POLLUTION PREVENTION

PETROLEUM REFINING AND PETROLEUM DISTRIBUTION SYSTEMS

Petroleum refineries and petroleum distribution systems generate a series of different kinds of hazardous wastes. This fact sheet characterizes the types and quantities of hazardous waste generated by these activities in Wyoming and provides an overview of the various methods that can be used to minimize hazardous waste in the industry.

The fact sheet is divided into the following four sections:

1. background information on Wyoming’s petroleum refining/distribution industry, including the types and quantities of waste generated;
2. a description of hazardous waste generating operations typically used by the industry and the resultant types of wastes;
3. a summary of techniques for waste minimization organized into three categories: source reduction techniques; recycling options; and management changes; and
4. a brief conclusion.

Background Information on Wyoming’s Petroleum Refining Industry

Wyoming has 5 petroleum refineries in operation with a cumulative refining capacity of approximately 165,000 barrels per day. The petroleum refining industry reported the generation of approximately 2,809 tons of hazardous waste in 1989 consisting of 8 different waste types. The quantities of each waste type are listed below:

1. Although petroleum distribution systems are generally considered to be a distinct industrial group from petroleum refineries, the kinds of hazardous waste generated by distribution facilities are similar to some of the waste generated by refineries. Therefore, the two industries will be considered together in this fact sheet.


<table>
<thead>
<tr>
<th>Description</th>
<th>Waste Code</th>
<th>Weight (tons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>API separator sludge</td>
<td>KO51</td>
<td>2,369</td>
</tr>
<tr>
<td>Leaded tank bottoms</td>
<td>KO52/D008</td>
<td>261</td>
</tr>
<tr>
<td>Slop oil emulsion solids</td>
<td>K049</td>
<td>105</td>
</tr>
<tr>
<td>Dissolved air flotation float</td>
<td>KO48</td>
<td>34</td>
</tr>
<tr>
<td>Cooling tower sludge</td>
<td>D007</td>
<td>17</td>
</tr>
<tr>
<td>Heat exchanger bundle cleaning sludge</td>
<td>K050</td>
<td>12</td>
</tr>
<tr>
<td>Ignitable wastes (catalyst and solvent)</td>
<td>D001</td>
<td>9</td>
</tr>
<tr>
<td>Contaminated soil</td>
<td>D009</td>
<td>2</td>
</tr>
</tbody>
</table>

The vast majority (99 percent) of these waste streams were disposed of in hazardous waste landfills with three exceptions. The dissolved air floatation float was recycled on-site. Four tons of the ignitable waste went to energy recovery. Twelve tons of catalyst (generated in 1988) were sent off-site for metals recovery. Given the promulgation of land disposal restrictions for listed wastes from the petroleum refining industry since 1989, it is likely that many of these waste streams previously managed in landfills are currently managed by incineration.4

**Overview of Industrial Processes in Petroleum Refineries and Petroleum Distribution Facilities**

Refineries are often classified by their processes and/or capacities. The U.S. EPA, for example, uses a five tier classification system in National Pollutant Discharge Elimination System (NPDES) permitting based on the types of refining processes occurring at the site. The five tiers, in increasing order of complexity, are as follows: topping; cracking; petrochemical; lube; and integrated (i.e., uses all of the above processes). The American Petroleum Institute has used a four tier system to classify refineries in terms of capacity. The tiers are from 0 - 50,000 barrels per day, 51,000 - 100,000 barrels per day, 101,000 - 200,000 barrels per day, and greater than 200,000 barrels per day. Four of the refineries in Wyoming have refining capacities of less than 50,000 barrels per day, while one refinery has a capacity of 54,000 barrels per day.5

Oil refining is composed of many complex processes. The aim of refining is to separate different organic compounds from the crude oil and convert less valuable compounds into more valuable ones. The general order of processing is desalting, distillation, and further refining (i.e., cracking, treating, reforming, etc.). Desalting is a washing process where water is added to the crude, mixed, and then separated to remove salt, clay, and other suspended particles. Distillation involves heating the crude so that different fractions (compounds that boil at different temperatures) can be recovered. Refinement is then performed on the individual fractions. Many different products result from refining: petroleum products with different octane ratings; a more consistent product (i.e., fewer impurities); or a product with enhanced value because of the addition of other compounds. Refining generally involves thermal treatment and/or the use of catalysts to change the form of the petroleum fractions.

Waste is generated throughout the refinery process. Major waste streams include process wastes (e.g., wastewaters from desalting operations, spent catalyst from refinement processes); equipment cleaning wastes (e.g., sludges from tank cleaning); and wastewater treatment wastes

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Petroleum distribution involves collecting crude oil from wellheads and ports and moving it to central locations via pipelines, trains, or trucks. There are various collection facilities along the way, though the final destination of the crude oil is a petroleum refinery. As a result of handling petroleum products, distribution facilities generate certain wastes that are similar to the wastes generated by petroleum refiners, including: equipment cleaning wastes (e.g., petroleum-contaminated wastewaters and sludges from cleaning tanks, tank truck or other containers), and wastewater treatment wastes.

**Opportunities for Source Reduction of Specific Petroleum Refining/Distribution Processes**

The primary hazardous wastes associated with petroleum refining can be classified into three main categories: process wastes; equipment cleaning wastes; and wastewater treatment wastes. The following is a description of these categories, as well as a presentation of certain source reduction options for each category. Refer to Table 1 for a summary of all of the options.

A. **Process Wastes**

Refining operations generate a series of wastes from each step in the refining process. Desalting operations generate both water and sludges contaminated with petroleum, while distillation and refinement operations generate wastewater, spent catalysts (which often contain heavy-metal constituents), spent caustics, and spent desiccant clays.

A series of minimization techniques have been identified for petroleum refining process wastes. These techniques tend to be quite technical and relate directly to the chemical reactions being utilized during the refining process. In general, the techniques revolve around the following approaches:

- Maximize the use of process materials such as catalysts or desiccant clays by following proper storage and use procedures.
- Ensure that all reaction processes are being run under optimal conditions (pressure, temperature, and mixing ratios).
- Select catalysts and associated materials based on their tendency to minimize the generation waste.
- Use cooling water for multiple cycles.
- Locate specific sources of wastewater contamination and segregate them.

B. **Equipment Cleaning Wastes**

Equipment cleaning wastes are generated from cleaning such items as heat exchangers, storage tanks, and tank trucks. The waste from cleaning the heat exchangers is classified as K050 waste and waste from cleaning leaded gasoline storage tanks is classified as K052 waste (leaded tank

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All other waste from cleaning petroleum storage equipment is potentially TC-hazardous waste due to the presence of benzene (D018).

Equipment cleaning wastes may be minimized by a series of techniques. For storage tank or other equipment cleaning wastes, some of the available waste minimization techniques are as follows.

- Filter the fuel going into the tanks (or other storage equipment) with reusable filters to avoid sludge buildup.
- Install floating tank covers and add secondary seals in the tanks to minimize water or solid entrainment.
- Install cathodic protectors in tanks, and/or use corrosion resistant materials to line the tanks.
- Use a filter press to recover petroleum from the cleaning sludge.
- Allow oil to separate from tank water draws before treating the water.

For heat exchanger bundle cleaning wastes, some available waste minimization techniques are as follows.

- Decrease the film (surface) temperature and increase the cooling liquid turbulence (velocity) to reduce cleaning frequency.
- Reduce deposit precursors (calcium or magnesium salts) in fluids to help prevent scale buildup and corrosion.
- Add water softeners to cooling water.
- Add corrosion inhibitors to cooling water.
- Use air coolers/electric heaters as alternatives to heat exchangers.
- Use smooth heat exchanger tube surfaces (e.g., teflon) to minimize the sites available for scale formation and to reduce the cleaning frequency.
- Use ozone destruction of microorganisms in cooling water rather than biocides.

C. Wastewater Treatment Wastes

Wastewater treatment at petroleum refineries generally involves API separators and other equipment such as dissolved air floatation units, oil slop tanks, vacuum filters, biological treatment systems, and stormwater settling basins. Distribution facilities may utilize some or all of these treatment techniques, although usually on a much smaller scale than most refineries. The following discussion will focus on petroleum refineries.

In most refineries, all wastewater is treated in a centralized system. Wastewater is collected from all processes and first treated by an API separator. The purpose of the API separator is to perform the initial separation of solids from liquids and oil from water. Solids that settle in the API separator are K051 wastes (API separator sludge). The sludge is removed from the API separators, the water is passed on to further treatment, and the oil is recycled.
In some refineries, the next treatment step for wastewater is “dissolved air floatation” or DAF, which removes additional oil and solids. The water is fed into a tank where air bubbles are formed, bringing solids and oil particles to the surface where they are skimmed off. Oil skimmed off the top is recycled and the remaining waste is classified as K048 waste (dissolved air floatation float).

The water effluent from these processes may be subject to further primary treatment, then to secondary treatment (biological treatment), and finally discharged to surface waters under a Clean Water Act (NPDES) permit, discharged to a sewer system, recycled, or impounded in a lagoon. Any sludges arising from primary treatment other than API separation or DAF is listed as F037. Sludges resulting from secondary treatment are listed as F038. (Note that these two listings apply only to refinery treatment, distribution facilities that perform similar primary or secondary treatment are not covered by the F037/F038 listings.)

The oil that has been recovered from the API or DAF treatment must go through further treatment in “slop oil tanks”, where it is again separated into oil, water, and emulsion. The oil is returned for reprocessing and the wastewater is recycled back to the API separator. The emulsion is classified as a K049 waste (slop oil emulsion solids).

Wastewater treatment wastes may be minimized by all of the following approaches.

1. Use better operating procedures to minimize the amount of wastewater requiring treatment. For example, segregate aqueous and oily wastes where possible; use only the amount of water required in refinery processes; insure that process system components are well serviced to avoid leakage and contamination of non-process waters; etc.
2. Retrofit API separators with coalescing plates (i.e., baffles) to increase separation efficiency or treatment volume.
3. Use pressurized air technology to increase API recovery efficiency.
4. Use alternative cleaning technologies where possible, especially DAF technology, which is more expensive but ten times more efficient than an API separator.
5. Use proper flocculants in API or other separation operations to increase the separation efficiency and reduce the amount of waste that is carried downstream.
6. Use a filter press to recover oil from wastewater sludges.
7. For facilities with cokers, use wastewater sludges to produce coke.

Opportunities for Recycling in the Petroleum Refining and Distribution Industry

In addition to direct source reduction activities listed above, the petroleum refining and distribution industry may also be able to reduce the amount of hazardous waste requiring disposal by taking advantage of certain recycling options. Much of the industry is currently involved in recycling efforts. American Petroleum Institute estimates that in both 1987 and 1988, the petroleum refining industry recycled approximately 1 million tons, or 7 percent of the total waste quantity, of RCRA hazardous waste, nonhazardous solid waste, and wastewaters. When the outlier waste streams
(Other Aqueous Wastes not otherwise specified generated by 4 large refineries) are removed from the calculations the percentage of waste streams recycled increases to 21 percent in 1987 and 23 percent in 1988.

The petroleum refining industry generates waste streams that are recycled in one of three ways: some oily wastes can be returned to the crude unit; other oily wastes can be processed in a coker; and caustics, acids, and catalysts can be regenerated or constituents (i.e., valuable metals) of these waste streams can be reclaimed. With regard to recycling activities, oily wastes more often are recycled on-site while caustics, acids, and catalysts are more often recycled off-site. Nationally for 1988, the waste streams recycled in the largest quantities are listed below along with the percentages of those waste streams that were recycled.

<table>
<thead>
<tr>
<th>Waste Stream</th>
<th>Quantity</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spent Caustics</td>
<td>497,000 tons</td>
<td>76 percent</td>
</tr>
<tr>
<td>DAF Float</td>
<td>96,000 tons</td>
<td>15 percent</td>
</tr>
<tr>
<td>API Separator Sludge</td>
<td>91,000 tons</td>
<td>21 percent</td>
</tr>
</tbody>
</table>


Ibid
The following is a summary of two recycling efforts available to the petroleum refining industry that have been identified in the literature. The potential for further recycling depends largely on the existence of markets for the hazardous materials generated as waste by petroleum refineries or distribution facilities.

A. Recycling of Catalysts and Spent Phenolic Caustic

In a sampling of six refineries (from moderate to large in size and from moderate to highly complex refineries) by the American Petroleum Institute, 65 percent of the catalysts and over 60 percent of the spent phenolic caustic at each refinery were recycled in 1988. According to the source of this information, the recycling of catalysts and of spent phenolic caustic may already be occurring at many refineries. Catalysts can be recycled in a variety of ways. Metals from catalysts in isomerization, reforming, and hydrodesulfurizing can be reclaimed off-site. Cat cracking catalyst can be used as a source of alumina in cement manufacturing. Caustics, as well, can serve a variety of purposes after their use in petroleum refining. Caustic wastewater can be used in wastewater treatment to adjust the pH (e.g., for enhanced bio-oxidation). Sulfidic caustics can be reused off-site by some paper manufacturers or, possibly, as a feedstock for manufacturing sulfuric acid.

B. Recycling Petroleum Refinery Hazardous Wastes that Contain Oil

Two techniques are commonly used to recycle oily wastes: feeding to a coker or reusing it the crude unit. During 1988, coking was a more common (185,400 tons of waste was recycled in cokers) way of recycling oily wastes than reprocessing the waste in the crude unit (86,710 tons of waste was recycled in crude units).

The 1984 RCRA amendments provided an exemption for petroleum refinery wastes containing oil (RCRA section 3004[q][2][A]). This exemption allows for refinery hazardous wastes that contain oil to be used as feedstock to a coker as long as the wastes are generated at the same facility at which the coker is located and the resulting coke does not exhibit a hazardous characteristic. The oily wastes that a coker can normally receive include DAF float (K048), slop oil emulsion solids (K049), API separator sludge (K051), tank bottom sludge and bio-sludge. According to the literature, the process modification necessary to recycle these wastes is relatively inexpensive. The process is currently used in the industry by Mobil, and has been shown to be “extremely effective” for recycling the above listed and non-listed hazardous wastes. In some cases, these materials may be suitable for feeding back into the crude unit. A number of refineries use the crude unit to recycle API separator sludge, DAF float, slop oil emulsion solids, other separator sludges, and non-leaded tank bottoms.

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The Role of Management Commitment to Waste Minimization

Some businesses have found that certain management decisions can help to promote adoption of the source reduction and recycling options identified above. These decisions include: developing a company waste minimization policy, performing an assessment of waste minimization opportunities, and establishing employee training and incentive programs on waste minimization.

**Developing a company policy**

A petroleum refining or distribution company can demonstrate a commitment to reducing the generation of hazardous waste by developing and following through with a formal strategy for waste minimization. The following is a list of possible components of a company’s waste minimization strategy.

- The company may want to develop a written statement of commitment to hazardous waste minimization. This statement will clarify the company’s position to employees, customers, and other interested parties.

- The company may want to set specific goals for waste minimization progress (e.g., a 50% reduction in the amount of hazardous waste being disposed). Goals can provide a standard to chart progress and an objective for employees to try to attain.

- The company may want to consider waste minimization opportunities when initiating new processes or designing new work areas. Incorporating waste minimization into new processes may add little to their construction costs and offer significant savings during operation.

- The company may want to track hazardous materials use and hazardous waste generation amounts. Simple inventory systems can help identify problem areas in hazardous waste generation.

**Assessing waste minimization opportunities**

An audit of operations for waste minimization opportunities can be very instructive in determining the factors influencing current waste generation and in establishing priorities for further action. To be most useful, audits should carefully examine all inputs, processes, and waste streams. A list of possible options for waste minimization can then be developed, using the assessment, as well as employee suggestions and ideas from technical or trade literature.
Employee Involvement

A company can involve its employees in hazardous waste minimization in a number of ways. A training program can be established to ensure that employees are aware of proper hazardous materials handling and hazardous waste minimization techniques.

An incentive program can be established to encourage employees to become involved with waste minimization techniques.

Employees can be regularly solicited for suggestions about ways to reduce hazardous and other wastes.

The company can designate a specific staff member to be the “waste minimization contact person.” This person would continue to keep abreast of new waste minimization products and technology, changes in costs, and promulgation of new regulations, so that the company could more easily implement new waste minimization options as they become available.

Conclusion

It appears that there is potential to minimize hazardous waste in the petroleum refining and distribution industry. Improved operating procedures and more efficient equipment are two types of waste minimization practices that the industry could adopt. To better estimate the potential to minimize waste in Wyoming, it is necessary to work with individual facilities to determine the specific activities they engage in, to estimate the amount of waste they generate and how it is managed, and to appraise the current level of waste minimization practiced.
List of Sources


County of Ventura Environmental Health Department, AB 685 Grant Project Report: Hazardous Waste Minimization Program Results and Case Studies, July 1987.


Huisingh, Donald, Division of University Studies, NCSU, Profits of Pollution Prevention.


Swartznbaugh, Joseph T., Peer Consultants, P.C., *Using an Audit to Identify Waste Minimization Opportunities*, no date.


United States Environmental Protection Agency, *Waste Minimization: Hazardous and Non-


United States Office of Technology Assessment, Serious Reduction of Hazardous Waste for Pollution and Industrial Efficiency, September, 1986.

SOURCES FOR ADDITIONAL HELP

Wyoming Solid and Hazardous Waste Division  (307) 777-7752
U.S. EPA  (800) 227-8917
RCRA/Superfund Hotline  (800) 424-9346
Trade Associations
Vendors
Consultants

SHARE INFORMATION: LET OTHERS KNOW WHAT WORKS (AND WHAT DOESN’T)

Department of Environmental Quality
Solid and Hazardous Waste Division
Herschler Building
122 West 25th Street
Cheyenne, WY 82002