services.

| | |
|---|---|
| Fuel, residential grade | $0.06/mmbtu<br>(or mcf) |
| Power | $0.06/kwh |
| Steam | $6.00/1000# |
| Lime, average quality | $15/ton |
| Cooling water, circulated | $0.06/1000 gal |
| Purchased water | $4.00/1000 gal |
| Operating labor | $15/hr |
| Engineering labor | $50/hr |
| Analytical tests | $250/test |

## Benefits

Benefits were determined based upon the added value of products produced or the avoidance value of waste not disposed of. These costs were based on mid 1990 commercially available values.

| | |
|---|---|
| Hazardous waste (9#/gal) with no long term liability(incinerated) | $380/barrel |
| Non-hazardous waste (9#/gal) with no long term liability, toxic | $250/barrel |
| Non-hazardous waste (9#/gal) with non toxic components | $1/barrel |
| Landfarming | $9/ton |
| LPG | $0.30/gal |
| Finished products, liquid | $0.50/gal |
| Coke | $70/ton |
| Mol sieve | $1/# |

## Brine Reduction

The capital costs were based on the equipment additions needed, due to the increase in residence time requirement, and the addition of an electric field Atmospheric level volume tanks for residence time improvement of 10 minutes would be on the order of 600 barrels or $10 K.

(85,000 b/d * d/24hr * hr/60 min * 10 min)

Electric field generation equipment, estimated using PEPCOST would cost approximately $25 K. The sum total would be $10 K + $25 K or $35 K. Rounding would result in $40 K.

The additional operating costs were:

Engineering studies at $50/hr. The number of hours needed were based upon complexity of the oil feedstock. Based upon the refinery model, 6 months for two men would be reasonable, therefore $140 K annually.

(6 months * 30days * 8 hrs * $50 * 2 men)

Tests and analysis costs at $250/test,$15/hr. The number of tests were based on each test being performed from composite samples at least six times. There were nineteen different items for review. Therefore the cost of analysis was $30 K.

(6 * 19 * $250)

The cost of obtaining the samples was $3 K.

(2 times each test * 1 hr * 6 * 19 * $15)

Electricity was based upon $0.06/kw. The added cost was based upon 85,000 bpd feed and 35 watts/inlet feed barrel, or $70 K annually.

(365 * 85000 bpd * 35 watts * kw/1000watts * $0.06)

The increased chemical usage depended upon analysis

findings. Based upon our feedstock, an increase of 1 #/b or $0.02/b was representative, therefore $620 K annually.
(85000bpd * $0.02/b * 365 days)
Therefor the total was $140 K + $30 K + $3 K + $70 K + $620 K or $863 K. Rounding would result in $860 K.

The increased benefits associated with these improvements were mostly intangibles; less operational problems in downstream units, less waste or sludge generated in downstream units, less utilities consumed, etc. All of these items could have been "estimated" or "calculated" based upon partial savings times large flowrates to generate numbers. But these numbers are historically never located when the refinery is audited. The changes were smaller than the level of counting employed in the refinery. The intelligent estimate of actual benefits was one of intangible improvement.

### Brine Recycling

The capital costs were due to storage requirements at both ends, the refinery and the reinjection. Seven days of storage were three times $15 K or $45 K. Rounding would result in $50 K.
(4100gpd * 7 days * b/42 gal = 6830 barrels)
This was a good fit with transport truck size. This

allowed one tank at the refinery and two at the reinjection point.

The operating costs were due to the additional transportation required. This was a function of the distance required for travel. For relatively close distances, water transport fees of $0.20 per gallon resulted in $300 K annually.
($0.20 per gallon * 4100 gpd * 365 days)

The benefits were due to the elimination of the current material disposed and the requirement to purchase water. Because the material was on the RCRA list of exemptions, the material was usually land disposed with an attendant cost or cost avoidance of $60 K.
(4100 gpd * 9#/gallon * 1#/2000tons * $9/ton * 365)
The cost of water not purchased due to this usage was $6 K.
(4100 gpd * $4/1000 gallon * 365)
The total benefits would be $60 K + $6 K or $66 K.
Rounding would result in $70 K.
The potential benefits if the RCRA exemption is removed during RCRA reauthorization would be $14000 K.
(4100gpd * b/42 gallon * 365 days * $380/b)
A more detailed economic analysis based upon specific refinery locations would allow individual refinery breakeven milage values to be calculated, assuming milage and cost values were significantly related.

### Brine Mineral By-Product Recovery

The capital costs were based on the literature estimate of $6000 K at 1974 dollars. This was for an entire plant. Therefore the 1990 dollars were $16000 K.

mid 1990 = $6000 K * (1226.5/468)

= 16,000 K

The operating costs were based on the 1966 dollars of the literature estimate. Therefore the 1990 dollars were $10 K.

mid 1990 = $3 K * (378.5/111.7)

= $10 K

The benefits were based upon 1966 dollars for the entire industry. The value for the refinery model of 85000 bpd was based upon that share of the entire feed.

mid 1990 = $3000 K * (378.5/111.7)

= $10,000 K

model refinery share = (85000/15557923) * $10000K

= $60,000

It was anticipated that the model refinery would be too small to develop a recovery plant for itself, but would utilize a plant others had constructed. Therefore the benefits were reduced in half or $30 K to account for other margins.

## Coke Fines Source Reduction

Capital costs were reference costs in Aug. 1990 dollars with no changes. Operating costs were for the new equipment. For example, a hood over a conveyer belt required no additional operating costs.

Benefits of a cost avoidance nature of $20 K were available.

(23 ton/yr * 2000#/ton * gallon/20# * $380/b * b/42 gallon)

A second benefit was additional product value available for sale of $2 K.

(23 ton * $70/ton)

## Amine Filter Elements Source Reduction

The capital costs were $50 K, installed for a charcoal filter. This was the only additional equipment. To meet the refinery need, four units or $200 K would be needed.

The operating costs were a reduction in the steam requirements to the reboiler of the stripper. These requirements were reduced 30 % maximum by usage of DEA versus MEA. This amount of steam was worth approximately $690 K.

(10 mmbtu/hr per unit * 6 units * .3 * #/963 btu * .7 efficiency of steam generation * $6/1000# * 24 * 365)

NOTE: Assume the additional cost of regeneration was equal to the value of final coke disposal.

The benefits based on the cost of current disposal was $38 K, rounded to $40 K.

(2,500 elements * barrel/ 25 elements * $380 /barrel)

## Amine Filter Wastes Recycling

The benefit was the added value of the steel. The capital costs did not change and the operating cost was still the same. The disposal cost was however off-set by the recovery value of the component steel. Therefore $7.5 K or rounded $8 K.

(1500 elements * $3/element)

The $3 per element was a commercially quoted price of July 1990 for a steel mill in Longview, Tx. location.

## Catalyst Cement Recycling

There was no change in capital requirements and operational costs. Some value was received for the catalyst which usually covers the cost of transportation. Because of the influx of material in to this mode of disposal, values for the catalyst materials were declining.

### Polymerization Fertilizer Replacement

There was no change in capital requirements and operational costs. Some value was received for the catalyst which usually covers the cost of transportation.

### Mol Sieve Reuse

The reuse suggested related to mol sieve used in less severe service than required by the refinery. This type of service would be available in gas field gathering operations. As such this option depended more upon the availability of the proper situation to an individual refinery operator than whether the economics of the specific location and distance was favorable. To provide numeric evidence of this, the following example has been offered:

| | |
|---|---|
| less severe service needed | yes - use if savings in disposal outweigh cost of transport<br>no - generate one by buying a gas field? |
| Mol sieve unit used in existing field | yes - use if savings in disposal outweigh |

cost of transport
no - build a $5,000 K
unit to utilize $2K
(cost of new sieve) of
material?

The benefits, if a opportunity exists, were in value or cost avoidance of 1 ton per year of hazardous waste disposal. This was worth $1 K.
(1 ton * 2000#/ton * 1 gallon/18 # * b/42gallon * $380/b)
The effect of reducing new purchases was not included, due to the poorer performance of the reused material and the minor amount (due to time value of money).

### HF Carbon Filters

The operating and capital costs were unchanged ( as in the amine filter recycle option above). The benefit was for filter component reclaiming of $0.30K, rounding resulted in $1 K.
(100 elements * $3/ element)

### HF $CaF_2$ Lime Solid/Sludge

There was no change to the equipment due to the change in the quality of lime used. The operating cost increase of eight percent was based upon three calls to Tulsa, Ok area vendors in the summer of 1991. These values were then factored to 1990 values.

| | percentage difference |
|---|---|
| vender #1 | 7.2 |
| #2 | 9.0 |
| #3 | 8.1 |

percentage 1990 = 8.1 * (230.9/233.6)

= 8.01

The actual value was $2 K based upon twice the sludge being used as raw feed.

(2 times 745 tons/year * .0801 * $15/ton)

The benefits were 50 % of the impurities reduced or $20 K.

(0.50 * 0.05 * 745 ton/yr * 2000#/ton * gal/9# * b/42 gal * $250 /b)

### Recycling $CaF_2$ into Steel or HF Acid Manufacturing

No additional equipment or capital costs occurred. Operating costs were a function of distance required. 1990 estimates of transportation in western Arkansas (for a 600 mile distance) would be $0.0004 per mile-pound (if all miles and pounds were considered equal). Based on 745 tons, this was $596 per mile. Based upon the benefit value of $400 K (below), this translated into approximately 650 miles.

The benefits were of a revenue generation and a waste disposal avoidance type. Revenue generation was estimated at $10 K for 1988. Therefore 1990 dollars were, rounded to the proper significant value, $10 K.

mid 1990 = $10 K * (230.2/213.9)

Waste disposal savings would be based on disposal of 745 tons per year of sludge (35 % precipitate) or $390 K.

(0.35 * 745 tons/yr * 2000#/ton * gal/9 # * b/42 gal * $280 /b)

The total benefit would be $10 K + $390 K or $400 K.

### Filter Clays

Each value was taken from the 1979 source and updated to current 1990 values.

capital 1990 = $150 K * (1225.8/748)
= $245.8 K
= $250 K

operating 1990 = $232 K * (400.5/283)
= $328 K
= $330 K

benefits 1990 = $104 K * (400.5/283)
= $147 K
= $150 K

## BTX Spills

The additional capital costs of the barrier to protect the environment from spill was estimated from the cost for a total refinery barrier construction of \$8000 K. The determination of how much of the total was for the BTX Complex was based on a ratio between the number of units in the BTX complex, 6, and the total for the refinery model, 28.

cost = (6/28) * (\$8000 K)
= \$1714 K
= \$1700 K

Additional compression, separation, and repiping was based upon generalized costs of \$500 K. The total would be \$1700 K +\$500 K or \$2,200 K.

Operating costs were based upon the cost of compression operation annually. According to manufacturer specifications, fuel usage at maximum 1200 RPM for a lean burn 7042 GL Waukasha will be 14,250 cu ft per hour. The actual time of usage was based upon the amount of spillage which occurred and therefore the amount of compression needed would probably be two hours per day, therefore, costs were calculated at \$60 K.

(14250 * 24 * 365 * \$6/mcf * (2/24))

The benefits based on in-situ costs were based upon a

1988 reference. These costs factored to 1990 dollars were $50 K.

dollar 1990 = $50 K (378.5/373.7)

= $50 K

The benefits based on avoidance costs would be $70 K.

(10 cu yds / spill * 4/year * 27 cu ft/ cu yd * 7.4805 * b/42 gal * $380/b)

### Spent Acids

The capital costs had no increase. The operating costs were due to transportation costs. These costs were variable based upon distance and location. One such estimate was $180 per barrel for a 700 mile distance commercially available in 1992. If the cost was based on a per mile basis then in 1992 dollars the transportation cost would be

cost 1992 = ($180/b * 1/700 miles)

= 0.2571 per barrel-mile

cost 1990 = (0.2571 per barrel-mile * (1226.5/1270))

= 0.2483 per barrel-mile

Therefore 1990 $/mile = (6000 ton/yr * 2000#/ton * gallon/9# * b/42 gallon * $0.2483)

= 7884.

Based upon $238 K benefits (below), a milage breakeven value would be 30 miles.

The benefits of sales were be based upon conversion of the sources dollars to 1990 or \$240 K.

1990 dollars = \$100 K * (230.2/96.7)

= \$238 K (Rounding to \$240 K)

## Neutralization and Land Disposal

The capital cost additions needed by this option was similar in nature to a fresh water treatment plant with mixers, lime feed, basins, etc. Therefore the 1991 cost was \$1,000 K.

cost 1990 = \$1000 K * (1226.5/1270)

= \$965 K

= \$970 K

The operating costs were based on lime costs plus electricity costs. Lime costs were \$90 K.

(6000 ton per year * \$15 per ton)

Electricity costs were \$10 K.

(18650 watts-hr * 24 * 365 * \$0.06/kwh * k/1000 watts)

The total would be \$90 K + \$10 K or \$100 K.

## SOx

The capital costs and operating costs were in 1988 dollars. Conversion to 1990 dollars resulted in $380 K and $50 K respectively.

improvement capital 1990 = $4000 * (1164.5/1226.5)
= $380 K

improvement operating 1990 = $50 K * (373.7/378.5)
= $50 K

Improvement benefits were based upon 1990 values of sulphur in the East Texas Area and the cost of a ton of emission under the new Clean Air Act of 1990.

The benefits of installation of new processes to reduce SOx were based on the Clean Air Act of 1990 and were calculated at $1 K.

(705.7 tons/yr * 0.06 * $25 per ton)

The limestone option benefits were based on the same act and were calculated at $20 K.

(705.7 tons/yr * $25 per ton)

### NSCR, SCR, & VOC Source Reductions

The cost items for these options were defined in the discussion text below.

### General Sludges Handling

Coker disposal benefits were based upon the following:

| | |
|---|---|
| API separator | 4100 t/yr |
| Air floc | 6300 t/yr |
| Sludge | 10055 t/yr |
| tank bottoms | 240 t/yr |
| total | 20695 t/yr |

cost 1990 = 20695 * $9/ton

= $190 K

Solvent extraction costs were from 1991 references with such detail that they were left with that detail. NOTE: cost ratio of 399.7/392.2 would not have changed $230 K values.

Hot water extraction costs were based on references and changed to 1990 values.

1988 capital cost = $465 K

1990 capital cost = $465 K * (1226.5/1164.5)

= $490 K

1988 operating costs = $121.5 K

1990 operating costs = $121.5 K * (378.5/373.7)

= $120 K

### Wastewater Recycle Benefits

The benefits were worth $684 K or $680 K. (171 mm gallons/yr * $4/1000 gallons)

## Heat Exchange Source Reduction

The capital costs were based on the cost of the replacement medium of \$260 K.
(\$0.20/gallon * 33000 gpm * 40 minutes)

The operating costs were approximately equal. The benefits were based on disposal avoidance of \$30 K.
(\$380/b * 80 t/yr * 2000#/ton * gallon/9# * b/42 gallon * 20 % solid )

## Brine Reduction

As mentioned above, the brine was a crude oil contaminant that was removed before crude processing. As produced fluids, the usual disposal method's were either injection into deep wells or discharge to a pit for leaching or evaporation (23). As a result of a refinery's unique extractive nature, normal source reduction implied poorer performance which resulted in more environmental problems (due to additional removal duties in the desulfurizer, heat exchangers, coking, and other downstream units). So source reduction for the brine solution from a desalter meant more waste stream generation. Therefore improved operations and source increases were regarded as an improvement in waste management. One option of Brine reduction was improved operations obtained by improvements in certain operating parameters which have been historically ignored (24). These parameters included:

(1) Evaluation of the incoming salts and matching the optimum pH, temperature, and pressure for the emulsion;

(2) Reduction of sludge layers by redesign of water phase residence time;

(3) Removal of inorganic sediment particles in the range of 20-200 microns in diameter in the desalter by horizontal injection into a electrical treating field;

(4) Identification of the filtrable solids (Table XIX) and specific chemical requirements for removal after identification.

As a result of following these four steps, the desalting process would be able to target and remove water-soluble contaminants such as :

Salts: water-soluble alkali-metal chlorides
water-soluble alkali-metal carbonates
water-soluble alkali-metal sulfates
low molecular weight organic soaps

## TABLE XIX

## TYPICAL EXAMPLES OF FILTERABLE SOLIDS FOUND IN DESALTED CRUDE OIL

| | |
|---|---|
| Small Particle Size | |
| Basic Sediment | $SIO_2$, Sand, Silt |
| Alkali-metal Salts | $CaCO_3$, $CaSO_4$, $BaSO_4$ |
| Metal Salts | FeS, CuS, $FeO_4$, $Fe_2O_3$ |
| (Source 23) | |

Acids: heavy metal chlorides

Bases: water-soluble hydroxides

Sediment: large particle size, water insoluble inert inorganic compounds

Filterable Solids: water-insoluble alkali-metal carbonates
water-insoluble alkali-metal sulfates

water-insoluble metal
sulfides
water-insoluble metal
oxides
silica and other inert
compounds (24)

Economic evaluation of the implementation of these parameters was very difficult and somewhat inconclusive. The capital costs of the additional requirements were small and estimated using current construction and analysis market values at less than $40 K. Most of the effort entailed analysis work and engineering implementation. The operating cost was an increase of $860 K annually. Improvements due to the additional removal were unquantifiable within reasonable actual parameters. In general, these benefits were nondetectable in the actual operation of the refinery. Its a good practice to do, but difficult to justify the relative large sums of money.

## Brine Recycling

The brine stream generated by the desalter was recycled for use with a secondary oilfield flood recovery project for increased crude production. The usage was similar in concept to injection well disposal but with a beneficial reusage. In general, approval of state regulating agencies for underground well injection was required before this process could be undertaken.

The costs of the project was due mainly to plant storage and transportation costs (It was assumed the waterflood project would be self justified and that waterflood associated equipment; storage, pumps, etc. would be available.). The capital cost, based on the 4,100 gallons per day volume, was approximately $50 K. The operating cost and the feasibility of this option was mainly dependent upon the distance required to transport the brine to the field for reinjection. Typical transport fees (25) for small distances of less than one hundred miles of $0.20 per gallon would result in $300 K costs. Benefits of this technology depended upon the current disposal method and its associated costs which were estimated at $70 K.

At the current time, no significant justification existed. If produced fluids were removed from the RCRA list of exceptions or an accounting of the risk of future liability for current land or injection disposal was made, then the possibility for this option would exist due to the additional potential benefits of $14,000 K.

## Brine Mineral By-Product Recovery

Brine has several minerals of sufficient quantity that was worth recovering. Table XX showed the products which were readily recoverable using existing technology (23).

TABLE XX

BRINE COMPONENTS AND THEIR ASSOCIATED SALABLE PRODUCTS

| ELEMENT | PRODUCT |
|---|---|
| Sodium | Sodium Chloride |
| Potassium | Potassium Chloride |
| Lithium | Lithium Chloride |
| Magnesium | Magnesium Chloride |
| Calcium | Calcium Chloride |
| Strontium | Strontium Chloride |
| Boron | Sodium Borate |
| Bromine | Bromine |
| Iodine | Iodine |
| Sulphur | Sodium Sulfate |

The Dow Chemical Company had mined iodine from California oil brines (26), however in general little activity in this area had been generated. It seems the main reasons for this lack of activity were:

(1) Ease of disposal by other non-capital means.
(2) Excessive amounts of brine available from natural wells.
(3) Relative small amounts of brine available from this source.
(4) High capital and operating costs.
(5) Oil contaminants can foul certain technologies such as chelation steps.
(6) Market was variable.

The economic value of the minerals was estimated at more than three million dollars annually (27). Using this value related to the model refinery resulted in an annual recovery value of approximately $30 K annually. Operating costs were estimated to be quite low, $10 K per year (27). However capital costs were very large, about $16,000 K (23).

## Brine Summary

At the current time, little economic incentives exists for minimization or usage of the waste stream generated. As new legislation reauthorizing the RCRA regulations is developed relating to the hazardous status of this material, available technology had been found to minimize and utilize this stream.

## Coke Fines Source Reduction

As discussed before, coke was produced by refineries as an industrial fuel, or for anode usage (electric power negative transmitting point). The waste stream for the coking operation was generated by spillage and contamination during loading and or storage operations. The most useful reduction was to eliminate the problem by:

(1) reducing the amount of fines generated and being released into waste streams
(2) collecting the fines generated for sale as a product (28).

The amount of fines generated can be reduced by installation of equipment used by other industries to control the formation of particles in solid handling machinery. The equipment included the use of plastic collars, smaller trays, conveyer hoods, seals, covers, and a suppression vacuum collection system (29). The above equipment prevented coke solids introduction into the oily water sewer system through the open system and its eventual deposition at the bottom of the API separator as an RCRA listed sludge.

Economically the coke usage had a product value which was used to offset the added capital cost. In addition the avoidance cost of disposing of the fines as hazardous waste had a value of $20 K annually. The value of the additional recovered coke was approximately $2 K annually. The cost of purchasing and installing the additional coke fines handling equipment was estimated at approximately $50 K for retrofitted equipment and possible half that for original design of new equipment installations.

## Amine Filter Elements Source Reduction

MEA filter requirements were eliminated by changing the treating medium to other chemicals. One of the nonproprietary alternatives was DEA (diethanol amine). DEA degenerates to form various nonregenerating compounds, eliminating the need for a reclaimer (12). The process used continuous filtration on a slip stream basis to remove degradation products. The filtration was achieved with activated carbon medium. The activated carbon was regenerated with final disposal as a fuel or feed to the coker. Some additives were required to improve the chemicals ability to resist deterioration.

Because of DEA's ability to release sour gases with less energy input and its ability to use the same process equipment as MEA, the conversion to DEA or other special treating chemical was easily done. The capital cost was for the cost of filters and vessels, approximately $200 K). Benefits included the elimination of waste and energy savings associated with stripper column operation worth $710 K.

## Amine Filter Wastes Recycling

Filter element recycling was an approach which has been used on a variety of elements. The elements were recycled to a steel mill which used the steel portion of the element. Because the mill used high temperatures to recycle and melt the scrap metal, all other materials were consumed. The benefit was dependent upon the distance to a recycler and was usually about three dollars per element or $5 K annually.

## Catalysts Cement Manufacturer

FCCU cracker fines were generated either by wet liquid entrapment and later separation or by cyclones and electrostatic precipitators located downstream of the cyclones. In either case collection of very fine particles was achieved which were too small for efficient usage in the FCCU unit. The majority of these fines were composed of the catalyst material itself. This was usually a silica and alumina sand mixture with a nickel trap (30). Small trace amounts of residual coke and metals such as vanadium, chromium, and nickel were also present.

Because these FCCU catalysts were non-hazardous at this time, most fines were currently sold to Portland Cement manufacturers. The catalyst was attractive to cement kilns as a source of alumina and the catalyst was chemically consumed in the cement making process (31). The cement has been tested and found to be of acceptable strength with no leachate when subjected to the EP toxicity extraction procedure (32). This option was economically superior to any other at this time. There was no capital investment and while little was paid for the fines, it usually covered the transportation and handling. HF alumina, which was spent, also was utilized in this fashion after defluorination.

Cat polymerization catalyst had been used after degradation as a pozzolan material in the manufacturer of concrete. This catalyst had been reported to fail the RCRA characteristic of corrosivity when wet (33). However concrete made with this catalyst exceeded normal standards for strength and did not exhibited leachate problems.

## Polymerization Fertilizer Replacement

A second usage of polymerization catalyst was a source of phosphorous fertilizer for agricultural crops (33). Current nutrient data indicated little difference between the polymerization catalyst and commercially available triple superphosphate fertilizer (0-46-0) (33). Economics for this fertilizer replacement were very attractive with little outlay of capital or operating cost and nominal revenue generated. Handling requirements were the majority of any cost.

## Spent Catalyst Reclamation

Treating the spent catalyst to reclaim the metals for sale to the general metals market and disposal of the remaining materials was an option gaining popularity. Catalysts which were candidates for this option included in the model refinery were:

FCCU Cracker Fines
HF Alumina Catalyst
Cobalt Molybdenum Catalyst
Polymerization Catalyst.

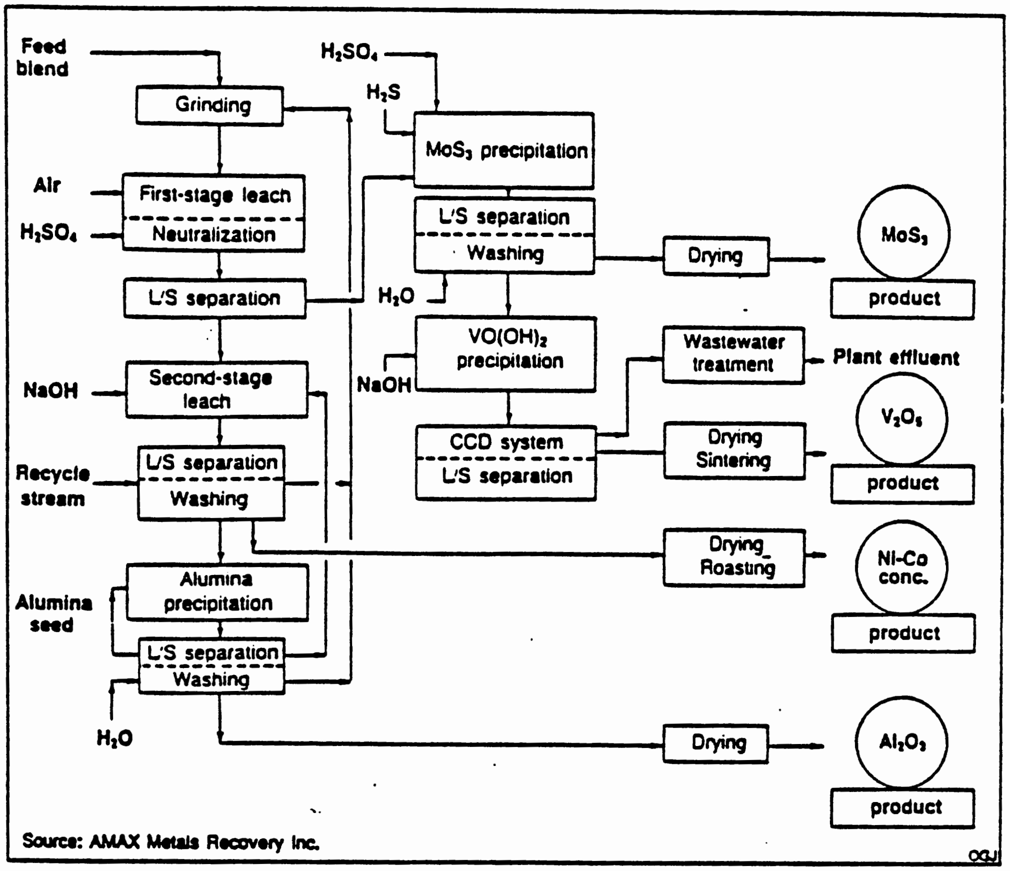
The products which were generated included:

Molybdenum Trisulfide
Vanadium Pentoxide
Alumina Trihydrate
Nickel Cobalt Concentrate (31).

The process was shown in Figure 21. Spent catalyst was separated from trash and dust. The catalyst was then mixed with a dilute caustic-alimunate solution, ground, and subjected to a series of high temperature oxidizing leaching processes. Standard solids handling operations including drying, roasting, sintering, separation, and precipitation were employed. The only waste stream generated by the process was treated wastewater (31).

Economics for the reclaimer process were difficult to estimate precisely. Using a similar process to regenerate solvents and scaling to the amount of equipment resulted in an equipment cost of approximately five million dollars (18). Using normal factors of 3-5 for installed, capital cost indicated a cost of approximately twenty million dollars. Operating costs, similarly estimated, were approximately $600 K annually. Using dollars per pound from the Chemical Marketing Reporter (34), resulted in a value of approximately $760 K annually, if all catalysts were replaced each year.

Spent catalyst recovery plant



Source: AMAX Metals Recovery Inc.

Figure 21

Spent Catalyst Recovery Plant

(Source 20)

## Mol Sieve Reuse

Mol sieve can be reused as a dehydration medium in less severe service, such as field gathering operations. No cost was involved and small nominal benefits were generated if the opportunity existed. The mol sieve material, if considered a waste would fail the TCLP test for metals.

## HF Carbon Filters

These filters were treated as amine filter elements above. The operating and capital costs were unchanged. Benefits of $1 K were possible.

## HF $CaF_2$ Lime Solid/Sludge

The lime solid or sludge was generated as part of the neutralization process for products. The sludge had approximately fifty percent water, five percent oil, and thirty five percent CaCO3 precipitate, with the remaining material of various impurities (18). These impurities were reduced by using a higher-grade of lime to neutralize the sludge. The capital cost was zero with an operating cost increase of $2 K or approximately eight percent. Savings were estimated at fifty percent of the additional impurities (five percent of the total produced per year) at \$20 K annually (35).

HF lime sludge was also be recycled for use in two different industries (36). $CaF_2$ (fluorspar) was utilized as a neutral flux to lower the slag-melting temperature during steel- manufacturing. The fluorspar also improved slag fluidity. The fluorspar was not hazardous per RCRA definitions which allowed this beneficial recycling.

The fluorspar is also a needed component of HF acid manufacturing. One of the basic steps in the manufacturing process of HF acid was the reaction of sulfuric acid with the fluorspar. This reaction produced HF and calcium sulfate. As noted above, the fluorspar usage was not hazardous.

Economics included no additional capital or operating costs. Transportation costs were a function of location, but this was offset by a decrease in the cost of the original disposal. Benefits included waste disposal plus revenue generation. Revenue generation was estimated at \$10 K annually (37). Waste disposal avoidance was estimated at \$390 K annually. Breakeven transportation costs have been estimated at 650 miles for some locations.

## Filter Clays

The clay filters were used as polishing agents for various hydrocarbon products. The clay used was either bentonite or montmorillonite. The clay adsorbed the impurities, usually by celation and was discarded when it became saturated with impurities. Most of the impurities were metals with some oil fractions. The percentage of water, oil, and solids in the resulting clay filter after use was 5, 22, and 73 percent, respectively (18). The clays were recycled using a thermal desorption process to drive off the impurities before reuse. The process used a slurry tank, mixers, centrifuge separations with rotary drying, steam heating and solvent regeneration. Metal removal was followed by separation and sale to the wholesale market. The value of the recovered metal was estimated at $150 K (18). Capital costs and operating costs annually were estimated at $2,500 K and $330 K, respectively (18).

## BTX Spills

Because of the liabilities and RCRA regulations associated with these hazardous waste producing products, spill clean up was expensive. Therefore the primary method of reducing costs was to limit the exposure to such spills. Limiting exposure usually has taken the form of providing a barrier between the environment (soil) and the product spill potential sites. One such barrier method consisted of a sealed, paved surface with vapor recovery and recompression and liquid reinjection into the process. The estimated detailed capital cost of this for an existing refinery was $2,200 K with approximately $60 K in annualized operating costs. Benefits were of the negative type, waste avoidance. Estimates of cleanup costs indicated a magnitude of $50 K annually if based on the clean up in situ cost or $70 K if based upon waste disposal (38).

## Spent Acids

Spent acids which were generated by the refinery were treated as additional products for sale or waste to be neutralized. The preferred method was sales to chemical companies as primary feedstock. Revenues on the order of magnitude of $240 K were estimated (36). Transport costs were variable depending upon distance and location. One such calculation indicated a breakeven value of 30 miles. This was a superior option to the neutralization and land disposal process. The capital cost of mixers, movers, and solid handling was estimated at $970 K. Operating costs included electricity and the cost of lime. These were estimated at $100 K annually. No tangible benefits were justified for this option. Intangible benefits included control of waste internally.

## Air Emission

Air emissions were generated from six basic sources:

(1) fired heaters exhaust
(2) compressor exhaust
(3) regeneration burn exhaust
(4) VOC
(5) SCOT unit tail off gas
(6) Carbon dioxide vent

The main constituents of these vapor streams were :

(1) NOx
(2) SOx
(3) CO
(4) Carbon Dioxide
(5) Hydrocarbon

### SOx

SOx emissions were reduced by the installation of improved or additional Claus tail gas units. Improvements were made to either the Claus or SCOT units. New technology was also used as a complete replacement. This was a very large area with many options. Only a few options for representative purposes were suggested. One improvement technique which has been used in refineries consisted of air enrichment. Included changes required for the process to the standard Claus unit included:

liquid oxygen enrichment of the feed
oxygen storage
new burners
new waste heat boiler
new condenser in SCOT unit for quenching
new structured packing
additional reflux

Improvements in emissions included complete destruction of any carryover ammonia and reduction of SOx emission by fifty percent (39). Benefits were approximately 15 LT/D incremental sulphur production with a reduction in SOx emissions of approximately 300 tons per year for the refinery model. Ammonia was also destroyed with no resultant operational problems. Direct benefit costs were approximately \$300 K annually at \$60 per LT and \$25 per ton emission per the Clean Air Act of 1990. Operating cost increases were estimated at \$50 K annually with an initial capital cost of \$380 K (39).

A completely new technology was the process developed at the University of California called UCBSRP. This process replaced all of the Claus, SCOT, and MEA or DEA units. The hydrogen sulfide was absorbed by a physical solvent and the resultant solution was mixed with a solution of $SO_2$ and solvent. The reaction of the two streams resulted in water and elemental sulphur. Part of the sulfur was burned to make the needed sulphur dioxide needed (40). Operating costs were revenue generating based on the stream available or $50 K annually. Capital costs were estimated at $5,000 K. Reduction of SOx emissions was approximately six percent. This value was approximately $1 K.

After the SOx was generated, various technologies were available to reduce the amount emitted. One such method was a fluid bed, dry limestone pollution control system to remove SOx from flue gas. Limestone was used by the system to form calcium oxide (lime), which reacted with the SOx to form calcium sulfate. Calcium sulfate has several usages. The calcium sulfate was not a hazardous waste (41). Uses for the calcium sulfate included:

(1) chemical fixation agent
(2) sludge stabilization agent
(3) pH control of runoff
(4) Road construction
(5) formulation of concrete.

The estimated cost of the system was approximately $500 K which depended upon the amount of ducting required. Operating costs were similarly dependent and were estimated at $50 K annually. Benefits were approximately $20 K, at $25 per ton permit emission cost (per the Clean Air Act of 1990).

SOx and NOx emission can both be treated by a plasma treatment process. Plasma technology has the advantage of removing simultaneously both SOx and NOx in a single-stage chemical process. A dielectric-barrier discharge chamber was used. Gas entered the plasma chamber through a side inlet. Electrical discharges were used to create $SO_3$ as an exhaust which was then be dissolved in water to form a saleable acid (42). At the level of current development, capital or operating costs were undefinable. Capital costs would be dependent on the type of plasma used. Benefits to justify the project were approximately $1,500 K if emissions can be eliminated.

NOx

NSCR is a NonSelective Catalytic Reduction technology which used a catalyst bed to reduce NOx to nitrogen and water. The catalyst used was an expensive noble metal such as platinum, rhodium, or palladium (42). Two major problems were catalyst poisoning and inadequate control of the amount of reducing agents in the feed to the catalyst.

Units were installed as needed on individual units. The model refinery required approximately 25 units at $30.2 K or $755 K in installed costs. Operating costs were $7 K per unit annually. Benefits consisted of approximately ninety percent reduction or at $25 per ton, $400 K annually (43).

SCR is a Selective Catalytic Reduction technology. It was a post combustion NOx control technology which handled a wide range of exhaust streams including ones with a significant oxygen content. The major components included a catalyst surface, reactor housing, ammonia system, continuous emission monitors, and a computer control system. The ammonia system consisted of a storage tank, vaporizer, injection grid, dilution air system, and a control system (43). In the process, ammonia was injected into the flue gas upstream of the catalyst reactor (44). On the catalyst surface, the NOx and ammonia reacted to form nitrogen and water. Oxygen was required for the reaction to occur. The process can removed approximately sixty percent of the NOx (40).

The capital cost for 25 units was $ 1,500 K with an operating cost of approximately $70 K per unit annually. The benefits of a sixty percent reduction of the available NOx was $950 K (43).

### VOC / Fugitive Emissions

The method of waste minimization which reduced the VOC emitted included a complete program of equipment coverage, piping components replacement, training of employees, testing, and maintenance. These techniques were difficult to generalize, being cost dependent upon each situation. Therefore, no cost values have been estimated.

An open-bed biofilter system was selected as a treatment method for reducing VOC emissions. Biofiltration is a method of treating large volume off-gases that contain low concentrations of the containments. Most organic air toxics and VOC's were biologically degraded into nontoxic by-products. This eliminated a typical disadvantage of many treatment systems of transferring the pollutants from one environmental media to another (45).

The biofilters were constructed of a series of beds of biologically active materials, such as peat or clay. The system consisted of a series of ducts to gather the gas, and a blower to direct the gas through a humidifier before the filter (Figure 22). In the filter, contaminants diffused into the wet film that covered the filter particles. The biologically active population was then allowed to metabolize the contaminants in this film area by aerobic processes. The results were be carbon dioxide, water, mineral salts, and a microbial biomass.

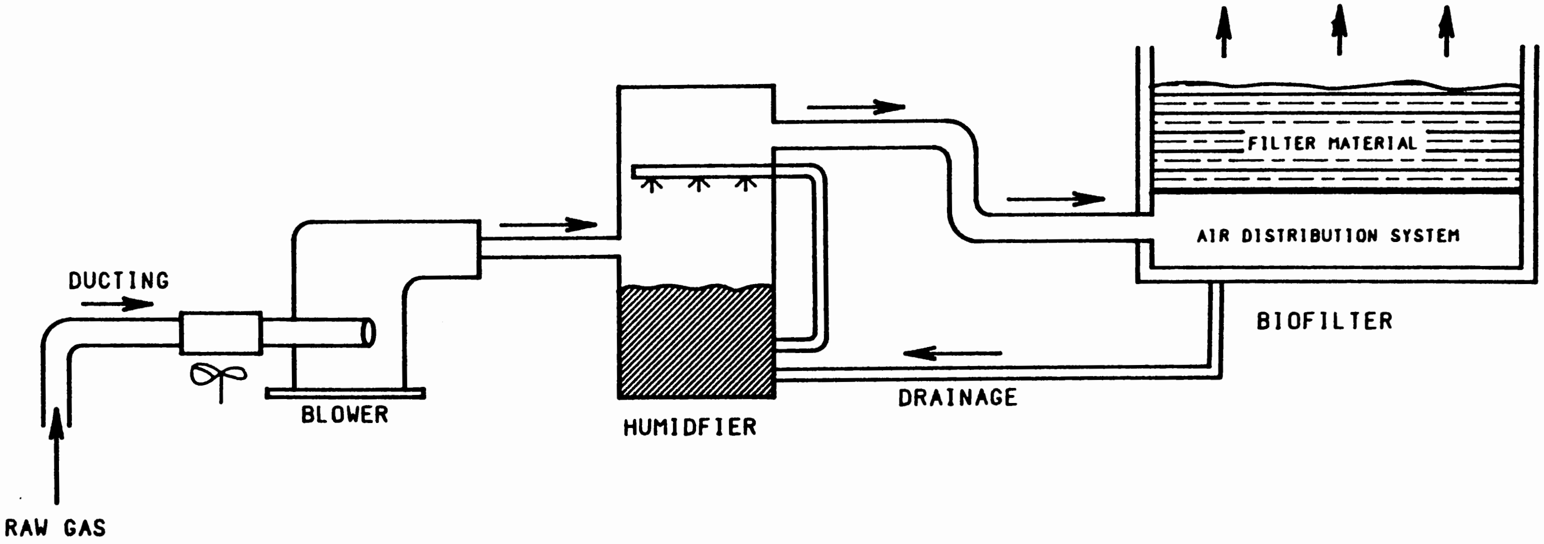


Figure 22 Open-Bed Biofilter Flow Diagram

The amount of filter mass required was based upon a rate of 100 grams/hour/meter cubed, which was the recommended rate for typical alcohols, ketones, aliphatic, and aromatic hydrocarbons. Based on a rate of 85 tons per year, the amount of filter was approximately 15 cubic feet. The capital cost of typical filters was $90 per cubic feet. Therefore, the capital cost was approximately was $1.3 K. The operating cost was reported as $1.00 per 100,000 cubic feet of off gas. This resulted in approximately 48.5 K per year. The cost of ducting and collection was estimated at $250 K. Benefits were approximately $2 K annually at $25 per ton.

#### $CO_2$

No items or regulatory limits (EPA) were identified for $CO_2$ emissions to the atmosphere. Because of the size of the stream, 1752 tons per year, and the degree of risk, it was anticipated no interest by private or government agency has been or will be shown.

### Sludge Waste Minimization Options

There were several wastes generated by units which were in sludges. These sludges consisted of varying proportions of oil, water, and solids. Most of these sludges were listed hazardous waste or were proposed for listing. The listing was due to the presence of heavy metals (1). Most contamination that was carried into the refinery by the crude or other streams usually ended up in one of the sludges. Before regulation, most refineries had one treatment unit for all wastewaters and sludges. As a result of listing, most refineries have or were installing programs designed to segregate waste streams and direct each to only the type of treatment required. Because these programs were individualized, this area will be of limited discussion.

### Coke Recycling

Because the model refinery has a coker, the refinery can use an exemption which occurs in 40 CFR 261.6 (a)(3) (46). This allows hazardous wastes that contain oil to be used as a feedstock for coker feeds as long as the wastes were generated at the same facility. The resulting coke product cannot exceed any of the characteristics of a hazardous waste (33). Because of the diluting effect of the normal feed, most sludges can be used in this manner. DAF float, slop oil, API separator, tank bottoms, and biosludge disposal was considered of in this manner. Process modifications were inexpensive, capital cost was estimated at $80 K. Additional operating costs were minimal while benefits can be quantified in relationship to the cost of alternate disposal. This was $190 K annually for secure land storage.

### Solvent Extraction

A second method of handling many of the same sludges (excluding leaded tank bottoms) was with solvent extraction. This system involved the use of four steps; dissolution of the oil, phase separation of the oil and solvent, recovery of the oil, and regeneration of the solvent (47). Some of the processes included a fixation step to reduce the leachability of any metals in the final compressed sludge (48). The estimated capital cost was $750 K for the model refinery (18). Operating costs were placed at $230 K. Benefits were estimated at $230 K annually.

### Hot Water Extraction

Another method, for the same four sludges as above; API separator, DAF floc, biosludge, and cooling tower sludge was hot water extraction (49). The process originated from the very common washing of dishes with hot soapy water. The process consisted of six main steps. The first step was a screening of the sludge. Then hot water was uniformly dispersed and a wetting agent added. A series of froth flotation and separations were made with tap water and air being added. The froth and liquid tailings were separated and the oil recycled. Capital costs were estimated at approximately

$490 K with operating costs of $120 K (49). Benefits accrued from this process were the recovery of approximately 90 percent of the available oil for reuse or $270 K annually at $20 per barrel.

### Specifically a Cooling Tower Sludge Option

This sludge while small in amount was particularly important in reducing chromium emissions from the refinery. Studies have shown that more than ninety percent of the chromium discharged from a refinery originated in additives to cooling towers to inhibit corrosion, scale, and slime (50). There were several strategies available to pursue to reduce this amount. Some of these were:

(1) Substitute phosphate based chemicals for chromium.

(2) Improve the quality of inlet water (also see next section on wastewater recycling).

3. Reduce the amount of water coolers needed by increasing utilization of air exchange.

The cost of the first item was negligible while the savings to the environment were quantified at approximately 70 % reduction in total actual pounds of chromium released by a standard refinery (50). Costs for the other items were individualized by refineries and could not reasonably be "typically" estimated.

## Wastewater Recycle

Refineries generated large quantities of wastewater which must be replaced with fresh water. The model refinery used approximately 800,000 tons per year or 170 mm gallons per year. Not only was there disposal costs, but freshwater must be purchased, treated, and incorporated into the refinery processes. In areas where water was scarce, recycling of a portion of this large amount of water was already implemented (51) (52). This idea should be considered at U.S. facilities. The complete recycle system, has been installed for larger flowrates (1833 gpm, six times the model refinery rate) included; covers to eliminate odors, two inclined plate separators to remove course material, two DAF units with pressurized air, sludge handling systems, chemical feeders, digesters, and final polishing cartridge filters (53). Some additional materials generated were listed wastes.

Costs of the water recycling system alone were approximately $3,000 K (capital) and $300 K annual (operating). Benefits, based on water replacement value of $4.00 per 1000 gallon were $680 K annually.

## Heat Exchanger Bundle Washings

Heat exchangers are cleaned to remove fouling or deposits of scale material on the tubes. Basically this material reduces the ability of the bundle to transfer heat. The wash from the cleaning was mostly water with small amounts of oil and solids. Usually several techniques for removal were used including sandblasting, brushing, jet water blasting, rodding, or chemical absorption. One method that significantly reduced the fouling problem and the resultant sludge was to replace water with various heat transfer fluids developed specifically for heat transfer (54). This was an expensive solution due to the usual differences in cost of treated waste ($4.06 per 1000 gallons) and cooling medium ($0.20 per gallon). Many solutions created other problems. For example solution leaks were usually hazardous waste. The benifit was that bundle sludge was made almost nonexistence using the heat transfer fluids. Capital costs were usually related to the addition of air cooling as an heat exhaust sink and purchase of the medium itself. These were estimated at $260 K. Operating costs were essentially the same. Benefits based on $380 per barrel were $30 K annually for the solid portion only.

Usually a variety of ideas and technologies were used to obtain partial solution to the problem (55) (56). They included:

(1) air cooler maximization
(2) improved inlet water or treatment facilities
(3) use lower pressure steam
(4) desuperheat steam
(5) minimize degradation by staging heating
(6) use on line cleaning techniques
(7) redesign exchangers to improve flow.

These have been applied to some degree to all refineries. Costs and benefits will be individualized by refinery.

## Leaded Tank Bottoms

Storage tanks which held lead containing petroleum products generated hazardous waste when they were cleaned. These wastes, or sludge, were listed as hazardous waste. There were several strategics which were used to reduce this emission (55) (56). They included:

(1) lining equipment
(2) clean in place
(3) reuse cleanup solvent
(4) optimize scheduling to reduce storage
(5) use in line blenders
(6) reduce storage before shut down

(7) use submerged jets to remix

(8) use crude mixers

These were available to reduce the amount of sludge or solid drop out or reduce the amount of tankage needed. Due to the individual nature of these items no costs or benefits were generated.

## Summary

Eighteen specific refinery generated wastes have been evaluated for current technology waste management options and economic incentive. In general, sufficient technology options existed to efficiently manage refinery wastes. Poor economic incentive existed for many options. Most of the economic incentives developed resulted from RCRA hazardous waste reduction.

Specific, developed waste management options, all refinery should be reviewing for incorporation into operations were:

* Coke fine reduction
* Change amine treating medium
* Recycle filter wastes
* FCCU catalysts capture and recycle to cement manufacturers
* Spent acids disposal as product sale

* NOx reduction with NSCR or SCR technology
* Coker recycling of sludges
* Chromium cooling tower replacement

Waste management options which refineries should review based upon the site location were:

* Brine waste recycling
* Mol Sieve reuse
* Recycle HF carbon filter wastes
* HF Lime quality upgrading
* Recycle waste water

Waste management options which refineries should review if RCRA hazardous waste rules are rewritten were:

* Brine wastes mineral by-product recovery
* Filter clay desorption and reuse
* BTX spill prevention

One waste management option which will require additional technological development, but has great potential is SOx and NOx air emission control with plasma treatment (destruction).

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# APPENDIXES

# APPENDIX A

## REFINERY SURVEY DEVELOPMENT DATA

Data from the Oil and Gas Journal annual refinery survey was developed in such a way to determine the frequency and size of the units that make up a refinery in the United States today. This information is presented in Table II and III following.

## TABLE II

## CRUDE PROCESSING CAPACITY IN BARRELS

## PER CALENDAR DAY

| TOTAL CAPACITY | VACUUM DISTILLATION CAPACITY | THERMAL OPERATIONS CAPACITY | THERMAL OPERATIONS TYPE | CAT CRACKING CAPACITY FRESH | CAT CRACKING CAPACITY TYPE | CAT CRACKING CAPACITY RECYCLE | REFORMING CAPACITY | REFORMING TYPE | HYDROCRACKING CAPACITY | HYDROCRACKING TYPE | HYDROREFINING CAPACITY | HYDROREFINING TYPE | HYDROTREATING CAPACITY | HYDROTREATING TYPE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BBL/CD | BBL/CD | BBL/CD | | BBL/CD | | BBL/CD | BBL/CD | | BBL/CD | | BBL/CD | | BBL/CD | |
| 14,250 | 14,000 | | | | | | | | | | | | | |
| 45,000 | 15,000 | 12,000 | 5 | | | | 6,000 | 2 | | | 9,800 | 2 | 6,000 | 1 |
| | | | | | | | | | | | 5,000 | 4 | 1,500 | 3 |
| 80,000 | 20,000 | | | | | | 20,000 | 2 | | | 15,000 | 3 | 2,000 | 2 |
| 12,000 | | 12,000 | 6 | | | | | | | | | | | |
| 16,000 | | 16,000 | 6 | | | | | | | | | | | |
| 22,000 | | | | | | | | | | | | | | |
| 102,000 | 6,000 | | | | | | | | | | | | | |
| 7,000 | | | | | | | | | | | | | | |
| 72,000 | | | | | | | 12,000 | 4 | 9,000 | 2 | | | 12,000 | 1 |
| 5,710 | 2,000 | | | | | | | | | | | | | |
| 8,000 | 6,000 | | | | | | | | | | | | | |
| 3,800 | 1,500 | | | | | | | | | | | | | |
| 6,770 | 4,000 | | | | | | | | | | | | 4,500 | 6 |
| 48,000 | 25,000 | | | 18,500 | 1 | 775 | 9,000 | 2 | | | | | 10,000 | 1 |
| 10,000 | 7,000 | | | | | | | | | | | | 5,500 | 5 |
| 220,000 | 112,000 | 56,000 | 5 | 82,000 | 1 | | 48,000 | 2 | 22,000 | 1 | | | 40,000 | 1 |
| | | | | | | | | | | | | | 10,000 | 2 |
| | | | | | | | | | | | | | 18,000 | 4 |
| | | | | | | | | | | | | | 8,000 | 5 |
| | | | | | | | | | | | | | 75,000 | 7 |

Source Ref. 7.

TABLE II (Continued)

| TOTAL CAPACITY | VACUUM DISTILLATION CAPACITY | THERMAL OPERATIONS CAPACITY | THERMAL OPERATIONS TYPE | CAT CRACKING CAPACITY FRESH | CAT CRACKING CAPACITY TYPE | CAT CRACKING CAPACITY RECYCLE | REFORMING CAPACITY | REFORMING TYPE | HYDROCRACKING CAPACITY | HYDROCRACKING TYPE | HYDROREFINING CAPACITY | HYDROREFINING TYPE | HYDROTREATING CAPACITY | HYDROTREATING TYPE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 14,200 | | | | | | | | | | | | | | |
| 286,000 | 114,000 | 54,000 | 4 | 62,000 | 1 | | 51,000 | 2 | 45,000 | 1 | 24,000 | 1 | 56,000 | 1 |
| | | | | | | | | | | | 60,000 | 2 | 14,000 | 4 |
| | | | | | | | | | | | 14,000 | 4 | | |
| 270,000 | 175,000 | | | 63,000 | 1 | | 50,000 | 2 | 45,000 | 1 | 60,000 | 2 | 66,000 | 1 |
| | | | | | | | | | 30,000 | 2 | 65,000 | 4 | 18,200 | 6 |
| | | | | | | | | | 30,500 | 3 | | | | |
| 9,500 | 7,800 | | | | | | | | | | | | | |
| 41,600 | 21,165 | | | | | | | | | | | | | |
| 128,000 | 67,000 | 27,500 | 4 | 64,000 | 1 | 11,000 | 32,000 | 3 | 32,000 | 1 | 37,000 | 1 | 27,000 | 1 |
| | | | | | | | | | | | | | 22,000 | 2 |
| | | | | | | | | | | | | | 12,500 | 4 |
| | | | | | | | | | | | | | 12,500 | 5 |
| | | | | | | | | | | | | | 17,000 | 7 |
| 26,500 | 17,000 | | | 12,000 | 1 | | 5,000 | 4 | | | 12,000 | 2 | 5,000 | 1 |
| 10,348 | 10,230 | | | | | | | | | | | | 900 | 6 |
| 40,600 | 25,000 | 13,800 | 3 | 13,500 | 1 | | 19,000 | 2 | 11,000 | 1 | | | 12,000 | 2 |
| 8,400 | 7,500 | | | | | | | | | | | | | |
| 5,500 | 5,000 | | | | | | | | | | | | | |
| 20,000 | | | | | | | 3,000 | 2 | | | | | 4,500 | 1 |
| 7,000 | 7,500 | | | | | | | | | | | | | |
| 123,000 | 95,000 | 48,000 | 5 | 63,000 | 1 | | 36,000 | 2 | 21,700 | 1 | 68,000 | 3 | 21,000 | 1 |
| | | | | | | | | | | | | | 16,000 | 3 |
| | | | | | | | | | | | | | 28,000 | 4 |
| 52,250 | 17,000 | 12,000 | 3 | | | | 15,000 | 2 | 3,500 | 1 | | | 15,000 | 1 |
| 42,700 | 29,000 | | | | | | 10,500 | 2 | | | 11,000 | 2 | 11,000 | 2 |
| | | | | | | | | | | | | | 7,000 | 4 |

Source Ref. 7.

## TABLE II (Continued)

| TOTAL CAPACITY | VACUUM DISTILLATION CAPACITY | THERMAL OPERATIONS |  | CAT CRACKING CAPACITY |  |  | REFORMING |  | HYDROCRACKING |  | HYDROREFINING |  | HYDROTREATING |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | CAPACITY | TYPE | FRESH | TYPE | RECYCLE | CAPACITY | TYPE | CAPACITY | TYPE | CAPACITY | TYPE | CAPACITY | TYPE |
| 46,550 | 26,000 | 10,400 | 5 | 12,500 | 1 |  | 9,000 | 2 | 8,000 | 1 | 13,500 | 3 | 8,500 | 1 |
|  |  |  |  |  |  |  |  |  |  |  | 6,000 | 4 | 7,000 | 5 |
| 18,000 | 14,000 | 10,000 | 3 |  |  |  |  |  |  |  |  |  |  |  |
| 140,100 | 98,000 | 22,000 | 4 | 67,000 | 1 | 1,000 | 28,000 | 3 | 27,000 | 1 | 50,000 | 3 | 17,000 | 1 |
|  |  |  |  |  |  |  |  |  |  |  |  |  | 18,000 | 3 |
|  |  |  |  |  |  |  |  |  |  |  |  |  | 21,000 | 4 |
|  |  |  |  |  |  |  |  |  |  |  |  |  | 6,300 | 6 |
|  |  |  |  |  |  |  |  |  |  |  |  |  | 15,000 | 7 |
| 139,000 | 75,000 | 53,000 | 5 | 42,000 | 1 |  | 24,000 | 2 |  |  | 11,000 | 3 | 25,000 | 2 |
|  |  |  |  |  |  |  |  |  |  |  |  |  | 14,000 | 3 |
|  |  |  |  |  |  |  |  |  |  |  |  |  | 54,700 | 4 |
| 15,000 |  |  |  |  |  |  | 1,500 | 2 |  |  |  |  | 1,500 | 2 |
| 4,000 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 48,000 | 23,000 | 13,000 | 5 |  |  |  | 22,000 | 2 | 14,300 | 1 | 15,000 | 2 | 14,000 | 1 |
| 75,000 | 42,000 | 48,000 | 5 | 28,000 | 1 |  | 38,000 | 2 | 20,000 | 1 |  |  | 18,000 | 1 |
|  |  |  |  |  |  |  |  |  |  |  |  |  | 12,000 | 4 |
| 131,900 | 118,000 | 46,000 | 4 | 60,000 | 1 | 2,000 | 20,000 | 2 | 27,000 | 1 | 50,000 | 2 | 12,000 | 1 |
|  |  |  |  |  |  |  | 23,000 | 5 |  |  |  |  | 22,000 | 4 |
| 68,000 | 42,000 | 24,000 | 5 | 38,000 | 1 |  | 14,500 | 6 |  |  | 42,000 | 3 | 15,000 | 1 |
| 108,000 | 83,000 | 20,000 | 3 | 47,000 | 2 |  | 52,000 | 2 | 22,000 | 2 |  |  | 54,000 | 1 |
|  |  |  |  |  |  |  |  |  |  |  |  |  | 36,000 | 5 |
| 113,100 | 74,100 | 46,900 | 5 |  |  |  | 34,000 | 2 | 32,500 | 1 |  |  | 23,000 | 1 |
|  |  |  |  |  |  |  |  |  |  |  |  |  | 12,000 | 5 |
|  |  |  |  |  |  |  |  |  |  |  |  |  | 14,500 | 6 |
| 28,000 | 10,000 |  |  | 8,500 | 1 |  | 9,000 | 2 |  |  |  |  | 9,000 | 1 |
| 48,000 | 23,000 |  |  | 17,000 | 1 | 1,000 | 10,000 | 2 |  |  |  |  | 10,000 | 1 |
|  |  |  |  |  |  |  |  |  |  |  |  |  | 11,800 | 4 |

Source Ref. 7.

TABLE II (Continued)

| TOTAL CAPACITY | VACUUM DISTILLATION CAPACITY | THERMAL OPERATIONS CAPACITY | TYPE | CAT CRACKING CAPACITY FRESH | TYPE | RECYCLE | REFORMING CAPACITY | TYPE | HYDROCRACKING CAPACITY | TYPE | HYDROREFINING CAPACITY | TYPE | HYDROTREATING CAPACITY | TYPE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 15,200 | 8,100 | 4,200 | 5 | | | | 3,400 | 2 | 5,000 | 1 | | | 3,400 | 1 |
| 140,000 | 95,000 | 46,000 | 4 | 65,000 | 1 | 5,000 | 18,000 | 2 | 19,000 | 4 | | | 55,000 | 1 |
| | | | | | | | 38,000 | 5 | | | | | 55,000 | 4 |
| 28,000 | | | | | | | | | | | | | | |
| 7,500 | | | | | | | | | | | | | | |
| 52,800 | 31,250 | | | 20,000 | 1 | | | | | | | | 3,500 | 3 |
| 77,000 | 40,000 | 13,000 | 3 | | | | 12,000 | 2 | 16,000 | 1 | | | 11,000 | 2 |
| 64,600 | 27,000 | | | 25,000 | 1 | 1,000 | 30,500 | 2 | 9,500 | 1 | | | 20,500 | 1 |
| 60,000 | 18,000 | 14,500 | 5 | 26,000 | 1 | 1,000 | 12,000 | 2 | | | | | 12,000 | 1 |
| | | | | | | | | | | | | | 4,000 | 2 |
| | | | | | | | | | | | | | 4,000 | 4 |
| | | | | | | | | | | | | | 8,000 | 5 |
| 195,000 | 62,000 | 4,000 | 3 | 42,000 | 1 | | 38,000 | 4 | 23,000 | 1 | 6,000 | 5 | 65,000 | 1 |
| | | 22,000 | 5 | | | | 41,000 | 5 | | | | | | |
| 180,000 | 88,000 | 38,000 | 5 | 98,000 | 1 | | 46,000 | 2 | | | | | 72,000 | 1 |
| | | | | | | | | | | | | | 9,000 | 2 |
| | | | | | | | | | | | | | 75,000 | 5 |
| 274,000 | 108,000 | 18,000 | 3 | 94,000 | 1 | | 18,000 | 2 | 33,500 | 1 | 29,000 | 3 | 64,000 | 2 |
| | | | | | | | 75,000 | | | | | | 79,500 | 4 |
| | | | | | | | | | | | | | 10,500 | 6 |
| 147,000 | 58,000 | 27,900 | 5 | 58,000 | 1 | 10,000 | 29,800 | 2 | | | | | 29,800 | 1 |
| | | | | | | | | | | | | | 22,200 | 2 |
| | | | | | | | | | | | | | 6,400 | 3 |
| | | | | | | | | | | | | | 39,000 | 5 |
| | | | | | | | | | | | | | 2,100 | 7 |
| | | | | | | | | | | | | | 4,300 | 7 |

Source Ref. 7.

TABLE II (Continued)

| TOTAL CAPACITY | VACUUM DISTILLATION CAPACITY | THERMAL OPERATIONS | | CAT CRACKING CAPACITY | | | REFORMING | | HYDROCRACKING | | HYDROREFINING | | HYDROTREATING | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | CAPACITY | TYPE | FRESH | TYPE | RECYCLE | CAPACITY | TYPE | CAPACITY | TYPE | CAPACITY | TYPE | CAPACITY | TYPE |
| 350,000 | 203,000 | 27,500 | 5 | 140,000 | 1 | 4,000 | 85,000 | 3 | | | 80,000 | 3 | 87,000 | 1 |
| | | | | | | | | | | | | | 24,000 | 2 |
| | | | | | | | | | | | | | 42,000 | 5 |
| | | | | | | | | | | | | | 4,300 | 6 |
| 20,600 | 7,200 | | | 7,000 | 1 | | 4,000 | 2 | | | | | 6,000 | 2 |
| 8,300 | 6,000 | | | | | | | | | | | | | |
| 48,000 | 17,000 | | | 19,500 | 1 | | 10,500 | 2 | | | | | 13,500 | 1 |
| 0 | | | | | | | 10,000 | 4 | | | | | 14,500 | 1 |
| 30,400 | 12,000 | | | 14,500 | 1 | | 4,500 | 2 | | | | | 4,000 | 4 |
| 29,925 | 10,000 | 5,500 | 5 | 19,000 | 1 | | 6,500 | 2 | | | | | 7,000 | 1 |
| 56,500 | 19,500 | 12,000 | 5 | 23,000 | 1 | 1,500 | 16,000 | 2 | | | | | 26,500 | 1 |
| 26,400 | 10,000 | | | | | | 5,300 | 2 | | | | | 7,500 | 1 |
| 70,900 | 27,000 | 22,000 | 5 | 20,000 | 1 | 1,000 | 15,000 | 4 | | | | | 10,000 | 1 |
| | | | | | | | | | | | | | 14,500 | 2 |
| | | | | | | | | | | | | | 13,000 | 4 |
| 78,000 | 32,000 | 12,500 | 5 | 31,500 | 1 | 2,500 | 18,500 | 2 | | | 44,000 | 3 | 20,000 | 1 |
| | | | | | | | | | | | | | 20,000 | 2 |
| | | | | | | | | | | | | | 9,000 | 4 |
| 56,000 | 16,150 | | | 19,500 | 1 | | 18,000 | 2 | 3,190 | 4 | | | 18,000 | 1 |
| 213,400 | 92,000 | 2,600 | 2 | 60,000 | 1 | | 25,000 | 2 | | | 40,000 | 3 | 60,000 | 1 |
| | | 55,000 | 6 | 40,000 | 2 | | 27,000 | 5 | | | | | 6,000 | 2 |
| | | | | | | | | | | | | | 6,000 | 3 |
| | | | | | | | | | | | | | 40,000 | 4 |
| | | | | | | | | | | | | | 29,000 | 7 |
| 5,500 | | | | | | | 1,000 | 2 | 400 | 1 | | | 1,300 | 1 |
| | | | | | | | | | | | | | 400 | 5 |

Source Ref. 7.

TABLE II (Continued)

| TOTAL CAPACITY | VACUUM DISTILLATION CAPACITY | THERMAL OPERATIONS CAPACITY | TYPE | CAT CRACKING CAPACITY FRESH | TYPE | RECYCLE | REFORMING CAPACITY | TYPE | HYDROCRACKING CAPACITY | TYPE | HYDROREFINING CAPACITY | TYPE | HYDROTREATING CAPACITY | TYPE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 46,200 | 24,300 | | | | | | 10,000 | 2 | | | | | 10,000 | 1 |
| | | | | | | | | | | | | | 3,400 | 6 |
| | | | | | | | | | | | | | 6,700 | 7 |
| 12,000 | | | | | | | | | | | | | | |
| 4,500 | 4,500 | | | | | | | | | | | | 4,500 | 6 |
| 9,865 | | | | | | | 1,900 | 1 | | | | | | |
| 320,000 | 83,000 | 63,000 | 5 | 150,000 | 1 | | 46,000 | 2 | 37,000 | 1 | 40,000 | 3 | 91,000 | 1 |
| | | | | | | | 45,000 | 5 | | | | | 14,000 | 4 |
| 159,500 | 63,000 | 12,000 | 2 | 42,500 | 1 | | 16,000 | 2 | | | | | 32,000 | 1 |
| | | 60,000 | 5 | | | | 12,000 | 5 | | | | | 109,000 | 5 |
| | | | | | | | | | | | | | 13000 | 7 |
| 421,000 | 183,000 | 90,000 | 5 | 188,000 | 1 | | 90,000 | 4 | 24,000 | 1 | | | 95,000 | 1 |
| | | | | | | | | | | | | | 2,500 | 3 |
| | | | | | | | | | | | | | 55,000 | 5 |
| | | | | | | | | | | | | | 17,000 | 6 |
| | | | | | | | | | | | | | 45,000 | 7 |
| 62,300 | 24,000 | | | 30,000 | 1 | | 12,500 | 2 | | | | | 12,500 | 1 |
| 40,000 | 20,000 | | | | | | | | | | | | | |
| 7,800 | | | | | | | | | | | | | | |
| 255,000 | 125,000 | | | 90,000 | 1 | | 48,000 | 5 | | | 71,000 | 2 | 48,000 | 1 |
| | | | | | | | | | | | 38,000 | 4 | 19,000 | 7 |
| 160,000 | 92,500 | 33,000 | 5 | 55,000 | 1 | | 28,000 | 2 | 18,000 | 1 | 43,000 | 3 | 45,000 | 1 |
| | | | | | | | 19,000 | 4 | | | | | 24,000 | 5 |
| 92,500 | 40,000 | | | 35,000 | 1 | 2,500 | 23,000 | 6 | | | 15,000 | 4 | 29,000 | 1 |
| 47,000 | 18,000 | | | 19,000 | 1 | 1,500 | 10,000 | 2 | | | | | 10,000 | 1 |
| 215,000 | 78,000 | 89,000 | 1 | | | | 18,000 | 2 | 35,000 | 1 | 70,000 | 3 | 29,000 | 2 |
| | | 21,000 | 5 | | | | 38,000 | 3 | | | | | 28,000 | 3 |

Source Ref. 7.

TABLE II (Continued)

| TOTAL CAPACITY | VACUUM DISTILLATION CAPACITY | THERMAL OPERATIONS CAPACITY | THERMAL OPERATIONS TYPE | CAT CRACKING CAPACITY FRESH | CAT CRACKING CAPACITY TYPE | CAT CRACKING CAPACITY RECYCLE | REFORMING CAPACITY | REFORMING TYPE | HYDROCRACKING CAPACITY | HYDROCRACKING TYPE | HYDROREFINING CAPACITY | HYDROREFINING TYPE | HYDROTREATING CAPACITY | HYDROTREATING TYPE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 17,700 | 6 | | | | | | | | | | | |
| 194,750 | 73,000 | 21,000 | 5 | 89,000 | 1 | 2,300 | 37,500 | 2 | | | | | 42,000 | 2 |
| | | | | | | | | | | | | | 24,000 | 4 |
| | | | | | | | | | | | | | 22,000 | 5 |
| 225,000 | 75,000 | 12,000 | 3 | 85,000 | 1 | 5,000 | 40,000 | 2 | 35,000 | 2 | | | 40,000 | 1 |
| | | | | | | | | | | | | | 37,000 | 4 |
| | | | | | | | | | | | | | 65,000 | 5 |
| 4,000 | | | | | | | | | | | | | | |
| 4,600 | | | | | | | 1,000 | 1 | | | | | | |
| 68,500 | 30,000 | | | 27,000 | 1 | 1,300 | 18,500 | 2 | | | 14,000 | 3 | 21,000 | 1 |
| | | | | | | | | | | | 2,000 | 4 | | |
| 45,600 | | | | 19,500 | 1 | | 14,000 | 2 | | | 3,800 | 2 | 21,000 | 1 |
| | | | | | | | | | | | 2,000 | 4 | 2,000 | 4 |
| 67,100 | 32,000 | | | 23,000 | 1 | | 23,500 | 2 | | | 23,000 | 3 | 24,500 | 1 |
| | | | | | | | | | | | | | 7,200 | 4 |
| | | | | | | | | | | | | | 8,300 | 7 |
| 218,500 | 160,000 | 58,000 | 5 | 55,000 | 1 | 1,000 | 26,000 | 6 | | | 63,500 | 3 | 26,000 | 1 |
| | | | | | | | 6,000 | 2 | | | | | 15,000 | 2 |
| | | | | | | | | | | | | | 46,000 | 4 |
| 30,000 | 20,000 | 8,000 | 4 | 16,000 | 2 | | 5,800 | 2 | | | | | 5,800 | 2 |
| | | | | | | | | | | | | | 6,000 | 4 |
| 295,000 | 243,000 | 62,000 | 5 | 58,000 | 1 | | 90,000 | 2 | 68,000 | 1 | 96,000 | 1 | 48,000 | 1 |
| | | | | | | | | | | | 63,000 | 3 | | |
| | | | | | | | | | | | 30,000 | 4 | | |
| 16,800 | 15,600 | | | | | | | | | | 5,000 | 5 | | |
| 5,800 | | | | | | | | | | | | | | |

Source Ref. 7.

TABLE II (Continued)

| TOTAL CAPACITY | VACUUM DISTILLATION CAPACITY | THERMAL OPERATIONS | | CAT CRACKING CAPACITY | | | REFORMING | | HYDROCRACKING | | HYDROREFINING | | HYDROTREATING | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | CAPACITY | TYPE | FRESH | TYPE | RECYCLE | CAPACITY | TYPE | CAPACITY | TYPE | CAPACITY | TYPE | CAPACITY | TYPE |
| 11,000 | | | | | | | | | | | | | | |
| 40,400 | 14,000 | | | 12,000 | 1 | 3,000 | 12,000 | 2 | | | 14,000 | 4 | 15,000 | 1 |
| 49,500 | 20,000 | | | 18,500 | 1 | 1,000 | 14,700 | 2 | | | | | 38,000 | 4 |
| | | | | | | | | | | | | | 4,500 | 5 |
| 42,000 | 18,000 | 7,700 | 4 | 21,000 | 1 | 3,500 | 10,000 | 1 | 4,900 | 1 | | | 15,500 | 2 |
| | | | | | | | | | | | | | 10,000 | 4 |
| | | | | | | | | | | | | | 10,000 | 5 |
| | | | | | | | | | | | | | 6,000 | 7 |
| 7,000 | 2,800 | | | 2,400 | 1 | 200 | 1,000 | 2 | | | | | 1,200 | 1 |
| | | | | | | | | | | | | | 1,300 | 4 |
| 4,500 | 2,500 | | | | | | | | | | | | | |
| 0 | | | | 50,000 | 1 | | | | | | | | | |
| 80,000 | 46,000 | | | | | | | | | | | | | |
| 109,250 | 45,000 | 10,000 | 3 | 50,000 | 1 | | 27,000 | 2 | | | | | 25,000 | 1 |
| | | | | | | | | | | | | | 14,000 | 4 |
| | | | | | | | | | | | | | 17,000 | 5 |
| | | | | | | | | | | | | | 4,800 | 7 |
| 130,000 | 66,000 | | | 120,000 | 1 | 25,000 | 28,000 | 4 | | | 50,000 | 2 | 29,000 | 1 |
| | | | | | | | | | | | | | 19,000 | 2 |
| | | | | | | | | | | | | | 65,000 | 5 |
| 100,000 | 62,400 | 21,500 | 5 | 36,000 | 1 | | 23,500 | 2 | | | 15,000 | 5 | 23,500 | 1 |
| | | | | | | | | | | | | | 42,000 | 5 |
| | | | | | | | | | | | | | 300 | 6 |
| 75,000 | 30,000 | | | | | | | | | | | | | |
| 16,800 | | | | 6,000 | 1 | 500 | 4,000 | 2 | | | | | 4,000 | 1 |
| 19,000 | 7,900 | | | 7,200 | 1 | 3,600 | 6,800 | 2 | | | | | 6,800 | 2 |

Source Ref. 7.

TABLE II (Continued)

| TOTAL CAPACITY | VACUUM DISTILLATION CAPACITY | THERMAL OPERATIONS | | CAT CRACKING CAPACITY | | | REFORMING | | HYDROCRACKING | | HYDROREFINING | | HYDROTREATING | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | CAPACITY | TYPE | FRESH | TYPE | RECYCLE | CAPACITY | TYPE | CAPACITY | TYPE | CAPACITY | TYPE | CAPACITY | TYPE |
| 38,000 | 6,000 | | | 14,500 | 1 | 2,500 | 7,800 | 2 | | | | | 10,000 | 1 |
| | | | | | | | | | | | | | 6,500 | 4 |
| | | | | | | | | | | | | | 3,000 | 5 |
| 6,500 | | 1,000 | 2 | | | | 2,500 | 2 | 1,000 | 2 | | | | |
| 42,500 | 27,000 | | | | | | | | | | | | | |
| 58,000 | | | | 26,000 | 1 | 5,200 | 12,100 | 4 | | | | | 16,600 | 2 |
| 66,000 | 33,000 | | | 25,000 | 1 | | 20,000 | 5 | | | 23,000 | 3 | 20,000 | 1 |
| | | | | | | | | | | | | | 7,000 | 4 |
| | | | | | | | | | | | | | 6,500 | 7 |
| 171,000 | 51,000 | 16,200 | 5 | 36,000 | 1 | 7,800 | 53,000 | 4 | 23,000 | 4 | | | 59,000 | 1 |
| 120,650 | 49,000 | 13,700 | 5 | 55,000 | 1 | | 23,000 | 3 | 35,000 | 4 | | | 37,000 | 1 |
| | | | | | | | 19,000 | 4 | | | | | | |
| 125,000 | 30,000 | | | 60,000 | 1 | 1,000 | 45,600 | 2 | 28,200 | 1 | | | 40,000 | 1 |
| 13,000 | | | | | | | | | | | | | | |
| 140,000 | 45,000 | 20,500 | 5 | 53,000 | 1 | | 36,000 | 2 | | | | | 36,000 | 1 |
| | | | | | | | | | | | | | 30,000 | 5 |
| 43,000 | 13,000 | | | 20,000 | 1 | | 8,500 | 2 | 5,000 | 1 | | | 9,000 | 1 |
| 50,000 | 26,500 | | | 18,000 | 1 | 5,000 | 12,000 | 2 | | | | | 12,000 | 1 |
| | | | | | | | | | | | | | 5,000 | 5 |
| 85,000 | 29,000 | | | 30,000 | 1 | 840 | 24,000 | 2 | | | | | 24,000 | 1 |
| | | | | | | | | | | | | | 10,500 | 6 |

Source Ref. 7.

## TABLE II (Continued)

| TOTAL CAPACITY | VACUUM DISTILLATION CAPACITY | THERMAL OPERATIONS | | CAT CRACKING CAPACITY | | | REFORMING | | HYDROCRACKING | | HYDROREFINING | | HYDROTREATING | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | CAPACITY | TYPE | FRESH | TYPE | RECYCLE | CAPACITY | TYPE | CAPACITY | TYPE | CAPACITY | TYPE | CAPACITY | TYPE |
| 60,500 | 32,000 | | | 23,500 | 1 | | 14,000 | 6 | | | 21,000 | 2 | 20,000 | 1 |
| 15,000 | 16,000 | | | | | | | | | | | | | |
| 125,000 | 83,000 | | | 29,000 | 1 | | 60,000 | 2 | 30,000 | 4 | | | 54,000 | 1 |
| | | | | | | | | | | | | | 50,000 | 4 |
| | | | | | | | | | | | | | 24,000 | 7 |
| 175,000 | 80,000 | | | 53,300 | 1 | 5,000 | 34,000 | 2 | | | | | 34,000 | 2 |
| | | | | | | | | | | | | | 30,000 | 4 |
| 15,700 | 6,500 | | | | | | 5,820 | 2 | | | | | 6,500 | 1 |
| | | | | | | | | | | | | | 7,800 | 6 |
| 6,500 | 2,680 | | | | | | 2,100 | 2 | | | | | 2,900 | 1 |
| 171,000 | 75,000 | | | 50,000 | 1 | 1,600 | 48,000 | 6 | 21,000 | 4 | 50,000 | 3 | 64,000 | 1 |
| | | | | | | | | | | | | | 22,000 | 4 |
| | | | | | | | | | | | | | 22,000 | 5 |
| 165,000 | 46,000 | | | 87,000 | 1 | | 39,600 | 2 | | | | | 54,300 | 1 |
| | | | | | | | | | | | | | 14,400 | 4 |
| | | | | | | | | | | | | | 13,000 | 5 |
| | | | | | | | | | | | | | 6,000 | 6 |
| 125,000 | 83,000 | | | 29,000 | 1 | | 50,000 | 2 | 30,000 | 4 | | | 54,000 | 1 |
| | | | | | | | | | | | | | 50,000 | 4 |
| | | | | | | | | | | | | | 24,000 | 7 |
| 64,600 | 27,000 | | | 20,000 | 1 | 200 | 16,000 | 2 | | | | | 20,000 | 1 |
| | | | | | | | | | | | | | 6,000 | 4 |
| 8,200 | | | | | | | 3,300 | 2 | | | | | | |
| 60,000 | 12,000 | | | 30,000 | 1 | | 10,000 | 2 | | | | | 10,000 | 1 |
| | | | | | | | | | | | | | 5,000 | 2 |
| | | | | | | | | | | | | | 16,000 | 5 |
| 415,000 | 195,000 | 37,000 | 5 | 195,000 | 1 | 43,000 | 160,000 | 4 | 60,000 | 1 | 85,000 | 3 | 140,000 | 1 |

Source Ref. 7.

TABLE II (Continued)

| TOTAL | VACUUM | THERMAL | | CAT CRACKING | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CAPACITY | DISTILLATION | OPERATIONS | | CAPACITY | | | REFORMING | | HYDROCRACKING | | HYDROREFINING | | HYDROTREATING | |
| | CAPACITY | CAPACITY | TYPE | FRESH | TYPE | RECYCLE | CAPACITY | TYPE | CAPACITY | TYPE | CAPACITY | TYPE | CAPACITY | TYPE |
| | | | | | | | | | 60,000 | 2 | | | 35,000 | 4 |
| | | | | | | | | | | | | | 35,000 | 5 |
| | | | | | | | | | | | | | 28,000 | 7 |
| 135,000 | 80,000 | 32,000 | 5 | 70,000 | 1 | | 52,000 | 5 | | | 55,000 | 2 | 54,000 | 2 |
| | | | | | | | | | | | 40,000 | 4 | | |
| 66,000 | 54,000 | | | 22,000 | 1 | | 25,000 | 2 | | | 19,000 | 4 | 25,000 | 1 |
| 329,000 | 163,200 | 34,000 | 5 | 110,000 | 1 | 6,000 | 23,000 | 2 | | | | | 67,100 | 2 |
| | | | | | | | 44,100 | 4 | | | | | 138,000 | 4 |
| | | | | | | | | | | | | | 13,900 | 6 |
| 90,250 | 53,000 | 11,000 | 3 | 18,500 | 1 | | 11,000 | 2 | 10,000 | 1 | | | 30,000 | 1 |
| | | 12,000 | 5 | | | | 17,500 | 6 | | | | | 20,000 | 4 |
| | | | | | | | | | | | | | 25,000 | 6 |
| 100,000 | 40,000 | 12,500 | 5 | 56,000 | 1 | | 14,000 | 2 | | | 10,000 | 4 | 26,000 | 1 |
| | | | | | | | 22,000 | 5 | | | | | | |
| 110,000 | 47,000 | | | 45,000 | 1 | | 29,000 | 2 | 20,000 | 4 | | | 33,000 | 1 |
| 50,000 | 20,000 | | | 20,000 | 1 | | 11,000 | 2 | | | | | 11,000 | 1 |
| 26,000 | | 4,400 | 5 | 10,800 | 1 | | 6,700 | 2 | | | | | 6,700 | 1 |
| 426,000 | 219,000 | 28,000 | 4 | 170,000 | 1 | 15,000 | 60,000 | 3 | 19,000 | 1 | 110,000 | 2 | 139,000 | 1 |
| | | | | | | | 63,000 | 4 | | | | | 23,500 | 3 |
| | | | | | | | | | | | | | 108,000 | 4 |
| | | | | | | | | | | | | | 80,000 | 5 |
| | | | | | | | | | | | | | 44,100 | 6 |
| 55,000 | 24,000 | | | 22,000 | 1 | | 20,000 | 2 | | | 6,000 | 2 | 25,000 | 1 |
| | | | | | | | | | | | | | 3,000 | 4 |

Source Ref. 7.

TABLE II (Continued)

| TOTAL CAPACITY | VACUUM DISTILLATION CAPACITY | THERMAL OPERATIONS |  | CAT CRACKING CAPACITY |  |  | REFORMING |  | HYDROCRACKING |  | HYDROREFINING |  | HYDROTREATING |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | CAPACITY | TYPE | FRESH | TYPE | RECYCLE | CAPACITY | TYPE | CAPACITY | TYPE | CAPACITY | TYPE | CAPACITY | TYPE |
|  |  |  |  |  |  |  |  |  |  |  |  |  | 15,000 | 5 |
| 110,000 | 50,000 |  |  | 36,000 | 1 |  | 34,000 | 5 |  |  | 18,000 | 2 | 40,000 | 1 |
|  |  |  |  |  |  |  |  |  |  |  | 13,000 | 3 | 28,000 | 5 |
| 66,000 | 28,000 |  |  | 50,000 | 1 |  | 13,500 | 2 |  |  |  |  | 14,000 | 1 |
|  |  |  |  |  |  |  |  |  |  |  |  |  | 23,000 | 4 |
|  |  |  |  |  |  |  |  |  |  |  |  |  | 7,000 | 7 |
| 123,000 | 64,000 | 21,000 | 3 | 50,000 | 1 |  | 11,000 | 2 |  |  |  |  | 23,000 | 1 |
|  |  |  |  |  |  |  | 12,000 | 6 |  |  |  |  | 29,000 | 4 |
| 2,900 |  |  |  |  |  |  | 1,200 | 1 |  |  |  |  |  |  |
| 125,000 | 42,000 | 12,000 | 5 | 40,000 | 1 | 800 | 15,000 | 3 |  |  |  |  | 49,500 | 1 |
|  |  |  |  |  |  |  | 33,500 | 6 |  |  |  |  | 8,000 | 56 |
| 49,500 | 16,000 | 6,000 | 5 | 17,000 | 1 | 850 | 4,500 | 2 |  |  |  |  | 20,800 | 2 |
|  |  |  |  |  |  |  | 11,700 | 5 |  |  |  |  |  |  |
| 10,000 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 265,000 | 129,000 | 40,000 | 5 | 90,000 | 1 |  | 110,000 | 2 |  |  | 48,000 | 3 | 110,000 | 1 |
|  |  |  |  |  |  |  |  |  |  |  | 46,000 | 4 | 10,000 | 3 |
|  |  |  |  |  |  |  |  |  |  |  | 35,000 | 5 | 43,000 | 4 |
|  |  |  |  |  |  |  |  |  |  |  |  |  | 7,000 | 7 |
| 69,500 | 27,000 |  |  | 38,000 | 1 | 1,000 | 10,000 | 1 |  |  |  |  |  |  |
| 275,000 | 86,000 | 29,500 | 5 | 102,000 | 1 |  | 57,000 | 2 | 32,000 | 1 |  |  | 92,000 | 1 |
|  |  |  |  |  |  |  | 46,000 | 5 |  |  |  |  | 116,000 | 5 |
|  |  |  |  |  |  |  |  |  |  |  |  |  | 3,500 | 6 |
|  |  |  |  |  |  |  |  |  |  |  |  |  | 2,150 | 7 |
| 105,000 |  |  |  | 60,000 | 1 | 10,400 | 26,000 | 2 |  |  | 50,000 | 1 | 26,500 | 2 |
|  |  |  |  |  |  |  |  |  |  |  | 40,000 | 4 |  |  |

Source Ref. 7.

## TABLE II (Continued)

| TOTAL CAPACITY | VACUUM DISTILLATION CAPACITY | THERMAL OPERATIONS |  | CAT CRACKING CAPACITY |  |  | REFORMING |  | HYDROCRACKING |  | HYDROREFINING |  | HYDROTREATING |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | CAPACITY | TYPE | FRESH | TYPE | RECYCLE | CAPACITY | TYPE | CAPACITY | TYPE | CAPACITY | TYPE | CAPACITY | TYPE |
| 175,000 | 83,000 |  |  | 87,000 | 1 | 12,000 | 36,000 | 2 |  |  | 75,000 | 1 | 53,000 | 2 |
|  |  |  |  |  |  |  |  |  |  |  | 50,000 | 4 |  |  |
| 44,100 | 12,000 |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 215,900 | 88,000 | 55,000 | 1 | 65,000 | 1 | 5,000 | 20,000 | 2 | 65,000 | 1 | 45,000 | 3 | 65,000 | 1 |
|  |  | 19,000 | 2 |  |  |  | 43,000 | 3 |  |  |  |  | 37,500 | 3 |
|  |  |  |  |  |  |  |  |  |  |  |  |  | 70,000 | 4 |
|  |  |  |  |  |  |  |  |  |  |  |  |  | 10,000 | 6 |
|  |  |  |  |  |  |  |  |  |  |  |  |  | 7,000 | 7 |
| 28,600 | 10,000 |  |  | 10,500 | 1 |  | 10,000 | 2 |  |  |  |  | 11,000 | 1 |
| 104,000 | 36,000 |  |  | 50,000 | 1 |  | 30,000 | 2 |  |  | 18,000 | 2 | 40,000 | 1 |
|  |  |  |  |  |  |  |  |  |  |  |  |  | 27,000 | 4 |
| 250,000 | 143,100 |  |  | 110,000 | 1 | 31,500 | 42,000 | 5 | 15,000 | 1 |  |  | 42,000 | 1 |
|  |  |  |  |  |  |  |  |  |  |  |  |  | 80,000 | 4 |
|  |  |  |  |  |  |  |  |  |  |  |  |  | 18,500 | 6 |
| 27,000 | 15,000 | 10,000 | 3 |  |  |  |  |  |  |  |  |  |  |  |
| 120,000 | 43,000 |  |  | 39,000 | 1 | 4,000 | 12,000 | 1 |  |  |  |  | 43,000 | 1 |
|  |  |  |  |  |  |  | 20,000 | 2 |  |  |  |  | 10,600 | 3 |
| 25,000 | 24,000 |  |  | 65,000 | 2 | 2,700 |  |  |  |  | 61,000 | 1 |  |  |
| 40,000 |  |  |  | 18,000 | 1 | 4,000 | 7,600 | 4 |  |  |  |  | 7,600 | 1 |
| 24,000 | 3,800 |  |  | 5,000 | 2 | 1,000 | 5,000 | 2 |  |  |  |  | 6,000 | 2 |
| 45,000 | 35,500 | 8,500 | 5 | 11,000 | 1 | 1,000 | 7,500 | 2 |  |  | 5,500 | 5 | 7,500 | 1 |
|  |  |  |  | 7,000 | 2 |  |  |  |  |  |  |  |  |  |
| 12,500 | 4,000 |  |  |  |  |  | 3,000 | 2 |  |  |  |  |  |  |
| 8,000 |  |  |  | 6,000 | 1 | 500 | 2,000 | 2 |  |  |  |  | 2,000 | 4 |

Source Ref. 7.

TABLE II (Continued)

| TOTAL CAPACITY | VACUUM DISTILLATION CAPACITY | THERMAL OPERATIONS CAPACITY | THERMAL OPERATIONS TYPE | CAT CRACKING CAPACITY FRESH | CAT CRACKING CAPACITY TYPE | CAT CRACKING CAPACITY RECYCLE | REFORMING CAPACITY | REFORMING TYPE | HYDROCRACKING CAPACITY | HYDROCRACKING TYPE | HYDROREFINING CAPACITY | HYDROREFINING TYPE | HYDROTREATING CAPACITY | HYDROTREATING TYPE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 25,000 | 4,800 | | | 8,400 | 2 | 2,600 | 6,000 | 4 | | | 1,600 | 4 | 11,000 | 2 |
| 53,000 | 29,000 | 13,500 | 5 | 27,500 | 1 | 2,000 | 10,200 | 2 | | | | | 10,000 | 1 |
| | | | | | | | | | | | | | 16,000 | 5 |
| 164,000 | 95,000 | 50,000 | 5 | | | | 56,000 | 2 | 52,000 | 1 | 18,000 | 4 | 38,000 | 1 |
| 5,000 | 6,000 | | | | | | | | | | | | | |
| 85,000 | 36,000 | | | 42,000 | 1 | 6,000 | 25,000 | 3 | | | 7,500 | 3 | 32,000 | 2 |
| | | | | | | | | | | | | | 20,500 | 4 |
| 77,000 | 28,000 | | | 25,500 | 2 | 2,000 | 11,800 | 4 | | | | | 13,500 | 1 |
| | | | | | | | | | | | | | 15,000 | 4 |
| 11,900 | 6,000 | | | | | | | | | | | | | |
| 117,000 | 50,000 | 22,000 | 5 | 45,000 | 1 | 4,000 | 7,000 | 1 | | | | | 22,000 | 1 |
| | | | | | | | 14,000 | 2 | | | | | 13,000 | 4 |
| | | | | | | | | | | | | | 15,000 | 5 |
| 32,775 | 19,500 | | | | | | 6,000 | 2 | | | | | 6,000 | 1 |
| | | | | | | | | | | | | | 1,000 | 2 |
| | | | | | | | | | | | | | 4,000 | 4 |
| 19,180 | 2,000 | | | | | | 1,500 | 1 | | | | | | |
| 10,500 | 8,850 | | | | | | 3,400 | 2 | 4,500 | 3 | | | 3,900 | 1 |
| 32,000 | 20,500 | | | 11,000 | 1 | 1,000 | 8,000 | 2 | | | 5,800 | 4 | 9,000 | 1 |
| 40,000 | 17,000 | | | 13,500 | 1 | 2,700 | 7,000 | 4 | | | | | 7,100 | 1 |
| 36,100 | 19,500 | 8,400 | 4 | 12,000 | 1 | 500 | 7,000 | 2 | | | 8,000 | 5 | 7,200 | 1 |
| 22,000 | 8,600 | | | 14,000 | 1 | 3,000 | 6,000 | 4 | | | | | 6,000 | 1 |
| | | | | | | | | | | | | | 3,750 | 2 |
| | | | | | | | | | | | | | 4,000 | 5 |
| 54,000 | 30,000 | | | 21,000 | 1 | 1,000 | 14,500 | 2 | | | 21,000 | 3 | 14,500 | 1 |
| | | | | | | | | | | | | | 12,000 | 4 |
| 12,500 | | | | 4,000 | 2 | 3,000 | 2,750 | 1 | | | | | | |

Source Ref. 7.

TABLE II (Continued)

| | TOTAL CAPACITY | VACUUM DISTILLATION CAPACITY | THERMAL OPERATIONS CAPACITY | THERMAL OPERATIONS TYPE | CAT CRACKING CAPACITY FRESH | CAT CRACKING CAPACITY TYPE | CAT CRACKING CAPACITY RECYCLE | REFORMING CAPACITY | REFORMING TYPE | HYDROCRACKING CAPACITY | HYDROCRACKING TYPE | HYDROREFINING CAPACITY | HYDROREFINING TYPE | HYDROTREATING CAPACITY | HYDROTREATING TYPE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| TOTAL | 15,557,923 | 7,132,525 | 1,972,400 | | 5,404,100 | | 287,865 | 3,930,470 | | 1,242,690 | | 2,411,000 | | 7,245,300 | |
| AVERAGE FOR 190 PLANTS | 81,884 | 37,540 | 10,381 | | 28,443 | | 1,515 | 20,687 | | 6,540 | | 12,689 | | 38,133 | |

LEGEND

THERMAL OPERATIONS

1 GAS/OIL CRACKING
2 THERMAL CRACKING
3 VISBRAKING
4 COKING (FLUID)
5 COKING (DELAYED)
6 OTHER

CATALYTIC CRACKING

1 FLUID
2 OTHER

CATALYTIC REFORMING

SEMIREGENERATIVE
1 CONVENTIONAL CATALYST
2 BIMETALLIC CATALYST

CYCLIC
3 CONVENTIONAL CATALYST
4 BIMETALLIC CATALYST

OTHER
5 CONVENTIONAL CATALYST
6 BIMETALLIC CATALYST

CATALYTIC HYDROCRACKING

1 DISTILLATE UPGRADING
2 RESIDUAL UPGRADING
3 LUBE OIL
4 OTHER

CATALYTIC HYDROREFINING

1 RESIDUAL DESULFURIZING
2 HEAVY GAS OIL
3 CAT CRACKER
4 MIDDLE DISTILLATE
5 OTHER

CATALYTIC HYDROTREATING

1 PRETREATING CAT FEEDS
2 NAPHTHA DESULFURIZING
3 NAPHTHA OLEFIN
4 STRAIGHT RUN DISTILLATE
5 OTHER DISTILLATE
6 LUBE OIL POLISHING
7 OTHER

## TABLE III

## PRODUCTS PROCESSING CAPACITY IN BARRELS

## PER CALENDAR DAY

| TOTAL CAPACITY | ALKLATION-POLYMERIZATION TYPE | ALKLATION-POLYMERIZATION CAPACITY | AROMATICS-ISOM CAPACITY | AROMATICS-ISOM TYPE | LUBES CAPACITY | ASPHALT CAPACITY | HYDROGEN MMCFD | HYDROGEN TYPE | COKE TON/DAY |
|---|---|---|---|---|---|---|---|---|---|
| BBL/CD | | BBL/CD | BBL/CD | | BBL/CD | BBL/CD | | | |
| 14,250 | | | | | | 10,000 | | | |
| 45,000 | | | | | | 9,500 | 6 | 1 | 400 |
| 80,000 | | | 7,000 | 6 | | | | | |
| 12,000 | | | | | | | | | |
| 16,000 | | | | | | | | | |
| 22,000 | | | | | | 6,000 | | | |
| 102,000 | | | 2,500 | 1 | | 2,000 | | | |
| 7,000 | | | | | | | | | |
| 72,000 | | | 4,000 | 6 | | | 13 | 1 | |
| 5,710 | | | | | | 1,000 | | | |
| 8,000 | | | | | 3,500 | | | | |
| 3,800 | | | | | | 1,000 | | | |
| 6,770 | | | | | 4,000 | 2,200 | 3 | 1 | |
| 48,000 | 1 | 4,800 | 3,000 | 6 | | 6,500 | | | |
| 10,000 | | | | | | 7,000 | | | |
| 220,000 | 1 | 14,000 | | | | | | | |
| | | 3,000 | | | | | 70 | 1 | 2,500 |

Source Ref. 7.

TABLE III (Continued)

| TOTAL CAPACITY | ALKLATION- POLYMERIZATION TYPE | CAPACITY | AROMATICS-ISOM CAPACITY | TYPE | LUBES CAPACITY | ASPHALT CAPACITY | HYDROGEN MMCFD | TYPE | COKE TON/DAY |
|---|---|---|---|---|---|---|---|---|---|
| 14,200 | | | | | | | | | |
| 286,000 | 1 | 8,000 | | | | | 130 | 2 | 2,900 |
| | | | | | | | | | |
| | | | | | | | | | |
| 270,000 | 1 | 7,000 | | | 11,000 | 11,000 | 150 | 1 | |
| | | 2,000 | | | | | | | |
| | | | | | | | | | |
| 9,500 | | | | | | 6,800 | | | |
| 41,600 | | | | | | 15,554 | | | |
| 128,000 | 1 | 14,000 | | | | | 104 | 1 | 1,100 |
| | | 2,000 | | | | | | | |
| | | | | | | | | | |
| | | | | | | | | | |
| | | | | | | | | | |
| 26,500 | | | | | | | | | |
| 10,348 | | | | | 5,100 | 4,000 | | | |
| 40,600 | 2 | 3,000 | | | | 4,000 | 11 | 1 | |
| 8,400 | | | | | | 4,500 | | | |
| 5,500 | | | | | | 3,500 | | | |
| 20,000 | | | | | | | | | |
| 7,000 | | | | | | | | | |
| 123,000 | 2 | 17,000 | | | | | 137 | 1 | 2,900 |
| | | | | | | | | | |
| | | | | | | | | | |
| 52,250 | | | | | | | | | |
| 42,700 | | | | | | 15,000 | | | |

Source Ref. 7.

## TABLE III (Continued)

| TOTAL CAPACITY | ALKLATION-POLYMERIZATION | | AROMATICS-ISOM | | LUBES | ASPHALT | HYDROGEN | | COKE |
|---|---|---|---|---|---|---|---|---|---|
| | TYPE | CAPACITY | CAPACITY | TYPE | CAPACITY | CAPACITY | MMCFD | TYPE | TON/DAY |
| 46,550 | 2 | 3,200 | 1,800 | 4 | | | 19 | 1 | 470 |
| 18,000 | | | | | 4,000 | 5,000 | | | |
| 140,100 | 1 | 8,000 | | | 4,500 | 11,000 | 110 | 1 | 127 |
| | | 3,200 | | | | | | | |
| 139,000 | 1 | 8,600 | | | | | 36 | 1 | 2,500 |
| 15,000 | | | | | | | | | |
| 4,000 | | | | | | 2,000 | | | |
| 48,000 | | | | | | | 21 | 1 | 690 |
| 75,000 | 1 | 4,400 | | | | | 48 | 3 | 1,650 |
| 131,900 | 1 | 13,000 | | | | | 80 | 1 | 1,500 |
| 68,000 | 2 | 10,500 | 9,000 | 4 | | | | | 1,200 |
| 108,000 | 1 | 10,000 | | | | | 49 | 1 | |
| 113,100 | | | 7,400 | 6 | 4,800 | | 65 | 1 | 2,620 |
| 28,000 | | 1,200 | | | | | | | |
| 48,000 | | 2,600 | | | | 5,000 | | | |

Source Ref. 7.

TABLE III (Continued)

| TOTAL CAPACITY | ALKLATION-POLYMERIZATION TYPE | ALKLATION-POLYMERIZATION CAPACITY | AROMATICS-ISOM CAPACITY | AROMATICS-ISOM TYPE | LUBES CAPACITY | ASPHALT CAPACITY | HYDROGEN MMCFD | HYDROGEN TYPE | COKE TON/DAY |
|---|---|---|---|---|---|---|---|---|---|
| 15,200 | | | | | | | 6 | 1 | 200 |
| 140,000 | 1 | 8,000 | | | | | 40 | 1 | 2,180 |
| | | 5,500 | | | | | | | |
| 28,000 | | | | | | 22,500 | | | |
| 7,500 | | | | | | 4,000 | | | |
| 52,800 | 1 | 4,500 | 1,500 | 4 | | 1,300 | 3 | 1 | |
| | | 1,125 | | | | | | | |
| 77,000 | | | | | | 1,100 | 18 | 2 | |
| 64,600 | 2 | 6,000 | | | | 4,500 | | | |
| 60,000 | 2 | 8,000 | 4,000 | 6 | | | 3 | 1 | 750 |
| 195,000 | 2 | 12,000 | 11,500 | 6 | | | 25 | 1 | 1,200 |
| 180,000 | 2 | 25,000 | | | | | | | 2,350 |
| 274,000 | 1 | 22,000 | 4,500 | 1 | 46,000 | 28,500 | 28 | 1 | |
| 147,000 | 2 | 18,000 | 3,500 | 1 | | 3,600 | 11 | 1 | 2,000 |
| | | | 7,400 | 6 | | | | | |

Source Ref. 7.

TABLE III (Continued)

| TOTAL CAPACITY | ALKLATION-POLYMERIZATION TYPE | ALKLATION-POLYMERIZATION CAPACITY | AROMATICS-ISOM CAPACITY | AROMATICS-ISOM TYPE | LUBES CAPACITY | ASPHALT CAPACITY | HYDROGEN MMCFD | HYDROGEN TYPE | COKE TON/DAY |
|---|---|---|---|---|---|---|---|---|---|
| 350,000 | 1 | 26,000 | 14,000 | 1 | 6,400 | 40,000 | | | 1,550 |
| | | | 21,000 | 6 | | | | | |
| 20,600 | 2 | 1,700 | 2,000 | 6 | | | | | |
| 8,300 | | | | | | 3,500 | | | |
| 48,000 | 2 | 6,000 | | | | 2,500 | | | |
| 0 | | | 6,500 | 6 | | | | | |
| 30,400 | 2 | 2,800 | | | | 2,500 | | | |
| 29,925 | 2 | 2,800 | | | | | | | 210 |
| | | 3,500 | | | | | | | |
| 56,500 | 2 | 6,000 | 8,000 | 6 | | | | | 600 |
| 26,400 | | | | | | 2,000 | | | |
| 70,900 | 2 | 6,000 | 2,000 | 4 | | | | | 650 |
| | | | 9,500 | 6 | | | | | |
| 78,000 | 2 | 12,500 | 15,000 | 6 | | | | | 610 |
| 56,000 | 2 | 5,500 | | | | | | | |
| 213,400 | 2 | 12,000 | 5,400 | 1 | 8,500 | 30,000 | | | |
| | | 1,000 | 12,000 | 6 | | | | | |
| 5,500 | | | 200 | 6 | | | | | |

Source Ref. 7.

TABLE III (Continued)

| TOTAL CAPACITY | ALKLATION-POLYMERIZATION | | AROMATICS-ISOM | | LUBES | ASPHALT | HYDROGEN | | COKE |
|---|---|---|---|---|---|---|---|---|---|
| | TYPE | CAPACITY | CAPACITY | TYPE | CAPACITY | CAPACITY | MMCFD | TYPE | TON/DAY |
| 46,200 | | | | | 8,500 | 600 | 6 | 1 | |
| 12,000 | | | | | | | | | |
| 4,500 | | | | | 4,500 | 900 | 5 | 1 | |
| 9,865 | | | | | | | | | |
| 320,000 | 1 | 20,200 | | | 9,000 | | | | |
| 159,500 | 1 | 7,500 | | | | | | | 3,650 |
| | | 2,100 | | | | | | | |
| 421,000 | 1 | 33,200 | 12,500 | 5 | 16,500 | 28,900 | | | 4,980 |
| | | 8,000 | | | | | | | |
| 62,300 | | 6,600 | | | | | | | |
| 40,000 | | | | | | | | | |
| 7,800 | | | | | | | | | |
| 255,000 | 2 | 26,000 | 18,500 | 4 | | 25,000 | | | |
| | | | 19,000 | 6 | | | | | |
| 160,000 | 2 | 19,000 | 7,000 | 1 | | | 24 | 1 | 1,550 |
| 92,500 | 1 | 8,700 | | | | | | | |
| 47,000 | 2 | 3,700 | | | | | | | |
| 215,000 | 1 | 15,000 | | | | | 70 | 1 | 1,000 |
| | | 9,400 | | | | | | | |

Source Ref. 7.

TABLE III (Continued)

| TOTAL CAPACITY | ALKLATION-POLYMERIZATION TYPE | ALKLATION-POLYMERIZATION CAPACITY | AROMATICS-ISOM CAPACITY | AROMATICS-ISOM TYPE | LUBES CAPACITY | ASPHALT CAPACITY | HYDROGEN MMCFD | HYDROGEN TYPE | COKE TON/DAY |
|---|---|---|---|---|---|---|---|---|---|
| 194,750 | 2 | 28,400 | 24,000 | 1 | | | | | 845 |
| | | | 6,300 | 2 | | | | | |
| 225,000 | 1 | 14,500 | 12,500 | 6 | | | 633 | 3 | |
| | | 4,000 | | | | | | | |
| 4,000 | | | | | | | | | |
| 4,600 | | | | | | | | | |
| 68,500 | 1 | 4,000 | | | | 10,000 | | | |
| 45,600 | 2 | 5,000 | 7,000 | 6 | | | | | |
| | | 1,000 | | | | | | | |
| 67,100 | 2 | 5,500 | 8,300 | 6 | | 14,000 | | | |
| | | 350 | | | | | | | |
| 218,500 | 1 | 8,500 | 15,000 | 6 | | 35,000 | 20 | 1 | 2,800 |
| | | 1,100 | | | | | | | |
| | | 3,700 | | | | | | | |
| 30,000 | 1 | 3,500 | | | | | | | 250 |
| 295,000 | 1 | 16,200 | 5,500 | 1 | | 20,000 | 215 | 1 | 3,200 |
| 16,800 | | | | | 5,000 | 12,000 | 3 | 1 | |
| 5,800 | | | | | | 3,500 | | | |

Source Ref. 7.

TABLE III (Continued)

| TOTAL CAPACITY | ALKLATION-POLYMERIZATION | | AROMATICS-ISOM | | LUBES | ASPHALT | HYDROGEN | | COKE |
|---|---|---|---|---|---|---|---|---|---|
| | TYPE | CAPACITY | CAPACITY | TYPE | CAPACITY | CAPACITY | MMCFD | TYPE | TON/DAY |
| 11,000 | | | | | | 5,100 | | | |
| 40,400 | 2 | 3,000 | 2,000 | 4 | | 6,000 | | | |
| 49,500 | 2 | 6,000 | 3,800 | 4 | | 6,500 | | | |
| 42,000 | 2 | 3,400 | | | | 11,000 | 19 | 5 | 435 |
| 7,000 | | 300 | 650 | 6 | | 1,200 | | | |
| 4,500 | | | | | | | | | |
| 0 | 1 | 4,500 | | | | | | | |
| | | 5,000 | | | | | | | |
| 80,000 | | | | | | 35,000 | | | |
| 109,250 | 1 | 4,000 | 2,000 | | | | | | |
| | | 2,500 | | | | | | | |
| 130,000 | 1 | 10,500 | 25,000 | 6 | | 38,000 | | | |
| 100,000 | 2 | 5,000 | | | 8,500 | | 11 | 1 | 1,010 |
| 75,000 | | | | | | | | | |
| 16,800 | | 2,000 | | | | | | | |
| 19,000 | 2 | 1,400 | 4,000 | 6 | | 700 | | | |

Source Ref. 7.

TABLE III (Continued)

| TOTAL CAPACITY | ALKLATION- POLYMERIZATION |  | AROMATICS-ISOM |  | LUBES | ASPHALT | HYDROGEN |  | COKE |
|---|---|---|---|---|---|---|---|---|---|
|  | TYPE | CAPACITY | CAPACITY | TYPE | CAPACITY | CAPACITY | MMCFD | TYPE | TON/DAY |
| 38,000 | 2 | 2,000 |  |  |  | 3,400 |  |  |  |
| 6,500 |  |  |  |  |  |  |  |  |  |
| 42,500 |  |  |  |  |  |  |  |  |  |
| 58,000 | 2 | 3,400 | 4,000 | 6 |  |  |  |  |  |
|  |  | 1,200 |  |  |  |  |  |  |  |
| 66,000 | 2 | 7,000 | 6,500 | 6 |  | 12,000 |  |  |  |
|  |  | 500 |  |  |  |  |  |  |  |
| 171,000 |  |  | 24,400 | 1 | 2,100 |  |  |  | 620 |
|  |  |  | 6,500 | 2 |  |  |  |  |  |
|  |  |  | 16,600 | 6 |  |  |  |  |  |
| 120,650 | 1 | 11,300 |  |  |  | 7,000 | 24 | 1 | 630 |
| 125,000 | 1 | 7,800 | 9,000 | 1 |  |  | 41 | 1 |  |
|  |  | 2,800 | 2,400 | 2 |  |  |  |  |  |
| 13,000 |  |  |  |  |  |  |  |  |  |
| 140,000 | 2 | 12,000 | 4,500 | 4 | 2,000 |  |  |  | 960 |
|  |  | 2,100 |  |  |  |  |  |  |  |
| 43,000 | 2 | 5,000 | 4,000 | 6 |  |  | 10 | 1 |  |
| 50,000 | 1 | 3,000 | 500 | 4 |  | 2,500 |  |  |  |
|  |  |  | 6,000 | 6 |  |  |  |  |  |
| 85,000 | 2 | 7,000 | 2,200 | 1 | 8,000 | 4,600 |  |  | 300 |
|  |  |  | 1,200 | 2 |  |  |  |  |  |
|  |  |  | 2,000 | 3 |  |  |  |  |  |
|  |  |  | 3,000 | 4 |  |  |  |  |  |

Source Ref. 7.

## TABLE III (Continued)

| TOTAL CAPACITY | ALKLATION- POLYMERIZATION | | AROMATICS-ISOM | | LUBES | ASPHALT | HYDROGEN | | COKE |
|---|---|---|---|---|---|---|---|---|---|
| | TYPE | CAPACITY | CAPACITY | TYPE | CAPACITY | CAPACITY | MMCFD | TYPE | TON/DAY |
| 60,500 | 2 | 7,000 | 6,000 | 6 | | 6,000 | | | |
| 15,000 | | | | | | 11,500 | | | |
| 125,000 | | | | | | 35,000 | 40 | 5 | |
| 175,000 | 2 | 18,000 | 4,000 | 1 | | | | | |
| | | | 1,300 | 2 | | | | | |
| 15,700 | | | 1,150 | 6 | 4,750 | | 4 | 1 | |
| 6,500 | | | 800 | 6 | 2,560 | | | | |
| 171,000 | 2 | 12,000 | | | | | | | |
| 165,000 | 1 | 12,000 | 7,000 | 1 | 10,000 | | 6 | 1 | |
| 125,000 | | | | | | 35,000 | 40 | 5 | |
| 64,600 | 1 | 3,000 | 6,800 | 6 | | 8,000 | | | |
| | | 2,000 | | | | | | | |
| 8,200 | | | | | 4,000 | | | | |
| 60,000 | 2 | 3,000 | 4,000 | 6 | | 3,500 | | | |
| | | 2,500 | | | | | | | |
| 415,000 | 1 | 22,000 | 45,000 | 1 | | | 180 | 1 | 1,900 |

Source Ref. 7.

TABLE III (Continued)

| TOTAL CAPACITY | ALKLATION-POLYMERIZATION TYPE | ALKLATION-POLYMERIZATION CAPACITY | AROMATICS-ISOM CAPACITY | AROMATICS-ISOM TYPE | LUBES CAPACITY | ASPHALT CAPACITY | HYDROGEN MMCFD | HYDROGEN TYPE | COKE TON/DAY |
|---|---|---|---|---|---|---|---|---|---|
| | 2 | 32,000 | 28,000 | 6 | | | | | |
| 135,000 | 2 | 19,000 | 5,000 | 1 | | | | | 1,800 |
| | | | 2,500 | 3 | | | | | |
| 66,000 | 1 | 5,500 | 3,000 | 4 | | 5,500 | | | |
| 329,000 | 2 | 16,900 | 7,095 | 1 | 10,000 | | | | 1,840 |
| | | | 2,905 | 2 | | | | | |
| | | | 2,500 | 3 | | | | | |
| | | | 7,200 | 5 | | | | | |
| 90,250 | 2 | 3,200 | 11,000 | 1 | | | 24 | 1 | 650 |
| | | 3,000 | 7,000 | 2 | | | 15 | 4 | |
| | | | 5,300 | 6 | | | | | |
| 100,000 | 2 | 13,000 | 2,000 | 1 | | | | | 350 |
| | | | 2,000 | 2 | | | | | |
| | | | 5,000 | 6 | | | | | |
| 110,000 | 1 | 8,700 | | | | 5,000 | | | |
| | | 4,600 | | | | | | | |
| 50,000 | 2 | 6,000 | | | 1,000 | | | | |
| 26,000 | 1 | 3,000 | 700 | 4 | | | | | 120 |
| 426,000 | 1 | 29,000 | | | 31,200 | 7,000 | 85 | 1 | 100 |
| 55,000 | 2 | 5,000 | 1,000 | 1 | | 7,000 | | | |

Source Ref. 7.

TABLE III (Continued)

| TOTAL CAPACITY | ALKLATION- POLYMERIZATION TYPE | CAPACITY | AROMATICS-ISOM CAPACITY | TYPE | LUBES CAPACITY | ASPHALT CAPACITY | HYDROGEN MMCFD | TYPE | COKE TON/DAY |
|---|---|---|---|---|---|---|---|---|---|
| 110,000 | 1 | 5,500 | 10,000 | 1 | | 2,000 | | | |
| | | | 8,500 | 6 | | | | | |
| 66,000 | 1 | 4,000 | 2,000 | 1 | | 5,000 | | | |
| 123,000 | 2 | 6,000 | | | | | | | |
| 2,900 | | | 1,000 | 1 | | | | | |
| 125,000 | 2 | 8,400 | 7,600 | 1 | | | | | 375 |
| | | | 3,200 | 2 | | | | | |
| 49,500 | 1 | 4,800 | 5,000 | 6 | | | | | 250 |
| 10,000 | | | | | | | | | |
| 265,000 | 1 | 14,000 | 11,000 | 1 | 6,000 | | | | 2,650 |
| 69,500 | 2 | 11,000 | 2,500 | 1 | | | | | |
| 275,000 | 1 | 13,000 | 20,000 | 5 | 94,000 | | 60 | 1 | 1,471 |
| 105,000 | 2 | 14,000 | 3,060 | 3 | | | 50 | 1 | |
| | | | 11,000 | 4 | | | | | |
| | | | 12,100 | 5 | | | | | |
| | | | 12,500 | 6 | | | | | |

Source Ref. 7.

TABLE III (Continued)

| TOTAL CAPACITY | ALKLATION-POLYMERIZATION TYPE | ALKLATION-POLYMERIZATION CAPACITY | AROMATICS-ISOM CAPACITY | AROMATICS-ISOM TYPE | LUBES CAPACITY | ASPHALT CAPACITY | HYDROGEN MMCFD | HYDROGEN TYPE | COKE TON/DAY |
|---|---|---|---|---|---|---|---|---|---|
| 175,000 | 2 | 15,000 | 5,575 | 1 | | | | 80 | 4 |
| | | | 7,630 | 3 | | | | | |
| | | | 9,100 | 5 | | | | | |
| | | | 7,800 | 6 | | | | | |
| 44,100 | | | | | | | | | |
| 215,900 | 1 | 8,100 | 20,000 | 1 | 12,500 | 7,400 | 65 | 1 | |
| 28,600 | 2 | 3,300 | 350 | 1 | | | | | |
| 104,000 | 2 | 7,000 | 6,500 | 1 | | | | | |
| | | 4,200 | | | | | | | |
| 250,000 | 1 | 9,000 | | | 17,400 | 14,000 | | | |
| 27,000 | | | | | | | | | |
| 120,000 | 1 | 4,200 | 6,000 | 1 | 3,100 | 2,500 | | | |
| | | 1,400 | 1,200 | 3 | | | | | |
| 25,000 | 2 | 9,500 | | | | | 64 | 1 | |
| | | 2,200 | | | | | | | |
| 40,000 | 1 | 4,000 | 3,000 | 4 | | | | | |
| 24,000 | 2 | 1,300 | 1,700 | 6 | | | | | |
| 45,000 | 2 | 4,300 | 750 | 4 | | | | | 350 |
| 12,500 | | | | | | | | | |
| 8,000 | | 2,600 | | | | | | | |

Source Ref. 7.

TABLE III (Continued)

| TOTAL CAPACITY | ALKLATION-POLYMERIZATION TYPE | ALKLATION-POLYMERIZATION CAPACITY | AROMATICS-ISOM CAPACITY | AROMATICS-ISOM TYPE | LUBES CAPACITY | ASPHALT CAPACITY | HYDROGEN MMCFD | HYDROGEN TYPE | COKE TON/DAY |
|---|---|---|---|---|---|---|---|---|---|
| 25,000 | 2 | 2,100 | 2,600 | 6 | | 1,700 | | | |
| 53,000 | | 2,400 | | | | | | | 750 |
| 164,000 | | | | | | | 80 | 1 | 2,500 |
| 5,000 | | | | | | 5,000 | | | |
| 85,000 | 1 | 11,000 | 2,750 | 4 | | | | | |
| 77,000 | 2 | 5,900 | | | | | | | |
| | | 1,200 | | | | | | | |
| 11,900 | | | | | | 3,600 | | | |
| 117,000 | 1 | 8,000 | | | | | | | 1,200 |
| | | 2,200 | | | | | | | |
| 32,775 | | | 1,500 | 6 | | 8,000 | | | |
| 19,180 | | | | | 2,000 | | | | |
| 10,500 | | | | | 4,440 | | 1 | 1 | |
| 32,000 | 2 | 1,300 | 2,000 | 5 | | 13,500 | | | |
| 40,000 | 1 | 2,500 | | | 1,500 | | | | |
| 36,100 | 2 | 3,000 | 1,200 | 4 | | 7,000 | | | |
| 22,000 | | | | | | 1,000 | | | |
| 54,000 | 1 | 3,500 | | | | 5,000 | | | |
| | | 700 | | | | | | | |
| 12,500 | 2 | 800 | | | | | | | |

Source Ref. 7.

TABLE III (Continued)

| | TOTAL CAPACITY | ALKLATION-POLYMERIZATION TYPE | ALKLATION-POLYMERIZATION CAPACITY | AROMATICS-ISOM CAPACITY | AROMATICS-ISOM TYPE | LUBES CAPACITY | ASPHALT CAPACITY | HYDROGEN MMCFD | HYDROGEN TYPE | COKE TON/DAY |
|---|---|---|---|---|---|---|---|---|---|---|
| TOTAL | 15,557,923 | | 1,135,075 | 785,915 | | 366,350 | 760,654 | 2,979 | | 71,397 |
| AVERAGE FOR 190 PLANTS | 81,884 | | 5,974 | 4,136 | | 1,928 | 4,003 | 16 | | 376 |

TABLE III LEGEND

ALKYLATION/POLYMERIZATION

1 SULFURIC ACID ALKYLATION
2 HYDROFLUORIC ACID ALKYLATION
3 POLYMERIZATION

AROMATICS/ISOMERIZATION

1 BTX
2 HYDRODEALKYLATION
3 CYCLOHEXAND
4 BUTANE FEED
5 PENTANE FEED
6 HEXANE PLUS FEED

HYDROGEN

1 STEAM METHANE REFORMING
2 STEAM NAPHTHA REFORMING
3 PARTIAL OXIDATION
4 CRYOGENIC
5 OTHER

# APPENDIX B

## CALCULATION OF EXHAUST VOLUMES AND COMPOSITIONS

FIRED HEATERS:

BASIS:

TOTAL MMBTU/HR HEAT DUTY REQUIRED IS 644.0 (THIS IS THE ADDED HEAT DUTIES OF ALL UNITS IN THE MODEL REFINERY)

| | |
|---|---|
| NTE OF FIRED HEATERS WITH CONVECTION SECTION | 80 % |
| EXCESS AIR USED IN ALL CASES | 20% |

FUEL COMPOSITION(CHAPTER 5 DEFINITION OF FUEL GAS)

| | |
|---|---|
| N2 | 5.22 MOL % |
| CO2 | 0.03 |
| C1 | 93.79 |
| C2 | 0.96 |

CALCULATION:

1. FUEL REQUIRED = HEAT REQUIRED/NTE

   = 644.0/0.8

   = 805 MMBTU/HR

2. BTU CONTENT OF FUEL GAS

| | NET BTU | MOL % | BTU/FT3 |
|---|---|---|---|
| N2 | 0 | | |
| CO2 | 0 | | |
| C1 | 909.4 | 93.79 | 852.9 |

| | | | |
|---|---|---|---|
| C2 | 1618.7 | 0.96 | 15.5 |
| | | TOTAL | 868.4 |

3. THE AMOUNT OF FUEL GAS VOLUME IS

= 805/868.4

= 0.927 MMCUBIC FEET PER HOUR

THE AMOUNT OF AIR IS EQUAL TO

PER MOLE OF C1, (1.2)(9.54 MOLES OF AIR ARE REQUIRED)

= 11.448 AIR MOLES

NOTE 9.54 = 2 MOLES O2* 1/.21 O2 AIR CONTENT

PER MOLE OF C2, (1.2)(3/.21)AIR MOLES ARE NEEDED

= 17.143 AIR MOLES

THERE ARE (0.927 MM CUBIC FEET/HOUR)(0.9379 C1)*

(1/23.654 POUNDS M/CUFT)(1/16.043 # M/#)

= 2291.1 # MOLES C1

THERE ARE LIKEWISE

(0.927)(0.0096)(1/12.62)(1/30.07)

= 23.45 # MOLES C2

THEREFORE THE AMOUNT OF AIR IS EQUAL TO

= (11.448) * 2291.1 + 17.143 (23.45)

= 26630.5 # MOLES PER HOUR

MMSCFH = 26630.5 * 28.9625 * 13.103

= 10.106

TOTAL VOLUME OF FUEL = 11.033 MMSCFH

4. THE DETAILED STORCHIOMETRY IS NOT NEEDED TO DEVELOP THE COMPOSITION OF THE FLUE GAS, AND APPROXIMATION BASED ON PUBLISHED LITERATURE (GPA DATA BOOK PG. 8-11) WILL BE USED:

PER CUBIC FEET OF GAS, DRY BASIS

| | |
|---|---|
| N2 | 86 % |
| O2 | 4 % |
| CO2 | 10% |

18 % H2O WOULD BE GENERATED, THEREFORE ON A WET BASIS

| | | |
|---|---|---|
| H2O | 18 % | 1.99 CUBIC FEET OF EMISSION |
| N2 | 70.5 % | 7.78 |
| O2 | .36 % | .36 |
| CO2 | 8.2 % | .90 |

ADDITIONALLY NOX AND CO WILL BE GENERATED ON A BASIS OF 0.01716 POUNDS AND .0005 RESPECTIVELY PER 100,000 BTU/HR

THIS WILL RESULT IN NOX EMISSIONS OF 13,814 #/HR AND CO EMISSIONS OF 414 #/HR.

COMPRESSOR DRIVERS (SOURCE COMPILATION OF EMISSIONS DATA FOR STATIONARY RECIPROCATING GAS ENGINES AND GAS TURVINES IN USE, NATIONAL GAS PIPELINE TRANSMISSION INDUSTRY)

BASIS: 89 UNITS WITH WASUKESHA L5108GU PRIME MOVERS

| | |
|---|---|
| BAROMETER, IN. HG. | 29.94 |
| AMBIENT TEMP F | 73 |
| INLET MANIFOLD TEMP F | 83 |
| EXHAUST WEL. FT/SEC | 71.00 |
| SP HUMIDITY GRAIN/# | 27 |
| ENGINE SPEED RPM | 822 |
| HORSEPOWER | 442 |

| | |
|---|---|
| SCAV.AIR PRESS IN. HG. | -11.0 |
| IGNIT. TIME DE BTBC | 20.0 |
| FUEL SPEC GR | .634 |
| CALC. EXH. FLOW #/HR | 2957 |
| AIR FLOW WET #/HR | 2785 |
| EXH H2O % | 19.09 |

EMISSIONS, #/HR

| | #/HR | TONS/YR | TOTAL TONS/YR |
|---|---|---|---|
| NOX | 3.222 | 14.1 | 1256 |
| HC | 3.849 | 16.9 | 1500 |
| CO | 37.250 | 250.8 | 22317 |

CATALYST REGENERATION EXHAUST (SOURCE DEVELOPMENT WORK INTERNAL COMMUNICATION K. ROCK TO R.CARVER, DAVY McKEE CORP., JAN. 1990)

BASIS: 8832 HOURS/YEAR
IN SCFH

| COMPONENT | START | 5 MIN | 10 MIN | 15 MIN | 20 MIN | 30 MIN | 60 MIN |
|---|---|---|---|---|---|---|---|
| N | 30240 | 30240 | 30240 | 35283 | 35283 | 74279 | 74279 |
| O | 240 | 480 | 7320 | 9378 | 9378 | 19145 | 19745 |
| CO2 | 10560 | 7920 | 1080 | - | - | - | - |
| CH | 3240 | - | - | - | - | - | - |
| OTHER | 30360 | 2400 | - | - | - | - | - |
| TOTAL | 74640 | 41040 | 38640 | 4661 | 44661 | 94024 | 94024 |
| MOL WT | 19.195 | 29.627 | 29.215 | 28.850 | 28.850 | 28.85 | 28.850 |

FLUE GAS REGENERATION CYCLE ONLY

| | |
|---|---|
| N | 23458 |
| O | 4681 |
| CO2 | 1753 |
| H2O | 1326 |
| NOX | 10.343 |

TOTAL 31228.3426 POUNDS PER HOUR

SCOT INCINERATOR

BASIS ONE UNIT FEED FROM FOUR AMINE UNITS AND ONE THREE BED CLAUS UNIT,

THE INCINERATION OF THE ABSORBER RESIDUE WILL RESULT IN

SOX 40 PPMV DRY PER "PROCESSES CLEAN UP TAIL GAS", OIL AND GAS JOURNAL, AUG.28, 1978, PAGE 161.

THEREFORE 40 PPMV SO2 IN THE TAIL GAS VERSUS INLET OF 4.3 WET PERCENT IN 85,000 B/D CRUDE (SP GR = 0.945)

= 85,000B/D * 42 G/B *(.945) (8.33 #/G)

= 28102504.5 #/DAY OF CRUDE

THEREFORE #/DAY S = 1208407.69

% OF SULPHUR RECOVERED IS =

$$.67 + .62(1-.67) + .82\ (1-.67-.2046) + .64\ (1-.9799) + .63\ (1-.991)$$

$$= \quad .9968 \text{ OR } 99.68\ \%$$

PERCENTS WERE TAKEN FROM CAPABILITY OF THE MODIFIED CLAUS PROCESSES , HAROLD G. PASKALL, PRESENTED TO THE 1979 GAS COND. CONF. NORMAN, OK.

BASED ON 40 PPMV SO2 IN TAIL GAS AND 0.32 % OF THE INLET GAS

THEN

#/DAY = (1208407.69 #/DAY) (.0032)

= 3866.9

OR 705.7 TONS PER YEAR OF SO2 COMPOUNDS EMITTED

# APPENDIX C

## CALCULATION OF RAIN/STORMWATER VOLUME

BASIS:

40 INCHES OF RAIN PER YEAR
1/4 SQUARE MILE SITE

CALCULATION:

= 1/4*(5280)**2FT**2 * 40 INCHES/YR * FT/12 INCH

= 23,232,000 CUBIC FEET PER YEAR

ASSUME 62.4 POUNDS PER CUBIC FEET

= 23232000 * 62.4 * TON/2000 POUNDS

= 724,838 TON PER YEAR

# VITA

Ronnie G. Carver

Candidate for the Degree of

Master of Science

Thesis: WASTE MANAGEMENT OPTIONS FOR UNITED STATES REFINERIES

Major Field: Environmental Engineering

Biographical:

Education: Received High School Degree from Pryor High School, Pryor Creek, Oklahoma in 1971.

Received B.S., Chemical Engineering, from Oklahoma State University, Stillwater, Oklahoma in 1975.

Received Masters of Chemical Engineering, from Oklahoma State University, Stillwater, Oklahoma in 1976.

Receiving a Masters of Science, Environmental Engineering, from Oklahoma State University, Stillwater, Oklahoma in December, 1992.

Profession Experience: I joined Cities Service Co. in 1976 as a project engineer. Named Operations Supervisor in 1978, and after a series of positions, named Manager, Measurement Development for the successor company, Occidental Oil and Gas Co. in 1985. I resigned in 1989 to pursue a M.S. in Environmental Engineering. While in school, I worked as Senior Process Engineer and later as Principal Environment Engineer for Davy McKee Ltd. In 1991, I was named to the position of Manager of Measurement and Environmental Affairs with Arkansas Western Gas Company. Areas of emphasis during my career include gas processing, MTBE/ETBE/STAR process development, custody transfer measurement, waste minimization, and major computer program development.

My registrations as a professional licensed to practice include:

| | |
|---|---|
| State of Oklahoma | 1984 |
| State of Texas | 1990 |
| State of Arkansas | 1991 |
| Registered Environmental Professional | 1992 |

My memberships in industrial societies includes:

American Institute of Chemical Engineers
American Petroleum Institute
Gas Processors Association
Air and Waste Management Association
Arkansas Federation of Land And Water Users