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WASTE MINIMIZATION PRACTICES IN THE PETROLEUM REFINING INDUSTRY

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INTRODUCTION

Waste minimization has moved to the forefront of environmental policies in the petroleum industry. In the past, waste minimization in the petroleum industry primarily meant conservation of hydrocarbons; more product out of every barrel of oil has been the goal of the industry since its inception. More recently, however, waste minimization has taken on a broader definition to encompass the reduction of all waste materials. At the same time, the industry is moving from the traditional view of the management of individual environmental impacts--water, air, and solid waste issues to one of the management of the overall environmental impacts. This change in viewpoint to a multi-media approach for environmental control has brought waste minimization to the forefront.

The incentives for waste minimization in the petroleum industry are: to reduce the environmental impacts of the operations, to reduce regulatory compliance paper work (an ever-increasing burden), reduce future liabilities that may be created when waste is stored or treated; increase the overall efficiency of the processing operations (the major goal of refining), and reduce costs (a goal of all manufacturing operations).

The petroleum industry encompasses four separate technology and business areas: 1) extraction of crude oil from the ground; 2) transportation to refineries and product distribution centers; 3) refining into finished products; and, 4) marketing, or sale of the products to consumers. Each segment of the industry generates different types of wastes because of the variation of the processes used in each area, and, therefore practices different waste minimization technologies. This paper focuses on waste minimization practices in the refining segment.

REFINERY OPERATION

In 1988, there were 182 refineries in the United States with a total capacity of 15.3 million barrels per day of crude oil. (One barrel is equivalent to 42 United States gallons.) The smallest refinery processed 300 barrels per calendar day and the largest almost 500,000 barrels per calendar day. There is no "typical" refinery. The types and designs of process operations at each refinery vary with the types of products generated and the types of crude oil processed.

The unit operations within a refinery can be classified into 4 types. Handling operations include storage, pumping, blending, and transportation within the refinery. If there are relatively few processes and products, handling can be simple. However, many operations and products can make handling operations complex. Thermal processes, such as distillation, are used to separate lighter products from heavier ones. Catalytic processes, such as cat cracking and reforming, are used to change the molecular structure of intermediate materials to make more saleable products, such as gasoline. Environmental operations, include the management of all emissions--air, water, and solids to the environment.

The simplified diagram in Figure 1 shows how the operations are interrelated. Crude enters the refinery, as shown on the left of the diagram, and is distilled in the crude unit. Various intermediate streams are generated depending on the type of crude processed and the type of downstream operations. Products that can be produced are also listed in Figure 1. Most refineries produce only some of the products from the list. As demand changes or the type of crude processed changes, the quantities and types of products can be adjusted, within the limits of the individual refinery.

WASTES AND OPPORTUNITIES FOR MINIMIZATION

Waste generated by refineries fall into four categories of materials: oily materials, spent chemicals, spent catalysts, and other residuals.

Oily Materials

Oily materials are the primary source of waste for most refineries and are generated when oil coalesces on solids, such as dirt particles. A large portion of the oily material is actually sand or grit covered with a small amount of oil. Because the oil acts as an adhesive, one kilogram of oil can generate 10 to 20 kilograms of residue. Oily residues are collected at several points within the refinery: oil/water separators; dissolved air flotation units which are part of the wastewater treatment process; heat exchanger cleanings, and tank bottoms cleanings.

Residues from oil/water separators that are used to treat process water from sewer systems represent the largest source of oily materials generated by most refineries. The residues are generated when oil coalesces on dirt particles that enter the sewer system from dust that falls on the process units or roadways and then is washed into the sewer systems.

The quantity of oily materials generated from one refinery to the next is highly variable. In a sampling of six refineries that varied in complexity from highly complex to simple ranged from 0.004 kg (1/100 lb) of residue per barrel of crude processed to almost 0.4 kg (1 lb) of residue per barrel of crude processed (a difference of two orders of magnitude). Some of the other factors affecting the quantity of materials generated are: the type of crude processed, the geographical location of the refinery, climatic factors, how often tanks are cleaned, the type of products generated, and the waste treatment system design. For example, crude varies in the amount of solids it contains and the type of emulsifiers that contribute to oily residues. The geographical location and climatic conditions of the refinery determine the type of soil and how readily it can be washed into the sewer system.

Minimization strategies for control of oily residue should be aimed at the three factors that contribute to formation: oil, dirt, and emulsifiers. Prevention can only vary from very simple methods such as the use of street sweepers to remove dirt from roads to more expensive methods, such as the redesign of piping. At one facility, 4500 to 9000 kg (5 to 10 tons) of solids can be removed per day from roadways by street sweepers. At 10 kg of residues per kg of solids (10 lbs residue per pound), that represents potentially 45,000 to 90,000 kg (50 to 100 tons) of oily sludge eliminated per day by street sweeping, or approximately 0.23 kg (0.5 lbs) of residue eliminated per barrel of oil processed.

Another method of preventing solids from entering the sewer system is to redesign storm catch basins to allow runoff but filter solids out. The amount of oil entering the sewer systems can be minimized by using a holding tank to separate oil and water drawn from storage tanks. Normally, water collects in crude oil and product storage tanks and is drawn off. This "tank water draw" is sent to the sewer system and then to the oil/water separator. By running the tank water draw to a collection tank prior to the sewer system, most of the oil can be separated and returned to the appropriate storage tank (Figure 2).

Segregating stormwater water runoff from the process wastewater prevents the mixing of dirt-containing water with process waters containing oil and emulsifiers. One method of segregating waters is to install above ground lines to prevent the commingling of process water with stormwater. Stormwater can be recycled for various uses within the refinery, such as fire water, with minimal pretreatment in the wastewater treatment system.

Emulsifiers enter the system from many sources, including the crude, and control requires careful monitoring of all sources. Because crudes contain naturally-occurring emulsifiers, mixing of many sources of crude can initiate emulsion formation. Rapid changes in the feed to desalters can increase emulsion formation. Better mixing in crude storage tanks can reduce the fluctuations in feed to the desalters and keep solids in suspension to minimize tank bottoms formation. Agitation in other storage tanks can reduce the amount of tank bottoms formation.

Oil Separation, Recycling, and Reprocessing

Once oil has formed, it can be managed by recycling and reprocessing. One very effective means of recycling oil from residue is filtration. For example, at one facility, oily residue is filtered with a recessed plate filter press. Ninety percent of the oil is recovered and recycled to the refinery for reprocessing. Water is returned to the wastewater treatment system and the filter cake is treated at a land treatment facility. (Land treatment facilities are used in the petroleum industry for treating oily materials using naturally occurring soil microorganisms to degrade oily residues.

The effectiveness of the filtration operation is illustrated in Figures 3 and 4. Figure 3 shows the residue before filtration and Figure 4 shows the material after the oil has been removed and it has applied to a land treatment unit.

With filtration, approximately 130,000 barrels of oil are recycled annually at this facility. At $10 a barrel for recycled oil, that represents a savings of $1.3 million annually.

Another method of recycling residue is to process it in an existing refinery unit. Not every refinery unit can be used to process residue because it can interfere with the operation of the unit. For example, some catalysts could be poisoned by materials in the residue. Options for reprocessing of residue must be evaluated carefully.

Cokers are process units that convert the heavy ends or bottoms of crude oil and, when heated with steam, generate lighter materials and coke (a fuel used in industrial applications). Some cokers can process oily residues, so the refinery that has a coker can use this method to effectively reduce its oily residues. However, some uses of coke limit the type of material that can be fed to the coker. Other process units, such as the cat cracker, are under investigation as potential methods of recycling oily materials.

Catalysts

Catalysts are used in numerous refining processes and are essential in producing many products, such as gasoline. In some cases, the catalysts remain in place for several years before they become inactive and must be replaced with new material. In other cases, the catalyst must be replaced more frequently, sometimes on a continuous basis. Some catalysts contain valuable metals, such as platinum, and the catalysts are treated to recover the metal for recycle. Catalyst treatment is usually done at a separate facility designed for metals recovery.

The types of refining processes that use catalysts are: catalytic cracking of oil to produce gasoline; sulfur removal from gas and liquid streams; treating to convert heavier products into lighter products (like gasoline); and, reforming of gases to produce liquid products.

In a sampling of six refineries, from moderate size to large, and moderate complexity to highly complex, 65 percent of the catalysts were recycled in 1988. Of the 35 percent that were not recycled, almost all was spent cat cracking catalyst. On the average of the six refineries, approximately 0.04 kg (0.1 lb) of spent cat cracking catalyst was generated per barrel of oil processed. However, the range of spent catalyst generated in the six refineries was almost 2 orders of magnitude on a capacity basis.

Spent cat cracking catalyst contains mostly aluminum oxide and is non-hazardous. Because it does not contain valuable metals, it has not been sought after by catalyst recycling companies. However, there are opportunities for recycling and reuse of the catalyst.

One possible method of reusing spent cat cracking catalyst is to substitute the catalyst for bauxite, which is a source of alumina, in the manufacture of cement.

Another method is to process the catalyst so it can be reused as cat cracking catalyst. At least one recycle process is under development and is in the pilot plant stage.[1]

Caustic Solutions

Caustic solutions are used in refining processes to absorb and remove contaminants from intermediate and final product streams. Caustic treating for removal of hydrogen sulfide and mercaptans from gas and liquid streams generates a sulfide caustic. Another type of caustic treatment removes phenolics, casylics, and napthenics from bases and distillate streams.

There are several methods for reducing and recycling the amount of spent caustic generated. Phenolic caustics can be sold to chemical recovery companies that specialize in extracting the phenolics. Usually a minimum of 5 percent phenolics and a maximum sulfide content of 0.5 percent is required for the recovery process. Sulfide caustics can be reused in paper manufacture or mining processes. However, these opportunities are more limited than those for phenolic caustics.

To maximize the opportunity for recycling caustics, it is critical to prevent the two types of caustics from mixing. More importantly, phenolic caustics should not be added to the wastewater treatment system because the addition of the increased surfactant load to the system which then adds to the production of emulsions and sludges.

In a survey of six refineries, the amount of spent caustic generated averaged 0.16 kg (0.35 lbs) per barrel of crude oil processed. Of the total generated, roughly 1/3 is phenolic and 2/3 is sulfidic. Currently, over 60 percent of the total spent caustic is recycled.

Identification and segregation of phenolic and sulfidic caustics are not trivial problems in a complex refinery. However, segregation may result in less fresh caustic makeup because spent caustic from one process may be reused in another that had been using fresh makeup.

Water Reuse

The quantities of water used vary with each refinery, the range based on capacity is very wide (almost two orders of magnitude). It is very difficult to generalize on water reuse opportunities, but one procedure that may aid in reuse is the segregation of stormwater and process water. As new oily water sewer systems are constructed, above ground lines can prevent the commingling of process water and stormwater. Stormwater is generally cleaner and can be recycled for various uses, such as firewater, with minimal pretreatment in the wastewater treatment system. A second method of water conservation is the use of multiple cycles in cooling towers.

The minimization of water in the refinery impacts almost all of the refinery processes and each method must be evaluated for potential downstream impacts.

RESEARCH AND DEVELOPMENT NEEDS

Although progress has been made by individual refineries in waste reduction, there are several generic areas where breakthroughs in research and development could impact the minimization of waste industry-wide. Examples are: the prevention of emulsions; the reuse of spent cat cracking catalysts; reprocessing in process units, such as cat crackers; and the reduction of tank bottoms formation. The industry is attacking these problems through cooperative research programs by the American Petroleum Institute (API) and the Petroleum Environmental Research Forum (PERF).

PERF is an organization that was formed to undertake environmental research by its members.[2] PERF has initiated a program on the reuse of spent cat cracking catalyst and has several other topics under discussion. The API has two programs underway that are aimed at increasing information available on waste reduction. One program is the publication of a compendium of waste minimization practices.[3] The second program is to establish a database of wastes generated by the industry.

SUMMARY

There are many opportunities for waste reduction in the industry, but the practicality of implementing these opportunities is dependent upon several factors. For example, the location of a particular refinery will determine what other manufacturing operations are nearby and what materials can be recycled offsite. The climatic factors, such as heavy rains, will directly impact the amount of residue generated. The type of crude processed will define the process operations required. For example, the sulfur content of the crude will impact the amount of treating required to remove sulfur from the products. The types of products generated by the refinery can impact the types of refinery processes that are needed for producing these products and the complexity of the refinery can limit the reprocessing options available. Whether or not a refinery has a coker, for example, can eliminate one potential method for residue processing.

The waste treatment systems available will affect the choices for waste handling.

Although much progress has been made recently, there are many areas under investigation that will continue to further the progress in waste reduction.

References

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2. Fenton, D. M. And Ouimette, J. R., The Petroleum Environmental Research Forum, Symposium on Refinery Waste Cleanup, American Chemical Society Meeting, New Orleans, August 30, 1987.

3. "Compendium of Waste Minimization Practices," Draft report to the American Petroleum Institute, November, 1988.

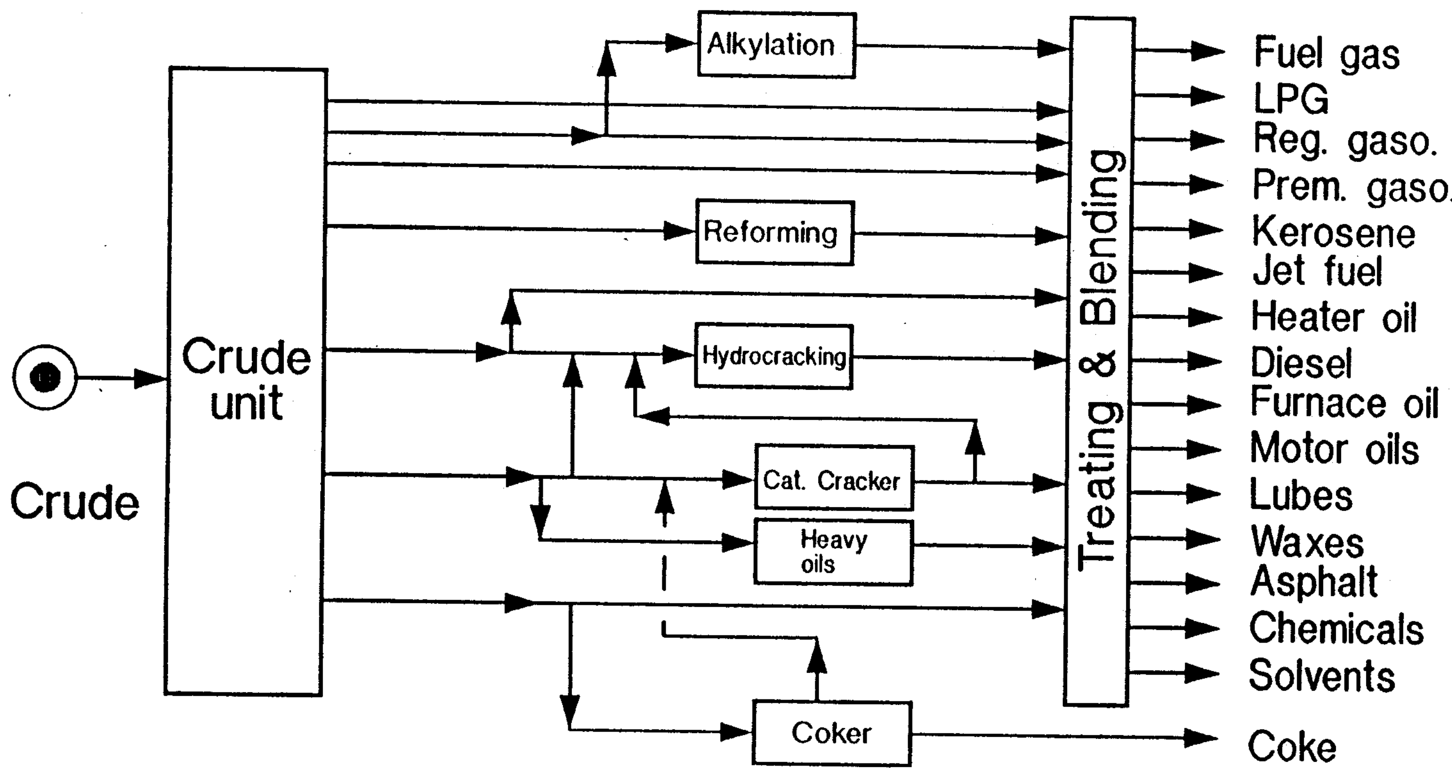

Figure 1 - Schematic Diagram of Refinery Operation

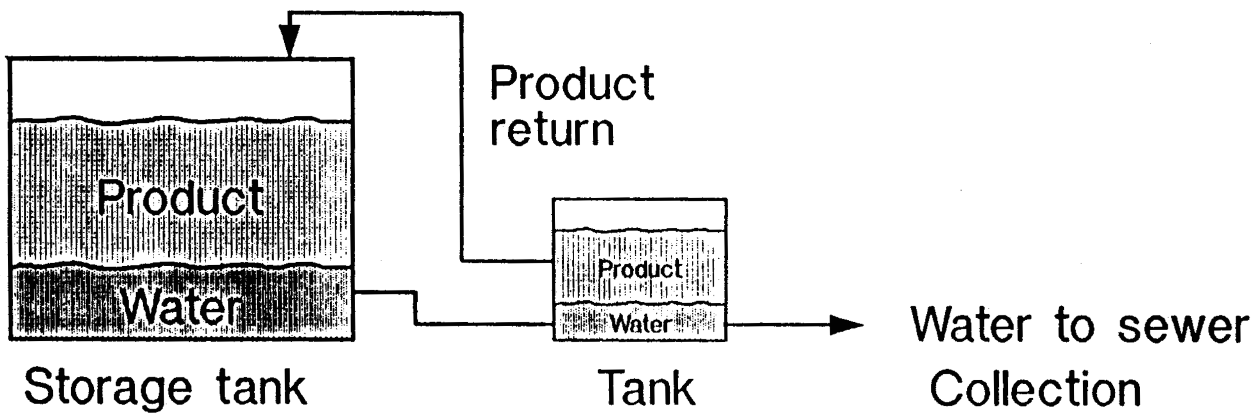

Figure 2 - Designs of Typical Tank Water Draw System and Modified System with a Collection Tank

Figure 3 - Oily Residue Prior to Filtration

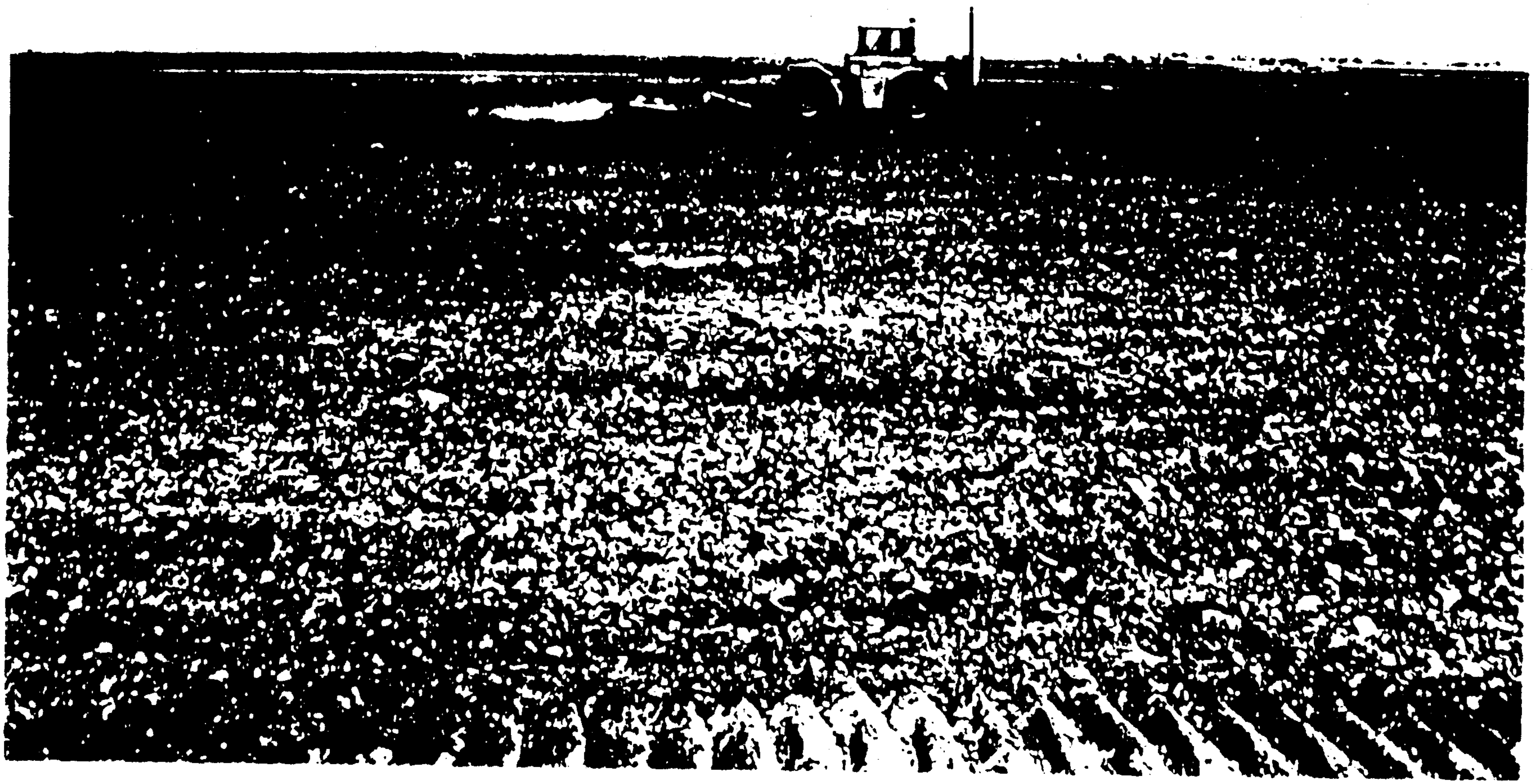

Figure 4 - Residue After Filtration Applied to a Landfarm