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# **Water Pollution Prevention Opportunities in Petroleum Refineries**

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# Table of Contents

Section	Page
<b>Acknowledgments</b>	<b>1</b>
<b>Introduction</b>	<b>2</b>
<b>A Summary</b>	<b>3</b>
Recent History of Pollution Prevention Activities in Refineries	3
Findings from Refinery Questionnaire	4
Selected Pollution Prevention Opportunities	5
Pollutants of Concern	5
<b>B Summary of Pollution Prevention Projects In The Refining Industry</b>	<b>7</b>
Pollution Prevention in U.S. Refineries Outside Washington	7
General Refinery Operating and Maintenance Practices	8
Minimization of Tank Bottoms	8
Improved Oil Recovery from Sludge	10
Minimization of Desalter Solids and Oil Under Carry	10
Minimization of Spent Filter Clay Disposal and Hydrocarbon Losses	11
Minimization of Loss of Solids from Heat Exchanger Cleaning	12
Control of Other Solids from Various Sources	13
Minimization of Surfactants in Wastewater	15
Minimization of Leaks, Spills and Other Losses to Sewer	15
Stormwater and Wastewater Segregation and Flow Reduction	16
Replacement of Drums with Storage Tanks	17
Minimization of Sample Losses to Sewer System	17
Minimization of Benzene Losses to Sewer System	17
Minimization of Spent Catalyst Waste	17
Alternative Disposal for Alkylation Unit Sludge	19
Minimization of Amine Losses and Sludge Generation in Amine Units	19
Minimization of Sludge from Residual Upgrading Processes	20
Minimization of Mercury Losses	20
Minimization of Hazardous Materials Use	20
Company Direction and Employee Motivation	21
Process Unit Design Modifications	21
Spent Caustic Recycle	21
Use of Oily Sludge as Coker Feedstock	21
Desalter Improvements	21
Alternative Projects	22
Plant-Wide Projects	22

## Table of Contents (continued)

Section	Page
<b>B</b>	
<b>Summary of Pollution Prevention Projects In The Refining Industry (continued)</b>	
Utility System Modifications	23
Minimization of Cooling Tower Blowdown Rates and Pollutants	23
Segregation of Boiler Blowdown	24
Pollution Prevention in European Refineries	24
Storage and Handling Systems	25
Crude Oil Desalting	25
Amine Treating	26
Sour Water Stripping	26
Optimization of Water Use	26
Pollution Prevention Programs of Washington Refiners	27
General Refinery Operating and Maintenance Practices	27
Minimization of Tank Bottoms	27
Improved Oil Recovery from Sludge	28
Minimization of Desalter Solids and Oil Under Carry	28
Minimization of Spent Filter Clay Disposal and Hydrocarbon Losses	28
Minimization of Loss of Solids from Heat Exchanger Cleaning	28
Control of Other Solids from Various Sources	28
Minimization of Leaks, Spills and Other Losses to Sewer	29
Stormwater and Wastewater Segregation and Flow Reduction	29
Replacement of Drums with Storage Tanks	29
Minimization of Sample Losses to Sewer System	30
Minimization of Benzene Losses to Sewer System	30
Minimization of Spent Catalyst Waste	30
Minimization of Amine Losses and Sludge Generation in Amine Units	30
Minimization of Mercury Losses	30
Minimization of Hazardous Materials Use	30
Process Unit Design Modifications	31
Spent Caustic Recycle	31
Use of Oily Sludge as Coker Feedstock	31
Dioxins and Furans	31
Reactor Optimization	31
Gasoline Treating Process Change	32
Utility System Modifications	32
Application of Pollution Prevention Principles in Process Design	32

## Table of Contents (continued)

Section	Page
<b>C</b>	<b>Key Findings From Refinery Questionnaires</b> <b>34</b>
	Wastewater Quantities and Sources 34
	Recovered Slop Oil 34
	Wastewater System Solid Waste Disposal 35
	Specific Pollutants 35
	Dioxin and Furan 35
	Mercury 35
	Polycyclic Aromatic Hydrocarbons (PAH) 37
	PCBs 37
	Miscellaneous Wastewater Pollutant Loads 37
	Soil 37
	Catalyst 37
	Scale and Rust 37
	Tank Bottoms 37
	Other Pollutants of Concern 38
<b>D</b>	<b>Analysis of Selected Pollution Prevention Opportunities in Refining</b> <b>39</b>
	Parallel Sour Water Stripping (Segregation) 39
	Eliminate Caustic Washing of Kerosenes and Medium Diesels as Part of Ultra-Low Sulfur Diesel Programs 41
	Secondary Benefits from Upgrading Olefinic FCC LPG Treating and Adding Alkylation Unit Feed Treating 43
	Examples of Pollution Prevention Opportunities Rejected by Refiners 45
	Washing and Steaming of Jet Fuel Treater Clay 46
	Use of Cyclones to Reduce Coke Fines 46
	Evaluate Various Oily Water Sewer Source Reduction Methods 46
	Purchase Crude Oil with Lower Solids Content, Tighten BS&W Specifications, and Change to Lighter Crude Oil Slate 46
	Reduce Cooling Tower and Boiler Blowdown 47
	Regenerate Spent Catalyst through Catalyst Suppliers 47
<b>E</b>	<b>Key Findings Relative to Pollutants of Concern</b> <b>48</b>
	Persistent Bioaccumulative Toxins 50
	Dioxin and Furan Formation in Refining Processes 50
	Catalytic Naphtha Reforming 50

## Table of Contents (continued)

<b>Section</b>	<b>Page</b>
<b>E</b>	<b>Key Findings Relative to Pollutants of Concern (continued)</b>
	Isomerization 53
	Polyaromatic Hydrocarbons 54
	Polychlorinated Biphenyls (PCBs) 54
	Toxic and Other Priority Metals 54
	Surfactants and Dissolved Solids 54
	Priority Pollutant Metals 55
	Metal Contaminants in Crude Oil 55
	Other Sources of Metals in Refining Effluent 57
	Mercury 57
	Chromium 57
	Antimony 58
	Chemicals Posing Threat of Wastewater Treatment Upset 58
	Other Pollutant Loadings to Wastewater Systems 58
	Soil and Sand 59
	Catalyst 59
	Coke Fines 59
	Scale and Rust 59
	Hydrocarbons and Tank Bottom Materials 59
	Stormwater Overflow to Wastewater System 60
	Materials Leading to Presence of Dangerous Wastes 60
<b>F</b>	<b>Summary of One-Day Workshop Results 61</b>
<b>G</b>	<b>Contractor's Assessment of Pollution Prevention Project Value 63</b>
<hr/>	
	<b>References / Bibliography 64</b>
	<b>Appendix 1: Refining Processes and Wastewater Sources 66</b>
	<b>Appendix 2: Washington Refinery Process Configurations 74</b>
	<b>Appendix 3: Workshop Presentation Materials 79</b>
	<b>Glossary 88</b>

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# Introduction

The State of Washington Department of Ecology retained the services of Jacobs Consultancy Inc. to perform a study for the purpose of identifying ways to reduce or avoid water pollution through pollution prevention opportunities that may be applicable to Washington refineries.

As stated by the Department of Ecology in its Request for Qualifications and Quotations (RFQQ) for this study, “pollution prevention strategies focus on selecting or changing in-plant processes or materials so as to avoid or reduce the use or generation of wastes harmful to the environment or to environmental control systems...[and] avoid shifting pollutants from one environmental medium to another.” Such strategies are aimed at source reduction rather than treatment or disposal and could include “changing process design, operational methods or procedures, maintenance practices, or selection of raw materials or chemicals used.” Other objectives are “to reduce the impacts of process-generated pollutants on treatment systems and the environment” and “to promote efficient use of materials through such methods as in-process or in-plant recycling of materials or wastes.”

The study consisted of the following basic steps:

- Identifying Candidate Pollution Prevention Strategies
  - Performing a literature search of past pollution prevention projects and philosophies in the refining industry
  - Determining the refining process configurations of the five Washington refineries
  - Developing a questionnaire to distribute to the refiners and requesting their voluntary responses regarding pollution prevention practices and data relative to the Pollutants of Concern defined by the Department of Ecology
  - Evaluating questionnaires and literature search results to identify pollution prevention opportunities and analyzing the applicability of the more promising opportunities, with special consideration given to the Pollutants of Concern
  - Addressing special topics, including the formation of dioxins and furans in catalytic reforming processes and means to reduce or eliminate their production, and others identified as relevant to Washington pollution prevention efforts.
- Conducting a One-Day Seminar
  - Conducting a one-day seminar for the Washington refiners and the Department of Ecology to present the findings of the study and to stimulate interaction and discussion about pollution prevention opportunities
  - Preparing a written summary of the seminar results to be included in the final report
- Preparing the Final Report

The following report presents the results of this study.



# Section A. Summary

A summary of the important findings and results of this pollution prevention study are presented below. References are given to the corresponding section of the report in which more detailed discussions are located.

## Recent History of Pollution Prevention Activities in Refineries

Based on a literature search and discussions with refiners, engineering design company technical staff, and selected refinery technology vendors, we find that refiners in the State of Washington, the rest of the United States, and Europe all appear to have examined very similar pollution prevention opportunities over the last decade or more. Section B of this report discusses these projects. The heaviest focus for pollution prevention activities in refineries has been in the area of general operating and maintenance practices and procedures, with much of the emphasis placed on reducing losses of hydrocarbons and solids to the wastewater systems. Loss of hydrocarbons results in both lost product and revenue, and loss of solids increases sludge formation and incurs additional disposal costs.

Some of the projects in this category are relatively inexpensive to implement (some involving primarily housekeeping improvements), and such projects have been widely adopted. In general, pollution prevention projects are selected based on economic considerations (expected cost to implement versus likelihood of achieving expected savings). Some projects that have been implemented in one or more refineries were rejected in others. The results of the literature search suggest that the operating and maintenance related projects attracting the greatest interest and activity include the following:

- Minimization of tank bottoms
- Improved oil recovery from sludge
- Minimization of desalter solids and oil under carry
- Minimization of solid losses from heat exchanger cleaning
- Control of solids from sources other than heat exchangers
- Minimization of leaks, spills, and other losses
- Segregation of stormwater and wastewater
- Stormwater and wastewater flow reduction
- Minimization of sample losses
- Minimization of spent catalyst waste
- Minimization of amine losses
- Minimization of cooling tower blowdown
- Segregation of boiler blowdown

Refiners have also looked at more fundamental changes involving design revisions and modifications to various refining processes. Such projects generally involve greater investment and are not always readily justifiable on an economic basis for existing, older facilities. The types of projects that have been evaluated in this category have been fairly wide ranging, but due to both feasibility and economic

considerations, these projects are not always found to be as attractive as those listed above for operating and maintenance procedures. Examples of process modifications evaluated include the following:

- Spent caustic recycle
- Use of oily sludge as feedstock to coking units
- Modifications to crude unit desalter internals
- Development of solid catalysts to eliminate liquid acid catalysts in alkylation units
- Modification or replacement of shell and tube exchangers
- Reactor optimization
- Evaluation of water reuse (process water minimization)
- Process energy or pinch analysis to reduce cooling tower and once-through water usage.

Although fundamental design changes to achieve pollution reduction are less prevalent than changes in plant operating and maintenance procedures, we find that refiners and the engineering design companies who design and construct refinery facilities now employ work processes and procedures that incorporate waste minimization and pollution prevention as inherent aspects in the evaluation and design of new facilities. Procedures are well established for the identification of pollutant sources and the thorough analysis of alternatives for source reduction and elimination. Pollution prevention strategies ensure first that regulatory compliance is achieved by a proposed new project and include additional measures based primarily on economic factors.

## Findings from Refinery Questionnaire

To assist in evaluating the status of pollution prevention activities in Washington refineries, the consultant distributed a confidential questionnaire to the five major refineries in the state. The questionnaire covered basic information of wastewater sources and flows, wastewater processing, handling of common sludges and solids sources, general data regarding various pollutant sources, and some of the pollution prevention techniques in place. The data received in the responses by the refiners is discussed further in Section C.

Key items from the survey are as follows:

- Major components of refinery wastewater include desalter effluent, cooling tower blowdown, stripped sour water, once-through cooling water, condensate and stormwater.
- Recovered slop oil is mainly routed back to the crude distillation unit, although some is sent to delayed cokers or various conversion units (*e.g.*, the fluid catalytic cracker) depending on composition.
- All of the refineries reporting have a method of dewatering API separator sludge. Sludge disposition is handled offsite by thermal desorption, cement kiln processing, or incineration. Where the alternative is available, primary sewer sludge is sent to a coker for use as feedstock. Otherwise, it is sent offsite for incineration or to a cement kiln for processing.
- All respondents report that the major source of mercury in their facilities is crude oil. Some reported past processing of crude oils with relatively high mercury levels, but they indicated that they no longer use these sources. None of the refineries is believed to be currently processing any crude oils with high levels of mercury.

## Selected Pollution Prevention Opportunities

Because most refiners have evaluated similar types of pollution prevention projects, and because there has already been extensive study of opportunities in basic plant operating and maintenance procedures, future developments in pollution prevention in refining will likely come in the form of future process modifications. We have identified in Section D some ideas that are being evaluated but, to the best of our knowledge, they have not yet been fully implemented in the refining industry. These potential projects include the following:

- Separation of wash water and sour water strippers
- Elimination of caustic washing of kerosenes and medium diesels
- Pollution prevention benefits from upgrading olefinic FCC LPG treating and adding alkylation unit feed treating.

## Pollutants of Concern

The Washington Department of Ecology had identified Pollutants of Concern in various categories, as discussed further in Section E. This is a broad list that encompasses pollutants from a variety of industries and is not limited to refining operations. We have reviewed this list and identified key pollutants that are refinery related for further discussion. The key findings from this review are as follows:

- Dioxins and furans are Pollutants of Concern in the category of Persistent Bioaccumulative Toxins. While generally not associated with refining operations, very small quantities of these compounds can form during catalyst regeneration in catalytic naphtha reformer units, and even smaller amounts can form in some isomerization units. With current technologies, it seems very unlikely that the conditions which promote dioxin and furan formation could be eliminated. However, it might be possible to divert regeneration flue gases from a catalytic reformer into a furnace firebox to destroy these compounds, or a filtration system might also be a potential means of removing them from the neutralization stream in the regeneration process.
- The quantities of dioxins and furans generated in reformers and isomerization units are extremely small. The wastewater treatment plants at the refineries that have undertaken dioxin and furan studies appear capable of removing most of these compounds from the wastewater systems, with much of them being captured in sludge, so that only a very small percentage of those that are fed to the wastewater treatment plant appears in the final effluent.
- Priority Pollutant Metals is another category of Pollutants of Concern. The largest single source of metals encountered in crude oil refining is the oil itself. Various crude oils have different levels of metal contaminants. The metal of most concern in crude oil is mercury, the concentration of which can vary widely from one crude oil source to another. Mercury is important to refiners as a pollutant, as a cause of corrosion in process units, and as a catalyst poison. Except for certain California crude oils, mercury levels in domestic crude oil are generally not of concern. Among imported crude oils, certain Asian oils have high mercury content, but most other sources are not of concern. Recent research has indicated that average levels of mercury in U.S. crude oil sources have generally been overestimated, and further work is underway to evaluate the mercury content of various U.S. crude oils.

- Amines are a group of organic compounds that represent a threat to the operation of wastewater treatment units. Their presence can raise the pH of the wastewater and release ammonia in excess of the levels needed by the biological organisms, thereby interfering with treatment operations in two ways. Amines are used to absorb hydrogen sulfide from by-product fuel gas, and various amines are available to meet the operating requirements of different units. In general, refiners maintain close control of amine units because of their ability to upset wastewater treatment operations. It is rare for a refinery to experience a major upset due to amine losses to the wastewater sewer.

## **Section B.**

# **Summary Of Pollution Prevention Projects In The Refining Industry**

The focus of pollution prevention activities in this study is on source reduction of both wastewater streams and solid wastes that affect the quality and quantity of refinery wastewater. This section of the report addresses the pollution prevention projects that have been undertaken in the refining industry over approximately the last ten to twelve years. We begin by reviewing projects in refineries outside the State of Washington. Information is most readily available for refinery projects in the United States, but we also identified information for European refineries. We then compare the programs outside Washington with those of Washington refiners. One topic of interest that arose during the study was the extent to which refiners and engineering design firms integrate pollution prevention practices into the evaluation and design of proposed new projects. We have therefore added a brief discussion of this topic at the end of this section.

In our review of various pollution prevention projects in refineries, we took note of those that may pertain to the specific Pollutants of Concern identified by the Department of Ecology. We found only limited references to these pollutants, and we mention them in the following discussion.

## **Pollution Prevention In U.S. Refineries Outside Washington**

Projects focusing on source reduction for pollution prevention have been undertaken in the U.S. refining industry for well over a decade. Most of this activity has been directed toward improvements in operating and maintenance practices requiring small to moderate levels of capital investment, but there has also been some emphasis on more basic processing modifications by refiners in conjunction with the licensors and contractors serving the industry. Not surprisingly, many refiners have evaluated similar projects. They have made decisions to implement or reject candidate projects based on site-specific, case-by-case evaluations. Thus, projects that have been adopted in one refinery may have been rejected in another based on the particular operating and financial conditions applicable at each refinery. (In Section D, we present examples of projects reported to have been rejected by some refineries. Similar projects can be found among those that have been implemented in other refineries.)

For the most part, source reduction efforts have been focused on general parameters (*e.g.*, reducing overall sewer flow rates, preventing hydrocarbon losses to the sewer, and limiting sludge formation by curtailing the flow of sand, soil and other solids into the sewer system). However, some projects have targeted specific pollutants. Described below are pollution prevention projects evaluated in one or more U.S. refineries outside the State of Washington. In many instances, refiners have reported proposed projects that were under study without indicating the eventual findings of their evaluations. Thus, the current status of many of these projects is not reported in the literature. It is beyond the scope of this project to track the current status of specific projects and to determine if they were actually implemented. However, as noted above, successful implementation of these projects in any specific refinery will depend on conditions applicable to that refinery. The main purpose of our literature search is to identify candidate projects that may be appropriate for consideration in the Washington refineries and not necessarily to identify projects that were eventually implemented elsewhere.

# General Refinery Operating and Maintenance Practices

The majority of pollution prevention activity described in the literature pertains to improved operating and maintenance practices. The loss of hydrocarbons to the oily water sewers, the prevention of sludge formation, and recovery of hydrocarbons from sludge are of great importance to refiners. These and other projects are summarized below.

## Minimization of Tank Bottoms

Storage tanks in refineries tend to collect solids and water over time. This tendency is especially prevalent in crude oil storage tanks and in intermediate to heavy product storage tanks (*e.g.*, residual fuel oil). Raw crude oil as produced contains small amounts of solids, salt, and water that are commonly referred to as bottoms sediments and water, or BS&W, that tend to corrode and foul downstream equipment and poison catalysts in processing units downstream of the crude oil fractionation unit. It is therefore necessary to remove this material somewhere in the process.

We note that lighter, more expensive crude oils generally contain less BS&W than heavier crude oils. However, light crude availability has been declining for many years, and heavier crude oils with more BS&W represent a larger portion of refinery feedstock. For most refiners, it is simply not economical to process lighter crude oils for the sole purpose of reducing crude tank bottoms and desalter sludges.

BS&W generally deposits in the bottoms of the crude oil storage tanks over time. Water that collects on the bottom of these tanks is generally drained off, but the solids will continue to accumulate in the bottom. This accumulation over a period of years will reach a level necessitating tank cleaning. Some refiners operate tank mixers that sweep across the crude tank bottoms to keep the BS&W in suspension with the crude oil so that the BS&W is transferred to the desalter. This practice does not reduce the quantity of waste that is generated; rather, it shifts this material to the desalter, where it is removed, treated, and collected for disposal. (See item 4 below.)

Since crude oil unloaded from tankers or received by pipeline has generally not undergone any processing, it is particularly likely to contain significant quantities of water and solids, including rust and scale washed from cargo holds of crude oil tankers after the crude oil has been unloaded. Any heavy metals that are present in the particular crude oil being refined may appear in the bottoms of the crude oil storage tanks. Projects that have been listed in the pollution prevention literature include the following<sup>1,2,5,6,15,17</sup>.

1. Evaluation of improved methods to separate oil and water layers in the bottom of tanks were reported by many refineries, including the use of surfactants and more efficient wash procedures when tanks are taken out of service for bottoms removal and cleaning. (Even though the Department of Ecology lists surfactants as a Pollutant of Concern, this is an application where their use can be beneficial in reducing overall pollutant loads to refinery wastewater. The cost of the surfactants must be weighed against possible reduction in tank cleaning costs.) Several refiners reported unspecified methods to improve procedures for tank cleaning and to improve means of separating water and solids from both tanks and process streams. One facility reports installing sumps and sloping tank bottoms in new storage tanks to facilitate draining of water and sediment layers, thereby improving separation and minimizing the amount of product that contaminates the wash water when tanks are emptied for cleaning. This practice will

reduce the oil content of the tank bottom sludges, possibly reducing future tank cleaning costs.

2. Use of filtration and/or centrifugation to recover oil from tank bottoms for recycling to the crude unit or other appropriate process unit has been considered in many refineries. Projects reported mention different types of filters and centrifuges, but insufficient details were reported to differentiate performance by type of unit. Applications are case specific and depend on the quantity and type of material processed. Projects for optimizing the use of filter pre-coat were reported both as cost reduction measures and as means to minimize solid waste generated from these oil recovery operations. The cost of filtration and/or centrifugation must be weighed against other tank sludge disposal methods, such as incineration. Whether this option is economical depends on the specific refiner's waste disposal volumes and costs.
3. Some crude oil storage tanks contain an external floating roof that floats on the surface of the oil and moves with the oil level in the tank. This design minimizes crude oil evaporation losses and VOC emissions to the atmosphere. (Environmental regulations require VOC emission controls such as floating roofs, internal floating covers, or high efficiency vapor recovery systems with vapor tight return lines for crude oil tanks. Specific requirements vary from state to state and are often a function of the size of tank, the specific material stored, and whether the tank is located in an ozone non-attainment area where greater restrictions apply to VOC emissions.) The external floating roofs are exposed to rain and must be equipped to allow drainage from the roof surface. Some tanks allow rain to drain directly into the crude oil, while others have flexible internal piping to allow the water to drain to the outside of the tank. If the tank roof is kept free of hydrocarbons, this water can be discharged as stormwater and can bypass the process wastewater system. Some refiners are installing geodesic domes over their external floating roof tanks to minimize air emissions. As a side benefit, these domes prevent rain from reaching the surface of the external floating roof tanks. Several refiners have noted projects to improve maintenance and repair of tank roofs to minimize rain as a source of water in tank bottoms, thereby minimizing the potential flow of water to the oily sewer system (or, in some cases, to off-site disposal as hazardous waste) and the quantity of water fed to oil recovery operations, such as noted in item (2) above. Decisions regarding implementation of such repairs are made based on case-by-case considerations of the extent of roof damage, the cost of repairs versus the cost of water recovery/disposal, average rainfall amounts, and related factors. Details regarding the extent of damage and the type of repairs needed were not cited.
4. Several refiners have evaluated the installation of permanent mixers in tanks to entrain solids and heavy hydrocarbons, thereby minimizing their separation from oil in the tanks. Such mixers minimize the quantity of solids and water and heavy hydrocarbon layers to be removed from a tank, but of course consideration must be given to the eventual destination of these materials and eventual distribution of these solids, heavy hydrocarbons and water in the downstream process units. The solids must be removed in downstream raw crude oil desalting. Two-stage desalting is generally required to lower the water and solids content to acceptable levels to minimize downstream fouling, corrosion, and catalyst poisoning.
5. At least one refiner has evaluated filtration of products and intermediates upstream of selected storage tanks to remove solids and prevent sludge buildup in the bottoms of these tanks, thereby eliminating a source of sludge to the oily water sewer system during

tank cleaning. This approach would generally be applicable only to less viscous streams with relatively small quantities of solids so that such filters would not be subject to high pressure drop or need frequent cleaning. Conclusions from this evaluation were not reported. Many refiners have upstream coalescers to minimize the water content in the hydrocarbon streams (other than crude oil) going to storage tanks. A coalescer takes advantage of the high surface tension of water to promote the combination of smaller water droplets into larger drops that can then disengage from the oil phase to form a separate water phase. This unit typically consists of a horizontal vessel with a series of parallel wire mesh screens that collect water droplets as the stream flows across the vessel. The water then drains down the screens and is collected in the bottom of the vessel.

## Improved Oil Recovery from Sludge

In addition to considering projects to recover oil from tank bottoms as noted above, numerous refiners have also evaluated means to improve recovery of oil from various sludges, including wastewater sludges<sup>1, 4, 5, 15</sup>. Projects have included the following:

1. Various refiners have considered installation of belt filter presses, rotary vacuum filters and other types of filters as well as centrifuges, driers, and centrifuge-drier combination units. Both batch and continuous operations have been studied.
2. Self-cleaning, reusable filters have been evaluated for some sludge filtration applications with mixed results.
3. Thermal treatment has been evaluated to minimize water and volatile components in sludges and to allow recovery of some of the hydrocarbons in a vapor phase. There are two general types of thermal desorption: low temperature and high temperature. In the low temperature process, water and light hydrocarbons are removed from sludge. The recovered water is treated in the refinery wastewater treatment unit, and recovered hydrocarbons are re-processed. High temperature thermal desorption processes heat the waste to over 1000°F, removing the water and most of the hydrocarbons. In many cases, high temperature thermal desorption can allow a listed hazardous waste to be de-listed, assuming the proper regulatory approvals are obtained. Thermal desorption can reduce the waste mass that has to be disposed by as much as 90%. However, the cost of thermal desorption has to be weighed against the cost for a more traditional hazardous waste disposal. (Generally, the refiner has to have a capacity of greater than 150,000 BPD for this approach to be economical.)

## Minimization of Desalter Solids and Oil Under Carry

Desalting of crude oil upstream of the crude distillation unit is a key process operation for the removal of undesirable components from crude oil before it reaches any of the major unit operations. Crude oil typically contains salts that can cause corrosion and fouling of equipment when deposited on heat transfer surfaces, metals that can deactivate catalysts, solid debris (rust, scale, trash, *etc.*) from washing of vessel cargo holds after crude oil is unloaded (such wash water is typically pumped out into the crude storage units since the vessels have no way to treat it and are not allowed to dump it into the waterways), and other contaminants. Desalting is carried out by creating an emulsion of crude oil and water. The salts,



including salts containing some of the metals that can poison catalysts, are dissolved in the water phase. Demulsifying chemicals and electric fields are commonly used to break the emulsion.

Crude oil desalters are typically sized to allow the water and oil to settle according to Stoke's Law. Solids present in the crude will accumulate in the bottom of the desalter vessel. The desalter must be periodically washed to remove the accumulated solids. A "mud washing" system is installed in the bottom of the vessel to periodically remove the solids. Mud washing consists of recycling a portion of the desalter effluent water to agitate the accumulated solids so that they are washed into the effluent water. These solids are usually routed to the wastewater system. Some units have "hydroclones" that use centrifugal force to concentrate the desalter solids for further disposal.

The desalter water is a major source of contaminated wastewater (as confirmed by the refinery questionnaires discussed in the next section of this report) and a source of hydrocarbons as oil under carry to the extent that emulsions are not completely broken. At least one refiner has reported finding oil under carry to be the single largest source of oil losses to the oily sewer system, and many, if not most, refiners would concur with this assessment. Thus, improved demulsification not only reduces sewer loadings but also recovers valuable raw material that would otherwise be lost.

Operating and maintenance related pollution prevention projects considered to minimize the quantity and improve the quality of desalter water include the following<sup>1, 2, 3, 4, 6, 17</sup>:

1. Projects have been evaluated to improve emulsion formation by using low shear mixing devices to mix wash water and crude oil and by using low-pressure water to minimize turbulence. Modifications to a desalter are generally not relatively expensive as long as the desalter vessel itself does not have to be replaced. However, the desalting unit must be shut down for modifications to be made, and opportunities to make modifications may therefore be available only every three to five years.
2. Similarly, mud rakes have been evaluated as replacements for water jets to reduce turbulence when removing settled solids. Vendors of desalter equipment have a variety of mud-washing technologies available to remove desalter solids as they accumulate in the vessel.
3. At least one refiner reported success in optimizing use of chemical demulsifiers to minimize oil under carry. The project reviewed both the selection of demulsifiers being employed and the quantities used as a function of each crude oil supply source. Details of the demulsifiers tested and test parameters were not disclosed. All desalting units employ demulsifiers to optimize oil recovery and minimize oil under carry with the desalter effluent water. In practice, most refiners evaluate the performance of their demulsifier program every one to three years because demulsifier chemical vendors are constantly improving their product formulations to remain competitive.

Design-related desalter projects are noted in a subsection below titled "Process Unit Design Modifications."

## **Minimization of Spent Filter Clay Disposal and Hydrocarbon Losses**

Clay filtration is generally a finishing step (*e.g.*, to remove color and to ensure product clarity) that is commonly seen for treating distillate streams, such as diesel and kerosene. Different types of clay from

various filters used for adsorption of impurities in product streams must be replaced periodically as the clay becomes saturated with these impurities. Spent clay may contain relatively low to relatively high concentrations of hydrocarbons and would generally be classified as a hazardous waste unless the clay is recovered and regenerated for further use. To minimize the hydrocarbon content of the spent clay, refiners may back wash the filter with steam or water, a step that could result in some of the hydrocarbons reaching the oily water sewer system<sup>4, 5, 6, 17</sup>. Backwashing with a light hydrocarbon (*e.g.*, naphtha) before using water or steam can result in a high level of hydrocarbon recovery without appreciable losses to the sewer. If steam were then used to evaporate the naphtha, the steam could be directed to a fired heater so that no hydrocarbon would be lost to the sewer.

As ultra-low sulfur diesel fuel standards are implemented, more distillate hydrotreating capacity will be installed, thereby reducing the need for clay treatment of distillate streams in the future.

## **Minimization of Loss of Solids from Heat Exchanger Cleaning**

Petroleum refining is an extremely energy intensive industry, and fuel gas purchases are typically one of the largest budget items for a refinery. As a result, refiners closely monitor fuel consumption. One carefully monitored factor in refinery fuel consumption is heat exchanger fouling. Fouled heat exchangers are inefficient and can result in higher energy consumption and lower production capacity. Furthermore, heat exchanger solids are a major source of waste in most refineries. Refiners closely monitor the condition of their heat exchangers to minimize the possibility that a fouled exchanger could increase energy usage and limit process capacity. To keep exchangers operating at peak efficiency, refiners periodically remove them from service for cleaning. Cleaning of exchangers generates solid waste (designated as hazardous waste by the EPA and as dangerous waste by the State of Washington) but also lowers energy consumption.

Fouled exchangers can also directly affect discharges to the wastewater system. The crude oil desalting operation is a prime example of such a situation. For optimum desalting, it is critical that the crude oil feed to the desalters be maintained in an optimal temperature range (generally 250 to 300°F). Fouled heat exchangers can result in feed temperatures below the optimal range. Low desalting temperatures limit the oil/water separating capabilities of the desalter. Poor separation results in loss of oil in the desalter water layer with increases in the loss of hydrocarbons to the sewer. It also results in salts and solids that should have been removed in the water layer instead remaining in the crude oil phase where they will foul and limit downstream processing equipment. Such fouling inevitably leads to generation of additional solid wastes when these equipment items must be cleaned and leads to the potential loss of even more wastes to the sewer system.

Shell and tube heat exchangers are used widely throughout the refining industry for heating and cooling of process streams. When exchangers become fouled, solids are often removed by taking the affected exchanger out of service, removing the tube bundle, and hydro-blasting the solids with a high-velocity water stream. In the past, these solids were typically washed into the sewer system, where they promoted the formation of sludge. Refiners have undertaken several measures to prevent such solids from entering the oily sewer system<sup>1, 17</sup>. (See also the discussion of design changes and design alternatives below under the heading “Process Unit Design Modifications.”)

1. Installation of concrete overflow weirs around exchanger pads as well as around drains in or near exchanger pads has been completed in several refineries to retain solids from tube bundle cleaning operations that could otherwise reach the sewer system.

2. Temporary covers have been installed over sewer drains in many refineries during cleaning operations to keep exchanger solids from being washed into the sewers.
3. Some refineries report increased use of anti-foulants to minimize solids build-up on exchanger bundles.
4. One of the most widespread approaches now in use in the industry to minimize exchanger solids in the sewer is to clean bundles only in designated cleaning areas designed for solids containment.
5. In crude fractionating units, good desalter operation reduces the levels of solids and salt in crude oil that can deposit on heat exchanger tubes and therefore minimizes heat exchanger fouling, which in turn reduces the need for cleaning and the quantity of hazardous waste generated in cleaning operations. For heavy, high salt crude oils, two-stage desalting is typically required to achieve adequate reduction.

## **Control of Other Solids from Various Sources**

In addition to exchanger cleaning solids, there are several other sources of solids to oily water sewer systems in refineries<sup>1, 2, 3, 4, 5, 6, 17</sup>. One refiner reported that unit washdown activity was the main source of sewer sludge in its refineries (after isolating exchanger cleaning to a designated, controlled area), and all refiners seem to agree that washdown is certainly a major source if not the single largest source. Projects to minimize the solids content of oily water sewer systems accordingly account for a large number of pollution prevention source reduction projects. Other key sources of solids include cleaning of equipment other than heat exchangers, boiler water blowdown streams, and coke fines as well as various other slurry, blowdown and wash water streams.

Among the many projects reported to minimize these sources have been the following:

1. Many of the reported projects focus on the reduction of soil, sand and trash entering the sewer systems. Several refiners cited the use of street sweepers on paved areas to remove trash before it can be washed into sewers. Paving or planting ground cover on unpaved areas near sewers, increased inspection and maintenance to identify and repair sewer line breaks, re-lining sewers where needed, cleaning solids from ditches and catch basins, and vacuuming of solids where feasible were all mentioned by multiple refiners. Several refiners have used beds of small rock installed on earthen tank farm floors to impede entrainment of soil and sand in rainwater that falls on the tank farm areas. Use of curbs and berms has been reported to protect some sewer drains from solids in stormwater runoff and wash water. Erosion control pipe trenches and catch basins have also been studied in some refineries.
2. Losses of solids to sewers during maintenance operations have been the focus of projects for a number of refiners. Several refiners have eliminated use of sandbags or burlap bags topped with sand as covers to plug sewers during maintenance to avoid potential deterioration of the sandbags and spillage of sand into sewers. They have replaced sandbags and burlap bags with temporary seals, lead blankets or other commercial devices.
3. In related projects, methods of controlling and containing sandblast grit (which contains metal, old paint, and primer, some of which may contain lead) to keep it out of the sewer

system have been studied in several refineries. At least one refiner has segregated toxic sand blast media as well as segregating sand by the type of paint it is used to remove (*i.e.*, leaded and non-leaded).

4. As in the case of heat exchanger cleaning discussed above, more refiners are now confining selected maintenance activities to dedicated areas that are designed for solids and waste containment and recovery.
5. Absorbents (*e.g.*, diatomaceous earth, vermiculite) rather than sand are now used in several refineries for cleaning up oily surfaces. Such absorbents are much easier to remove than sand and require relatively little water wash for final cleanup. Some refiners have used detergents to clean-up oily spills, but this approach adds surfactants to the wastewater treatment loading.
6. One project reported was to identify by sampling any equipment clean-out material having a relatively low solids content that could be returned to the appropriate processing unit instead of being treated as waste for disposal. This approach would reduce potential losses to the sewers (and subsequent sludge formation), eliminate quantities of waste for offsite disposal, and recover material that can be further processed. Candidate streams would include recovered oil streams from numerous items of equipment removed from service. Each would be evaluated on an individual basis to determine if the solids content was low enough for return to the process. Candidates for sampling could include skim oil from oil/water separators, laboratory samples, the recovered oil tank at the wastewater treatment plant, material recovered from vacuum trucks, and others. There was no indication of which, if any, of these materials had been found to have a low solids content.
7. One refiner has been evaluating the use of cyclonic separators upstream of the API gravity separators to reduce the quantity of fines contributing to sludge formation in the separators. The success of such a project would be heavily dependent on the flow rates, concentrations of solids, and cost of installation and operation.
8. Fluid catalytic cracking units (FCCU) use a fluidized reactor bed with a catalyst similar in texture to fine beach sand. (Spent catalyst is typically land filled, but some refiners sell the catalyst to cement manufacturers as admix.) FCCU catalyst spills must be carefully controlled. While the catalyst itself is not hazardous, many refiners formerly washed the catalyst down the oily water sewer where it became hazardous sewer sludge. Most refiners now sweep and shovel all FCCU catalyst spills to minimize hazardous waste generation. The use of cyclonic separators has also been considered in catalytic cracking operations as a means of recovering catalyst fines and sending them to the FCCU regenerator, thereby keeping them out of the decant oil, where they would also promote the formation of sludge.
9. Several refineries have reported a reduction in the frequency of washing down process areas as a routine housekeeping method and instead use dry sweeping or other techniques to remove trash, dirt, and other debris.
10. Many refiners have emphasized projects for the recovery of catalyst fines around fluid catalytic cracking unit (FCCU) catalyst hoppers and coke fines around coking units and storage areas. Depending on the recovered material, it could be recycled, disposed of as a non-hazardous waste, or used as fuel. Refiners also reported modifications to

transportation and handling methods for FCCU catalyst fines removed in the unit's electrostatic precipitator to reduce spillage onto the ground and into the sewer systems.

11. Projects have also been evaluated to employ filters at sewer drains in coking units to keep coke fines out of the oily water sewer. The use of hydroclones to recover fines that do escape into the sewer has also been evaluated in at least one refinery.

## **Minimization of Surfactants in Wastewater**

Surfactants entering the refinery wastewater system will increase the amount of emulsions and sludges generated<sup>1, 17</sup>. Surfactants are one of the Pollutants of Concern listed by the Department of Ecology because of their potential to pose a toxicity threat to aquatic organisms and to the biomass in activated sludge treatment processes and because they can interfere with the settling processes in wastewater treatment systems. Surfactants are used in various cleaning and washing operations and in high end point gasoline treating operations. Although surfactants are necessary for refining operations, refiners recognize the need to control surfactant use more closely. In particular, they have promoted efforts to educate and supervise operators to prevent overuse in cleaning operations. Dry cleaning techniques and use of high-pressure water or steam to clean oil and dirt where practical have also been promoted. Conventional degreasers can be replaced in many applications with power washers that do not generate spent solvents for disposal and treatment.

## **Minimization of Leaks, Spills and Other Losses to Sewer**

Pollution prevention programs have prompted many refiners to intensify efforts to find and eliminate potentially numerous small sources of hydrocarbon losses to the sewer systems. In aggregate, such losses can result in noticeable increases in sludge formation and wastewater treatment loads. Many of the potential sources (*e.g.*, valves, pump seals, flanges) are already monitored periodically for fugitive air emission losses, but there are also other sources, such as underground piping. Projects to address potential sources include the following<sup>1, 4, 6, 17, 21</sup>:

1. Most refiners have undertaken projects for periodic inspection and repair of underground piping and/or replacement of such piping with above ground piping. Replacement has generally been the preferred option, especially in older refineries with known areas of soil and groundwater contamination from past operations. Many refineries have already completed projects to replace all of their underground piping.
2. Numerous refiners report on projects to monitor equipment more closely for sources of liquid leaks (*e.g.*, pump seals and lubricating systems at pump pads) and promptly repair any leaks that are found. Refiners have also eliminated oil leaks from pump seals by installing mechanical seals on selected pumps to replace the older style oil seal systems.
3. One refiner reported a project to identify all open-ended valves and ensure that plugs have been installed and are maintained on such valves. Valves in light ends service are required by environmental air regulations to be blinded or capped.
4. Several refiners have evaluated installation of tank overfill prevention systems in selected tanks to shut off flows into the tank automatically at a certain level. At least one proposed system was rejected for a crude oil storage tank, but the basis for the decision was not given,

and the specific refinery was not identified. It is not known whether any of these projects were implemented and if so, what shutoff system was selected.

5. At least one refiner has evaluated the benefit of installing pavement in place of bare ground or other surfaces under major pipe racks to facilitate leak detection.
6. One refinery considered and rejected the use of detectors to reduce oil drainage during tank draws and the use of automated water draws on product and crude oil tanks. The refinery concluded that for its circumstances, these measures would not be sufficiently reliable or cost effective.

## **Stormwater and Wastewater Segregation and Flow Reduction**

Almost all refineries have undertaken programs to separate stormwater and oily water sewers to reduce wastewater flows to the treatment plant, contamination of stormwater with hydrocarbons, and sludge formation<sup>2, 3, 4, 5, 15, 17, 21</sup>. Among the projects reported for this purpose are the following:

1. Dikes have been installed in selected process areas to prevent drainage of hydrocarbon bearing streams into stormwater sewers.
2. A common practice employed in many refineries is to impound stormwater from areas of potential contamination (*e.g.*, tank farms) for sampling to verify whether treatment is necessary (*e.g.*, the so-called first flush runoff from areas that may be somewhat oil contaminated but that are unlikely to produce contaminated runoff after a certain initial amount of rain has fallen).
3. A few refineries have evaluated use of collected rainwater as wash water for process use to minimize runoff flow rates, although the potential is largely limited to clean stormwater runoff that does not contain entrained soils and sand.
4. Projects have been reported to divert waste streams with primarily inorganic contaminants (*e.g.*, streams such as stripped sour water or boiler blowdown) directly to biological treatment downstream of the API separator and dissolved air flotation (DAF) unit to minimize sludge formation in these units.
5. Several refiners have evaluated methods to reuse and recycle wash water to the maximum extent possible. Applications as desalter feed water and wash water for further unit and tank washing were two key examples. One source noted that water injected into the crude and vacuum distillation unit overhead streams for corrosion control and condensed stripping steam are often suitable as desalter makeup water. Several sources noted that stripped sour water is also an excellent source of makeup water for the desalter.
6. Some older refineries have undertaken programs for surveying oily water and stormwater sewers with cameras and dyes to detect cross connections between the two systems. Eliminating cross connections will reduce stormwater intrusion into the oily water system and reduce the amount of hazardous waste generated in the oily water system.

## **Replacement of Drums with Storage Tanks**

Most refineries handle at least some bulk materials in drums. Proper storage and monitoring of drums generally minimizes leaks and spills, but the potential remains for losses due to improper handling and accidents, and operators must continually deal with inventory issues, removal of emptied drums, *etc.*<sup>1</sup>. Most refineries have evaluated the replacement of drums with small bulk storage tanks whenever it would be cost effective to do so.

## **Minimization of Sample Losses to Sewer System**

In the past (generally before 1990), samples of various process streams were often taken from sample lines by allowing the stream being sampled to flow into the sewer long enough to flush the line and then rinsing and emptying the sample container into the sewer several times to ensure that a representative sample had been collected. After analysis, the remaining sample was usually dumped to the sewer. With a large number of samples collected in various process units, sample stream losses became an appreciable source of hydrocarbon losses. Two measures have been reported by most refineries to control these losses<sup>2,4</sup>:

1. Closed loop sampling systems have been installed so that sample streams return to the process and are not sent to the sewer. In many cases, such systems were originally installed for benzene containing streams due to Benzene NESHAPS rules, but they are now employed in many refineries for all hydrocarbon streams. Closed loop systems can easily be installed to flow from a pump discharge line to a suction line on the same pump or to flow around a control valve.
2. Most refineries report that they now recycle laboratory samples of crude oils and samples of refined and intermediate product streams to their oil recovery systems after the laboratory has finished its analyses.

## **Minimization of Benzene Losses to Sewer System**

Benzene is one of the Pollutants of Concern as listed by the Department of Ecology. In addition to closed loop sampling systems noted above, projects to reduce benzene flows to the sewer system include the following<sup>1,3,4</sup>:

1. Several refiners have specifically noted that they segregate and recycle high benzene content streams, and it is our impression that virtually all refineries now do so.
2. Treatment of isolated benzene sources upstream of the wastewater treatment plant has been evaluated in some refineries, although no details of sources or treatment methods were reported.
3. In some cases, benzene containing wastewater streams have been isolated and fed to a stripping unit to recover the benzene before the stream goes to the treatment plant.

## **Minimization of Spent Catalyst Waste**

Crude oil as produced contains only relatively small amounts of two very important products, gasoline and diesel fuel. Catalytic processes have therefore been developed over the past 60 years to maximize the

yield of these products. These catalytic processes can generally be broken down into four major categories: reforming, cracking, hydrotreating, and alkylation.

- In the reforming process, light gasoline boiling range components (naphtha) are upgraded to high-octane blending stocks by processing the naphtha over a precious metal catalyst.
- In the cracking processes, heavy oils consisting of large molecular compounds are broken up (“cracked”) into smaller molecules, thereby producing lighter, more valuable products. The two predominant cracking processes are hydrocracking (at high pressure with hydrogen) and fluid catalytic cracking. The former process is used for more difficult-to-crack feedstocks, such as cycle oils and coker distillates, while the latter is used for easier-to-crack atmospheric and vacuum gas oils.
- The hydrotreating processes remove sulfur and other contaminants from petroleum products by reacting them with hydrogen.
- Alkylation in refining refers to the reaction of low-molecular weight olefins (*e.g.*, propylene, isobutylene) with isoparaffins (*e.g.*, isobutane) to form higher-molecular weight isoparaffins. Alkylation is unique compared to the other catalytic processes in that alkylation uses a liquid acid catalyst instead of a solid catalyst (although as discussed later in this section, there are ongoing projects to develop a solid acid catalyst for alkylation).

Even though catalysts are not consumed in the chemical reactions they promote, they can be deactivated and diluted by contaminants present in the feed streams to the catalytic processes, and eventually all catalysts must be replaced. Over the last 10 to 15 years, catalyst recyclers have made progress in making recycling more economical relative to disposal in landfills. For many years, spent reformer catalyst, which contains platinum, a valuable precious metal, has been reclaimed to recover the platinum for re-use. Catalyst recycling facilities are now available for hydrotreating catalyst, where nickel, cobalt, and molybdenum can be recovered for recycle. These metals have considerably less value than platinum, and the decision to recycle such catalyst rather than dispose of it is based strictly on economics. Also, as noted in our discussion of rejected pollution prevention ideas in Section D, the inventory costs associated with regenerated catalyst can be high for catalysts with a long service life. Depending on the status of the metals markets, there are thus times when disposal of hydrotreating catalysts is more economical than recycling, while at other times refiners may actually show a slight profit by sending these spent catalysts to recyclers.

Numerous projects have been contemplated to minimize waste disposal of spent catalysts, which represent a major disposal cost and potentially large savings to the extent that catalysts can be recycled and their useful life extended<sup>2, 4, 15</sup>. Spent catalyst disposal is largely a solid waste and dangerous waste issue, but catalysts also impact the wastewater systems of refineries in several ways. First, the regeneration of catalytic reformer catalyst can produce dioxins and furans as unintended by-products that can reach the sewer system (as discussed in more detail in Section E of this report). Second, FCCU catalyst fines can pose a solids control problem and can be washed into the sewer system (see above discussion of modifications to FCCU fines transportation and handling under “*Control of Other Solids from Various Sources*”). Third, change out of catalysts can release dust and fines that eventually wash into the sewer system. Among the pollution prevention projects reported to address catalyst issues that affect wastewater systems are the following:

1. Refiners have universally noted the need to optimize operating parameters affecting catalyst life in all major processing units, to provide better removal of catalyst poisons from feed streams, and to upgrade feedstock quality where feasible to extend catalyst life.



2. At least one refiner has addressed improvements in hydrocarbon recovery from spent sulfuric acid in alkylation units (*e.g.*, by contacting alkylate product with primary settler acid discharge so that heavy hydrocarbons in the product absorb light hydrocarbons in the spent acid). Improved hydrocarbon recovery would decrease sewer losses and reduce sludge formation.
3. One refiner reported plans to begin agricultural use of spent polymerization unit catalyst, which is composed of phosphoric acid on a silica-alumina base. The phosphoric acid is a good source of phosphorous for cultivated plants.

Numerous other projects address minimizing catalyst losses and ways to regenerate and reuse catalyst, but these projects for the most part do not affect refinery wastewater.

### **Alternative Disposal for Alkylation Unit Sludge**

Several refiners have addressed projects specific to sludge formation from alkylation unit operations <sup>2,6</sup>:

1. One refiner reports evaluating various alternative uses for alkylation unit sludge, including use as a fluxing substitute in metal refining and as a raw material for manufacturing hydrofluoric acid.
2. Sludge generation has been decreased in some units by replacing insoluble neutralizing agents (*e.g.*, lime) with soluble agents (*e.g.*, sodium hydroxide), although this approach increases fluoride levels in the wastewater and refinery outfall, for which permit limits for fluoride may be in place. Some refineries neutralize with agents that precipitate fluoride in the form of a marketable by-product (*e.g.*, as calcium fluoride).
3. Sludge generation has also been decreased in some refineries by sending acid regenerator bottoms to other processing units rather than to the neutralization pit, where the sludge forms.

### **Minimization of Amine Losses and Sludge Generation in Amine Units**

Amine treating units are used to remove hydrogen sulfide (H<sub>2</sub>S) from different refinery sour gas streams, producing a low-sulfur fuel gas and, after regeneration of the amine in a stripper, an acid gas stream containing the H<sub>2</sub>S that is sent to the sulfur recovery unit. The main solvents involved in amine systems in refineries are monoethanol amine (MEA), diethanol amine (DEA), diglycol amine (DGA), di-isopropanol amine (DIPA), methyl diethanol amine (MDEA), and various proprietary formulations of these amines and additives. Selection of the amine for a given application is typically a function of selectivity of absorption to H<sub>2</sub>S and CO<sub>2</sub>.

A portion of the recovered amine stream from the regenerator is blown down to the sewer system to prevent buildup of impurities. The amines in this blowdown stream can interfere with performance of biological organisms in the wastewater treatment plant. Refiners have addressed several proposed projects to reduce amine losses as well as to minimize sludge generation <sup>4</sup>:

1. One method reported for capturing amines for recycling is to employ a sump to retain amines drained from sludge filters in the Claus/tail gas unit during filter bag change-outs. These amines would otherwise be lost to the wastewater treatment unit.
2. A method under evaluation for potentially minimizing amine losses is to replace cloth filters with metal filters for sludge filtration to reduce maintenance and eliminate amine discharges associated with filter change-outs.
3. Replacement of MEA with MDEA to reduce formation of heat stable salts and minimize quantities of amine sludge and spent amine solution from tail gas units is also under study, as is the use of additives to minimize heat stable salts in MDEA systems. MEA has had widespread use. It is inexpensive and highly reactive. However, it is irreversibly degraded by impurities. MDEA has the advantage of a high selectivity to H<sub>2</sub>S but not to CO<sub>2</sub>.

### **Minimization of Sludge from Residual Upgrading Processes**

Residual upgrading units (solvent deasphalting, ROSE units, *etc.*) basically separate gas oil streams from asphalt components. Sludges from these refining processes may be generated and released during unit upsets, in surge and knockout drums, and during unit turnarounds. Such sludges are a source of polyaromatic hydrocarbons (PAHs), another of the Pollutants of Concern listed by the Department of Ecology. Projects have been noted to address unspecified improvements in process controls and “housekeeping” in these units to minimize formation of such sludges.

### **Minimization of Mercury Losses**

Mercury is another Pollutant of Concern listed by the Department of Ecology that is addressed in some pollution prevention projects. However, mercury is much less of a problem in refineries today than in the past when it was widely used both in process control and laboratory equipment. The references found mainly note that refiners now minimize or have eliminated altogether the purchase of mercury-containing equipment, such as thermometers and switches in process control apparatus. (We note that some electrical power systems require the use of mercury containing switches that cannot be replaced without completely replacing the associated electrical power systems.) Some refiners may inventory their mercury containing equipment, but we do not believe this practice is common. Other than continuing to minimize use of such equipment whenever possible, refiners have generally not focused on mercury in their pollution prevention programs. (A separate discussion of the presence of mercury in crude oils is presented in Section E under “Priority Pollutant Metals.” We did not find any discussion of mercury in crude oil in any pollution prevention literature.)

### **Minimization of Hazardous Materials Use**

Many refiners now select catalysts, chemicals and associated materials with consideration given to their tendency to generate wastes <sup>6,15</sup>. Non-hazardous alternatives are sought and evaluated to minimize use of hazardous materials. While no refiners reported specific examples, the reference to such activities reflects a growing awareness of waste minimization requirements and costs in aspects of refining operations other than plant operations (*e.g.*, in purchasing and procurement).

## **Company Direction and Employee Motivation**

Management guidelines and employee training and incentive programs have been widely implemented to promote awareness of the importance of controlling wastewater flow rates and minimizing losses to the sewer systems. In general, most refiners have developed formal policy statements and company guidelines for waste minimization, and many have instituted incentive programs that reward the successful implementation of new ideas for waste minimization. Most refiners have made waste minimization training and education programs a standard part of ongoing employee training in order to enhance employee awareness of pollution prevention opportunities.

## **Process Unit Design Modifications**

Refiners have gone beyond the improvements in operating and maintenance procedures described above to evaluate design modifications for source reduction. Some of the projects listed above require a basic level of engineering involvement (*e.g.*, to prepare equipment specifications for filters, mixers and centrifuges or to design piping to reroute wastewater streams), but they generally do not involve more detailed or fundamental changes such as those listed below.

## **Spent Caustic Recycle**

Caustic treating is used throughout a refinery to remove hydrogen sulfide and phenolic compounds from various streams. Spent caustic streams are generally treated in the wastewater treatment facilities. Various possibilities for recycling and minimizing spent caustic are reported<sup>1, 6, 15</sup>. Cascading of caustic streams from one unit to another provides an opportunity to optimize caustic use while reducing the quantity of fresh caustic needed as well as the total wastewater treatment load. Some specialty chemical companies will buy spent caustic streams from refiners to recover the phenol value, although the cost effectiveness of this approach depends on several factors, including proximity of the recovery facilities to the refinery. Refiners have also evaluated installation of commercial caustic regeneration units.

## **Use of Oily Sludge as Coker Feedstock**

Refineries with coker operations can in many cases utilize relatively small quantities of waste and residual streams as coker feedstock without affecting petroleum coke product quality<sup>2, 4, 5, 15, 17</sup>. Oil-containing sludge is an example of a potential coker feedstock that would otherwise have to be disposed of as a hazardous waste or fed to a process (such as a filter press or other option discussed above) to recover the oil. Sludge sources that have been successfully fed to a coker unit include exchanger bundle sludge, filter cake from tank cleaning, primary treatment sludge, oil emulsions and slop oil emulsion solids, laboratory wastes, *etc*). Coke product specifications are typically the limiting factor in determining how much of this material can be processed. One refiner has considered installing a separate sludge coker, but we would not expect such units to be cost effective in most cases due to capital cost and the small scale of the operation.

## **Desalter Improvements**

As discussed above in the section “General Refinery Operating and Maintenance Practices,” desalter operations are a significant source of contaminated wastewater. In addition to implementing the operating and maintenance improvements noted earlier, several refiners have evaluated desalter modification or

replacement<sup>2,3,4</sup>. Successful modifications of desalter internals have been made to improve efficiency, including replacement of internals with more efficient electrical equipment to improve the ability to coalesce water droplets in the emulsion, thereby improving oil-water separation. Refiners have also evaluated the elimination of desalters by replacing them with other processes, including dehydration of oil with emulsion breakers. However, we are not aware of any extensive move away from desalting operations in the industry.

Another approach has been to evaluate the use of various processing steps to treat desalter water before it enters the sewer system to recover remaining oil and reduce waste loads. One refiner in particular cited centrifugation and air flotation as potential steps to reduce sewer loads.

## Alternative Catalysts for HF Alkylation Units

Alkylation catalysts are one of two strong acids, hydrofluoric acid (HF) or sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). In both of these systems, acid is added continuously as a liquid. Care must be taken not to allow these acids to reach the wastewater treatment system. In sulfuric acid units, spent acid is recycled to produce fresh sulfuric acid. The HF units use less acid per volume of alkylate produced, and the HF acid is consumed by feed contaminants. Thus, HF units do not recycle the acid as do sulfuric acid units.

New processes have been evaluated that would employ solid acid catalysts and small quantities of liquid acid catalysts to replace HF and H<sub>2</sub>SO<sub>4</sub>, thereby eliminating the acid soluble oil stream, the neutralization of which generates sludge. Use of solid acid catalyst may also reduce quantities of adsorbents (such as mole sieves, alumina, sand and salt) used and the quantity of spent adsorbents to be disposed of as hazardous waste.

## Plant-Wide Projects

- **Heat Exchangers** – As discussed above, heat exchanger solids from tube bundle cleaning are a significant source of sludge in most refineries. Refiners have evaluated the replacement of some of their shell and tube heat exchangers with air-cooled exchangers and electric heaters to reduce this source of sludge<sup>5,15</sup>. Such applications are not always feasible due to both economics and the general suitability of air coolers and electric heaters for the types of service considered. For shell and tube exchangers that cannot be replaced, the use of smooth exchanger tube surfaces where practical to minimize sites for scale formation has been suggested<sup>15</sup>. Optimization of key heat exchanger design parameters (film temperatures, velocity profiles, *etc.*) has also been undertaken to minimize conditions favorable to fouling.
- **Reactor Optimization** – Projects have reportedly been undertaken to ensure that reaction processes are optimized to achieve maximum catalyst life consistent with overall operating requirements, although (not unexpectedly) refiners do not report specific examples or results of reactor optimization studies<sup>6,15</sup>. We note that conditions which optimize reactor conversion and throughput do not always optimize catalyst life, and the economic optimization of a reactor operation may therefore call for conditions that do not maximize catalyst life. This result is not a new development, and refiners have always engaged in programs to optimize economics. However, the increasing importance of waste minimization and spent catalyst disposal costs add economic incentives to operate under conditions more favorable to extended catalyst life. While such projects are not strictly pollution prevention activities but rather represent refinery economic optimization efforts, refiners now tend to note their relationship to pollution

prevention and recognize that the economics of waste disposal and waste minimization are an important part of refinery optimization.

- **Caustic and Rinse Water** – Projects have been evaluated to minimize caustic and rinse water use throughout a refinery by ensuring that efficient contacting and proper process controls are employed in all applications.
- **Overall Water Reuse Evaluation** – Overall water reuse evaluations within refineries are based on influent water purchase and treatment costs, wastewater treatment costs, permit limitations, and various non-economic factors (*e.g.*, community relations). The basic scope of such a program is to identify all of the major influent streams to and effluent streams from each process and utility unit as well as from the waste treatment area. Each stream is then characterized in terms of pollutants, composition, flow characteristics and other parameters. Matching influent requirements to effluent parameters will identify effluent streams that are potential candidates for reuse as influent streams to other units (*e.g.*, stripped sour water, an effluent stream, as a candidate for desalter feed water, an influent stream). A potential candidate would be an effluent stream that already matches influent requirements in one or more other units or one that with relatively minor treatment steps would match influent requirements. Such steps might include treatment with biocides, pH adjustment, filtration or other procedures that generally do not entail high capital or operating costs.

## Utility System Modifications

Utility systems that directly impact the wastewater treatment operations consist mainly of cooling towers and boilers. Reducing total flows from both cooling tower and boiler blowdown, reducing pollutants, and minimizing the impact of these streams on sludge formation are the primary focus of most reported pollution prevention projects.

### Minimization of Cooling Tower Blowdown Rates and Pollutants

Cooling tower blowdown typically represents an important source of water to the wastewater treatment system. The purpose of the blowdown stream is to prevent the buildup of dissolved solids and other components that would lead to fouling and corrosion in the cooling water system. The blowdown not only increases total wastewater flow but also adds solids that can promote sludge formation. Among programs undertaken to allow cooling water systems to operate with reduced blowdown rates are the following<sup>1, 4, 5, 15, 17, 21</sup>.

1. A common approach is to reduce the dissolved solids level in the cooling tower make-up water. Traditional methods include water softening, reverse osmosis and electro dialysis. Use of make-up water sources having a low dissolved solids content has also been reported, with availability of such sources, of course, being a limiting factor at most refineries.
2. The use of corrosion inhibitors in industrial cooling water systems is fairly common as a means of sustaining acceptable corrosion rates.
3. Another means of reducing blowdown rates is to reduce cooling water demand. Use of air-cooled exchangers as an alternative to water-cooled heat exchangers has been successful in

selected cases, and this evaluation is now typically made in the early stages of most new design projects.

4. Careful control and optimization of cooling water systems will maximize the number of cycles in a cooling water system, thereby minimizing blowdown.

In addition to minimizing blowdown rates from cooling towers, refiners have also focused on reducing the pollutants contained in such blowdown. Refiners have converted their cooling water treatment programs to non-chromate based treatment as required by EPA regulations, thus eliminating a key source of a toxic metal pollutant. (Chromium is one of the Pollutants of Concern listed by the Department of Ecology.) Also, refiners have evaluated using ozone rather than biocides or chlorine to eliminate microorganisms, thereby eliminating potentially toxic chemicals from the refinery wastewater.

### **Segregation of Boiler Blowdown**

The possibility of segregating hard water from boiler blowdown has been examined as a means to reduce sludge formation<sup>2,3,4</sup>. In order to reduce sludge formation caused by deposition of solids from boiler blowdown, one refiner has evaluated isolating such blowdown from the wastewater system and redirecting it to a location in the treatment plant downstream of the API separator and DAF unit or determining some other disposal alternative. Another refiner reported implementing diversion of both boiler blowdown and stripped sour water to the bio-treatment operations in the wastewater treatment plant.

## **Pollution Prevention In European Refineries**

Information on pollution prevention activities in European refineries is generally not as readily available on a refinery-by-refinery basis as information in the United States, but general information is available through the European Commission (EC) Directorate General Joint Research Centre (JRC), which analyzes and recommends Best Available Techniques (BAT) for pollution prevention and control in the EC refining industry. The JRC has evaluated numerous proposed methods for both general and specific pollution prevention practices and reportedly considered practices from the approximately one hundred European refineries as well as from refining operations in other parts of the world. The JRC gave consideration to practices that provided good environmental performance while also evaluating effects on other forms of pollution (cross-media effects) and overall economic factors.

The following summary describes some of the pollution prevention projects that the JRC has reviewed favorably while recognizing that the application of such projects in any particular EC refinery must be based on relevant conditions (*e.g.*, economics and cross-media considerations)<sup>18,19</sup>. In general, many proposed projects are viewed by the JRC as more likely to be applicable to new units or major revamps but worth considering for older units. A cost-effective application to an existing unit may not achieve the same level of results as in a new unit. On the whole, we do not find any particular types of pollution prevention efforts in Europe that are not found in the United States, and in fact, some of the pollution prevention opportunities cited by the JRC appear to draw heavily from U.S. publications and experience.

## Storage and Handling Systems

1. Use double tank bottoms as retrofits to existing tanks or for new tanks to prevent leakage. In a retrofit, the installed floor becomes the primary tank bottoms and can represent an upgrade from carbon steel (the most likely material of construction of the original floor) to, for example, stainless steel or fiberglass reinforced epoxy coated carbon steel. Installing a second impervious tank bottom provides protection against non-catastrophic releases due to corrosion, faulty welds, or other material or construction problems. The secondary bottom also provides a means of allowing detection of a bottom leak that is not obviously visible by, for example, maintaining a slight vacuum between the two floors so that failure of either floor will cause loss of vacuum and indicate a problem.
2. Use an impervious membrane liner on the floors of storage tanks to prevent leakage.
3. Use various leak detection devices and methods along with overflow alarms and pump shut-off devices to prevent loss of tank contents to soil, groundwater or sewer systems.
4. Use cathodic protection for storage tanks to prevent loss of material due to corrosion and subsequent leakage.
5. Use filters and centrifuges to minimize tank bottoms by recovering and recycling oil and sending the water, scale, rust and other bottoms sediments to the desalter.
6. Use larger containers (preferably small bulk storage tanks) instead of drums for liquid raw materials that are consumed in small quantities to avoid the problems of storing and handling drums and to reduce the likelihood of leaks and spills.
7. Store drums above floor or ground level to minimize corrosion and leakage.
8. Monitor corrosion of underground piping and tank floors, and employ cathodic protection where appropriate.
9. Prevent leaks and spills by installing self-sealing hose connections and utilizing proper line draining procedures.

In addition to the above possibilities, the EC guidelines recommend numerous procedures for preventing spills that are standard safety procedures employed in major refineries throughout the world, such as installing barriers and interlock systems to prevent movement of rail cars and trucks during loading and unloading that could lead to spills, accidents, fires, *etc.* and employing instruments and level alarms to prevent overflow from tank filling.

## Crude Oil Desalting

1. Use multistage desalters with combined AC and DC electric fields, recycling a portion of the effluent brine back to the first desalter to provide high efficiency and energy savings and to minimize wash water usage.
2. Use low shear mixing devices to mix wash water and crude oil.

3. Use low-pressure water to minimize turbulence.
4. Replace water jets with mud rakes to minimize turbulence.
5. Enhance oil-water separation before discharging water to the sewer by using a settling drum, upgrading the interface level controller, using wetting agents to release oil bound to solid contaminants in the crude oil, and optimizing the use of demulsifying agents.
6. Use a pressurized plate separator for the water phase or a combination hydroclone desalter-deoiler to enhance oil-water separation.
7. Use a sludge wash system to remove solids accumulated on the bottom of the desalter.
8. Reuse water from other processes for desalter wash water, such as water from the crude distillation unit overhead drum, steam condensates from the light and heavy gas oil driers and vacuum distillation overhead, stripped sour water and other solid-free process water streams, and blowdown from cooling water and boilers. (We note that these projects do not include the reuse of treated refinery effluent in the process units. In general, the reuse of treated effluent would be cost prohibitive since it would require steps such as reverse osmosis or desalination to remove solids and salts that would otherwise build up in the units.)
9. Strip desalter brine before sending it to wastewater treatment.

## **Amine Treating**

To minimize the impact of amines on the wastewater treatment unit, the EC guidelines call for improved control of amine flow by use of a surge tank and/or tighter production planning to ensure a smaller, steadier flow of amine to the treatment plant.

## **Sour Water Stripping**

To minimize the impact of sour water stripping on the wastewater treatment plant, a refiner can do the following:

1. Replace single-stage stripping with two-stage stripping, thereby reducing both the sulfur and ammonia content of the blowdown stream to the sewer (assuming that not all stripped sour water is recycled to the desalter and/or other process units).
2. Replace live steam stripping with a stripper having a steam reboiler to reduce the blowdown rate.

## **Optimization of Water Use**

Optimization of water use reduces make-up water requirements by recycling process water, rainwater, and cooling water and minimizes the amount of wastewater to be treated by optimizing the use and re-use of all water streams in the refinery. A water balance must be developed for the refinery to allow identification of all requirements and sources of water. Opportunities to reduce water use within process units and to evaluate all sources of water are thus identified. Techniques may include the following:



1. Substitute wet cooling processes with dry processes (*e.g.*, air cooling).
2. Maximize recirculation of cooling water.
3. Use treated process water as cooling water.
4. Use condensate stream as process water.
5. Use rainwater as process water.

Applications may include the use of stripped sour water, crude unit overhead condensate, boiler blowdown, *etc.* as desalter water and the use of phenolic spent caustic for stripped water neutralization and subsequent desalter wash to allow phenol resorption into the crude oil.

## **Pollution Prevention Programs of Washington Refiners**

We have reviewed the various pollution prevention reports filed by the five Washington refiners with the Department of Ecology and the pollution prevention opportunities listed by the Department of Ecology on the Internet <sup>7</sup>. We have compared these projects with those reported by other refiners and discussed above. As has been found in other U.S. refineries, Washington refiners have focused heavily on improvements in operating and maintenance practices, but they have also emphasized process modifications. Examples of pollution prevention projects that pertain to reducing wastewater sources and that either have been considered recently or are now under review by Washington refiners are discussed below. To the extent applicable, we have utilized the same subheadings as in the review of other U.S. refinery projects above. In this manner, we are able to illustrate parallels between the overall U.S. projects and the Washington projects. In general, we find that the Washington refiners have undertaken pollution prevention efforts that are very similar to those of other U.S. refiners in terms of both the categories and the specific projects.

### **General Refinery Operating and Maintenance Practices**

#### **Minimization of Tank Bottoms**

1. Reclaim oil from storage tank bottoms with a filter press or centrifuge and return it to the appropriate process units
2. Improve crude tank cleaning by use of a warm water chemical cleaning process using a circulating stream of a hydrocarbon diluent, warm water and emulsion breaking chemicals to achieve almost 90% reduction in tank sludge volume
3. Installed automatic crude tank dewatering equipment (oil-in-water monitor and controller to close the tank drain valve) in a crude oil tank for testing
4. Evaluate use of FCCU clarified slurry oil sediment (which contains polyaromatic hydrocarbons, listed as a Pollutant of Concern by the Department of Ecology) for use as a feedstock in cement manufacturing based on high alumina-silica content.

## **Improved Oil Recovery from Sludge**

1. Reclaim oil from desalter sludge, slop oil emulsion solids and other sludges with a filter press (One refinery reported that 85% of the sludge was recovered as oil and recycled during the last turnaround.)
2. Employ other methods for oil recovery from various sludges (centrifuges, *etc.*)
3. Considered use of non-toxic substitutes for emulsion breakers, but none could be identified.

## **Minimization of Desalter Solids and Oil Under Carry**

1. Improved controls and wash water sequence (changes not specified) in desalter area to minimize oil loss to oily water sewer and maximize reuse of wash water
2. Implemented continuous diversion of brine to increase settling time and minimize oil and grease loading to sewer system during desalter upsets
3. Considered removal of desalter solids upstream of sewer, but no economically feasible method was found.

## **Minimization of Spent Filter Clay Disposal and Hydrocarbon Losses**

1. Reduced spent clay generation after installation of a new product treating unit
2. Evaluated steam cleaning of spent clay to reduce toxicity, but the test was only partially successful.

## **Minimization of Loss of Solids to Sewers from Heat Exchanger Cleaning**

1. Heat exchanger operating parameters optimized to reduce fouling rates
2. Tube bundles from heat exchangers cleaned only in designated area with concrete pad and containment for solids

## **Control of Other Solids from Various Sources**

1. Paved refinery road surfaces and other areas in and around sewers to minimize solids entering wastewater system during storms
2. Periodically clean roads and concrete surfaces to minimize solids subject to washing into wastewater system during storms
3. Replaced sand/dirt surfaces in loading rack areas with rock
4. Increased frequency of cleaning process wastewater and stormwater systems
5. Evaluated use of inline filters to remove coarse sediment but rejected due to high initial cost, short expected service life, incompatibility of materials with sewer contents and high manpower costs for servicing and maintaining filters

6. Install cyclones for removal of coke fines from cooling tower blowdown to reduce solids loading on wastewater sewer (project evaluated and rejected because of poor return on investment)
7. Evaluating modification to wash water flow and decoking procedures to minimize the loss of coke fines to the sewer
8. Evaluating control of losses of catalyst fines to sewer system, including debris catchers and other methods
9. Installed sediment trap for stormwater runoff
10. Evaluating all potential sources of sediments to API separator to better define future source reduction opportunities
11. Installed inlet screen boxes and catch basins to prevent solids from entering sewer openings
12. Optimize corrosion control procedures to minimize loss of corrosion products to sewer systems
13. Use caustic as a replacement for lime for neutralization of spent acid to minimize solids formation in the wastewater system

### **Minimization of Leaks, Spills and Other Losses to Sewer**

1. Evaluating temporary measures to minimize losses to sewer during maintenance outages
2. Install sensor and alarm in caustic tank to prevent losses due to overflow when tank is filled
3. Review spill prevention control measures to minimize losses of various hydrocarbons, chemicals, and additives to sewer system
4. Install process unit pump-out system to capture and divert from the sewer system any hydrocarbons in process vessels prior to maintenance
5. Replace flush oil pump seals with mechanical seals to reduce oil loss to sewers
6. Plan turnarounds and shutdowns to minimize waste generation and maximize recycling
7. Monitor strength of alkylation unit sodium and potassium hydroxide (KOH) streams to minimize spent caustic and KOH disposal

### **Stormwater and Wastewater Segregation and Flow Reduction**

Several Washington refineries have addressed sewer segregation projects. There appears to be a consensus that preventing clean stormwater runoff from entering the oily water sewer systems is a high priority matter. Several projects have been implemented to isolate stormwater flows and reduce silt and sediment that could potentially reach the oily water sewer during heavy rainfalls.

### **Replacement of Drums with Storage Tanks**

- Convert from drummed to bulk storage for various chemicals and additives where possible to reduce losses, improve inventory control and minimize spills and leaks.

## **Minimization of Sample Losses to Sewer System**

1. Installed closed loop sampling stations
2. Analytical laboratory waste reduced by modifying analytical methods, changing from daily to weekly analyses of less critical parameters, and reducing frequency of other sampling programs
3. Programs underway to minimize use of solvents for cleaning and other purposes and use of other hazardous reagents and materials to the extent possible.

## **Minimization of Benzene Losses to Sewer System**

- Use heavy gas oil in place of lighter naphtha stream as extractant in brine deoiler, thereby reducing slop oil emulsion and benzene content of desalter brine.

## **Minimization of Spent Catalyst Waste**

Washington refineries have addressed methods similar to other refineries to minimize catalyst waste, including optimization of unit operating conditions and recycling catalysts to vendors for regeneration and recovery of valuable metals content. Other projects cited include the following:

1. Regeneration and reuse of spent acid in the alkylation unit
2. Using spent polymerization catalyst as a phosphate nutrient source at a landfarm operation.

## **Minimization of Amine Losses and Sludge Generation in Amine Units**

1. Evaluating MDEA as a replacement for DEA to minimize impact of amine losses
2. Installed filters and process controls to reduce contaminants in amine systems to extend useful life and reduce blowdown rate to sewer
3. Evaluating replacing a DEA containing neutralizer with a non-DEA containing neutralizer in different processing units
4. Evaluating methods to control formation of heat stable salts causing intermittent foaming and resultant amine losses.

## **Minimization of Mercury Losses**

1. Mercury thermometers replaced by non-mercury thermometers and/or thermocouples to the extent possible
2. Eliminated processing of a crude oil believed to contain significant levels of mercury and considered a potential source of mercury to the wastewater system.

## Minimization of Hazardous Materials Use

Like most other U.S. refiners, all Washington refiners report that they select catalysts, chemicals and associated materials with consideration given to their tendency to generate wastes and review all hazardous chemical purchases with due consideration given to non-hazardous alternatives and to minimization of hazardous chemical use. These programs apply to all materials needed for process, maintenance, laboratory and other applications. Inventory control programs are also reported to minimize the presence on-site of unused and excess hazardous chemicals and materials as well as any materials for which the useful shelf life has expired.

## Process Unit Design Modifications

### Spent Caustic Recycle

- Spent caustic sent to reclaiming operation to recover phenols and other chemicals

### Use of Oily Sludge as Coker Feedstock

1. API separator sludge used as feedstock to delayed coking unit and a coke calciner
2. Slop oil emulsion solids recycled as feedstock to delayed coking unit and fuel blended as fuel for cement kiln
3. DAF float recycled as feedstock to delayed coking unit

### Dioxins and Furans

1. Evaluated various treatment alternatives for treating dioxins and furans, including thermal destruction, chemical substitution, process changes, and others; rejected because of favorable results of evaluation of wastewater treatment plant performance in removing these compounds
2. Evaluating segregation of catalytic reformer regeneration wastewater and unspecified pretreatment options to destroy/remove dioxins before release to wastewater treatment plant

### Reactor Optimization

1. Replaced reaction section of butane isomerization unit with new technology that no longer requires use of a catalyst that had represented a source of antimony to the wastewater system and in sludges generated in the refinery
2. Considered replacement of HF catalyst in alkylation unit with another acid catalyzed process; studies of solid acid catalyst systems reported to be continuing (see “*Alternative Catalysts for HF Alkylation Units*” above under “Pollution Prevention in U.S. Refineries Outside Washington”)
3. Considered alternative to antimony based passivation system for catalytic cracking unit, but no suitable alternative could be found

## **Gasoline Treating Process Change**

- Switched from caustic treating of gasoline to Merox treating, thereby reducing discharge of phenols to sewer system and spent caustic disposal needs

## **Utility System Modifications**

Washington refiners have undertaken programs similar to those in other refineries to minimize the impact of utility systems on the refinery wastewater system. All refineries have eliminated the use of chromium based treatment in cooling towers as mandated by the EPA. Other projects include the following:

1. Evaluation of alternatives to use of chlorine for control of microorganisms in cooling towers, including substitution of bromine based compounds and hypochlorite
2. Modification of boiler water demineralization to reduce both caustic and acid usage
3. Considered replacement of boiler water treatment chemicals with non-toxic alternatives, but no suitable candidates could be identified

## **Application Of Pollution Prevention Principles In Process Design**

Due to the competitive nature of the petroleum refining business, refiners have begun to view pollution prevention less as a cost of doing business and more as a cost reduction method. With hazardous waste disposal costing upwards of \$1,000 per ton, many refinery wastes cost far more for disposal than the materials to be disposed of cost initially. As refiners have undertaken projects to reduce waste disposal costs, they have reduced the quantities of waste produced.

In the area of process design, refiners and engineering companies have formalized the work process that takes a project from an initial concept all the way to plant start-up. The work process is similar from one refiner to another and from one engineering company to another. Waste minimization and pollution prevention have now become an integral part of these work processes. Most processes follow a six-step regimen consisting of the following phases:

- Phase 1 – Project Feasibility Study
- Phase 2 – Project Conceptual Study
- Phase 3 – Preliminary Engineering
- Phase 4 – Detailed Design and Procurement
- Phase 5 – Construction
- Phase 6 – Start-up

During the initial phases, regulatory compliance, including waste minimization and pollution prevention, is an integral part of the analysis determining the life cycle cost for the project.

The work processes provide documented methods for choosing the optimal project characteristics and for clarifying project scope. Emphasis is placed on performing enough work in the front-end phases of the

project for the refiner to determine whether the project should proceed (a practice known as “front-end loading”).

As part of the front-end study, all waste streams that will be generated are identified and quantified. A strategy is then developed to reduce or eliminate each stream, and options for achieving this goal are evaluated on the basis of the extent to which they reduce the project costs. Source reduction methods are explored, recycling opportunities are identified, and other alternatives (including, in some cases, alternative processes) are considered. The feasibility and economics of the various processing and source reduction alternatives are carefully explored. This evaluation process and its results are thoroughly documented. The recommended pollution prevention and waste minimization strategy is officially adopted and incorporated as part of the overall design basis and implemented in the final design and construction.

## Section C.

# Key Findings From Refinery Questionnaires

To obtain additional information concerning the Washington refineries, questionnaires were prepared and distributed on a confidential and voluntary basis to each refiner. With all five refineries reporting back, we have summarized our findings in the following section. To provide a comparative basis for assessment, we have converted many of the reported parameters to relative values based on barrels of crude oil processed. Crude oil capacities of the five refineries are indicated below:

### Responding Washington Refineries: Crude Oil Capacities

Company	Location	Crude Capacity (BPD)
BP PLC	Ferndale	222,720
Shell Oil Products USA	Anacortes	148,600
Tesoro West Coast Co.	Anacortes	114,500
ConocoPhillips	Ferndale	89,000
US Oil & Refining Co.	Tacoma	43,700

Source: *Oil & Gas Journal*, Dec. 24, 2001

## Wastewater Quantities And Sources

Total representative daily wastewater discharge rates ranged from 0.4 to 3.7 MM GPD. Major contributions to wastewater sources were reported to be contaminated stormwater, desalter effluent, cooling tower blowdown, stripped sour water, once-through cooling water, and process and steam condensate.

Of these contributions, we noted differences mainly in the cooling tower blowdown and process/steam condensate categories. Differences can exist in cooling tower blowdown control methods based on the cooling tower chemical vendor treatment programs. Refineries with relatively higher condensate blowdown rates may have potential for flow reductions, but depending on specific boiler blowdown requirements as well as energy savings and capital requirements, reductions in condensate rates may not be justifiable.

## Recovered Slop Oil

Rates for recovered slop oil ranged from 0.02 to 0.11 barrel of recovered oil per thousand gallons of wastewater. Most of the refiners reroute slop oil back to the crude unit, while a few send slop oil to a downstream conversion unit. Our experience is that most refiners route recovered slop oil back to the crude unit. Alternatively, the delayed coker may also receive some of this oil. If the composition suits a



specific process unit, the oil can be routed to a downstream conversion unit, such as “dirty gas oil” to the FCCU. The key to rerouting to a downstream conversion unit is whether the candidate stream will be detrimental in terms of expected yield performance, corrosion, or other factors in the downstream unit to which it is sent.

## **Wastewater System Solid Waste Disposal**

Two refineries reported having surge capacity upstream of the API separator. For these refineries, the skimmed oil recovery ranged from 5,000 to 50,000 barrels per year, while solids removal recovery ranged from 1,500 to 2,000 barrels/year. Surge capacity can be useful for providing additional hold-up and equalization capacity, especially during periods of high rainfall.

For 2000 and 2001, API separator sludge ranged from 0.1 to 17 pounds of sludge annually per daily barrel of crude oil capacity. All of the refineries have a method of dewatering the sludge, most commonly a plate and frame filter press and/or a centrifuge. Sludge disposition was handled off site with the options varying among incineration, cement kiln processing, calcining and thermal desorption.

Three of the refineries have air flotation systems: two are induced systems and the other a direct flotation system. Primary sewer sludge quantities ranged from 0.1 to 0.64 pound annually per daily barrel of crude oil capacity. After filter pressing or centrifuging to dewater, most plants send primary sewer sludge off site for incineration or to a cement kiln. Two of the Washington refineries keep the material on site and feed it to a downstream conversion unit. Waste tank sludge is dealt with in a similar manner. Depending on the tank cleanout schedule, reported annual averages of quantities generated ranged from 1.4 to 12.7 lb per barrel of crude. Depending on the tank service, one of the refiners routes this material to incineration, cement kilns or landfill.

Biosolids and biological sludge at the refineries are not designated as dangerous waste. The generated quantities at the refineries ranged from 6 to 55 pounds annually per daily barrel of crude oil capacity. The refineries generally thicken or concentrate the solids by draining, decanting or naturally deliquescent. One refinery reported that it filter presses solids and places them on a controlled landfarm site within the facility. Another sprays decanted sludge onto a lined biosolids landfarm with leachate collection. Another refinery dredges its wastewater ponds annually and applies the sludge to a non-hazardous waste landfarm.

## **Specific Pollutants**

### **Dioxin and Furan**

The questionnaire results validate the *Oil & Gas Journal* Refinery Survey data that are also presented in Section E of this report. The following table shows the types of catalytic naphtha reformers that are found in the State of Washington:

## Responding Washington Refineries: Reformers

Company	Location	Catalytic Reforming	
		Semi Regen	Cyclic
		BPD	BPD
BP PLC	Ferndale	60,480	
Shell Oil Products USA	Anacortes	32,200	
Tesoro West Coast Co.	Anacortes		24,300
ConocoPhillips	Ferndale		15,500
US Oil & Refining Co.	Tacoma	5,750	
Source: <i>Oil &amp; Gas Journal</i> , Dec. 24, 2001			

Three of the refineries are using bimetallic catalyst and are not using pure oxygen during the regeneration cycle. All five refineries are using perchloroethylene as their chloride source for regeneration. The semi-regenerative naphtha reformers are all using caustic as the neutralizing agent during regeneration. After circulation through the naphtha reformer process equipment, the caustic is routed to the primary wastewater treatment facility. The neutralizing agent is tested during disposal prior to release to the sewer. Neither of the cyclic naphtha reformer operators mentioned contaminant testing during catalyst regeneration.

## Mercury

All of the refineries indicated that their primary source of domestic crude oil is Alaskan North Slope (ANS). All have tested for mercury in their waste water systems as well as crude oil receipts. As noted in the responses, the Western States Petroleum Association completed a survey of ANS crude oils with a mean mercury content reported at 1.98 nanograms of mercury per gram of crude oil (ng/g), or 1.98 parts per billion (ppb) by weight. (The number of samples and the range of results were not stated.) Some of the refiners have tested the product streams, but all report numbers below the suggested API guideline of 17 mg/kg (numerically equivalent to 17,000 ng/g). One refiner reported finding mercury levels on the order of 2 ppb in the fresh caustic supply, a concentration similar to that found in the crude oil, but, of course, the quantity of caustic consumed is small relative to that of crude oil.

Testing indicates that mercury levels in crude oil are well within current acceptable limits. Most of the refineries mentioned ongoing EPA studies to continue contaminant metal testing in crude oil, and most refineries appear to believe that the major source of mercury in their operations is crude oil. As a result of laboratory and field instrument upgrades to nonmercury-containing equipment (except, as discussed in Section B, for certain mercury containing switches that cannot be replaced), there is a common belief that such equipment is not a source of mercury. Two of the respondents specifically noted having programs in place to segregate, collect and manage as hazardous waste any mercury from instrumentation (*e.g.*, broken thermometers) generated in the laboratories and elsewhere in the refinery. In general, it is our impression that U.S. and European refiners have been very aware of equipment-related mercury sources and keep tight control of the mercury-containing equipment that remains in use in their facilities. Some refiners may even maintain inventories of such equipment, but mercury inventorying does not appear to be a widespread or common practice.

## **Polyaromatic Hydrocarbons (PAH)**

As the refineries all pointed out, polyaromatic hydrocarbons are an inherent part of the overall refinery operations. Of the refineries that have analyzed for PAH, the common response is that the concentration levels of PAH are at or below detectable limits. Analyses of PAH were reportedly made in various product and waste streams throughout the refinery.

With respect to methods of controlling PAH-containing streams from spills, *etc.*, all the refineries were consistent in using the following documents and programs: Facility Oil Spill Response Plan, Spill Prevention Control and Countermeasures (SPCC) Plan, Marine Terminal Operations Manual, Facility Oil Handlers Training and Certification Program, Triennial Spill Drill Program, Operating Procedures and Standing Orders. These documents address the EPA, Coast Guard, RSPA DOT and Department of Ecology regulations as well as good industrial operating practices.

One refinery mentioned that PAH laden soil would be sent to a soil burner to destroy PAHs.

## **PCBs**

Four of the refineries have tested for PCBs in recent years. The results were below detectable limits. One refinery has not tested for PCBs in wastewater on the basis that they have no PCB-containing transformers. Two refineries have reported still having PCB containing transformers (one reporting only one still in service and the other not specifying the number). Two of the other three specifically noted that they had not had such transformers for more than ten years.

## **Miscellaneous Wastewater Pollutant Loads**

Under the category of miscellaneous wastewater pollutant loads, refiners were asked to address sources of soil, catalyst, scale and rust, and tank bottoms.

### **Soil**

All five refineries reported using berms and curbs at drains to minimize soil losses to the sewer systems. The level of usage varies somewhat, but it appears that most facilities use berms and curbs fairly extensively. One refiner noted that berms are used throughout the tank farm areas whereas curbing (or equivalent) is more prevalent within the process units. All refineries conduct street sweeping. Sanding of streets occurs during the summer and during icy winter conditions as required. Sewers are covered during maintenance as necessary.

### **Catalyst**

Depending on the FCC technology licensed by the refinery, most FCCUs have either electrostatic precipitators or wet gas scrubbers to control particulates in FCCU flue gas. During unit turnarounds, catalyst is offloaded from the unit back to storage hoppers or silos located near the unit. Spent regenerated catalyst is then either offloaded to railcars or trucks depending on the refinery's physical layout and access to rail facilities. The same loading procedure is followed for introducing fresh catalyst to the unit. Opacity meters are provided on FCCU flue gas emission points to detect changes in solids as a result of changes in unit performance. Each licensor in cooperation with the individual refiner set up best practices

to optimize unit performance while minimizing operations that are detrimental to the surrounding environment.

For other fixed bed reactors catalyst, such as that used in hydrotreaters and naphtha reformers, catalyst is dumped directly into drums or flow bins. On occasion, this catalyst is run through a “shaker” to separate the ceramic support media from the catalyst. The shaker is staged in an enclosed shed or other temporary structure to provide protection from rain as well as to help mitigate the migration of any dust that may be generated during the shaking process. When the operation is completed, any catalyst dust that was deposited within the shed or temporary structure is cleaned up and placed into appropriate containers.

## **Scale and Rust**

Isolated areas or containment pads for exchanger bundle cleaning are utilized in all of the refineries. Likewise, sewers, where and when appropriate, are covered for sandblasting. Other control measures include containment of hydroblasting and collection of scale and rust generated by tank or vessel cleaning.

## **Tank Bottoms**

Most of the refineries cited procedures requiring operators to be physically present to observe tank draws to prevent unnecessary releases of oil to the sewers. As tanks are taken offline for repair and inspection, maintenance practices include coating the tank bottoms and walls with corrosion resistant paints. Depending on the service of the tank being cleaned, disposition of the solids will vary between incineration and cement kiln processing.

## **Other Pollutants of Concern**

Surfactants and dissolved solids were identified in various locations and attributed to various sources. The potential sources for surfactants included cleaning materials and antifoams. For dissolved solids, boiler and cooling tower blowdowns were believed to be the potential sources. Other potential toxic threats included salt from product driers and caustic from product treaters.

The only toxins that were reported in the final effluent were the metal toxins cadmium, lead and mercury, and not all of the refineries reported finding detectable levels. The refineries generally believe that the sources for these toxins are tied to crude oil or plant metallurgy. The highest cadmium result reported was less than 5 µg/l, well below the API guidance value of 26 mg/kg. The highest lead result was less than 50 µg/l, well below the API guidance value of 300 mg/kg. The highest mercury result was less than 0.2 µg/l, well below the API guidance value of 17 mg/kg.

Refinery amine systems can be located near the product recovery gas plants and/or the sulfur recovery and tail gas treating units. Depending on the application, the Washington state refineries are utilizing both diethanol amine (DEA) and methyl diethanol amine (MDEA). The potential sources for pollutants are the amine sump systems that are located near this equipment to recover amine from drum, tower and drain connections.

## **Section D.**

# **Analysis Of Selected Pollution Prevention Opportunities In Refining**

Refiners throughout the United States have undertaken similar pollution prevention programs over the last ten to twelve years. Most refiners have explored all of the various types and categories of projects discussed in Section B of this report and have thus evaluated many of the same possibilities. This situation is particularly the case in terms of operating and maintenance practices, but it also applies to many of the process unit modifications previously discussed (*e.g.*, spent caustic recycle, use of sludges as coker feedstock, desalter modifications, and others).

While continued focus on the same types of activities may result in incremental improvements in pollution prevention, the achievement of more substantial progress will require new approaches to refining practices. Some of the newer innovations were identified in Section B, such as use of alternative catalysts in HF alkylation units. In the following discussion, we present three additional topics that refiners may be starting to explore but that we did not find among the ongoing pollution prevention activities listed in the literature. The applicability of these approaches to pollution prevention in any refinery will depend on refinery configuration, crude slate and co-product slate. Because of the large capital requirements, these approaches may be more appropriate within the framework of a new grass-roots refinery or the addition or expansion of major units in an existing refinery.

As refiners pursue programs to reduce pollutant loads further, consideration must also be given to the needs of the wastewater treatment facilities. While it is not our purpose in this study to focus on the details of the operation of refinery wastewater treatment facilities, we note that a typical secondary wastewater treatment plant in a refinery is a continuous activated sludge system in which aerobic biological organisms are mixed with pretreated wastewater. The incoming wastewater provides the organisms with essential nutrients that ensure both their survival and the proper functioning of the treatment plant. An insufficient supply of nutrients can weaken the organisms so that they are unable to respond adequately to increased COD and BOD loads caused by upset conditions. (For example, the growth of the organisms and the ability of the sludge to settle in the downstream clarifier will be impeded if there is an inadequate supply of nitrogen or phosphorus.) It is not uncommon for refinery wastewater treatment operators from time to time to add low levels of chemicals (*e.g.*, isopropyl alcohol) to the wastewater to supply nutrients during periods when wastewater loads are reduced (*e.g.*, during partial refinery shutdowns) to maintain healthy levels of biological activity. It is therefore important when evaluating and implementing projects that reduce the loading of various wastewater pollutants to be certain that the reduction will not compromise the nutritional needs and health of these organisms.

## **Parallel Sour Water Stripping (Segregation)**

In most refineries, stripped sour water is the second largest wastewater stream generated. Sour water is created when wash water contacts refinery-produced gas streams and absorbs from them hydrogen sulfide (H<sub>2</sub>S) and ammonia (NH<sub>3</sub>), which are byproducts of various cracking and hydrotreating operations. The use of wash water minimizes equipment fouling and corrosion in these operations.

Sour waters are generated by many of the processing units within refineries and contain various concentrations of dissolved  $\text{NH}_3$  and  $\text{H}_2\text{S}$  along with much smaller amounts of other water-soluble acid gases. Certain sour waters also contain light and heavy soluble organics and some benzene, which is one of the few hydrocarbons containing only hydrogen and carbon that exhibits enhanced solubility in water. Certain fractions of these soluble organics are designated as phenolic compounds, or “phenolics.” Phenolics are aromatic compounds that are poisonous to aquatic life. Discharges of phenolic compounds in refinery wastewater streams are severely restricted.

Sources of sour waters in refineries can be divided into two broad categories: sour waters from processes with incidental or intentional thermal character (*i.e.*, processes that involve thermal cracking of large molecules into smaller compounds, such as fluid catalytic cracking, visbreaking, and delayed coking) and sour wash waters from hydrotreaters and catalytic gas oil hydrocrackers. (Gas oil hydrocrackers crack larger molecules but do not fall in the category of thermal processes, relying instead on the high hydrogen pressure maintained in the reactor to crack molecules.)

Sour wash waters from distillate and heavy oil hydrotreaters contain nearly an equal ratio of ammonia and acid gases. The acid gases are composed primarily of  $\text{H}_2\text{S}$  but may also contain small quantities of hydrogen chloride (HCl) and hydrogen cyanide (HCN). Such sour waters are essentially free of soluble organics such as phenolic compounds. By contrast, sour waters from processes with thermal character tend to be imbalanced, having more dissolved  $\text{H}_2\text{S}$  than  $\text{NH}_3$  and containing significant quantities of soluble organics and phenolic compounds. (In some hydrocracker operations, there is a possibility that wash water could have contacted heavy oils containing phenolic compounds.)

A potential means of pollution prevention and waste minimization would be to segregate the two types of sour water mentioned above. Hydrotreater and hydrocracker sour waters would thus be processed in one stripper, and FCCU, coker, and other thermal process sour water would be processed in another. Since the hydrocracker and hydrotreater sour waters do not contain highly soluble organic and phenolic compounds, this water could be recycled back to the hydrotreaters and hydrocrackers after it had been stripped to remove ammonia and hydrogen sulfide. The sour waters generated by the thermal processes that contain soluble organics and phenolic compounds would be stripped in a separate hydrotreater wash water stripper (WWS) to operate in parallel with the Sour Water Stripper (SWS), thereby providing the following benefits:

- Most of the water in hydrotreater sour wash water can be recycled back to the source hydrotreaters as wash water since it would contain no soluble organics. This approach would greatly reduce net sour water disposal.
- Wash water rates can be increased to help distribution, to mitigate corrosion and to prevent leakage since most of the wash water would be recycled back to the unit rather than being sent to the sewer.
- Fouling, corrosion and leakage of the colder end reactor effluent exchangers and air coolers would be minimized with wash water that is entirely free of heavier soluble organics.
- Steam requirements for stripping wash water are lower on a per gallon basis in a WWS than in a SWS so that both steam generation and boiler blowdown rates would diminish.
- Essentially all of the soluble organics would be sent to the SWS so that WWS stripped wash water would be free of soluble organics.

- Overhead vapors from the separate SWS would be enriched in light soluble organics (while remaining relatively lean in ammonia, as noted above). As a result, organic vapors would be more completely combusted in the special burners of the Claus Sulfur Recovery Plant since there would be no competition from hydrotreater-derived ammonia incineration.
- The stripped sour water flow rate from a separate SWS would generally match up well with the water requirements of the crude unit desalters. Overall desalter operations are typically optimized at about 5 barrels of total water feed per 100 barrels of crude oil feed. About 80% of the water could be stripped sour water. Fresh water would be directed to the front end of the crude preheat train, with stripped sour water going to a mixing device ahead of the second stage desalter.
- The residual heavier soluble organics that remain in stripped sour water would be recycled by being absorbed into the crude oil in the desalter.

In terms of process configuration, the Wash Water Stripper and the Sour Water Stripper would be similar except that the SWS should have an API specification storage tank to serve as an equilibration tank (with internal “oil” skimmer, a secondary containment wall, and a double bottom). Nominal capacity of the API equilibration tank should equate to 4 to 7 days of normally expected general service sour water production. Similarity of process schemes would allow the WWS to be temporarily re-aligned to back up the SWS during scheduled and forced outages of the primary SWS.

Wash water going to the reactor effluent air coolers in hydrotreaters and gas oil hydrocrackers should be a mixture of (a) sour water decanted from an associated steam stripper or complex steam stripper/splitter, (b) stripped wash water from the dedicated WWS, and (c) clean steam condensate as required and as a back-up source. Today’s common practice of substituting stripped sour water from a general service SWS for stripped wash water from a dedicated WWS could be halted with improved hydrotreater reliability, risk management and wastewater management.

We note that modifying a refinery for parallel stripping operations and isolating the stripped water for return to specific units as described above would represent a major capital investment that may be economically justifiable only as part of a larger revamp or expansion. Nonetheless, it is an approach that merits consideration and should be examined when future revamps and expansions are evaluated.

## **Eliminate Caustic Washing of Kerosenes and Medium Diesels as Part of Ultra Low Sulfur Diesel Programs**

In traditional refining operations, dilute caustic prewash systems have been widely employed for treating jet fuel grade kerosene and to a lesser extent fuel grade kerosene and medium diesel cuts. Dilute caustic interacts with naturally occurring naphthenic acids to form sodium naphthenates, which are fairly soluble in water and which add to the loading of the wastewater treatment plant.

Traditional waxy crude oils have very low acidity, and the modest quantities of sodium naphthenates that are generated in caustic washing are strongly soluble in the caustic (aqueous) phase. The spent caustic carrying these dissolved organics and modest amounts of entrained emulsions is drawn off either to a spent caustic tank or directly to the oily water sewer.

Typically, a spent caustic tank will also receive spent caustics from other units (such as Merox™ or Mericat™ units treating jet fuel, FCC gasoline and/or coker gasoline streams as well as Merox™ or Thiolex™ treating systems for olefinic LPG). Any emulsified diesel fuel, kerosene or gasoline will tend to separate in the spent caustic tank. They can thus be skimmed off and recycled (*e.g.*, for transfer to the light slops tank or for use as rerun material spiked into crude oil). From the spent caustic tank, dilute spent caustic is typically continuously spiked into the wastewater treatment facilities. Sulfuric acid is added as necessary to neutralize remaining free caustic. Sodium naphthenates in the spent caustic will generally undergo complete biological destruction in the wastewater treatment plant.

For many refineries, crude oil slates with some degree of increased acidity are often encountered, causing the quantity of sodium naphthenates to increase greatly. In the caustic treating operations, formation of three-phase emulsions can occur involving diesel/kerosene, partially spent dilute caustic aqueous phase, and sodium naphthenates. These emulsions tend to disrupt spent caustic tank operations, force the dumping of emulsion layers to the oily water sewer, and disrupt wastewater treatment operations.

A potential means of reducing the additional wastewater loads that are associated with processing higher acidity crude oils is therefore to eliminate the dilute caustic treating of jet fuels, kerosenes and medium diesels by installing additional hydrotreating capacity. However, major capital investment would be required, and the refinery must have or add capacity to produce substantially greater quantities of hydrogen. The economic justification would generally derive from regulatory mandates for low sulfur and ultra low sulfur (ULS) fuels, with the investments likely viewed as a requirement for staying in business. The mitigation of sodium naphthenate loadings on the wastewater treatment operations would be a secondary benefit of such investments and would not be sufficient by itself to justify these projects. The scope of such a project would involve some or all of the following:

- Jet Fuel Hydrotreater – This unit would be dedicated to processing straight-run kerosene suitable for jet fuel in lieu of operating dilute caustic pre-wash or other caustic treatment units.
- ULS Kerosene Hydrotreater – This unit would process fuel-quality straight-run kerosene, perhaps with direct spiking of coker light kerosene if this cut were available from a coker fractionator.
- As an alternative to the above, a larger, multi-purpose jet fuel and ULS kerosene hydrotreater could be added with two feed tanks and a product tank for the ULS kerosene. This combination unit would permit batch operations to make Jet A (having 200 to 400 ppm by weight of sulfur residual) and ULS kerosene (with a sulfur residual of around 5 ppm by weight).
- A medium to high pressure ULS light distillate hydrotreater would be able to make ULS diesel blending stock with sulfur residuals of 5-7 ppm by weight from mixtures of medium and heavy diesel, FCC light cycle oil, and/or FCC light coker gas oil.

Caustic treating still remains the technology of choice for many applications, including processing olefinic LPG co-products (*e.g.*, from FCC and coking units), processing light FCC gasoline, and cleaning up certain vent gas streams. Economic justification to replace caustic treating for these applications would likely be much more elusive.



## Secondary Benefits From Upgrading Olefinic FCC LPG Treating and Adding Alkylation Unit Feed Treating

A number of secondary benefits can accrue when treatment systems for olefinic FCC LPG are upgraded and when systems are added to treat alkylation unit feed. Economic benefits can include the following:

- More consistent and/or improved quality and potentially higher output of high purity chemical grade propylene co-product can be achieved. (Propylene is derived from a high purity propylene plant located downstream of the FCCU gas plant.)
- Acid consumption in the alkylation unit may be significantly lower. For sulfuric acid alkylation units, this result will sharply reduce the annual out-of-pocket expenses for regeneration of spent sulfuric acid and mitigate hydrocarbon losses in spent acid.
- Reduction may occur in the high boiling tail of alkylate gasoline blendstocks, providing greater opportunities for optimizing the upper cut point of desulfurized FCC gasoline and improving octane values.
- The volume of spent sulfidic caustic sent to the spent caustic tank and refinery wastewater system could be reduced.
- Consumption of fresh amine could be reduced with a corresponding reduction in the quantity of amine entering the refinery wastewater system.

Below are several ideas for improving treatment of olefinic LPG streams from the FCC gas plant, with allowance for the fact that some refiners also process coker LPG in their FCC gas plants:

- Upgrade the stripper, primary absorber, and mix drum system in the FCC gas plant to mitigate the levels of H<sub>2</sub>S, CO<sub>2</sub>, and ethylene in the mixed propylene and butylene LPG from the FCC gas plant debutanizer.
- Upgrade distributors and contacting internals in the olefinic LPG and amine wash tower or replace the tower with a larger diameter vessel having state-of-the-art internals.
- Use a higher flow of amine solution to the wash tower to permit acid gas pick up of less than 0.15-0.20 mole of H<sub>2</sub>S and CO<sub>2</sub> per mole of amine in this service.
- Retrofit an in-line coalescer and/or special water wash system for amine-washed olefinic LPG to recapture the amine solution that is absorbed and entrained.
- Retrofit the amine flash drum on the hydrocarbon-bearing semi-rich amine solution to direct hydrocarbon-rich vapors back to the interstage of the FCC wet gas compressor, or retrofit the FCC fuel gas amine contactor to permit mid-way injection of semi-rich amine solution. In the latter case, the hydrocarbons in the semi-rich amine will overlay into refinery sweet fuel gas, and as a trade-off benefit, the semi-rich amine can be loaded up to accept rich amine loadings of H<sub>2</sub>S and CO<sub>2</sub> inside the FCC fuel gas amine contactor. Overall amine circulation and regeneration requirements would be reduced as a result.

- Install a dilute caustic prewash system upstream of an olefinic LPG treatment unit. Such a unit would use a recirculating dilute caustic stream with a make up of about 2-3 weight % caustic.
- Upgrade catalyzed caustic treating systems with new distributors and contactors and other internals plus improved air-based regeneration and disulfide oil separation systems.
- Retrofit or upgrade the post-water wash step for the olefinic LPG en route to the C<sub>3</sub>/C<sub>4</sub> splitter tower, superceding in some cases in-line coalescers or sand filters.
- Upgrade the overhead system of the downstream C<sub>3</sub>/C<sub>4</sub> splitter or depropanizer to ensure the best possible segregation and decanting of residual soluble water stripped out of the olefinic C<sub>4</sub> alky feed fraction of olefinic LPG feed and to provide carrier purge venting of much of the nitrogen, oxygen and hydrogen residuals in olefinic LPG feed.

Upgrades to the olefinic LPG/amine wash tower and addition of dilute caustic prewash would be expected to minimize the discharges, purges, water washes and activation requirements with respect to the olefinic LPG treatment units, thus minimizing disruptions to the refinery wastewater treatment system.

The following steps can optimize the overall performance and consumption of acid in the alkylation unit associated with the FCCU:

- Upgrades to the tower internals and control systems for the FCC debutanizer and C<sub>3</sub>/C<sub>4</sub> splitter will minimize propylene in the C<sub>4</sub> alky feed and ensure that only the lightest amylenes are lifted. Impurities and contaminants will increase rapidly in C<sub>4</sub> alky feed if the fractionation is poor in the FCC debutanizer or if more than about 10-20% of amylenes are lifted into the C<sub>4</sub> alky feed (thereby sharply reducing the Reid vapor pressure of the remaining FCC gasoline bottoms).
- Upgrades to the FCC riser reactor and feed injector system will mitigate the butadiene, cyclopentene and pentadiene content of the alky feed.
- The retrofit of a selective hydrogenation unit (SHU) for olefinic C<sub>4</sub> alky feed will reduce the quantity of di-olefins (mainly butadiene) and reactive sulfur species fed to the unit.
- Improved control over and monitoring of the quality of purchased mixed butanes, which are often used to balance requirements for fresh isobutane to match fresh olefins in alkylation reactors, will also contribute to improved alkylation unit performance and reduced acid consumption. Purchased mixed butanes can be quite variable in terms of the content of C<sub>3</sub>S and C<sub>5</sub>S, olefins, and sulfur. Significant olefin levels in particular can create serious problems in alkylation units.

The economic justifications for these changes must derive from improvements in quality or quantity of intermediate blending stocks. The pollution prevention benefits would be secondary and would include reduced loading of caustic, caustic derivatives, amines, and soluble organics in the refinery wastewater treatment system.

## Examples of Pollution Prevention Opportunities Rejected by Refiners

As noted in Section B, many refiners have evaluated similar projects, and projects that were favorably regarded in some refineries have been evaluated and rejected in others, largely based on economic and/or operating factors that can vary from one facility to the next. The states of Washington<sup>7</sup> and California<sup>17</sup> have issued lists of projects rejected by refiners. The types of projects listed in these references are for the most part similar to those discussed in Section B.

We emphasize that, in most cases, rejection of a pollution prevention idea does not mean that higher levels of pollution will be released to the environment than if the idea had been adopted. Common reasons for rejecting pollution prevention ideas include the following:

- In many cases, the idea represents an alternative approach that was expected to be less costly than a pollution control method already successfully employed. However, after study, the alternative approach may prove to be more costly than expected. For example, a source reduction method to recover and recycle material in a process unit may turn out to be more costly than the current method of treating that material as a pollutant in the wastewater treatment plant.
- Some methods and ideas may prove to be infeasible or impractical. For example, a recovery and recycle method simply may not work efficiently enough to justify the cost of the project because of low concentrations of the material to be recovered, interference from other materials present in the stream, or a variety of other factors. As another example, attempts to replace certain chemicals and additives used in refining operations with similar products that would result in less pollution may be unsuccessful because the substitute materials may not exist or may not perform as needed or expected.
- In other instances, a source reduction method may cause unexpected technical problems and side effects. For example, a recovered hydrocarbon stream may cause unexpected corrosion or otherwise upset operations when recycled to a processing unit that was expected to use it successfully as a feedstock.
- Some pollution prevention ideas represent secondary benefits of capital intensive projects that could not be justified by the pollution prevention aspects alone. For example, the opportunities to eliminate caustic wash operations as part of low sulfur fuels projects described above in this section would reduce wastewater loading, but the main purpose of the project would be to produce low sulfur diesel fuel and gasoline. In such cases, only if the investment can be justified on other grounds will the pollution prevention benefits will be achievable.

While we cannot review all of the rejected projects in the scope of this study, we have selected some as examples to review the types of factors that might cause them to be rejected in some refineries.

## **Washing and Steaming of Jet Fuel Treater Clay**

As discussed in Section B, clay filtration is often used as a finishing step for some refined products. To minimize the hydrocarbon content of spent clay, refiners may backwash or steam the clay to recover the hydrocarbons. In one case, a refiner attempted extended steaming to reduce the hydrocarbon content and lower the toxicity level to a point where the spent clay would not be considered a hazardous waste. After repeated tests, the steamed clay still failed toxicity tests, and the project was considered unsuccessful. In another refinery, extensive water washing was studied to achieve a similar result. In that case, we believe that either the desired level of toxicity could not be achieved, or the quantity of water needed put too great a load on the wastewater treatment plant (details of the tests were not reported). Yet another refiner reported that it had explored unspecified ways to modify jet fuel clay washing procedures without success.

## **Use of Cyclones to Reduce Coke Fines**

As reported in Section B, many refiners have emphasized projects for the recovery of coke fines around coking units and storage areas. One refiner evaluated the installation of cyclones to remove coke fines from cooling water, which would be a source of coke fines to the wastewater treatment plant through the cooling tower blowdown stream. Because the level of coke fines in the cooling water was small (due to the large volume of water circulated through the cooling water system), the cyclones were not able to remove enough coke fines to justify the investment cost. In such cases, the savings that would justify such a project would typically be the reduction in costs of sludge removal and disposal. If the cost of the upstream removal system is great enough, the savings will be small or non-existent.

## **Evaluate Various Oily Water Sewer Source Reduction Methods**

Source reduction efforts were under study in a refinery to reduce the flow of certain oily sludge forming materials that were reaching the sewer system and incurring sludge removal and disposal costs. This pollution prevention project was dropped when another approach was adopted. It was found that the oily sludge was suitable as feed to a delayed coker in another refinery operated by the same company. The various regulatory approvals required were obtained for transporting the material to and processing it at the affiliated refinery. Thus, the material that formerly was treated as a hazardous waste is now a feedstock to a unit producing a useful product.

## **Purchase Crude Oil with Lower Solids Content, Tighten BS&W Specifications, and Change to Lighter Crude Oil Slate**

Several refiners have considered the possibility of running only crude oils with relatively low solids levels and changing purchasing requirements for crude oil by reducing the bottoms sediment and water (BS&W) specifications. While such attempts are commendable, they are generally impractical. Lighter crude oils that yield more motor fuel and other light products and less heavy residual materials are less available than heavier crude oils that require upgrading processes such as coking to meet demand for light products. The better quality light crude oils can be hard to obtain since they are not available in sufficient quantities

to meet the needs of all refiners that would like to acquire them. Also, BS&W cannot always be separated or controlled, especially in crude oil receipts from vessels that have no way to remove and dispose of sediment and water other than pumping it out with the crude oil (since they are not allowed to dump it in the harbors or oceans).

## **Reduce Cooling Tower and Boiler Blowdown**

Closed water systems, such as boiler systems that collect condensed steam from the process units and recycle it as boiler feed water or cooling water systems that cool return water in a cooling tower and recycle it back to the process units, tend to build up levels of dissolved solids (*e.g.*, from treatment chemicals that must be added to the water) and other contaminants. Blowdown streams from these systems are needed to remove these materials from the system at a controlled rate so they do not accumulate to a level that would create problems (*e.g.*, corrosion or fouling of piping and heat exchanger surfaces). Reduction of blowdown rates would reduce the hydraulic load and the quantity of pollutants requiring treatment in the wastewater treatment plant. Methods to reduce blowdown rates usually focus on modifying chemical treatment methods for the circulating water and evaluating control systems to be sure that the rate of blowdown does not exceed that required to protect the system.

Such projects have succeeded in many refineries, which have found more effective treatment methods and have improved control of blowdown rates. In some cases, however, alternative chemical treatments have caused problems due to insufficient or unstable control of water quality parameters with unfavorable results, such as corrosion and rupture of boiler tubes, corrosion and leakage of heat exchanger equipment, or other technical problems. In other cases, alternative treatment methods have simply proven more costly than the incremental cost of treating higher blowdown flow rates at the wastewater treatment plant.

## **Regenerate Spent Catalyst through Catalyst Suppliers**

As noted in Section B, refiners have gone to great lengths to reduce spent catalyst wastes. One of the measures taken has been to return catalyst to the vendor for regeneration and recycle. While such programs have been successful in some cases, certain types of catalysts cannot be readily regenerated at a cost less than that of new catalyst. Insufficient details were provided concerning this specific example, but in general, due to the physical condition of the catalyst and the steps required for recovery, shipment to the supplier, and regeneration, not all catalysts can effectively be regenerated.

Another factor may be the length of time between catalyst replacements. In the case of a catalyst with a relatively long life (*e.g.*, naphtha hydrodesulfurization catalyst, which typically runs for five years or more), the refiner will have less economic incentive to regenerate spent catalyst that will then have to be placed in inventory and not used for many years. For a catalyst with a shorter life (*e.g.*, one to two years), regeneration and storage until the next change out may be more practical.

## **Section E.**

# **Key Findings Relative To Pollutants Of Concern**

The State of Washington Department of Ecology has identified pollutants in six different categories that are considered to be “Pollutants of Concern.” Table E-1 lists the specific Pollutants of Concern in each of the categories, which are identified below:

- Persistent Bioaccumulative Toxins
- Surfactants and Dissolved Solids causing threat of toxicity of wastewater treatment effluent to aquatic organisms
- Priority Pollutant Metals
- Chemicals causing threat of wastewater treatment upset
- Certain pollutant loadings to wastewater collection system
- Materials designated as Dangerous Waste or that would cause generation of Dangerous Waste when spilled to oily water or storm sewers.

In our review of the pollution prevention projects that have been undertaken in refineries as presented in Section B, we have noted projects that pertain to these pollutants. In this section, we address the prevalence of these pollutants as indicated by the results of the refinery questionnaires received from the Washington refineries, and we discuss the possible sources of and the means of avoiding some of these pollutants.

**Table E-1.**  
**Pollutants of Concern**  
 (Listed by the State of Washington Department of Ecology)

<b>Persistent Bioaccumulative Toxins</b>		
Aldrin	Lead <sup>1</sup>	
4-Bromophenyl phenyl ether	Methoxychlor	
Cadmium <sup>1</sup>	Mercury <sup>1</sup>	
Chlordane	Pendimethalin	
DDT / DDD / DDE	Pentabromo diphenyl ether	
Dicofol	Pentachlorobenzene	
Dieldrin	Pentachloronitrobenzene	
Dioxins & furans	Polyaromatic hydrocarbons (PAH)	
Endosulfan	Polychlorinated biphenyls (PCBs)	
Heptachlor epoxide	Toxaphene	
Hexachlorobenzene	Trifluralin	
Hexachlorobutadiene	1,2,4,5-Tetrachlorobenzene	
Hexachlorocyclohexane (Lindane)		
<sup>1</sup> Also listed below as a Priority Metal Pollutant		
<b>Surfactants and Dissolved Solids Causing Threat of Toxicity to Aquatic Organisms</b>		
Surfactants / Detergents	Dissolved Solids	
<b>Priority Pollutant Metals</b>		
Antimony	Copper	Selenium
Arsenic	Lead <sup>2</sup>	Silver
Beryllium	Mercury <sup>2</sup>	Thallium
Cadmium <sup>2</sup>	Nickel	Zinc
Chromium		
<sup>2</sup> Also listed above as Persistent Bioaccumulative Toxin		
<b>Chemicals Posing Threat to Wastewater Treatment</b>		
Diethanol amine (DEA)		
Other amines <sup>3</sup>		
• Monoethanol amine (MEA)		
• Methyl diethanol amine (MDEA)		<sup>3</sup> Added to list by Jacobs
Consultancy Inc.		
• Diglycol amine (DGA)		
• Di-isopropanol amine (DIPA)		
<b>Other Pollutant Loadings to the Wastewater System</b>		
Solids		
• Soils		
• Catalysts		
• Coke fines		<sup>3</sup> Added to list by Jacobs
Consultancy Inc.		
• Scale and rust		
Hydrocarbons (preventable / recoverable)		
Stormwater overflow to wastewater sewer system <sup>3</sup>		

**Table E-1** (continued)

<b>Spills and Other Releases of Dangerous Wastes and Their Precursors</b>
RCRA Listed Refinery Wastes
RCRA Designated Wastes
Refinery Wastes, WAC Dangerous Waste Rule
<ul style="list-style-type: none"><li>• DAF float</li><li>• Slop oil emulsion solids</li><li>• Heat exchanger bundle cleaning sludge</li><li>• API separator sludge</li><li>• Tank bottoms (leaded)</li><li>• Crude oil storage tank sediment</li><li>• Clarified slurry oil tank sediment and/or inline filter/separation solids</li><li>• Spent hydrotreating and hydrorefining catalysts, including guard beds but excluding inert support media</li></ul>
Other Dangerous Wastes, WAC Rule

## **Persistent Bioaccumulative Toxins**

As shown in Table E-1, there are twenty-five pollutants in this category. However, relatively few are believed to be associated with refinery operations. The surveys from the Washington refiners listed only the three toxic metals (cadmium, lead and mercury), dioxins and furans, polyaromatic hydrocarbons, and polychlorinated biphenyls (PCBs) as pollutants in this category that have been identified in the wastewater streams of these refineries. We are not aware of the other pollutants listed in this category having a significant presence in refining operations, either as raw materials, by-products, products, or pollutants associated with any refinery operation, and none of the refiners reported any of the other compounds to have been identified in their wastewater streams.

Some of these materials are pesticides, herbicides or related products that might be used at times for pest control, weed control, *etc.* in a refinery. In such cases, they could enter the oily water or stormwater systems in trace quantities as a result of rain or wash down of an area for housekeeping or maintenance purposes. Otherwise, we would not expect to find these materials in refinery wastewater systems or effluent streams.

The pollutants in this category that are relevant to refinery operations are discussed in more detail below.

## **Dioxin and Furan Formation in Refining Processes**

Two refining processes are associated with the formation of dioxin and furan compounds. The more significant of the two by far is catalytic naphtha reforming, a process in which these compounds can form during catalyst regeneration. Lesser amounts may also be associated with some isomerization units. These processes are discussed below.



## Catalytic Naphtha Reforming

### *Background Information*

The naphtha produced in the crude distillation unit and in other refining units is a very poor quality gasoline blending stock due to its low octane value. Strong demand for gasoline provides favorable economic incentives to upgrade naphtha to high-octane products. The catalytic reformer is the process that upgrades naphtha into aromatic compounds (*i.e.*, compounds with a benzene ring), which have very high octane values. They are valuable both as gasoline blending components and as feedstocks for the manufacture of various petrochemicals.

The conversion of naphtha to aromatic compounds occurs via a complex series of reactions, including the dehydrogenation of alkylcyclohexanes, the dehydroisomerization of alkylcyclopentanes, the dehydrocyclization of paraffins, and the isomerization of alkylcyclopentanes. To optimize the value of the reformat product stream, the refiner must maintain careful control of reactor operating conditions with close attention paid to operating pressures, temperature profiles and other key parameters.

The reforming process uses a precious metal based catalyst, typically platinum or platinum-rhenium, operating at temperatures between 925°F and 1000°F to convert naphthenes to the corresponding aromatics and to isomerize paraffinic structures to isomeric forms. Both the conversion and isomerization reactions lead to a marked increase in octane number, although at the cost of volume shrinkage. As a result of these and other reactions associated with the process, coke will deposit on the catalyst. The catalyst must be reactivated or regenerated by burning off the coke in an inert atmosphere with low concentrations of oxygen to remove the coke buildup.

Depending on the reforming technology licensed, regeneration may be one of three types: semi-regenerative, cyclic, or continuous. Semi-regenerative units are typically regenerated every six to twelve months. Cyclic and continuous reformers can regenerate catalyst while the unit is still in operation.

The following table shows the types of catalytic naphtha reformers that are found in the State of Washington:

### **Responding Washington Refineries: Catalytic Naphtha Reformers**

<b>Company</b>	<b>Location</b>	<b>Crude Capacity (BPD)</b>	<b>Catalytic Reforming Process (BPD)</b>	
			<b>Semi Regen</b>	<b>Cyclic</b>
BP PLC	Ferndale	222,720	60,480	
Shell Oil Products USA	Anacortes	148,600	32,200	
Tesoro West Coast Co.	Anacortes	114,500		24,300
ConocoPhillips	Ferndale	89,000		15,500
US Oil & Refining Co.	Tacoma	43,700	5,750	
Source: <i>Oil &amp; Gas Journal</i> , Dec. 24, 2001				

From the above data, we conclude that BP, Shell and U.S. Oil have the type of regeneration process that requires the unit to come off line for a short duration to complete catalyst regeneration, a procedure typically scheduled in conjunction with a maintenance turnaround. Experience indicates that a semi-regenerative unit can be regenerated in about three to five days from time of feed out to time of feed in if the turnaround is taken for catalyst regeneration only.

With respect to Tesoro and ConocoPhillips, their cyclic units employ a swing type reactor, such as that licensed from ExxonMobil (Powerforming™) or BP (Amoco) (Ultraforming™). It appears from the *Oil & Gas Journal* survey that none of the refiners uses the continuous catalyst regeneration processes offered by either UOP or IFP.

In the late 1980s, the presence of trace amounts of dioxin in catalytic naphtha reformer regenerator wastewater was observed in some Canadian refineries. This finding has caused refiners to review their regeneration procedures with the licensors to determine root causes.

### ***The Regeneration Process***

At one time, catalyst regeneration referred only to burning off carbon. Regeneration now refers to a sequence of procedures, and carbon burn is only one step in the process. Each licensor and catalyst supplier (in some instances the same company) has developed proprietary procedures for completing the regeneration process. There are variations, but the general procedure is similar for bimetallic and multi-metallic catalysts. The order of events is as follows: shutdown and purge, carbon burn, oxidation or proof burn, rejuvenation, reduction, chloriding and sulfiding. We will focus on the parts of the regeneration process in which we perceive dioxin formation may occur.

The carbon burn is usually the most time-consuming step in regeneration. The burning (oxidation) of carbon must be strictly controlled to avoid excessive temperatures that could damage the catalyst. The temperature of regeneration gas flowing out of any reactor is customarily limited to 850°F maximum. The need for caution during a carbon burn must be strongly emphasized. Some refiners have learned to their dismay that it is not wise to raise the oxygen percentage to speed up coke burning. If the oxygen content is increased, temperatures rise rapidly. The carbon burn is assumed to be complete when the temperature change across the reactor falls to nearly zero.

The next step in regeneration is the cleanup or proof burn to ensure that a catalyst is thoroughly cleaned of carbon. Unless the catalyst is to be cooled and unloaded, this step immediately follows the carbon burn. The reactor inlet temperatures are gradually raised to 900 to 950°F until the temperature increase across the reactors is essentially zero. The oxygen concentration is gradually raised to 5-6 mole percent in the regeneration gas. When the temperature differential and the oxygen content of the outlet gas of the last reactor indicate no carbon burning, the catalyst is ready for the rejuvenation step.

The significant contribution of rejuvenation is that it re-disperses the agglomerated metal or metals of the catalyst. This metal redistribution essentially restores the catalyst structure to that of fresh catalyst. Rejuvenation is accomplished by contact of the catalyst with a gaseous mixture of oxygen and chloride at an elevated temperature. The procedure is to continue circulation of the regeneration gas containing 5 to 6 mole percent oxygen and to inject chloride for a period of several hours while maintaining the catalyst at 900 to 950°F.

To prevent corrosion downstream of the reactors, a dilute solution of sodium carbonate or sodium hydroxide is circulated from the product separator to the inlet of the reactor effluent/feed heat exchangers. This neutralizing solution is maintained at a pH of 6-7 by the addition of fresh caustic. The amount of chloride injected is proprietary with each catalyst supplier. Dioxin and furan compounds tend to concentrate during regeneration in this neutralization solution, which is subsequently treated in the refinery wastewater system.

Dioxin is a chlorinated, hydrogen-deficient, polynuclear aromatic compound. Furan is a five-member ring compound that contains oxygen. Conditions conducive to dioxin and furan formation can occur during the carbon burn, oxygen soak and rejuvenation phases of catalyst regeneration. Online process severity may increase the coke formation rate, and any reactor bed maldistribution may result in abnormal localized coke formation. Both situations can contribute to additional operational problems encountered during the carbon burn and can contribute to the formation of dioxin and furan.

With current catalytic reforming technologies, it may be nearly impossible to eliminate dioxin or furan production during regeneration. The continuous processes seem to have eliminated dioxin and furan emissions to wastewater by routing the regenerator flue gas directly to the reformer heater firebox. The semi-regenerative processes require a neutralization stream to protect unit metallurgy from corrosive regeneration gases. It might be possible to divert regeneration flue gases from a catalytic reformer into a furnace firebox to destroy these compounds, or a refiner might consider installing a filtration system as was done at one of the Canadian refineries involved in the 1980s study. Another alternative that was utilized in dealing with cooling water systems might be to replace chlorine with an alternative halogen, but the licensors of reforming technology have generally had a lukewarm response to the feasibility of this step.

## Isomerization

Butane isomerization is a process to convert straight chain n-butane to the branched chain molecule isobutane, a feedstock used in making both alkylate and MTBE. Light straight run naphtha (pentane and hexane) isomerization converts straight chain C<sub>5</sub> and higher hydrocarbons to a branched chain molecular structure, significantly raising the octane value in the process. In the most commonly employed units, butane or pentane/hexane is combined with hydrogen and flows through a fixed bed reactor(s) over a precious metal catalyst. The presence of hydrogen in the butane isomerization process suppresses the polymerization of olefin intermediates, while in naphtha isomerization, it inhibits coke formation on the catalyst. The product from butane isomerization is typically fed to the alkylation unit, and the naphtha isomerization product is sent to gasoline blending operations.

The addition of a small, continuous stream of a chlorinated hydrocarbon compound, such as perchloroethylene, provides a source of hydrogen chloride required for proper catalyst activity in both the butane and naphtha processes. Lighter hydrocarbons (C<sub>4</sub> and C<sub>5</sub>) do not cause coke to form on the catalyst, but heavier compounds, especially benzene, do promote minor levels of coke formation. While some dioxin can be produced in naphtha isomerization catalyst regeneration, under even the most conducive conditions, the quantity is very much less than that produced during the regeneration of a semi-regenerative catalytic naphtha reformer.

Coking does not occur in the butane isomerization process, and conditions there are not conducive to dioxin formation.

According to the latest annual refinery survey in the *Oil & Gas Journal*<sup>22</sup>, there are three refineries in Washington with isomerization units – U.S. Oil, ConocoPhillips and Tesoro. The unit at U.S. Oil reportedly uses a C<sub>5</sub>/C<sub>6</sub> feedstock, while those at ConocoPhillips and Tesoro use C<sub>4</sub> feedstock.

## **Polyaromatic Hydrocarbons (PAH)**

The responses of the Washington refiners to the questionnaire indicate that crude oil supplies and thermal and catalytic cracking operations are the primary sources of PAH in the refineries. Water separated from crude oil storage tanks was cited by one refinery as a likely source of PAH losses to the sewer system. Another refinery reported numerous potential sources for PAH, but it also reported that after testing various product and waste streams for PAH a number of years ago, it could find no detectable concentrations. The respondents indicated that control of PAH in spills was adequately addressed in the various spill control and spill response preparedness programs that the refineries are required to undertake by the EPA, U.S. Coast Guard, U.S. Department of Transportation, and Washington Department of Ecology. Such programs include the Spill Prevention Control and Countermeasures (SPCC) Plan, Facility Oil Spill Response Plan, Dock Operations Manual, Facility Oil Handlers Training and Certification Program, Triennial Spill Drill Program, Operating Procedures and Standing Orders and others.

Thus, while the refineries are generally aware of PAH sources, there are no ongoing programs or studies to test for PAH on a routine or regular basis. No programs are in place specifically to address PAH source reduction.

## **Polychlorinated Biphenyls (PCB)**

Two Washington refineries have reported having PCB containing electrical transformers still in service, although in one case, only a single transformer remains. These two refineries report that they have tested for PCB; one reported finding no PCB, while the other did not specifically indicate results.

Very few U.S. refineries are believed to have PCB containing transformers still in service, and there are no other sources of PCB in refining operations. Refineries are thus not regarded as significant sources of PCB in wastewater effluent. The source reduction efforts needed are adequate maintenance to prevent loss of transformer oil and eventual replacement of the remaining transformers.

## **Toxic and Other Priority Metals**

The discussion of the metal toxins is combined with that of the Priority Pollutant Metals presented below.

## **Surfactants and Dissolved Solids**

Many of the process chemicals used in the refinery processes have surface-active (surfactant) characteristics, and, as do other hazardous chemicals, they require proper handling. Inventories of these chemicals tend to be small, and their purchase costs tend to be high. Furthermore, loss of a large quantity of surfactant can quickly interfere with operation of the wastewater treatment plant. Thus, from both a cost and pollution prevention aspect, it is in the best interest of the refiner to properly contain storage areas of these chemicals so that they cannot enter inadvertently the wastewater treatment system.

Refiners have multiple incentives to prevent surfactants from entering the sewer system and have undertaken appropriate measures to do so. Whereas they have historically used strong detergents to clean oily residues from refinery structures and walkways, the trend today is to emphasize mechanical methods, such as absorbents and hydro-blasting, for removing oily residues. Inventories of surfactants are more closely controlled and minimized.

Refinery operations are not typically sources of large quantities of dissolved solids. The responses to our questionnaire indicated that dissolved solids are not generally monitored in the influent to wastewater treatment operations. Potential sources of dissolved solids were listed as the incoming refinery water supply, corrosion inhibitors, boiler and cooling tower blowdown streams, and possibly other sources. None of the refiners had any particular concerns with regard to dissolved solids, as is typical of most refineries.

## **Priority Pollutant Metals**

The Persistent Bioaccumulative Toxins listed in Table E-1 include three metals – cadmium, lead and mercury. These three metals are also listed in Table E-1 under Priority Pollutant Metals along with ten other metals. All thirteen metals were reported to be present in varying concentrations in the wastewater systems of the Washington refineries.

A primary source of toxic and other priority pollutant metals in refinery wastewater effluent is the crude oil that is processed in the refinery. Corrosion, catalyst additives, various other refinery raw materials, and even the public water supply are other sources of some metals. Both crude oil and other sources of metals found in refinery wastewater are discussed below:

### **Metal Contaminants in Crude Oil**

All crude oils contain trace quantities of naturally occurring metals. Other than crude oil trader or proprietary oil company crude oil assay information, very little data have been published on the specific metal content of crude oils. In 1999, member companies in cooperation with the Petroleum Environmental Research Forum published a study that involved 26 crude oils from various parts of the world. Crude oils, which ranged in API gravity from 12° (very heavy crude oil) to 46° (very light crude oil), were examined with respect to 18 metals. The results of the study indicated that many metals are present at such low levels that there is no need to consider them as chemicals of concern for purposes of site characterizations and risk assessments at sites where accidental and/or historical crude oil releases have occurred. Mercury is by far the most significant metal in crude oil and is discussed in the following paragraphs.

In a group of related papers<sup>13</sup>, Mercury Technology Services reports that there is wide variation in the distribution of mercury compounds in petroleum samples. According to this source, crude oil may contain mercury in several forms, including dissolved elemental mercury, dissolved organic compounds that are highly soluble in crude oil, inorganic salts that are soluble in condensate and that migrate to the water phase when it separates, suspended compounds, and mercury adsorbed on suspended solids. The organic compounds are reported to partition to particular product streams. The papers also report that the mean concentrations of mercury in crude oil applied by U.S. regulatory agencies have generally been in error due in large measure to the over-weighting of data for certain California crude oils that have extremely high mercury levels but that represent only a small fraction of the crude oil processed in U.S. refineries.

(One paper suggests that using proper weighting would reduce the estimated mean concentration of mercury by a factor of around 30).

The EPA has recently issued a study entitled “Mercury in Petroleum and Natural Gas: Estimation of Emissions from Production, Processing and Combustion”<sup>23</sup>. This study reports that the major concentration of mercury compounds occurs in material boiling at less than 170°C (338°F). It also reports that crude oils exhibiting the largest concentration of mercury originate from Far East condensates.

Our understanding is that a project is currently underway in cooperation with the U.S. EPA, the American Petroleum Institute (API), two laboratories in Seattle (Frontier Geosciences and CEBAM Analytical) and Texas A&M University to determine the mercury content of crude oil processed in the United States. The focus of the project is to determine the mean concentration and range of concentrations of total mercury in crude oil in a statistical fashion.

Domestically, some states, including California, Louisiana and Texas, track the composition of crude oils run in their state’s oil refineries. The State of Washington does not require refiners to provide this information. Based on our discussions with WSPA and other sources, we expect that the majority of domestic crude oil processed in Washington is Alaskan (Alaskan North Slope) delivered via the TAPS pipeline. Imported crude oils are tracked by the U.S. Energy Information Agency and have been summarized for the Washington state refineries by refinery, source and year in Table E-2, “Import Crude to Washington, 1996 to 2001.”

**Table E-2.  
Sources of Foreign Crude Oil  
Processed in Washington Refineries (1996-2001)**

<b>Source by Country</b>	<b>1996</b>	<b>1997</b>	<b>1998</b>	<b>1999</b>	<b>2000</b>	<b>2001</b>
Argentina		X	X	X	X	X
Australia	X	X	X	X	X	X
Bolivia		X				
Brunei				X	X	X
Canada	X	X	X	X	X	X
Colombia		X				
Ecuador						
Guinea	X		X		X	
Indonesia				X	X	
Iraq					X	X
Malaysia	X		X	X	X	X
Nigeria						X
Oman	X				X	
Papua New Guinea	X			X		
Saudi Arabia					X	X
United Kingdom			X			
Venezuela	X	X	X	X	X	

*Source: U.S. Energy Information Agency (EIA)*

With respect to refinery wastewater, the largest concentration of mercury compounds will typically occur in process water that contacts crude oil in the desalter. Secondary sources of these mercury compounds will occur in the refinery light ends fractionation sections that concentrate wash water used to control corrosion or concentrate it as a result of water/steam added to the process. Mercury removal systems have been patented and discussed in the refinery trade magazines, such as the article “Conceptual Design of Mercury Removal Systems for Hydrocarbon Liquids in Gas Processing Facilities” that was published in *Hydrocarbon Processing* <sup>24</sup>. Because very few commercial applications have been documented, this paper reviews the conceptual design approach for mercury removal systems. The paper examines process locations for mercury removal systems and compares them based on technical and practical limitations. The papers by Mercury Technology Services report that mercury removal systems based on the use of sorbents are usually only partially effective and do not work on all mercury compounds, particularly the suspended forms and organic mercury compounds.

Mercury is of concern to refiners not only as a pollutant but also as a cause of corrosion of processing equipment. The corrosive effects of dimethyl mercury (DMM) on carbon steel and aluminum make it one of the most significant mercury containing components of crude oil. In addition, mercury is a poison to many catalysts used in refining processes.

## **Other Sources of Metals in Refining Effluent**

### **Mercury**

Sources of mercury in refinery operations other than crude oil supply include laboratory and process control equipment. Thermometers and other precision analytical equipment often contain elemental mercury, and mercury electrical switches are sometimes used in control equipment. Other types of laboratory equipment and electrical switches using non-mercury materials are becoming more common, but older equipment containing mercury is still found in refineries, and for some applications (such as certain electrical switches), there are no substitutes. Equipment breakage and damage remain potential sources of loss of elemental mercury into building and unit drains.

### **Chromium**

Chromium in the past was present in chromate based cooling water treatment chemicals, but the EPA now mandates non-chromate based treatment programs. It has now been about eight to ten years since the conversion of these treatment programs in the various refineries, and residual chromium from treatment chemicals should no longer be present in refinery wastewater.

Chromium is also present in stainless steel and other alloy piping and equipment used in refinery processing equipment to minimize corrosion in selected applications. Such applications are not always successful in eliminating corrosion, however, and chromium can therefore be present as a corrosion product in both refined products and wastewater streams. Chromium may also be present in crude oil.

The Washington refineries reported levels of chromium in wastewater effluent ranging from below the detectable limit to values generally less than 10 micrograms per liter. Since the refineries have ceased chromate based water treatment, corrosion of stainless steel and alloy equipment and crude oil are the only likely sources of chromium.

## **Antimony**

Antimony or antimony/bismuth is used as a liquid additive in the FCCU process to inhibit the deleterious effects that metals such as nickel and vanadium can have on FCC catalyst. A metals passivator, antimony adheres to the FCC catalyst and can be found in that form both in FCC slurry bottoms and in spent regenerated FCC catalyst. Other than a liquid chemical spill, perhaps the only other source of antimony present in refinery wastewater would be spent FCC or equilibrium catalyst that has been washed to the sewer. Antimony is generally not found in crude oil.

## **Chemicals Posing Threat Of Wastewater Treatment Upset**

The Department of Ecology lists only diethanolamine (DEA) as a specific pollutant of concern in this category. Other common amines that may be used by the Washington refiners include monoethanolamine (MEA), diglycol amine (DGA), di-isopropanol amine (DIPA), and methyldiethanolamine (MDEA). Refiners typically use amines to remove hydrogen sulfide from refinery-produced fuel gas and mixed propane/butane streams.

Good engineering practice dictates that amine units have closed drain systems segregated from the plant wastewater treatment system. Amine discharges to the wastewater treatment system are usually the result of leaks outside the closed drain system. Amines cause two major problems when they enter a wastewater treatment system. Being alkaline compounds, amines will raise the pH of the wastewater and thus interfere with the operability of the treatment plant, and they are converted to ammonia in the wastewater treatment plant's biological treatment system, thereby threatening the organisms that consume various hydrocarbon wastes. When amines are present in the wastewater, the ammonia content of the treated wastewater may be higher than that of the influent to the treatment plant.

The questionnaires returned by the Washington refiners indicate that small concentrations of any of these amines could be expected (trace or part per million levels were cited) due, for example, to the blowdown streams from the amine systems. None of the refineries indicated any particular problems controlling amine levels, nor have they experienced upsets of the wastewater treatment operations due to amine loadings. Three refineries indicated that they use both DEA and MDEA, while the others use only one or the other. None of Washington refineries reported using MEA, DGA or DIPA.

## **Other Pollutant Loadings To Wastewater Systems**

Other pollutants that can overload or otherwise adversely affect wastewater collection and treatment operations include various solids (*e.g.*, soils, catalysts, coke fines, scale and rust), hydrocarbons, and tank bottoms that can contribute to sludge formation. In many cases, these pollutants could, with proper action, be prevented from entering the sewers or be recovered and reprocessed before they affect wastewater treatment operations.



## **Soil and Sand**

The questionnaires returned by the Washington refiners show a number of procedures and methods being employed to minimize the quantities of these materials reaching the sewer systems. Control of soils is achieved by use of berms and curbs at sewer drains, street sweeping, and covering sewers during maintenance activities. Sanding of roadways was noted as a particular source of solids during both winter for traction on icy roads and summer for protection of hot road surfaces from deterioration by truck traffic. Such sanding is considered essential. However, sand used for absorbing spills in a loading rack area has been replaced with rock to minimize the potential for sand being tracked onto plant roads and washed into the sewer system by rainfall in at least one refinery. Control of erosion by spraying asphalt onto tank berms to stabilize the soil is being studied in one refinery as a means of minimizing soil losses to the sewer system.

## **Catalyst**

Control of catalysts is reported by Washington refiners to be achieved by dust collection methods, use of dry catalyst dumping procedures in lieu of wet (wash out) procedures for certain catalysts, controlled collection of catalyst in containers for off-site disposal, and performing some used catalyst handling and loading in covered buildings to confine fines that would otherwise be exposed to wind and rain and lost to the sewer system.

## **Coke Fines**

Control of coke fines is achieved in a manner similar to that for control of soil and sand. Berms and curbs are used at drains, streets are swept in areas where coke trucks operate, sewers are covered where appropriate during maintenance, and the coke pile is kept wet to control fugitive dust.

## **Scale and Rust**

Scale and rust are present to some extent in crude oil and are generated in the refining operation. Washington refiners report the use of isolated areas that are set aside for cleaning scale and solids from heat exchanger tube bundles with fixed overflow weir systems employed to minimize sludge losses to the sewer. During sandblasting operations, sewers are covered to prevent loss of sand, used paint, metal, and other debris to the sewers. Sand blasting operations in open areas may utilize a vacuum system to collect dust and spent grit.

## **Hydrocarbons and Tank Bottom Materials**

Hydrocarbons can reach the sewer system from multiple sources in a refinery. One of the more important sources is loss to tank bottoms when the bottoms (water phase) is drawn off and separated from the oil phase above it. One of the key means of controlling hydrocarbon losses in Washington refineries is control of tank bottoms separation to the sewer system. Methods for controlling losses from crude oil and heavy oil product tanks include use of mixers to suspend material in the oil phase, close monitoring of drawdowns by operating staff, and coating crude tank bottoms and walls with corrosion resistant paint to minimize corrosion products in tank bottoms.

Best operating practices call for loss of oil to the deck to be minimized when process unit drains are checked to ensure that water has been removed from equipment during startup. Likewise, best efforts should be followed to minimize oil losses to the deck or pad upon shutdown.

## **Stormwater Overflow to Wastewater System**

The subject of the potential for stormwater overflow into oily water sewer systems was not directly addressed in the questionnaire sent to the Washington refiners. As discussed in Section D, refiners generally have taken steps to segregate stormwater and oily water to reduce sludge formation and to prevent excessive hydraulic loading of the wastewater treatment operations. In addition to the use of physical barriers to keep stormwater out of the oily water systems, it is also important to address the possibility of crossover connections that may have been overlooked, especially in older facilities where buried crossovers could exist that are no longer shown on drawings of the sewer systems. To the extent that such projects may not have already been undertaken, they are recommended.

## **Materials Leading To Presence Of Dangerous Wastes**

In Table E-1 we list both general categories of wastes and specific sources of refinery wastes that either are classified as Dangerous Wastes or would result in generation of Dangerous Waste as defined in the Washington Dangerous Waste Regulations, WAC 173-303<sup>11</sup>. All of the refineries in Washington as in other states have procedures and programs in operation to prevent the materials listed in this category from entering their oily and stormwater sewers. Most of these materials are removed for collection and disposal only during maintenance turnarounds, and none are continuously removed. Any releases or spills of any of these materials should therefore only be the result of accidents, failure of operating staff to follow documented procedures, or equipment failure. The focus for prevention of such spills and releases would therefore be the training of staff in procedures, the review of procedures by management and technical staff, safety training, training in the proper use of the equipment used to collect these materials, and proper maintenance of this equipment.

Most refineries today have trained hazardous materials response teams as a part of the refinery's total emergency response effort. These teams are trained and equipped to handle most spills and releases of hazardous materials. For large releases, most refineries have contracted with a hazardous spills contractor for additional support. In areas with a high refinery concentration, the refiners may pool their efforts and resources in a formalized mutual aid organization. It was beyond the scope of this study to review these aspects of the refinery operations, but we believe that the proper programs are in place to achieve these objectives.

## **Section F.**

# **Summary of One-Day Workshop Results**

The original RFQQ issued by the Department of Ecology for this study called for the contractor to conduct a one-day workshop in Washington for the Department of Ecology and refinery representatives to explain and field questions concerning the project results. On October 8, 2002, this workshop was held in Mount Vernon, Washington with staff from the Department of Ecology, Northwest Air Pollution Authority, Western States Petroleum Association, and all five major refineries operating in the State of Washington in attendance. The workshop presentation materials are contained in Appendix 3.

The workshop, which was conducted as an informal forum to encourage discussion and interaction by the participants, began with a review of the past activities of U.S., and Washington refiners in wastewater pollution prevention. The discussion demonstrated the close parallels between the Washington refiners and their counterparts in other locations. A brief review was then conducted of examples of projects evaluated and rejected in various refineries. These reviews focused on the similarities of these projects to those implemented elsewhere where economic incentives and local economic factors were more favorable.

The discussion then moved to the subject of the three pollution prevention opportunities that are discussed in Section D – parallel sour water stripping, elimination of kerosene and diesel caustic washing, and upgrading of olefinic LPG produced in fluid catalytic cracking. The participants in the workshop suggested that while these projects might have merit, the high capital cost associated with them would likely limit their application to grassroots projects, revamps, or major expansions. (Their conclusion is thus consistent with the observations in the second paragraph of Section D.) Specific points raised in the workshop are as follows:

- Parallel sour water strippers were suggested as a means of isolating wash waters that contain soluble organics and phenolic compounds from those that do not, rather than combining them as feed to a single sour water stripper. Stripped wash waters could thus be recycled back to the various processes without introducing these soluble organics and phenolic compounds into processes in which they are incompatible. One of the participants pointed out that in their experience, wash water from hydrocrackers, which was included in the group of wash waters not containing these organic and phenolic compounds, could, in fact, contain such compounds. The comment points out that in any evaluation of separate sour water stripping facilities, care must be taken to analyze all wash water streams thoroughly to verify those that should be directed to each stripper. Another participant indicated that the need to operate and maintain two separate systems would be a potential disincentive.
- Participants acknowledged that there has been a general trend toward eliminating caustic wash operations in favor of additional hydrotreating, but there was agreement that reduced caustic wash water loading on the wastewater treatment operations alone cannot justify the investment required for hydrotreating capacity increases. As ongoing clean fuels projects (ULS diesel fuel and gasoline) that require more hydrotreating capacity are completed, any further justification to expand hydrotreating will likely diminish.

The workshop next addressed the results of the surveys sent to the refiners, all of whom participated by returning completed survey forms. The survey results are covered in Section C of this report. The only comment offered during the workshop regarding topics covered in the surveys was the following:

- Regarding sources of mercury, one participant noted that while the refinery had reduced the number of mercury-containing electrical controls in the facility, some of these control devices could not be replaced since there are no non-mercury switching devices available. Thus, there will always be some mercury-containing devices in the facility. These switches are not considered a high potential source of mercury spills. At least one other refinery representative voiced agreement with this observation.

The last portion of the workshop dealt with special topics – dioxin and furan sources (with emphasis on catalytic reforming), metal contaminants in crude oil (with emphasis on mercury), and the application of pollution prevention principles in process design. Key points discussed in this session were as follows:

- Regarding dioxin and furan formation during catalytic reformer catalyst regeneration, the basic conditions and mechanisms were reviewed, and the differences among the three types of reformers (semi-regenerative, cyclic and continuous) were discussed. Much of the discussion centered on differences in the catalyst rejuvenation step with regard to the use of caustic wash to neutralize the regenerator flue gases (resulting in the absorption of dioxin and furan in the neutralizing stream) versus diverting the flue gases to a hot reactor heater firebox, where the dioxin and furan are destroyed. (Refer to the discussion in Section E.)
- Regarding mercury in crude oil, there was general agreement that the five Washington refineries do not rely on crude oil from sources with high mercury contents.
- The steps involved in formal process design activities for major projects were reviewed and illustrated the ways in which most engineering and construction companies integrate pollution prevention into process design. The ways in which waste minimization, source reduction, and waste disposal alternatives are applied in all steps from the initial feasibility study through detailed design, construction and start-up were discussed.

## **Section G.**

# **Contractor's Assessment of Pollution Prevention Project Value**

The RFQQ for this study calls for the final report to include the contractor's opinions concerning the usefulness of the project and the value of the information yielded to refinery environmental programs and to environmental improvement. We believe that the findings of this study are useful in characterizing ongoing refinery wastewater pollution prevention efforts in the State of Washington and in demonstrating that these efforts have in general been as thorough as those of refiners elsewhere and have led to similar types of results and improvements. We believe the study is also useful in identifying and clarifying sources of key toxic pollutants in refining and the control measures used by refiners to minimize their impact. We refer below to specific objectives of the study (as given in the RFQQ) and the findings presented in this report as follows:

1. The overall objective of the project was to identify water pollution related pollution prevention opportunities applicable to Washington refineries, beyond those identified in available literature, together with the conditions under which their feasibility would be more or less likely. The study has investigated pollution prevention activities by refiners outside Washington and, by comparing them with projects evaluated by Washington refiners, has provided assurance that there are no categories of projects evaluated outside the state that have been overlooked by Washington refiners. The study has further provided assurance that opportunities for major new breakthroughs, such as those identified in Section F, do exist, although for the most part, such opportunities will require design modifications and will be one aspect of major capital programs that cannot be justified by wastewater impacts alone.
2. Due to public and Department of Ecology interest in controlling dioxin and furans in the environment, one objective of the study was to address catalytic reformer process alternatives that could reduce or eliminate dioxin formation during reformer catalyst regeneration. This topic has been examined in Section E with the conclusion that while dioxin formation during regeneration cannot be avoided, diversion of regenerator flue gas to the reformer furnace firebox has the potential to destroy dioxin in continuous or cyclic units. We thus believe that the study has successfully addressed this key topic.
3. The Department of Ecology identified the Pollutants of Concern that are important to address in pollution prevention efforts (refer to Table E-1). The study has addressed these pollutants in Section E by identifying those that are likely to be significant in refining operations, reviewing the sources of these pollutants in refineries, and discussing the possible ways for refiners to control these pollutants. Particular attention was paid to mercury sources and control measures, and we believe that the study has properly characterized the present level of understanding of these sources and important ongoing programs to clarify data regarding the levels of mercury in crude oil.

# References / Bibliography

U.S. EPA and Other Governmental References (suggested by the State of Washington Department of Ecology):

- 1 <http://es.epa.gov/oeca/sector/sectornote/pdf/petrefsn.pdf> - "Profile of the Petroleum Refining Industry" – Section V (Pollution Prevention Opportunities)
- 2 <http://www.dtsc.ca.gov/PollutionPrevention/assessment-petroleum-industry2.pdf> - "Assessment of the Petroleum Industry Hazardous Waste Source Reduction Planning Efforts" – Sections IV & V
- 3 <http://es.epa.gov/techinfo/facts/amova-d.html> - "Amoco/USEPA P2 Project: Executive Summary" – Table 3.2, *Selected Pollution Prevention Engineering Projects*
- 4 <http://es.epa.gov/techinfo/facts/cheklst5.html> - "Refining Industry Pollution Prevention Opportunities Checklist"
- 5 <http://es.epa.gov/techinfo/facts/epa/petroleum.html> - "Pollution Prevention Opportunities In Petroleum Refining"
- 6 <http://www.epa.gov/epaoswer/hazwaste/minimize/petro/ptrlm.txt> - "Waste Minimization for Selected Residuals in the Petroleum Refining Industry" – Section III

State of Washington Pollution Prevention, Guidance Manuals and Regulations (suggested by the State of Washington Department of Ecology):

- 7 <http://www.ecy.wa.gov/pubs/0207009b.pdf> - "Pollution Prevention (P2) Opportunities Implemented and Rejected – A Summary of Information from Petroleum Refinery Pollution Prevention Plans in Washington"
- 8 <http://www.ecy.wa.gov/pubs/0207009c.pdf> - "Major Refinery Processes at Refineries in Washington State"
- 9 <http://www.ecy.wa.gov/biblio/912.html> or <http://www.ecy.wa.gov/pubs/912.pdf> - "Pollution Prevention Planning Guidance Manual"
- 10 <http://www.ecy.wa.gov/biblio/93015.html>, or <http://www.ecy.wa.gov/pubs/93015.pdf> - "Guidance Manual for Developing a Stormwater Pollution Plan for Industrial Facilities"
- 11 <http://www.leg.wa.gov/wac/index.cfm?fuseaction=chapterdigest&chapter=173-303> - "Dangerous Waste Regulations"

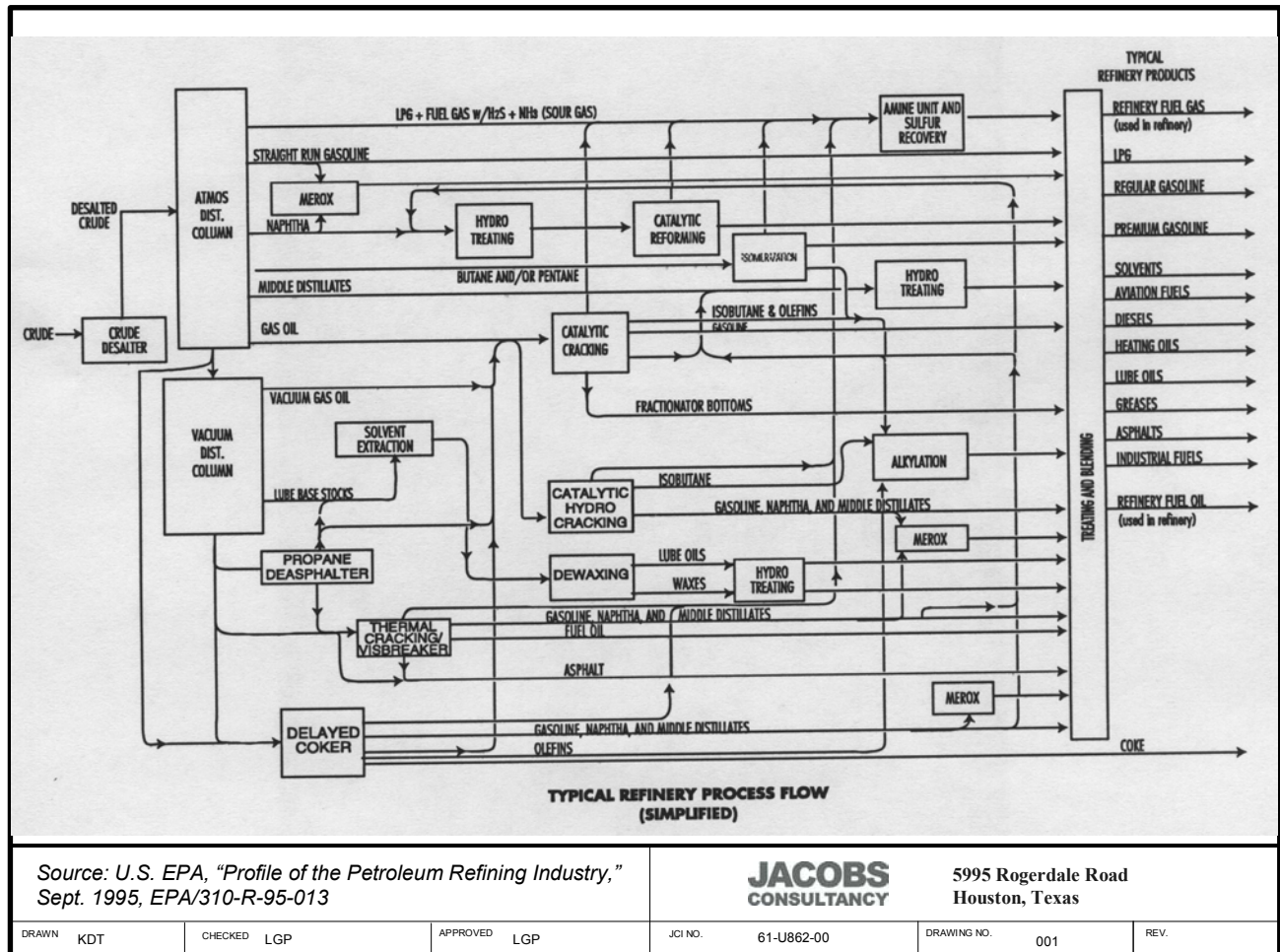
Other Reference Sources:

- 12 <http://es.epa.gov/techinfo/techinfo.html> - "Technical/R&D Information" (includes links to various other Pollution Prevention topics)
- 13 <http://hgtech.com/Basic/frame.htm> - Mercury Technology Services, including links to various articles by Wilhelm, S. M. on mercury in petroleum
- 14 <http://www.p2.org/> - National Pollution Prevention Roundtable
- 15 <http://www.p2pays.org/ref/01/00592.pdf> - "Petroleum Refining And Petroleum Distributing Systems"

- 16 <http://www.p2pays.org/ref/02/01881.pdf>, <http://www.p2pays.org/ref/02/01882.pdf> - “Study of Selected Petroleum Refining Residuals - Industry Study” – Parts I and II”
- 17 <http://earth2.epa.gov/program/regional/state/cali/petrsb14.pdf> - “Assessment of the Petroleum Industry Facility Planning Efforts” by California EPA, Department of Toxic Substances Control, Office of Pollution Prevention and Technology Development
- 18 <http://eippcb.jrc.es/pages/FActivities.htm> - The European Integrated Pollution Prevention and Control (IPPC) Bureau with a link to the IPPC BREF Outline and Guide, November 2000
- 19 <http://europa.eu.int/comm/environment/ippc/index.htm> - EC IPPC Directive (common rules on permitting)
- 20 “Pollution Prevention Report and Two-Year Work Plan – Review Draft,” California Department of Toxic Substances Control, January 2002
- 21 Eble, K. S. and Feathers, J., “Water Reuse Within a Refinery,” NPRA AM-92-08, 1992 NPRA Annual Meeting
- 22 *Oil & Gas Journal*, “2001 Worldwide Refining Survey,” December 24, 2001
- 23 U.S. EPA, “Mercury in Petroleum and Natural Gas: Estimation of Emissions from Production, Processing and Combustion,” EPA-600/R-01-066, September 2001
- 24 *Hydrocarbon Processing*, “Conceptual Design of Mercury Removal Systems for Hydrocarbon Liquids in Gas Processing Facilities,” April 1999

# Appendix 1. Refining Processes and Wastewater Sources

The following discussion is intended to provide an overview of refining operations by describing the steps in the refining of crude oil and the various products that can be made in a modern petroleum refinery. It is also intended to summarize the wastewater sources associated with various refinery operations. The purpose of this discussion is to explain some of the technical references to refining in the accompanying report on wastewater pollution prevention opportunities in the refining industry. The refinery processes are discussed in the general sequence in which crude oil flows through the refinery. Emphasis is placed on the purpose of each processing step and its interactions with other processes. For more details, we refer the reader to the U.S. EPA reports "Profile of the Petroleum Refining Industry"<sup>1</sup> and "Study of Selected Petroleum Refining Residuals - Industry Study"<sup>16</sup>.



**Figure App 1-1. Block Flow Diagram**



We refer the reader to Figure App 1-1, a block flow diagram of a representative refinery having most of the major processing units available to the industry today. As this figure indicates, refining is a complex operation. First, there are multiple options for feeding different feedstocks to various units. Intermediate streams can usually be processed in more than one unit depending on the target slate of products that the refinery finds most profitable to produce. Second, there are many different crude oils available to refiners. The capacities and other characteristics of the various units in the refinery will limit the number of crude oils that are suitable for a given refinery. Conversely, the specific mix selected from this group of suitable crude oils will affect how various units are run in terms of the feed rates and operating parameters needed to produce the desired products.

## **Crude Desalting**

### **Process Description**

Desalting of crude oil upstream of the crude distillation unit is a key process operation for removal of undesirable components from crude oil before it reaches any of the major unit operations. Crude oil as received at a refinery contains various contaminants that must be removed before it is processed. Various salts, clay, rust and debris from cargo holds, and other types of suspended solids can cause equipment to plug and corrode. The water and inorganic salts in the crude oil are the result of naturally occurring brine associated with the oil reserves, but additional water and salt may be added in the form of seawater ballast in the cargo hold of the oil tanker that delivered the oil to the refinery. The desalter removes these materials by a combination of water washing and emulsification of crude oil with water to promote thorough contact of the water and oil. Electrostatic separation and demulsification are then used to break the emulsion and separate the two phases.

### **Wastewater**

Desalter water is one of the larger volume streams to the refinery wastewater treatment plant. Rates vary with the water content of the crude oil and the degree of difficulty in desalting the crude, but a representative rate would be around 2-2.5 gallons of wastewater per barrel of crude oil feed to the unit. Desalter water contains salt, sludge, rust, clay, and varying amounts of emulsified oil (oil under carry). Depending on the crude oil source, it may or may not contain significant levels of hydrogen sulfide (H<sub>2</sub>S), ammonia, and phenolic compounds. Relatively high levels of suspended and dissolved solids are usually observed.

## **Crude Distillation**

### **Process Description**

After desalting, crude oil is distilled in an atmospheric distillation column to separate the different crude oil fractions by boiling point. The overhead product consists of light ends (basically the C<sub>1</sub> through C<sub>4</sub> compounds, including refinery fuel gas and LPG). Side streams include straight run gasoline, naphtha, and light and heavy atmospheric gas oil (also known as middle distillate). Atmospheric resid is the bottoms fraction that is sent to the vacuum distillation column. (Vacuum distillation is necessary for the heaviest material since fractionating it at atmospheric pressure would require temperatures so high that it would decompose, or crack, before it could distill. While thermal cracking is desirable in other refinery units designed to promote cracking, it would only serve to damage and plug a fractionation column. Fractionation under vacuum conditions reduces the temperature at which distillation occurs.) The products from the vacuum tower include light and heavy vacuum gas oil and vacuum resid, the heaviest fraction of crude oil.

## Wastewater

Wastewater from the crude oil distillation process contains H<sub>2</sub>S, ammonia, suspended and dissolved solids, phenol, and mercaptans (organic sulfur compounds). It is generally alkaline. Because live steam is fed to the atmospheric and vacuum towers as a heat source and stripping medium as well as being used to draw a vacuum on the latter tower, there is a significant flow of wastewater from condensed steam in the overhead reflux drums and from the vacuum system. Flow rates on the order of 20-25 gallons per barrel of crude oil feed are representative, but wide variations among units are typical.

## Catalytic Cracking

### Process Description

Catalytic cracking converts the heavier distillates streams, such as atmospheric and vacuum gas oils, to lower boiling compounds (naphtha, *etc.*) that can be further processed into more valuable products, such as gasoline. Catalytic cracking is primarily conducted in fluidized catalytic cracking units (FCCU) using a fluidized bed reactor in which a catalyst consisting of very fine particles flows continuously between the reactor and catalyst regeneration sections. Regeneration serves mainly to burn off the coke that forms on the catalyst surface in the reactor. The flue gas from the regenerator typically passes through dry or wet fines removal equipment to prevent loss of catalyst to the atmosphere. This flue gas contains a large quantity of carbon monoxide that is burned in a waste heat boiler, and the hot exhaust from this CO boiler is used as an energy source (*e.g.*, to generate steam, to compress regeneration air, and/or to generate electricity) before it is exhausted to atmosphere.

## Wastewater

Wastewater from the unit typically contains oil, suspended solids (*e.g.*, catalyst fines), ammonia, sulfides, phenols and cyanides released from the cracking of heavier petroleum cuts. Flow rates are relatively high at around 15 gallons per barrel of feedstock due to the use of catalyst stripping steam in the bottom of the reactor and stripping steam used in the main fractionator.

## Hydrotreating and Hydrorefining

### Process Description

Hydrotreating and hydrorefining are catalytic processes that stabilize petroleum products and remove impurities by reacting them with hydrogen over a fixed bed catalyst typically composed of nickel, molybdenum and/or cobalt. Stabilization generally involves hydrogenation of olefins and diolefins. Sulfur, oxygen, nitrogen, halides and metals are typical impurities. Hydrotreating operating conditions (*e.g.*, pressure, temperature, hydrogen feed rates) vary with the type of stream being treated and the desired product specifications. Gas oil hydrotreating is used to treat cat cracker and hydrocracker feedstock. Naphtha and thermal naphtha (catalytic reformer feed) hydrotreating removes sulfur, nitrogen, oxygen, metals, and, in the case of thermal naphtha, olefins and di-olefins, all of which are impurities that would poison the precious metal catalyst in the reformer. Various other intermediate and product streams are also hydrotreated.

## Wastewater

Wastewater from hydrotreating generally originates in the fractionation of the treated product stream. Stripping steam condensed in the product stripper reflux drum is the primary source of wastewater. The wastewater stream is usually alkaline and contains suspended solids, ammonia, and H<sub>2</sub>S. It may contain phenols if the feed to the unit includes cracked products. Flow rates vary from unit to unit but are on the order of one gallon per barrel of feedstock to the unit.

## Hydrocracking

### Process Description

Hydrocracking is a much more severe process than hydrotreating and is a companion process to cat cracking in that it serves the same purpose of cracking heavier feedstocks to more valuable lighter components. However, the feedstocks are the refractory streams (*e.g.*, light cycle oil from the cat cracker and distillate fuel oils) that resist catalytic cracking and require the extremely high hydrogen partial pressure associated with hydrocracking. The operation is flexible and versatile, permitting various yield patterns depending on the feedstock and chosen operating severity. Although cat cracking and hydrocracking are similar processes, the former produces by-product hydrogen due to the hydrogen release from coking offsetting the hydrogen consumption in cracking, while the latter process, which is controlled to prevent coke formation on the catalyst, consumes large quantities of hydrogen.

## Wastewater

Wastewater from hydrocracking is often similar to that described above for catalytic cracking in that it contains products released from cracking heavier cuts of petroleum. Flow rates are lower than in a typical FCCU since there is less steam used in the process. They are generally on the order of 2 gallons per barrel of feed.

## Catalytic Reforming

### Process Description

Catalytic reforming is the process that converts paraffinic and naphthenic compounds to aromatics in the presence of a precious metal catalyst in a series of reactor vessels. The main products are the C<sub>6</sub>, C<sub>7</sub> and C<sub>8</sub> aromatics. The only C<sub>6</sub> aromatic is benzene, the only C<sub>7</sub> aromatic is toluene (methyl benzene), and there are four C<sub>8</sub> aromatics, including ethylbenzene and three isomers of xylene (di-methyl benzene). These aromatic compounds are valuable both as high octane blending components for gasoline and as petrochemical feedstocks. Benzene, toluene and xylene products are often referred to together as BTX.

Catalytic reforming consists of multiple reactions in parallel, including dehydrogenation of cyclic C<sub>5</sub> and C<sub>6</sub> compounds, isomerization of normal and iso-paraffins, dehydrocyclization of paraffins, hydrocracking of paraffins and naphthenes, and hydrodealkylation of naphthenes and aromatics. Most units in service today are semi-regenerative operations in which all reactors operate simultaneously until they are shut down for catalyst regeneration. There are also cyclic and continuous units. A cyclic reformer has a spare reactor so that one reactor is always off-line for regeneration. A continuous unit is designed for continuous removal and regeneration of the catalyst while the unit remains in full operation.

## Wastewater

The process wastewater from a catalytic reformer is typically a very small stream since the naphtha feedstock has been hydrotreated and pre-fractionated. The effluent produced generally contains negligible quantities of phenols and H<sub>2</sub>S.

## Isomerization

### Process Description

Isomerization converts straight chain (normal) paraffins with low octane values (*e.g.*, 62 RON for normal pentane) in gasoline feedstocks into isomers with high octane values (*e.g.*, 92 RON for isopentane). The catalyst is similar to that used in catalytic reforming, but conditions are less severe, and only one reactor is typically used. Butane isomerization converts butane to isobutane, which is used in making alkylate and MTBE. C<sub>5</sub>/C<sub>6</sub> (light straight run) isomerization converts normal pentane and hexane into branched chain isomers that are used in gasoline blending.

## Wastewater

Isomerization typically produces an acidic wastewater stream that is relatively high in dissolved solids (chlorides). Since the feed to the unit must be desulfurized, the wastewater is low in H<sub>2</sub>S and ammonia. Flow rates are usually very low.

## Coking

### Process Description

Coking processes are intended to minimize refinery yields of residual fuel oil (mainly vacuum tower bottoms) by severe thermal cracking of streams that are too heavy and too contaminated with impurities to be processed in any other manner. Fluid coking is a continuous process, whereas delayed coking is a batch process and is the more common of the two. These processes yield a full spectrum of products from gases (C<sub>3</sub> and lighter), LPG and naphtha to gas oils. These streams are similar to the products from crude distillation, but they contain components (*e.g.*, olefins and di-olefins) that require more severe hydrotreating before they can be used as feedstocks to units such as a catalytic reformer. The heavy residue is recycled to extinction, and the remaining material that cannot be cracked further is basically a carbon by-product (petroleum coke) containing absorbed high boiling hydrocarbons. (These hydrocarbons can be recovered by calcining at very high temperatures.)

## Wastewater

Coking units produce wastewater that is usually alkaline and contains high levels of suspended solids (coke fines) along with ammonia and H<sub>2</sub>S. COD loads are typically high. Water use is high in delayed coking units, in which steam is fed to a coke drum to remove hydrocarbon vapors at the end of the coking cycle after which the coke drum is filled with water to cool the contents. High-pressure water jets are then used to cut out the coke. However, much of this water is recycled within the unit, and typical wastewater flow rates from the unit may be on the order of one gallon per barrel of feed.

## Visbreaking

### Process Description

In addition to coking, there are other thermal processes of significance in refining. Visbreaking is a common thermal process. It is a bottoms upgrading process for thermally cracking vacuum resid, deasphalter bottoms, and/or other heavy cuts. It is typically used to produce gasoline, naphtha, middle distillates, fuel oils, and asphalt. Conditions and severity can vary widely depending on the purpose for which the unit is used.

### Wastewater

The visbreaking process yields a wastewater stream that is alkaline and that contains high levels of ammonia, H<sub>2</sub>S, phenol, and suspended solids. It also represents a significant source of BOD and COD. Flow rates are on the order of two gallons per barrel of feed to the visbreaker. The source of wastewater is primarily stripping steam condensate.

## Alkylation

### Process Description

The term alkylation refers to any reaction that adds an alkyl group to a molecule. To the refiner, it means the reaction of a low molecular weight olefin (*e.g.*, propylene, isobutylene) with an isoparaffin (*e.g.*, isobutane) to form heavier isoparaffins with high octane values. Either sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) or hydrofluoric acid (HF) catalyst is used in the process. The process yields a wide range of products, and conditions are controlled to maximize octane values rather than to yield specific chemical compounds.

### Wastewater

The alkylation unit produces an acidic wastewater stream with significant levels of dissolved and suspended solids and COD. Minimal quantities of H<sub>2</sub>S, ammonia, and phenols are usually present. Wastewater from a sulfuric acid alkylation unit will contain spent sulfuric acid.

## Polymerization

### Process Description

Propylene and butylenes, separately or mixed, can be polymerized to form high octane blending components. Phosphoric acid in either solid or liquid form is used to catalyze the reaction. The reaction is highly exothermic, and temperature control is achieved by recycling cold propane or butane to the reactor inlet to intermediate points in the reactor bed. Spent catalyst is generally replaced rather than regenerated.

### Wastewater

Wastewater from the polymerization process is alkaline and contains ammonia, H<sub>2</sub>S, and mercaptans. Flow rates are minimal.

## Sulfur Recovery

### Process Description

Some crude oils typically contain high levels of sulfur, whereas most refined product specifications call for low sulfur levels. Sulfur is therefore removed in various processes and typically is converted to H<sub>2</sub>S, which is sent to the fuel gas system. These so-called sour gases are sweetened by removing H<sub>2</sub>S in an absorber using an amine absorbent, or scrubbing media. The choice of amine depends on the composition of the gas being treated and the final purity required. Amines commonly used in refining operations include monoethanolamine (MEA), diethanolamine (DEA), methyl diethanol amine (MDEA), diglycol amine (DGA), and di-isopropanol amine (DIPA). The sweetened fuel gas is burned as fuel (*e.g.*, in refinery furnaces, boilers, and flares), the H<sub>2</sub>S rich amine solution is fed to a stripper to regenerate lean amine solvent for recycle to the absorber, and the concentrated H<sub>2</sub>S stream from the stripper is typically fed to a Claus plant (sulfur recovery unit, or SRU) for conversion to elemental sulfur through a process of partial combustion and catalytic conversion. The process produces very high purity sulfur. Off-gases from the Claus plant typically are processed in a tail gas treating unit for additional sulfur recovery.

### Wastewater

The wastewater stream from a sulfur recovery unit is dependent on the SRU technology employed. One of the more common tail gas units is the SCOT process, which employs a quench tower with a circulating water spray for direct contact cooling of the reactor effluent. A portion of this circulating stream is blown down to the sewer system. Other processes use heat exchange for indirect cooling and may not have significant discharges to the sewer system.

## Light Ends (Vapor) Recovery

### Process Description

Gases and unstabilized liquids from various refining processes are charged to the gas recovery unit for stabilization and recovery of products that have greater value as feedstocks in various units than they have as refinery fuel gas. Fractionation and absorption followed by stabilization in a de-butanizer and de-propanizer yields a stabilized liquid product (*e.g.*, for gasoline blending) plus propane-propylene and butane-butylene streams that can be further processed to yield light olefins (propylene and butylenes), isobutane, n-butane, and propane for use in other units. Caustic treating is used as needed to remove sulfur compounds.

### Wastewater

Gases from the crude unit contain varying quantities of water in the form of steam condensate due to the use of live steam in the crude distillation process. Depending upon the quantity of steam used in the crude unit and on the degree of condensate collection and removal in the crude unit overhead, the light gases sent to gas recovery will have more or less water to be removed and blown down from the light ends recovery operation.

# Residual Upgrading

## Process Description

In addition to the processes discussed above (*e.g.*, coking, visbreaking), there are other processes in which vacuum distillation bottoms and other residual feeds can be upgraded. One of the more common is solvent deasphalting, which recovers lubricating oil feedstocks from residual streams and leaves most of the metals and sulfur in the asphalt product. Deasphalted oil (DAO) can be hydrotreated to yield a range of light to heavy products, including high quality lube oil feedstocks. Live steam stripping may be used to separate solvent from the heavy product streams produced in residual upgrading.

## Wastewater

To the extent that live steam stripping is employed in the process, condensate from the solvent stripper overhead is routed to the sewer system. The quantity depends on the type of upgrading technology employed. The organics content of this stream will be relatively high.

# Appendix 2. Washington Refinery Process Configurations

Figures App 2-1 through App 2-5 depict the fundamental block flow diagrams for the five Washington petroleum refineries. These representations are based on publicly available documents, including pollution prevention plans filed by the refineries with the State of Washington Department of Ecology and data available from published industry sources, such as the *Oil and Gas Journal's* latest annual refining survey<sup>22</sup>.

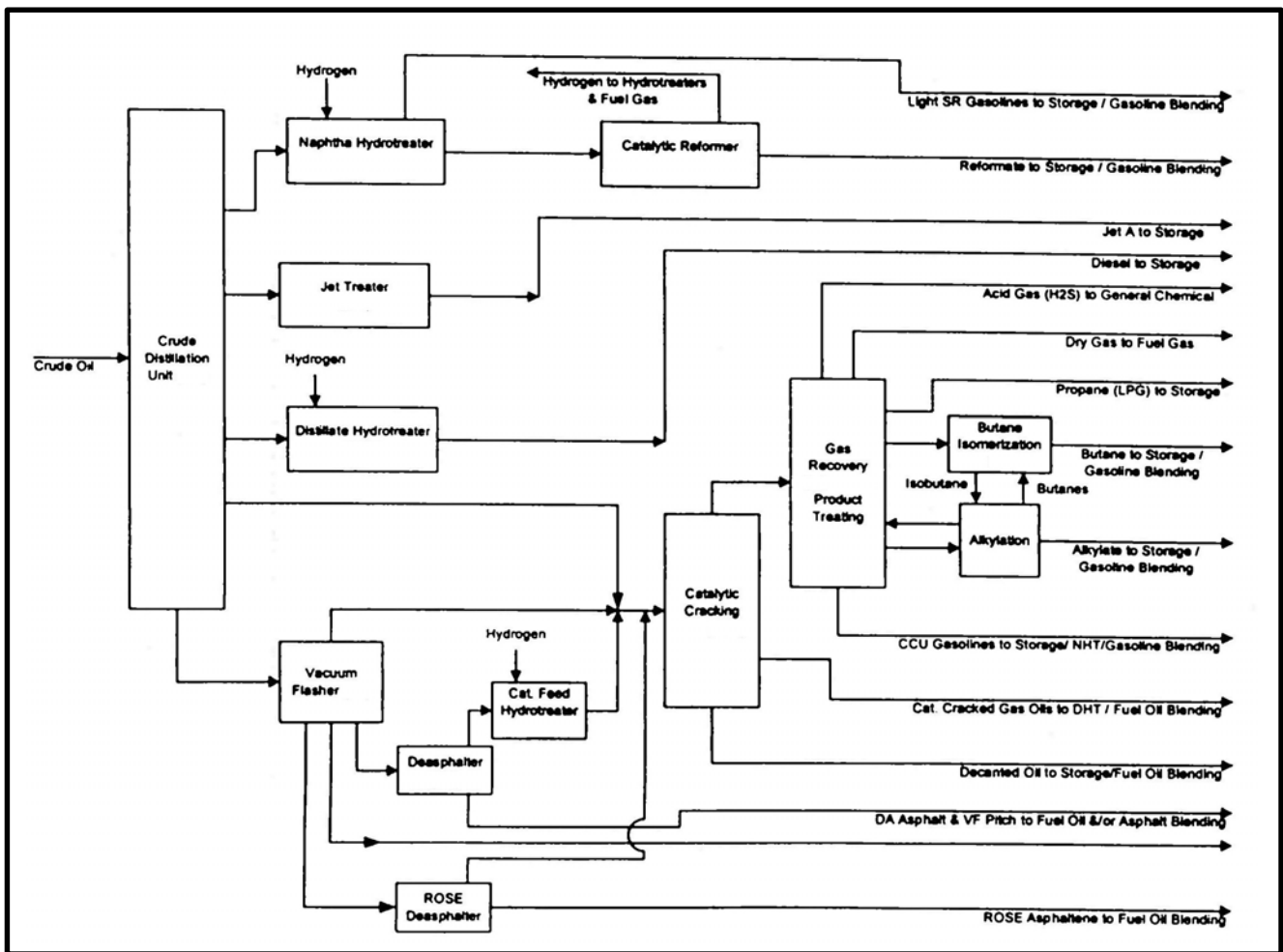


Figure App 2-1.  
Tesoro Anacortes Refinery  
Basic Configuration



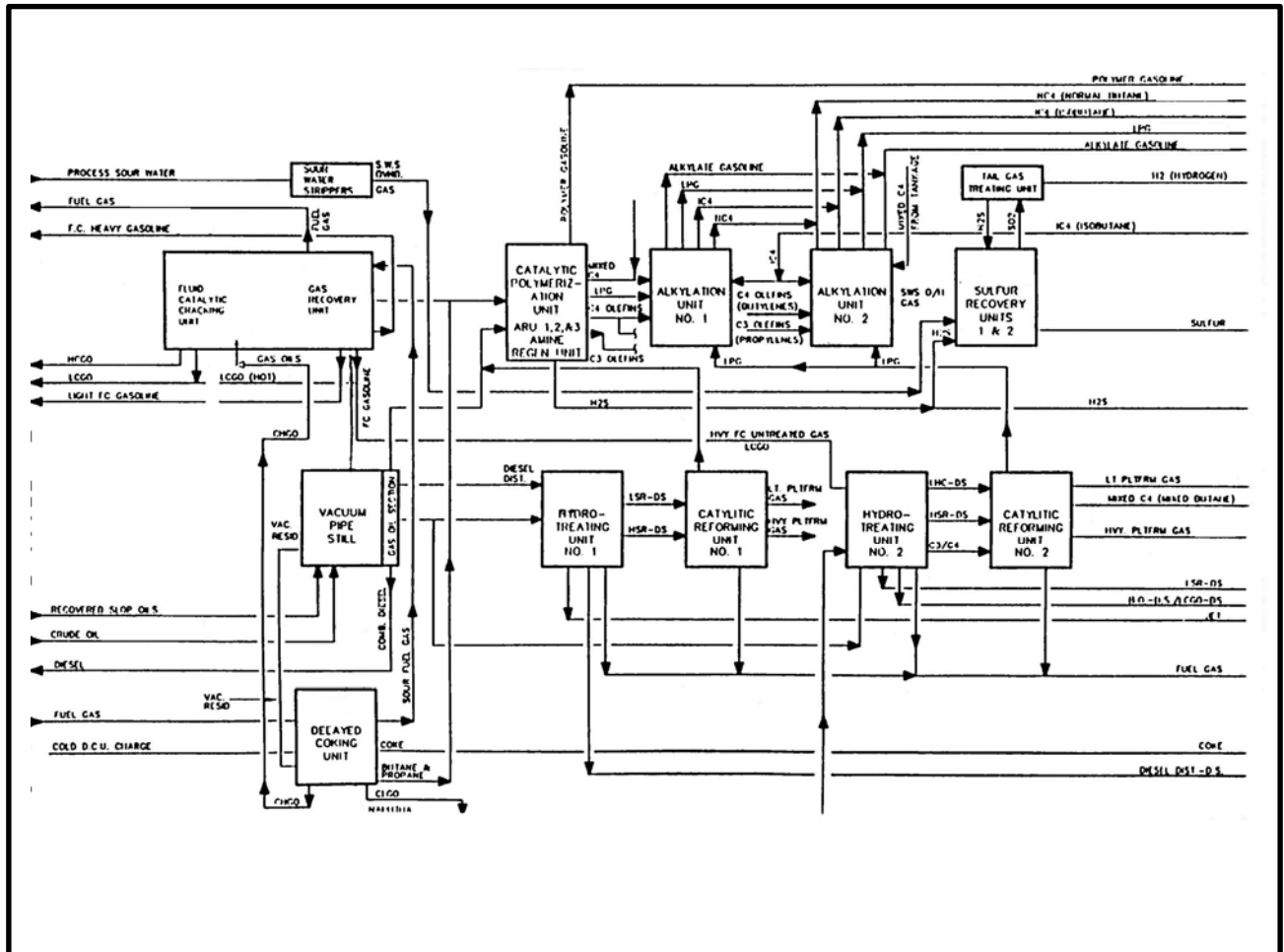


Figure App 2-2.  
 Shell Oil Products US Anacortes Refinery  
 Basic Configuration

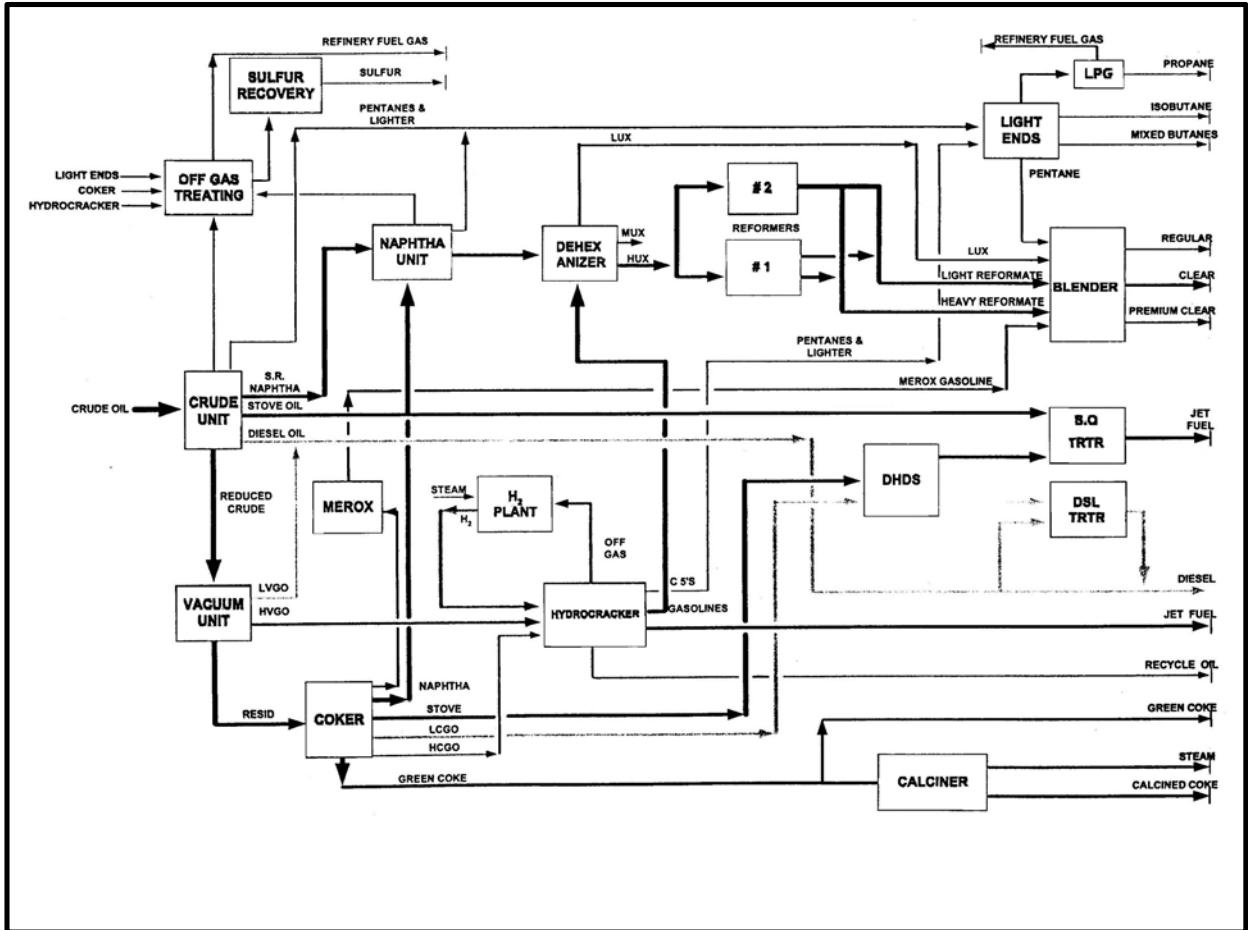


Figure App 2-3.  
bp Cherry Point Refinery  
Basic Configuration

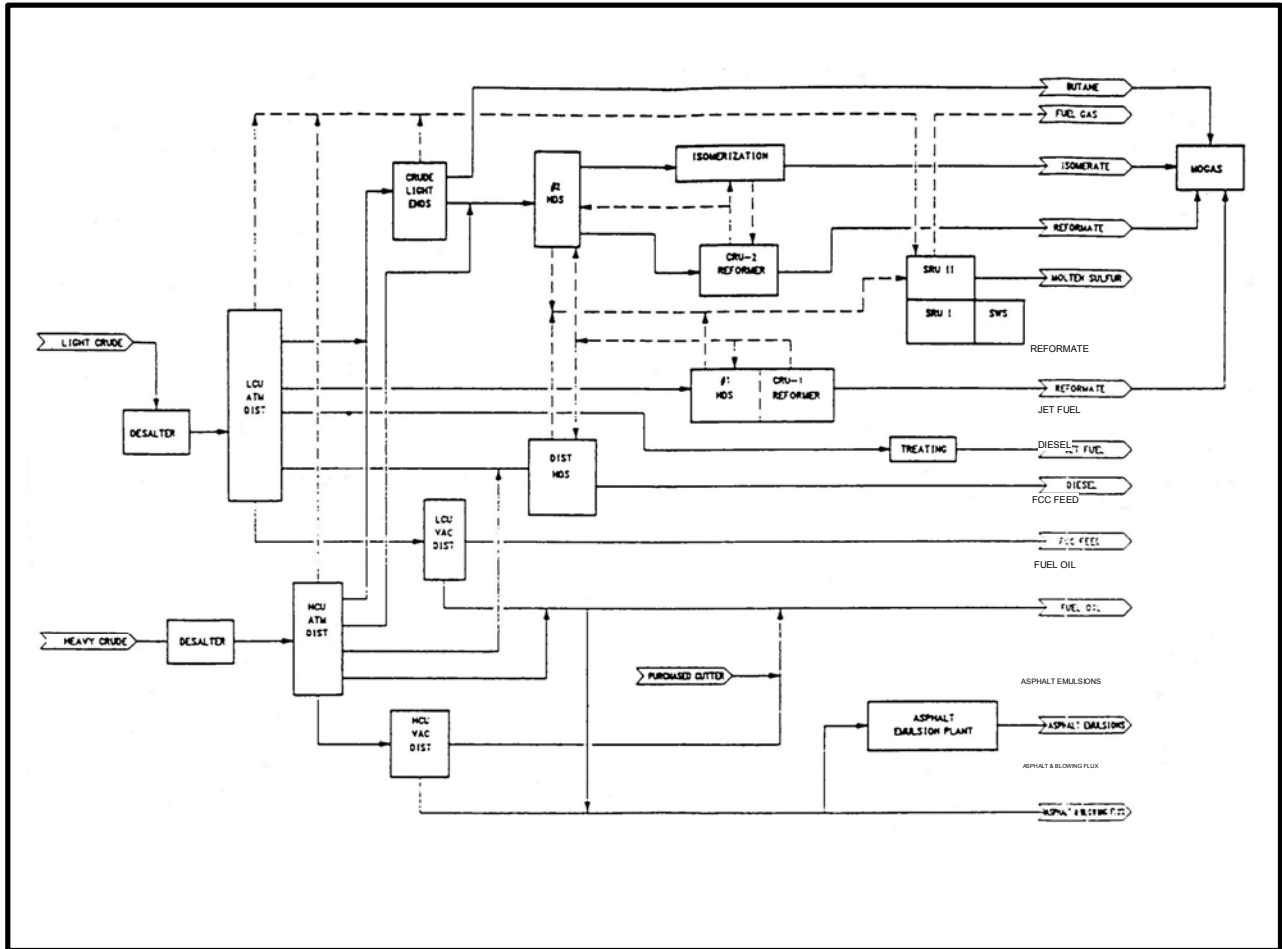
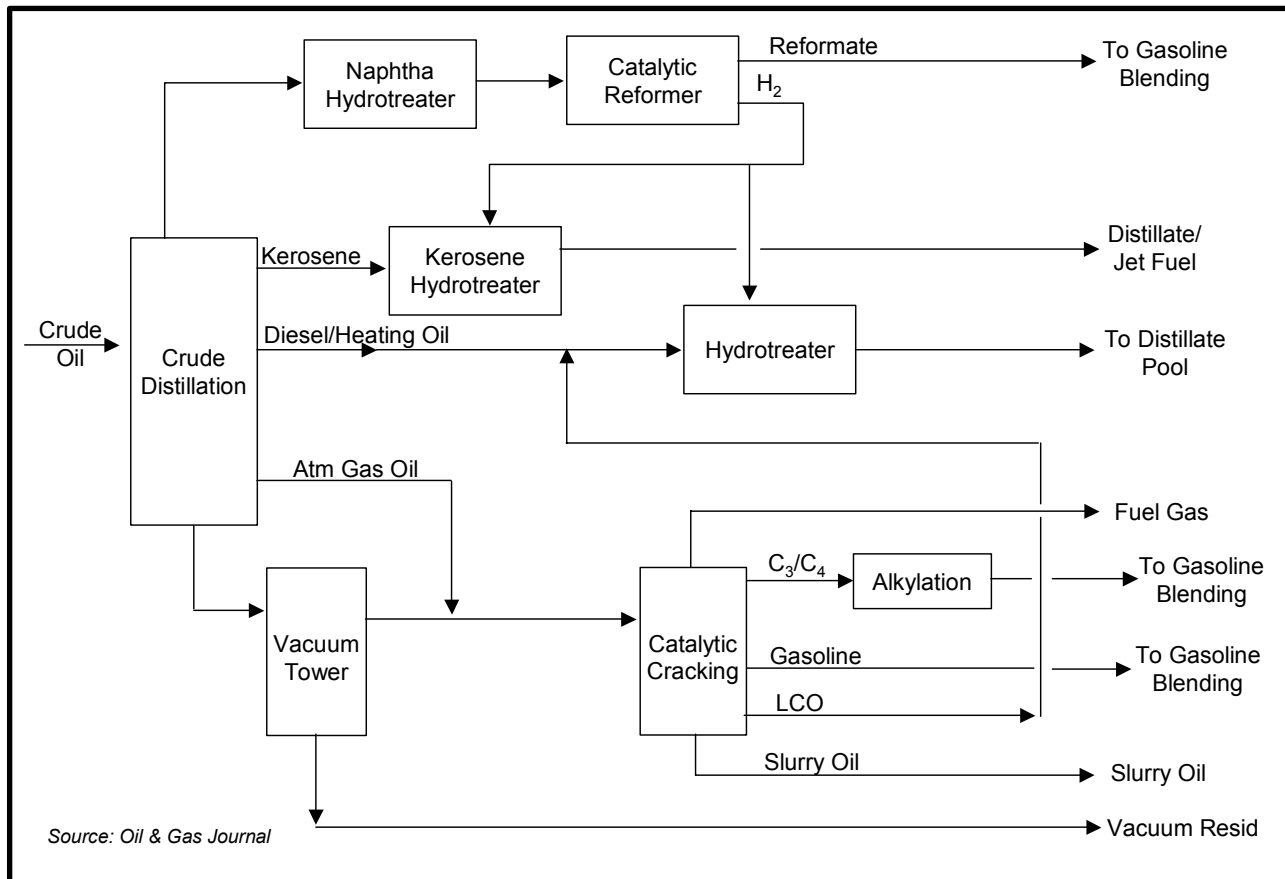


Figure App 2-4.  
 U.S. Oil & Refining Tacoma Refinery  
 Basic Configuration



**Figure App 2-5.**  
**ConocoPhillips Ferndale Refinery**  
**Basic Configuration**

## **Appendix 3.**

# **Workshop Presentation Materials**

This appendix contains the presentation materials used at the October 8, 2002 Pollution Prevention workshop held in Mount Vernon, Washington. Refer to Section F for further information regarding the workshop.

## **REFINERY WATER POLLUTION PREVENTION OPPORTUNITIES**

A Workshop Presented to the Washington State  
Department of Ecology and the Washington  
Petroleum Refineries

October 8, 2002

## **Agenda**

- Summary of past wastewater related refinery pollution prevention projects
- Feasibility of specific examples of P2 opportunities
- Survey results from Washington refiners
- Special topics
  - Dioxin and Furan generation
  - Metal contaminants
  - P2 principles in process design

## **Pollution Prevention**

Pollution prevention minimizes releases of pollutants to the environment, but to a plant operator, it can also mean \$saving\$:

- Waste minimization = reduced waste disposal costs
- Source reduction = preservation of feedstocks, utilities, catalysts, & other raw materials

## **Past Refinery Pollution Prevention Projects**

- United States (outside Washington)
- Europe
- State of Washington

## **Historical Focus of P2 Activities in Refineries**

1. Operating & maintenance practices – minimal capital, relatively easy to implement
2. Process modifications
  - Minor – more capital needed, but no major revisions to fundamental operations
  - Major – more fundamental changes requiring significant capital; likely to be part of a revamp or expansion program

## **Operating & Maintenance Practices – U.S.**

- Usually require minimal capital investment
- Relatively easy to implement
- Category most thoroughly explored
- Similar approaches adopted by many refiners

## Operating & Maintenance Practices – U.S.

- Tank bottoms
- Improved oil recovery from sludge
- Desalter solids, oil under carry
- Spent filter clay disposal
- Solids from heat exchanger cleaning
- Control of solids from other sources

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## Operating & Maintenance Practices – U.S.

- Surfactants in wastewater
- Leaks, spills & other losses
- Stormwater & wastewater segregation and flow reduction
- Replacement of drums with storage tanks
- Sample losses
- Benzene losses

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## Operating & Maintenance Practices – U.S.

- Spent catalyst waste
- Alternative disposal for alky sludge
- Amine units – losses & sludge generation
- Sludge from resid upgrading
- Mercury losses

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## Operating & Maintenance Practices – U.S.

- Hazardous materials use
- Cooling tower blowdown
- Segregate boiler blowdown
- Employee training & motivation

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## Process Modifications – U.S.

- Spent caustic recycle
- Oily sludge as coker feedstock
- Desalter improvements
- Alternative alky catalyst
- Heat exchanger modifications
- Reactor optimization
- Caustic and wash water optimization

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## Pollution Prevention in Europe

- EC Joint Research Centre evaluates and recommends Best Available Techniques
- BAT focus:
  - Environmental performance
  - Economics
  - Cross-media effects
- Very similar to U.S. programs

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## Pollution Prevention in Europe

- Storage & handling practices
- Crude oil desalting
- Amine treating
- Sour water stripping
- Optimizing water use

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## Pollution Prevention - State of Washington

- Washington refiners have undertaken programs similar to other U.S. refiners:
  - Operations & maintenance in basically the same categories as the list for overall U.S.
  - Minor & major process modifications

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## Projects Evaluated & Rejected

- Numerous reports of projects considered by refiners and eventually rejected
  - Most rejected due to poor economics
  - A few found not technically feasible
- Most of these projects were similar or identical to projects implemented in other refineries (refer to Section F of report)

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## Pollution Prevention Opportunities

- Parallel sour water stripping
- Eliminate caustic washing of kerosene and diesels
- Benefits from upgrading Olefinic FCC LPG

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## Parallel Sour Water Stripping

- Sour water – produced when process-required wash waters have contacted hydrocarbon streams containing hydrogen sulfide and ammonia. Sour water must be treated or “stripped” before discharge to the refinery’s treatment system

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## Parallel Sour Water Stripping

- Sour water sources
  - Process units with an incidental or intentional thermal character
    - Fluid Catalytic Cracking Units
    - Visbreakers
    - Delayed cokers
  - Hydro-processing units
    - Hydrotreaters
    - Hydrocrackers

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## Parallel Sour Water Stripping

- Sour water characteristics
  - Sour waters from “thermal” processes (FCC, Visbreaking, Coking)
    - Contain more hydrogen sulfide than ammonia
    - Contain significant quantities of organics such as benzene and phenolic compounds
  - Hydro-processing units
    - Equal quantities of hydrogen sulfide and ammonia
    - Essentially free of soluble organic and phenolic compounds

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## Parallel Sour Water Stripping

- Advantages of parallel sour water stripping (SWS)
  - Hydro-processing wash waters can be stripped in a separate SWS and recycled as wash water
  - Overall SWS steam requirements are reduced
  - Phenolic stripped sour waters can be re-used as crude oil desalter water make-up
  - Phenolic compound discharges are reduced
  - Overall water discharged to the plant waste water treatment unit should be reduced

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## Parallel Sour Water Stripping

- Disadvantages of parallel sour water stripping
  - Higher capital cost associated with having two parallel sour water strippers
  - More equipment to operate and maintain

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## Eliminate Caustic Washing of Kerosene and Diesel

- Caustic treating provides a means of “sweetening” and stabilizing kerosene and diesel streams
- Waste caustic stream that contains sodium naphthenate, sodium sulfide, and sodium phenolate is produced and must be treated in the refinery waste water treatment unit.

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## Eliminate Caustic Washing of Kerosene and Diesel

- Hydrotreating will eliminate the need for caustic treating
- Ultra-low sulfur diesel regulations will require more hydrotreating of diesel and kerosene streams

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## Benefits of Upgrading Olefinic FCC LPG

- FCC Units produce propane/propylene and butane/butylene streams
- These streams must be treated before being processed in downstream units
  - Caustic treating
  - Amine treating
- Propane → LPG
- Propylene → Alkylation unit feed or polymers
- Butane → Gasoline blending
- Isobutane/Butylenes → Alkylation unit feed

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## Benefits of Upgrading Olefinic FCC LPG

- Removing and controlling contaminants such as hydrogen sulfide, mercaptans, other sulfur compounds, diolefins, acid esters, and heavy ends can provide the following benefits:
  - Lower alkylation unit acid consumption
  - Lower caustic and amine consumption
  - Reduced load on the refinery waste water treatment unit
  - Higher alkylate product quality
- Disadvantages
  - Capital and operating costs

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## Survey Results from Washington Refiners

- Major wastewater sources
  - Contaminated stormwater
  - Desalter effluent
  - Cooling tower blowdown
  - Stripped sour water
  - Once-through cooling water
  - Condensate (process & steam)

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## Survey Results from Washington Refiners

- Recovered slop oil
  - Most slop rerouted to crude unit (same as in rest of U.S.)
  - Some sent to downstream units (e.g., FCCU, coker)

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## Survey Results from Washington Refiners

- Wastewater system solid waste disposal
  - Some surge capacity upstream of API separator
  - Sludges are dewatered (centrifuge or filtration)
  - Offsite disposal by incineration, cement kiln processing, & thermal desorption
  - Most WA refineries employ air flotation
  - Situation similar to other U.S. refineries

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## Survey Results from Washington Refiners

- Dioxin & Furan
- Mercury
  - Respondents indicate that crude oil is the main source of mercury
  - All report ANS to be main domestic crude oil
  - All report that laboratory and field instruments are no longer significant sources of mercury

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## Survey Results from Washington Refiners

- Polyaromatic hydrocarbons
  - Generally reported PAH to be at or below detectable levels in samples at various locations
- Polychlorinated biphenyls
  - 2 refineries still have PCB-containing transformers in operation
  - No detectable PCB in wastewater samples

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## Survey Results from Washington Refiners

- Soils
  - All report using berms & curbs at drains to minimize soil losses
  - All sweep streets to remove soil and other debris that could wash into sewers
- Catalyst
  - FCCU catalyst controls in loading & unloading
  - Other catalyst fines minimized (e.g., by handling in enclosed sheds)

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## Survey Results from Washington Refiners

- Scale & rust
  - Isolated areas & containment pads used for heat exchanger cleaning
  - Sewers covered during maintenance activities that produce scale & rust (e.g., sandblasting)
- Tank bottoms
  - Operators must be present to observe tank draws
  - Coating interior with corrosion resistant paint

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## Survey Results from Washington Refiners

- Surfactants – potential sources
  - Cleaning materials
  - Antifoams
- Dissolved solids – potential sources
  - Boiler and CTW blowdown
  - Salt from product driers
  - Caustic from product treating

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## Survey Results from Washington Refiners

- Toxins – potential sources
  - Only cadmium, lead & mercury reported to be found in final effluents (all below API guidance levels)
  - Crude oil and metallurgy cited as sources
- Amines (DEA, MDEA) – potential sources
  - Amine sump systems

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## Dioxin and Furan Generation

- Predominant source of dioxin and furan in refineries
  - Catalytic reforming
  - Isomerization
- Reforming processes
  - Semi-regenerative
  - Cyclic
  - Continuous

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## Dioxin and Furan Generation

- Reformer catalyst regeneration process
  - Carbon burn
  - Proof burn
  - Rejuvenation
  - Reduction
  - Chloriding
  - Sulfiding

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## Dioxin and Furan Generation

- Dioxin
  - Chlorinated, hydrogen deficient, polynuclear aromatic compound
- Furan
  - Five member ring containing oxygen
- Coke on catalyst + chloride on catalyst + oxygen deficient atmosphere = dioxin and furan

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## Dioxin and Furan Generation

- Reformer catalyst regeneration flue gas treatment
  - Caustic scrubbing
  - Incineration in reformer heater firebox

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## Metal Contaminants in Crude Oils

- All crude oils contain trace quantities of naturally occurring metals
  - Nickel
  - Vanadium
  - Copper
  - Iron
  - Mercury

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## Mercury

- Mercury occurs in crude oils in the following forms:
  - Dissolved elemental mercury
  - Dissolved organic mercury compounds
  - Inorganic mercury salts
  - Mercury adsorbed on suspended solids
- Organic mercury compounds may partition into product streams
- Whereas the inorganic mercury salts will migrate to the desalter water phase

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## Mercury

- Mercury containing crudes
  - Certain California crudes
  - Far East condensates
- Alaskan North Slope
  - 1.98 ng/g mercury concentration (as reported by WSPA)
  - Washington refiners' product streams – less than 17 mg/kg Hg
- Mercury containing equipment
  - Thermometers
  - Instrumentation
  - Electrical equipment

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## Application of Pollution Prevention Principles in Process Design

- Pollution prevention principles are now incorporated in formalized work processes for project development
- Formalized work processes
  - Feasibility
  - Conceptual
  - Preliminary engineering
  - Detailed design
  - Construction
  - Start-up

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## Application of Pollution Prevention Principles in Process Design

- Life cycle costs
  - Capital
  - Operating and maintenance costs
  - Waste disposal
- Formalized work process
  - Life cycle costs are reviewed
  - Waste minimization/pollution prevention is an integral part of the process
  - Waste streams are identified and quantified
  - Reduce waste generated → reduce project life cycle cost

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# Glossary

**Absorbent** – a material that retains or receives a substance by chemical or molecular action; in petroleum refining, typically a liquid stream used to absorb one or more selected components of a multi-component gas stream

**AGO** – atmospheric gas oil (see definition)

**Alkylate** – the product of an alkylation reaction; usually refers to the high octane isoparaffin product from alkylation units used in blending high octane gasoline that is blended with motor and aviation gasoline to improve the antiknock value of the fuel

**Alkylation Unit** – a refining process unit for chemically combining isobutene with olefin hydrocarbons (*e.g.*, propylene, butylene) through the control of temperature and pressure in the presence of an acid catalyst, usually sulfuric acid or hydrofluoric acid, to produce alkylate (see definition)

**Amine** – any of several compounds including, but not limited to, monoethanolamine,  $\text{HOC}_2\text{H}_4\text{NH}_2$ , (MEA), employed in treating natural gas; generally used in water solutions as an absorbent (see definition) to remove hydrogen sulfide and carbon dioxide from gas and liquid streams; other amines include DEA, DGA, DIPA, and MDEA

**Amylene** – any of five unsaturated isomeric hydrocarbons having the formula  $\text{C}_5\text{H}_{10}$

**API Separator** – American Petroleum Institute unit designed for settling basins or tanks that separate oil from water by taking advantage of their specific gravity difference, as referenced originally in API Volume 1, *Manual on Disposal of Refinery Wastes*

**Aromatic Compounds** – hydrocarbon compounds characterized by unsaturated ring structures of carbon atoms; commercial petroleum aromatics are benzene, toluene, and xylene (BTX)

**Atmospheric Gas Oil** – a hydrocarbon stream typically having a boiling range of 455°F to 800°F; usually divided into atmospheric gas oil from the bottom side stream of the atmospheric tower of a crude distillation tower and vacuum gas oils (light and heavy) from the top of the vacuum tower

**Benzene ( $\text{C}_6\text{H}_6$ )** – an aromatic hydrocarbon naturally present in small proportion in some crude oils and made commercially from petroleum by the catalytic reforming of naphthenes in petroleum naphtha; also made from coal in the manufacture of coke; used as a solvent, for manufacturing detergents, for the production of synthetic fibers, for various petrochemicals, and in limited amounts as a high-octane gasoline component

**Blowdown** – a stream used to prevent the accumulation of impurities by diverting a small portion of a larger recycle stream in which impurities build up; in the utility systems of a refinery, the cooling tower water and boiler water streams that are diverted to the sewer system to prevent the accumulation of dissolved solids and various other impurities

**BS&W** – bottoms sediment and water, usually applied to the such materials when they accumulate in the bottom of storage tanks, cargo holds of vessels, *etc.*

**Calcining** – with reference to petroleum coke, a process whereby green or raw petroleum coke is thermally upgraded to remove associated moisture and volatile combustion matter and to otherwise improve critical physical properties (e.g., electrical conductivity, real density, and oxidation characteristics)

**Catalyst** – a substance that can greatly increase the rate of a chemical reaction without itself being consumed in the reaction

**Catalyst Regeneration** – the utilization of onsite refinery process equipment or offsite process equipment (e.g., operated by the vendor of the catalyst or a licensed specialty reclaimer) to restore a refinery process catalyst to its original or near original condition

**Catalytic Hydrocracking** – a refining process using hydrogen and one or more catalysts at relatively low temperatures and high pressures to convert middle boiling or residual material to high octane gasoline, reformer charge stock, jet fuel, and /or high grade fuel oil; characterized by ability to handle high sulfur feedstocks without prior desulfurization

**Catalytic Hydrotreating** – a refining process for treating petroleum fractions from atmospheric or vacuum distillation units (e.g., naphthas, middle distillates, reformer feeds, residual fuel oil, heavy gas oil) and other petroleum streams (e.g., cat cracked naphtha, coker naphtha, coker gas oil) in the presence of catalyst and substantial quantities of hydrogen; includes desulfurization, removal of substances (e.g., nitrogen compounds) that deactivate catalyst, conversion of olefins to paraffins to reduce gum formation in gasoline, and other processes to upgrade the quality of the fractions

**Catalytic Reforming** – a catalytic refining process using controlled heat and pressure to rearrange certain hydrocarbon molecules, thereby converting paraffinic and naphthenic type hydrocarbons (e.g., low-octane gasoline boiling range fractions) into petrochemical feedstocks and high-octane stocks suitable for blending into finished gasoline

**Cathodic Protection** – protection of ferrous metals against electrolysis by the attachment of sacrificial anodes; also called electrolytic protection

**Caustic** – any strongly corrosive chemical substance, especially one that attacks organic matter; caustic alkali – a metal hydroxide, especially that of an alkali metal; caustic soda – sodium hydroxide; caustic potash – potassium hydroxide

**Centrifuge** – a device using centripetal force to separate two or more substances of different density, such as two liquids or a liquid and a suspended solid, and consisting of a fixed base or frame with a rotating part in which the mixture is placed and spun at high speed

**Cetane Number (or Rating)** – a technical measure of the value of diesel fuel and its various blending components

**CGO** – coker gas oil (see definition)

**Clarified Slurry Oil** – the bottoms or “cycle oil” from a FCC unit, usually having high viscosity, which contains sulfur, small ring aromatics, polynuclear aromatics (see definition), and catalyst fines; “clarified” refers to FCC slurry oil that has been processed through a mechanical liquid-solids separation device, such as a slurry settler or electrostatic precipitator, to supply a low solids liquid product suitable as needle coker feedstock

**Coker Gas Oil** – a hydrocarbon stream typically having a boiling range of 650°F to 1050°F that originates from the main fractionation column in either a fluid or delayed coking unit

**Coking** – in petroleum refining, referring to the processes of Delayed or Fluid Coking, or to the phenomena of catalyst coking with regard to catalytic operations (*e.g.*, FCC, naphtha reforming, hydrocracking) in which carbon is deposited on the catalyst, thus deactivating it (such catalyst being reactivated by burning off the carbon, which is not recoverable as a coke by-product)

**Condensate** – the liquid formed by the condensation of a vapor or gas; specifically, the hydrocarbon liquid separated from natural gas because of changes in temperature and pressure when gas from the reservoir is delivered to surface separators; also, water that is condensed and returned to boilers in a steam system

**Crude Distillation Unit** – a refining process unit which separates crude oil components at atmospheric pressure by heating to temperatures of about 600° to 750°F (depending on the nature of the crude oil and desired products) and subsequent condensing of the fractions by cooling

**CSO** – clarified slurry oil (see definition)

**DAF** – dissolved air flotation, a process accomplished by introducing pressurized wastewater (saturated with gas) to atmospheric pressure so that it releases the dissolved gases (The attachment of fine gas bubbles to suspended or oily material reduces its specific gravity and enhances flotation separation. There are three basic flotation design schemes: dissolved air flotation with pressurization of all or part of the influent flow, dissolved air flotation with recycle pressurization, and induced air flotation.)

**DEA** – diethanol amine

**Dehydrocyclization** – with regard to catalytic naphtha reforming, the reaction of paraffins to naphthenes (for example, normal heptane rearranging to saturated ring structures of either ethyl-cyclopentane or methyl-cyclohexane), which increases the aromatic content of the reformat product and yields excess hydrogen as a by-product

**Dehydrogenation** – a reaction that removes hydrogen atoms from an organic molecule to produce an unsaturated bond and yield hydrogen gas as a by-product (a catalytic reaction favored by high temperature); in the context of catalytic naphtha reforming, the reaction of naphthenes to aromatics (see definitions; *e.g.*, methyl-cyclohexane, a naphthene, is dehydrogenated to methyl-benzene (toluene), an aromatic)

**Dehydroisomerization** – a coupling of the dehydrogenation and isomerization reactions (see respective definitions; *e.g.*, conversion of n-butane, an abundant raw material from natural gas and LPG, to isobutene)

**Delayed Coking** – a process by which heavier crude oil fractions can be thermally decomposed under conditions of elevated temperatures and pressure to produce a mixture of lighter, oils that can be processed further to more valuable products and petroleum coke that can be used either as a fuel or in other applications, such as the manufacturing of steel or aluminum

**Demulsifier** – a chemical substance used to separate oil and water bound together in an emulsion



**Desalter** – process equipment used in petroleum refineries, usually upstream of crude distillation units, primarily to remove inorganic salts from incoming crude oil; of the two basic types of desalters, chemical and electrical, the latter is more prevalent

**DGA** – diglycol amine

**Diatomaceous Earth** – a chalk-like material composed of the shells of diatoms (single celled algae having siliceous cell walls) used to filter solid wastes from wastewater treatment plants; also found in powdered pesticides and in various other applications for filtration, absorption, and insulation

**Diolefin** – an unsaturated organic compound containing at least two carbon-to-carbon double bonds with no aromatic or naphthenic rings (*e.g.*, butadiene and pentadiene)

**DIPA** – di-isopropanol amine

**Electrodialysis** – a process that uses electrical current applied to permeable membranes to remove minerals from water; often used to desalinate salt water or brackish water

**Electrostatic Precipitator** – an air pollution control device in which solid particulate matter and/or liquid mist carried in a gas stream is charged as it passes through an electric field and precipitates on a collection surface

**Emulsion** – a mechanical mixture of two liquids that do not naturally mix, such as oil and water

**External Floating Roof Tank** – a type of liquid storage tank that consists of a cylindrical steel shell equipped with a roof that floats on the surface of the stored liquid, thereby minimizing the presence of a vapor space above the liquid and eliminating the displacement into the atmosphere of vapors saturated with molecules of the liquid stored in the tank when the tank is being filled; used extensively as an air pollution control device

**FCC** – fluid catalytic cracking (see definition)

**Filter Pre-coat** – a thin coating of material that is applied uniformly to the surface of a filter that enables the filter to perform more efficiently

**Floating Roof Tank** – a liquid storage tank that is either an internal or external floating roof tank

**Fluid Catalytic Cracking** – a petroleum refining process employing a fluidized bed of finely powdered catalyst that breaks down larger, heavier, and complex hydrocarbon molecules from fresh and recycled feedstocks into simpler, lighter molecules and that is highly effective in increasing the yield of gasoline from crude oil

**Fluidized Bed** – a process in which very fine particles behave as a flowing fluid when aerated with a vapor stream and carried by the drag force of the vapor stream; used in petroleum refineries for fluid catalytic cracking and in other industrial applications, such as fluidized bed combustion, in which fine particles of solid fuel (*e.g.*, coal or petroleum coke) are burned to generate steam for power generation or heating; also known as an expanded bed

**Gas Oil** – a generic term for refinery process streams that originate from atmospheric crude distillation units, vacuum distillation units, visbreakers, and fluid or delayed coking units; the boiling range varies depending on the source of the stream, but typically is in the range of 650°F to 1050°F

**Heat Exchanger** – a device that allows two fluids to exchange heat by passing on opposite sides of a metal surface, thereby cooling the hotter fluid and heating the cooler fluid

**Hydroclone** – a mechanical device that operates as a thickener for a slurry feed stream, producing a thickened underflow stream for subsequent filtration or centrifugation and an overflow stream containing suspended solids, the amount of which varies with the flow rate and particle size distribution of the feed slurry

**Internal Floating Roof** – a type of storage tank having both a permanent fixed roof and an internal floating deck that floats on the stored liquid; used as an air pollution control device

**Isomerization** – an acid catalyzed petroleum refining process that rearranges the shape and structure of a molecule without adding or removing any atoms; used to convert normal butane into isobutane, an alkylation process feedstock, and normal pentane and hexane into the high-octane gasoline blending components isopentane and isohexane, respectively

**Landfarm** – a waste disposal area in which biodegradable hazardous material is applied to soil and monitored as it naturally decomposes until it is no longer hazardous

**LCO** – light cycle oil (see definition)

**Light Cycle Oil** – the distillate or diesel fraction from the FCC, usually having a low cetane number because of the aromatic content; may be added to the refinery diesel pool, although the low cetane number lowers the pool quality; may have high concentrations of sulfur

**Liquefied Petroleum Gas** – a group of hydrocarbon-based gases derived from petroleum refining or natural gas fractionation (including ethane, ethylene, propane, propylene, normal butane, butylene, isobutane and isobutylene) that, for convenience in transportation and storage, are liquefied through pressurization

**LPG** – liquefied petroleum gas (see definition)

**MDEA** – methyldiethanol amine

**MEA** – monoethanol amine

**Molecular Sieves** – compound with molecule-size pores, such as some sodium aluminum silicates, that chemically lock molecules in the pores; used in purification and separation processes

**MTBE** – methyl tertiary butyl ether,  $(\text{CH}_3)_3\text{COCH}_3$ , an ether intended for gasoline blending that, when added to the gasoline blend, increases the amount of oxygen in the blend; used to reduce air pollution from gasoline powered internal combustion engines

**Naphtha** – a generic term applied to a petroleum fraction with an approximate boiling range between 122° and 400° F.

**Naphthenes** – saturated organic compounds with five and six member carbon ring structures; also known as cycloparaffins; includes the common naphthenes cyclopentane, cyclohexane and their homologues (molecules created by the addition of side chains to cyclopentane and cyclohexane); in the gasoline boiling range, valuable compounds that can be converted to high octane aromatics by dehydrogenation (see definition)

**NESHAP** – National Emission Standards for Hazardous Air Pollutants (federal air pollution regulations for hazardous pollutants)

**Octane Number (or Rating)** – a technical measure of the value of gasoline and its various blending components

**Olefins** – hydrocarbon compounds that contain at least one double carbon-to-carbon bond with no aromatic or naphthenic rings

**Organic** – in chemistry, referring to the chemistry of carbon compounds

**Overflow Weirs** – a dam designed to retain a solid or liquid and to regulate its flow; used on trays in distillation columns and in API separators (see definition)

**PAH** – polyaromatic hydrocarbon (see definition)

**Paraffins** – a saturated hydrocarbon molecule that is a member of the alkane series, such as butane, pentane, and hexane

**PCB** – Polychlorinated biphenyls, a mixture of compounds composed of the biphenyl molecule that has been chlorinated to varying degrees; not present in petroleum refinery feedstocks, but formerly used as transformer oil in electrical transformers in refineries and other industrial operations; now banned as a pollutant, but a few older transformers that have not yet been phased out still contain PCB in some industrial operations

**Petroleum Coke** – a residue high in carbon content and low in hydrogen that is the final product of thermal decomposition in the condensation process or in cracking; a marketable by-product from delayed or fluid coking units that may be recovered as relatively pure carbon; “green” coke may be sold as is or further purified by calcining (see definition)

**Phenol** –  $C_6H_5OH$ , a colorless, crystalline unsaturated organic compound consisting of a hydroxyl group (OH) attached to a benzene ring; a solid at room temperature that melts at about  $41^\circ C$ , boils at  $182^\circ C$ , is soluble in ethanol and ether and is somewhat soluble in water; an aromatic alcohol that exhibits weak acidic properties and is corrosive and poisonous; sometimes called carbolic acid, especially when in water solution; important in the production of certain artificial resins (e.g., Bakelite<sup>TM</sup>) and in the synthesis of many drugs, dyes, weed killers, insecticides, and explosives; phenol and its derivatives are generically referred to as phenols or phenolic compounds (see definition)

**Phenolic Compounds** – refers to a group of materials including phenol (see definition), cresols, xylenols, etc.; usually associated a refinery’s thermal and catalytic cracking processes

**Pinch Analysis** – a process integration technique originally used in heat exchange optimization to balance hot (or source) heat loads against cold (or sink) heat loads; as characterized on a graph of temperature versus enthalpy in which the distance between curves is manipulated, the point of closest approach between the curves is called the “Pinch” at which the utility requirements decrease and the

potential process heat exchange increases, so that locating the Pinch is critical to achieving an optimized design for both energy and capital costs; similar analytical procedures apply to optimization of hydrogen utilization, wastewater, and other aspects of refining

**PNA** – polynuclear aromatic (see definition)

**Polyaromatic Hydrocarbon** – a member of a highly reactive group of organic compounds (some of which are carcinogens) having multiple ring structures

**Polynuclear Aromatic** – a hydrocarbon compound that has two or more aromatic rings and having low hydrogen-to-carbon ratios, with hydrogen percentage by weight between 9% and 12%

**Residuum** – residue from crude oil after distilling off all but the heaviest components, with a boiling range greater than 1000°F

**Reverse Osmosis** – an advanced method of waste treatment that uses a semi-permeable membrane to separate water from pollutants

**ROSE™ Unit** – Residuum Oil Supercritical Extraction, a deasphalting process that produces asphaltene and an upgradeable oil product and upgrades residue by separating the heavy fraction from the lighter fraction using a variety of solvents

**Saturated** – in chemistry, referring to a molecule containing no double or higher bonds between atoms and thus having all valence bonds filled

**Shell and Tube Exchanger** – a heat exchanger consisting of numerous metal tubes fitted inside a large metal shell so that a fluid flowing through the shell on the outside of the tubes exchanges heat with another fluid flowing on the inside of the tubes

**Slop Oil** – recovered hydrocarbon oil streams that are recovered from the wastewater treatment facility or from a process unit after an emergency upset, unit startup, unit shutdown or other situation resulting in production of off-specification material; such slop oil streams are generally reprocessed

**Sludge** – any solid, semisolid or liquid waste generated from a municipal, commercial, or industrial wastewater treatment plant, water supply treatment plant, or air pollution control facility exclusive of the treated effluent from a wastewater treatment plant

**Solvent Deasphalting** – a refinery process using light hydrocarbons such as propane or butane to remove asphalts from lube oil feedstocks, improve gas oil recovery from heavy feedstocks, and make commercial asphalts from vacuum distillation unit bottoms

**Sour Water** – condensate from steam used in refinery processes to strip hydrocarbons or to change hydrocarbon partial pressure and containing dissolved hydrocarbons, H<sub>2</sub>S and NH<sub>3</sub> that give it a foul or sour smell

**Sour Water Stripping** – process equipment in petroleum refineries and petrochemical facilities for removing H<sub>2</sub>S and NH<sub>3</sub> from sour water streams, usually involving the downward flow of sour water through a trayed or packed tower in counter current flow against stripping steam or gas that removes the contaminants from the aqueous phase to the gaseous phase

**Stoke's Law** – the physical law stating that the force that retards a sphere moving through a viscous fluid is directly proportional to the velocity of the sphere, the radius of the sphere, and the viscosity of the fluid

**Stripped Sour Water** – see “Sour Water Stripping”

**Stripper** – process equipment, usually a fractionation column, used in refinery processes to separate or strip light components from heavy components in a liquid stream using steam or another refinery gas stream as the stripping medium

**Surfactant** – a surface active chemical agent, usually made up of phosphates, used in detergents to cause lathering; the phosphates may contribute to water pollution

**Thermal Desorption** – refers to the separation of volatile and semi-volatile constituents from a solid matrix through heat induced volatilization

**TDS** – total dissolved solids, as determined by use of the test method specified in 40 CFR Part 136

**TSS** – total suspended solids, as measured by a standard test method utilizing glass fiber disks

**ULS** – ultra-low sulfur; as applied to gasoline and distillates, sulfur levels measured in the 5 to 30 ppm by weight range

**Vacuum Distillation Unit** – distillation process unit occurring under reduced pressure (less than atmospheric) that lowers the boiling temperature of the liquid being distilled to prevent cracking or decomposition of the feedstock

**Vacuum Gas Oil** – the hydrocarbon stream originating in a refinery vacuum distillation unit with a boiling range generally of 650°F to 1100°F

**Visbreaking** – a thermal cracking process in which heavy atmospheric or vacuum-still bottoms are cracked at moderate temperature to increase production of distillate products and reduce viscosity of the distillation residues

**VGO** – vacuum gas oil (see definition)

**Wash Water** – water that is injected into refinery processes to control contaminant buildup, such as ammonium chloride in reactor effluent condensers or salt from crude oil in the desalter