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DA-069  
c.4

Chapter 10, Petroleum Industry  
from AP40, Air Pollution Engineering Manual  
2nd Edition. May 1973  
pp 581-698

**U.S. DEPARTMENT OF COMMERCE  
National Technical Information Service**

PB-225 132

**AIR POLLUTION ENGINEERING MANUAL (SECOND EDITION)**

**LOS ANGELES COUNTY AIR POLLUTION CONTROL DISTRICT**

**PREPARED FOR  
ENVIRONMENTAL PROTECTION AGENCY**

**MAY 1973**

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## CHAPTER 10 PETROLEUM EQUIPMENT

### GENERAL INTRODUCTION

Operations of the petroleum industry can logically be divided into production, refining, and marketing. Production includes locating and drilling oil wells, pumping and pretreating the crude oil, recovering gas condensate, and shipping these raw products to the refinery or, in the case of gas, to commercial sales outlets. Refining, which extends to the conversion of crude to a finished salable product, includes oil refining and the manufacture of various chemicals derived from petroleum. This chemical manufacture is often referred to as the petrochemical industry. Marketing involves the distribution and the actual sale of the finished products. These activities and their sources of air pollution are briefly discussed in this introduction. In the remainder of the chapter, they are discussed much more thoroughly, and adequate air pollution controls are recommended.

### CRUDE OIL PRODUCTION

The air contaminants emitted from crude oil production consist chiefly of the lighter saturated hydrocarbons. The main sources are process equipment and storage vessels. Hydrogen sulfide gas may be an additional contaminant in some production areas. Internal combustion equipment, mostly natural gas-fired compressors, contributes relatively negligible quantities of sulfur dioxide, nitrogen oxides, and particulate matter. Potential individual sources of air contaminants are shown in Table 153.

Contribution of air contaminants from crude-oil production varies widely with location and concentration of producing facilities. In isolated or scattered locations, many of the sources cannot be controlled feasibly. Control and pretreatment facilities such as natural gasoline plants are more likely to be located in more developed or highly productive areas. These factors are significant in determining where air contaminant emissions from production equipment must be minimized by proper use of air pollution control equipment. Control equipment for the various air pollution sources associated with crude-oil production are listed in Table 153. Their application can usually result in economic savings.

### REFINING

Oil companies have installed or modified equipment not only to prevent economic losses but also to try to improve community relations, prevent fire hazards, and comply with air pollution laws. The air contaminants emitted from equipment associated with oil refining include hydrocarbons, carbon monoxide, sulfur and nitrogen compounds, malodorous materials, particulate matter, aldehydes, organic acids, and ammonia. The potential sources of these pollutants are shown in Table 154.

### Flares and Blowdown Systems

To prevent unsafe operating pressures in process units during shutdowns and startups and to handle miscellaneous hydrocarbon leaks, the refinery must provide a means of venting hydrocarbon vapors safely. Either a properly sized elevated flare using steam injection or a series of venturi burners actuated by pressure increases is satisfactory. Good instrumentation and properly balanced steam-to-hydrocarbon ratios are prime factors in the design of a safe, smokeless flare.

### Pressure Relief Valves

In refinery operations, process vessels are protected from overpressure by relief valves. These pressure-relieving devices are normally spring-loaded valves. Corrosion or improper reseating of the valve seat results in leakage. Proper maintenance through routine inspections, or use of rupture discs, or manifolding the discharge side to vapor recovery or to a flare minimizes air contamination from this source.

### Storage Vessels

Tanks used to store crude oil and volatile petroleum distillates are a large potential source of hydrocarbon emissions. Hydrocarbons can be discharged to the atmosphere from a storage tank as a result of diurnal temperature changes, filling operations, and volatilization. Control efficiencies of 85 to 100 percent can be realized by using properly designed vapor recovery or disposal systems, floating-roof tanks, or pressure tanks.

Table 153. SOURCES AND CONTROL OF AIR CONTAMINANTS FROM CRUDE-OIL PRODUCTION FACILITIES

Phase of operation	Source	Contaminant	Acceptable control
Well drilling, pumping	Gas venting for production rate test	Methane	Smokeless flares, wet-gas-gathering system
	Oil well pumping	Light hydrocarbon vapors	Proper maintenance
	Effluent sumps	Hydrocarbon vapors, H <sub>2</sub> S	Replacement with closed vessels connected to vapor recovery
Storage, shipment	Gas-oil separators	Light hydrocarbon vapors	Relief to wet-gas-gathering system
	Storage tanks	Light hydrocarbon vapors, H <sub>2</sub> S	Vapor recovery, floating roofs, pressure tanks, white paint
	Dehydrating tanks	Hydrocarbon vapors, H <sub>2</sub> S	Closed vessels, connected to vapor recovery
	Tank truck loading	Hydrocarbon vapors	Vapor return, vapor recovery, vapor incineration, bottom loading
	Effluent sumps	Hydrocarbon vapors	Replacement with closed vessels connected to vapor recovery
	Heaters, boilers	H <sub>2</sub> S, HC, SO <sub>2</sub> , NO <sub>x</sub> , particulate matter	Proper operation, use of gas fuel
Compression, absorption, dehydrating, water treating	Compressors, pumps	Hydrocarbon vapors, H <sub>2</sub> S	Mechanical seals, packing glands vented to vapor recovery
	Scrubbers, KO pots	Hydrocarbon vapors, H <sub>2</sub> S	Relief to flare or vapor recovery
	Absorbers, fractionators, strippers	Hydrocarbon vapors	Relief to flare or vapor recovery
	Tank truck loading	Hydrocarbon vapors, H <sub>2</sub> S	Vapor return, vapor recovery, vapor incineration, bottom loading
	Gas odorizing	H <sub>2</sub> S mercaptans	Positive pumping, adsorption
	Waste-effluent treating	Hydrocarbon vapors	Enclosed separators, vapor recovery or incineration
	Storage vessels	Hydrocarbon vapors, H <sub>2</sub> S	Vapor recovery, vapor balance, floating roofs
	Heaters, boilers	Hydrocarbon, SO <sub>2</sub> , NO <sub>x</sub> , particulate matter	Proper operation, substitute gas as fuel

### Bulk-Loading Facilities

The filling of vessels used for transport of petroleum products is potentially a large source of hydrocarbon emissions. As the product is loaded, it displaces gases containing hydrocarbons to the atmosphere. An adequate method of preventing these emissions consists of collecting the vapors by enclosing the filling hatch and piping the captured vapors to recovery or disposal equipment. Submerged filling and bottom loading also reduce the amount of displaced hydrocarbon vapors.

### Catalyst Regenerators

Modern refining processes include many operations using solid-type catalysts. These catalysts become contaminated with coke buildup during operation and must be regenerated or discarded. For certain processes to be economically feasible, for example, catalytic cracking, regeneration of

the catalyst is a necessity and is achieved by burning off the coke under controlled combustion conditions. The resulting flue gases may contain catalyst dust, hydrocarbons, and other impurities originating in the charging stock, as well as the products of combustion.

The dust problem encountered in regeneration of moving-bed-type catalysts requires control by water scrubbers and cyclones, cyclones and precipitators, or high-efficiency cyclones, depending upon the type of catalyst, the process, and the regenerator conditions. Hydrocarbons, carbon monoxide, ammonia, and organic acids can be controlled effectively by incineration in carbon monoxide waste-heat boilers. The waste-heat boiler offers a secondary control feature for plumes emitted from fluid catalytic cracking units. This type of visible plume, shown in Figure 430, whose degree of opacity is dependent upon atmospheric humidity, can be eliminated by using the carbon monoxide waste-heat boiler.

Table 154. POTENTIAL SOURCES OF EMISSIONS FROM OIL REFINING

Type of emission	Potential source
Hydrocarbons	Air blowing, barometric condensers, blind changing, blowdown systems, boilers, catalyst regenerators, compressors, cooling towers, decoking operations, flares, heaters, incinerators, loading facilities, processing vessels, pumps, sampling operations, tanks, turnaround operations, vacuum jets, waste-effluent-handling equipment
Sulfur oxides	Boilers, catalyst regenerators, decoking operations, flares, heaters, incinerators, treaters, acid sludge disposal
Carbon monoxide	Catalyst regenerators, compressor engines, coking operations, incinerators
Nitrogen oxides	Boilers, catalyst regenerators, compressor engines, flares
Particulate matter	Boilers, catalyst regenerators, coking operations, heaters, incinerators
Odors	Air blowing, barometric condensers, drains, process vessels, steam blowing, tanks, treaters, waste-effluent-handling equipment
Aldehydes	Catalyst regenerators, compressor engines
Ammonia	Catalyst regenerators



Figure 430. A fluid catalytic cracking unit as a source of a visible plume. Use of a carbon monoxide waste-heat boiler eliminates this plume formation.

Other processes in refining operations employ liquid or solid catalysts. Regenerating some of these catalysts at the unit is feasible. Other catalysts are consumed or require special treatment by their manufacturer. Where regeneration is possible, a closed system can be effected to minimize the release of any air contaminants by venting the regenerator effluent to the firebox of a heater.

#### **Effluent-Waste Disposal**

Waste water, spent acids, spent caustic and other waste liquid materials are generated by refining operations and present disposal problems. The waste water is processed through clarification units or gravity separators. Unless adequate control measures are taken, hydrocarbons contained in the waste water are emitted to the atmosphere. Acceptable control is achieved by venting the clarifier to vapor recovery and enclosing the separator with a floating roof or a vapor-tight cover. In the latter case, the vapor section should be gas blanketed to prevent explosive mixtures and fires. Spent waste materials can be recovered as acids or phenolic compounds, or hauled to an acceptable disposal site (ocean or desert).

#### **Pumps and Compressors**

Pumps and compressors required to move liquids and gases in the refinery can leak product at the point of contact between the moving shaft and stationary casing. Properly maintained packing glands or mechanical seals minimize the emissions from pumps. Compressor glands can be vented to a vapor recovery system or smokeless flare.

The internal combustion engines normally used to drive the compressors are fueled by natural or refinery process gas. Even with relatively high combustion efficiency and steady load conditions, some fuel can pass through the engine unburned. Nitrogen oxides, aldehydes, and sulfur oxides can also be found in the exhaust gases. Control methods for reducing these contaminants are being studied.

#### **Air-Blowing Operations**

Venting the air used for "brightening" and agitation of petroleum products or oxidation of asphalt results in a discharge of entrained hydrocarbon vapors and mists, and malodorous compounds. Mechanical agitators that replace air agitation can reduce the volumes of these emissions. For the effluent fumes from asphalt oxidation, incineration gives effective control of the hydrocarbons and malodors.

#### **Pipeline Valves and Flanges, Blind Changing, Process Drains**

Liquid and vapor leaks can develop at valve stems as a result of heat, pressure, friction, corrosion, and vibration. Regular equipment inspection followed by adequate maintenance can keep losses at a minimum. Leaks at flange connections are negligible if the connections are properly installed and maintained. Installation or removal of pipeline blinds can result in spillage of some product. A certain amount of this spilled product evaporates regardless of drainage and flushing facilities. Special pipeline blinds have, however, been developed to reduce the amount of spillage.

In refinery operation, condensate water and flushing water must be drained from process equipment. These drains also remove liquid leakage or spills and water used to cool pump glands. Modern refining designs provide waste-water-effluent systems with running-liquid-sealed traps and liquid-sealed and covered junction boxes. These seals keep the amount of liquid hydrocarbons exposed to the air at a minimum and thereby reduce hydrocarbon losses.

#### **Cooling Towers**

The large amounts of water used for cooling are conserved by recooling the water in wooden towers. Cooling is accomplished by evaporating part of this water. Any hydrocarbons that might be entrained or dissolved in the water as a result of leaking heat exchange equipment are readily discharged to the atmosphere. Proper design and maintenance of heat exchange equipment minimizes this loss. Advancement of the fin-fan cooling equipment has also replaced the need of the conventional cooling tower in many instances. Process water that has come into contact with a hydrocarbon stream or has otherwise been contaminated with odorous material should not be piped to a cooling tower.

#### **Vacuum Jets and Barometric Condensers**

Some process equipment is operated at less than atmospheric pressure. Steam-driven vacuum jets and barometric condensers are used to obtain the desired vacuum. The lighter hydrocarbons that are not condensed are discharged to the atmosphere unless controlled. These hydrocarbons can be completely controlled by incinerating the discharge. The barometric hot well can also be enclosed and vented to a vapor disposal system. The water of the hot well should not be turned to a cooling tower.

**EFFECTIVE AIR POLLUTION CONTROL MEASURES**

Control of air contaminants can be accomplished by process change, installation of control equipment, improved housekeeping, and better equipment maintenance. Some combination of these often proves the most effective solution. Table 155 indicates various methods of controlling most air pollution sources encountered in the oil refinery. These techniques are also applicable to petrochemical operations. Most of these controls result in some form of economic saving.

**MARKETING**

An extensive network of pipelines, terminals, truck fleets, marine tankers, and storage and loading equipment must be used to deliver the

finished petroleum product to the user. Hydrocarbon emissions from the distribution of products derive principally from storage vessels and filling operations. Additional hydrocarbon emissions may occur from pump seals, spillage, and effluent-water separators. Table 156 lists practical methods of minimizing these emissions from this section of the industry.

**WASTE-GAS DISPOSAL SYSTEMS****INTRODUCTION**

Large volumes of hydrocarbon gases are produced in modern refinery and petrochemical plants. Generally, these gases are used as fuel or as raw material for further processing. In the past, however, large quantities of these gases

Table 155. SUGGESTED CONTROL MEASURES FOR REDUCTION OF AIR CONTAMINANTS FROM PETROLEUM REFINING

Source	Control method
Storage vessels	Vapor recovery systems; floating-roof tanks; pressure tanks; vapor balance; painting tanks white
Catalyst regenerators	Cyclones - precipitator - CO boiler; cyclones - water scrubber; multiple cyclones
Accumulator vents	Vapor recovery; vapor incineration
Blowdown systems	Smokeless flares - gas recovery
Pumps and compressors	Mechanical seals; vapor recovery; sealing glands by oil pressure; maintenance
Vacuum jets	Vapor incineration
Equipment valves	Inspection and maintenance
Pressure relief valves	Vapor recovery; vapor incineration; rupture discs; inspection and maintenance
Effluent-waste disposal	Enclosing separators; covering sewer boxes and using liquid seal; liquid seals on drains
Bulk-loading facilities	Vapor collection with recovery or incineration; submerged or bottom loading
Acid treating	Continuous-type agitators with mechanical mixing; replace with catalytic hydrogenation units; incinerate all vented gases; stop sludge burning
Acid sludge storage and shipping	Caustic scrubbing; incineration; vapor return system; disposal at sea
Spent-caustic handling	Incineration; scrubbing
Doctor treating	Steam strip spent doctor solution to hydrocarbon recovery before air regeneration; replace treating unit with other, less objectionable units (Mercox)
Sour-water treating	Use sour-water oxidizers and gas incineration; conversion to ammonium sulfate
Mercaptan disposal	Conversion to disulfides; adding to catalytic cracking charge stock; incineration; using material in organic synthesis
Asphalt blowing	Incineration; water scrubbing (nonrecirculating type)
Shutdowns, turnarounds	Depressure and purge to vapor recovery

Table 156. SOURCES AND CONTROL OF HYDROCARBON LOSSES FROM PETROLEUM MARKETING

Source	Control method
Storage vessels	Floating-roof tanks; vapor recovery; vapor disposal; vapor balance; pressure tanks; painting tanks white
Bulk-loading facilities	Vapor collection with recovery or incineration; submerged loading, bottom loading
Service station delivery	Vapor return; vapor incineration
Automotive fueling	Vapor return
Pumps	Mechanical seals; maintenance
Separators	Covers; use of fixed-roof tanks
Spills, leaks	Maintenance; proper housekeeping

were considered waste gases, and along with waste liquids, were dumped to open pits and burned, producing large volumes of black smoke. With modernization of processing units, this method of waste-gas disposal, even for emergency gas releases, has become less acceptable to the industry. Moreover, many local governments have adopted or are contemplating ordinances limiting the opacity of smoke from combustion processes.

Nevertheless, petroleum refineries are still faced with the problem of safe disposal of volatile liquids and gases resulting from scheduled shutdowns and sudden or unexpected upsets in process units. Emergencies that can cause the sudden venting of excessive amounts of gases and vapors include fires, compressor failures, overpressures in process vessels, line breaks, leaks, and power failures. Uncontrolled releases of large volumes of gases also constitute a serious safety hazard to personnel and equipment.

A system for disposal of emergency and waste refinery gases consists of a manifolded pressure-relieving or blowdown system, and a blowdown recovery system or a system of flares for the combustion of the excess gases, or both. Many refineries, however, do not operate blowdown recovery systems. In addition to disposing of emergency and excess gas flows, these systems are used in the evacuation of units during shutdowns and turnarounds. Normally a unit is shut down by depressuring into a fuel gas or vapor recovery system with further depressuring to essentially atmospheric pressure by venting to a low-pressure flare system. Thus, overall emissions of refinery hydrocarbons are substantially reduced.

Refinery pressure-relieving systems, commonly called blowdown systems, are used primarily to ensure the safety of personnel and protect equipment in the event of emergencies such as process upset, equipment failure, and fire. In addition, a properly designed pressure relief system permits substantial reduction of hydrocarbon emissions to the atmosphere.

The equipment in a refinery can operate at pressures ranging from less than atmospheric to 1,000 psig and higher. This equipment must be designed to permit safe disposal of excess gases and liquids in case operational difficulties or fires occur. These materials are usually removed from the process area by automatic safety and relief valves, as well as by manually controlled valves, manifolded to a header that conducts the material away from the unit involved. The preferred method of disposing of the waste gases that cannot be recovered in a blowdown recovery system is by burning in a smokeless flare. Liquid blowdowns are usually conducted to appropriately designed holding vessels and reclaimed.

A blowdown or pressure-relieving system consists of relief valves, safety valves, manual bypass valves, blowdown headers, knockout vessels, and holding tanks. A blowdown recovery system also includes compressors and vapor surge vessels such as gas holders or vapor spheres. Flares are usually considered as part of the blowdown system in a modern refinery.

The pressure-relieving system can be used for liquids or vapors or both. For reasons of economy and safety, vessels and equipment dis-

charging to blowdown systems are usually segregated according to their operating pressure. In other words, there is a high-pressure blowdown system for equipment working, for example, above 100 psig, and low-pressure systems for those vessels with working pressures below 100 psig. Butane and propane are usually discharged to a separate blowdown drum, which is operated above atmospheric pressure to increase recovery of liquids. Usually a direct-contact type of condenser is used to permit recovery of as much hydrocarbon liquid as possible from the blowdown vapors. The noncondensables are burned in a flare.

A pressure-relieving system used in one modern petroleum refinery is shown in Figure 431. This system is used not only as a safety measure but also as a means of reducing the emission of hydrocarbons to the atmosphere. This installation actually includes four separate collecting systems as follows: (1) The low-pressure blowdown system for vapors from equipment with working pressure below 100 psig, (2) the high-pressure blowdown system for vapors from equipment with working pressures above 100 psig, (3) the liquid blowdown system for liquids at all pres-

ures, and (4) the light-ends blowdown for butanes and lighter hydrocarbon blowdown products.

The liquid portion of light hydrocarbon products released through the light-ends blowdown system is recovered in a drum near the flare. A backpressure of 50 psig is maintained on the drum, which minimizes the amount of vapor that vents through a backpressure regulator to the high-pressure blowdown line. The high-pressure, low-pressure, and liquid-blowdown systems all discharge into the main blowdown vessel. Any entrained liquid is dropped out and pumped to a storage tank for recovery. Offgas from this blowdown drum flows to a vertical vessel with baffle trays in which the gases are contacted directly with water, which condenses some of the hydrocarbons and permits their recovery. The overhead vapors from this so-called sump tank flow to the flare system manifold for disposal by burning in a smokeless flare system.

The unique blowdown system shown in Figure 432 was installed primarily as an air pollution control measure. The system serves a delayed cok-

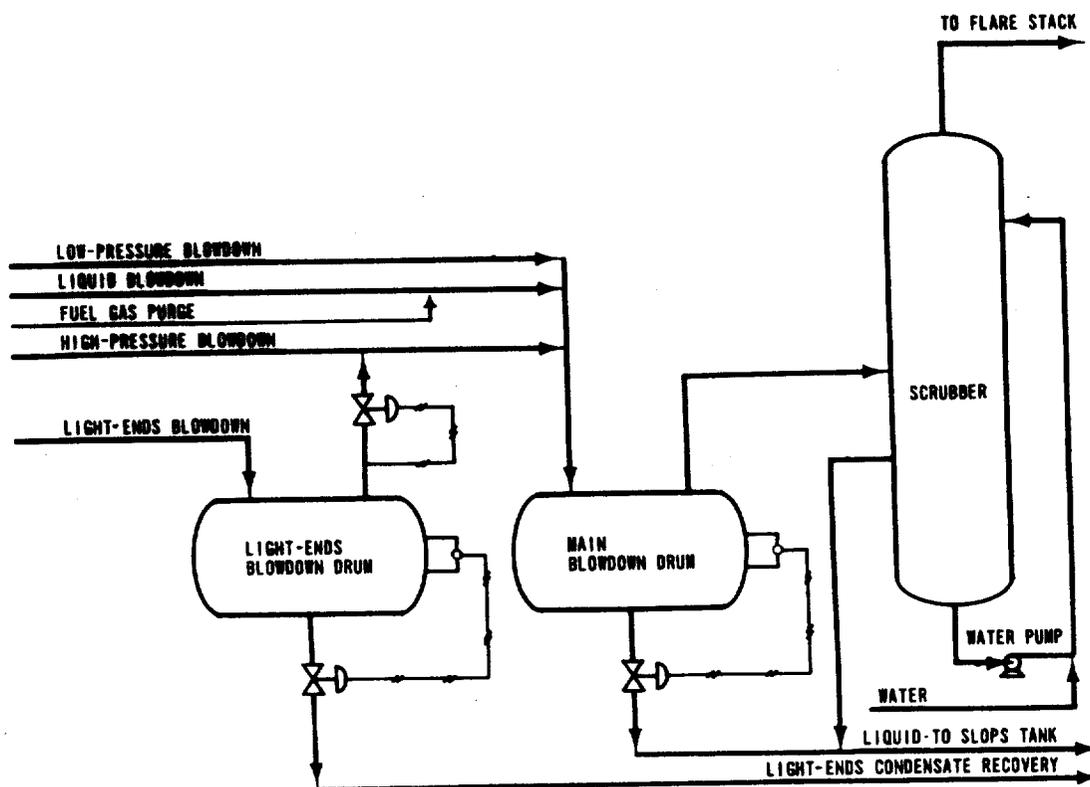


Figure 431. Typical modern refinery blowdown system.

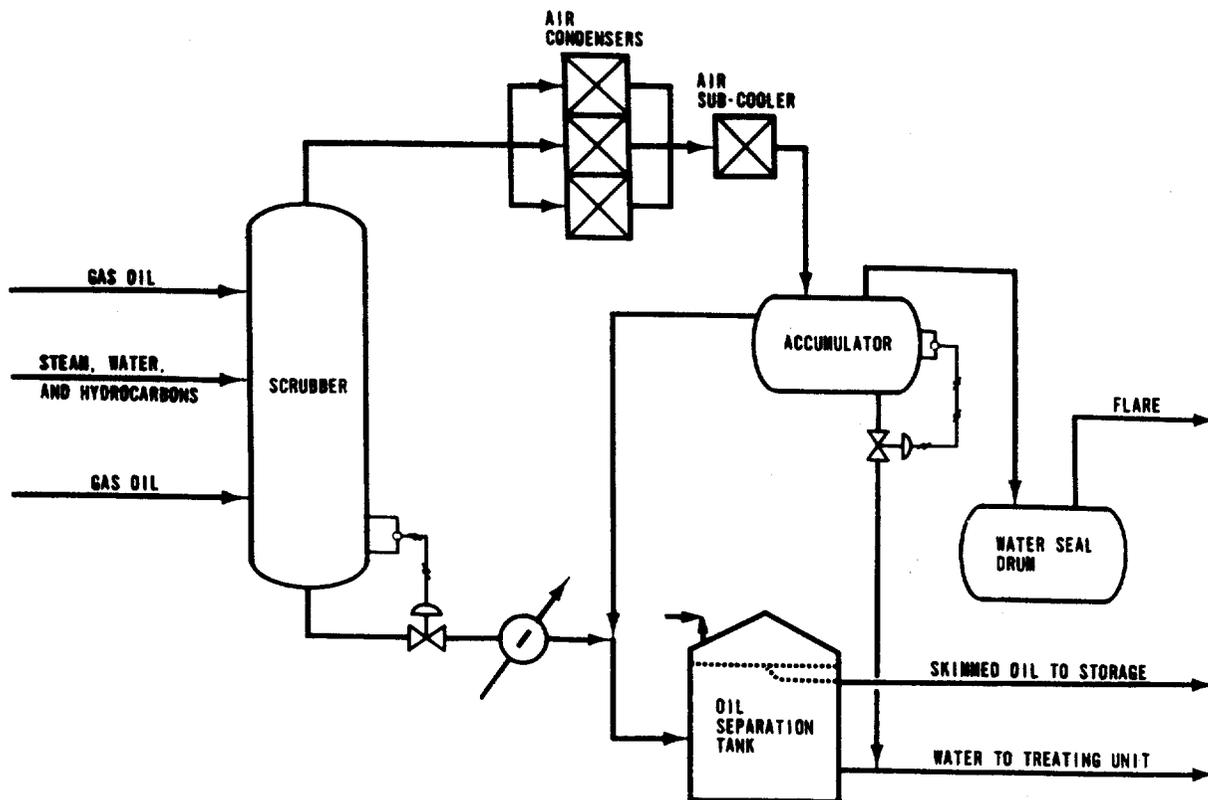


Figure 432. Coke drum blowdown system.

ing unit. In this process, each drum is taken off the line as it is filled with coke. The drum is then purged with steam and cooled with water. The steam-water-hydrocarbon mixture flows to a gas oil scrubber whose primary purpose is to remove entrained coke fines. At the same time some heavier hydrocarbons are condensed, and the mixture is pumped to a settling tank. The scrubbed gases flow to an air-cooled condenser and then through an air-cooled subcooler to an accumulator drum.

The air condenser sections are controlled by temperature and used as needed. The design outlet temperature range of the condensers is 212° to 270°F, and about 200°F for the sub-cooler.

The oil layer in the accumulator is skimmed off and pressured to the oil-settling tank while the water phase is sewered. Offgas flows through a water seal to a smokeless elevated flare. The oil-settling tank is a 3,000-barrel fixed-roof tank equipped with an oil skimmer. The oil phase is pumped to storage, and the water is sewered for further treatment at a central waste-water facility.

This installation has eliminated a previous nuisance from heavy oil mist and the daily emission of approximately 5-1/2 tons of hydrocarbons.

#### Design of Pressure Relief System

The design of a pressure relief system is one of the most important problems in the planning of a refinery or petrochemical plant. The safety of personnel and equipment depends upon the proper design and functioning of this type of system. The consequences of poor design can be disastrous.

A pressure relief system can consist of one relief valve, safety valve, or rupture disc, or of several relief devices manifolded to a common header. Usually the systems are segregated according to the type of material handled, that is, liquid or vapor, as well as to the operating pressures involved.

The several factors that must be considered in designing a pressure relief system are (1) the governing code, such as that of ASME (American Society of Mechanical Engineers, 1962); (2) characteristics of the pressure relief devices; (3) the design pressure of the equipment protected by

the pressure relief devices, (4) line sizes and lengths; and (5) physical properties of the material to be relieved to the system.

In discussing pressure relief systems, the terms commonly used should be defined. The following definitions are taken from the API Manual (1960).

1. A relief valve is an automatic pressure-relieving device actuated by the static pressure upstream of the valve. It opens further with increase of pressure over the set pressure. It is used primarily for liquid service.
2. A safety valve is an automatic relieving device actuated by the static pressure upstream of the valve and characterized by full opening or pop action upon opening. It is used for gas or vapor service.
3. A rupture disc consists of a thin metal diaphragm held between flanges.
4. The maximum allowable working pressure (that is, design pressure), as defined in the construction codes for unfired pressure vessels, depends upon the type of material, its thickness, and the service condition set as the basis for design. The vessel may not be operated above this pressure or its equivalent at any metal temperature higher than that used in its design; consequently, for that metal temperature, it is the highest pressure at which the primary safety or relief valve may be set to open.
5. The operating pressure of a vessel is the pressure, in psig, to which the vessel is usually subjected in service. A processing vessel is usually designed to a maximum allowable working pressure, in psig, that will provide a suitable margin above the operating pressure in order to prevent any undesirable operation of the relief valves. (It is suggested that this margin be approximately 10 percent higher, or 25 psi, whichever is greater.)
6. The set pressure, in psig, is the inlet pressure at which the safety or relief valve is adjusted to open.
7. Accumulation is the pressure increase over the maximum allowable working pressure of the vessel during discharge to the safety or relief valve expressed as a percent of that pressure or pounds per square inch.
8. Over pressure is the pressure increase over the set pressure of the primary relieving device. It is the same as accumulation when the relieving device is set at the maximum allowable working pressure of the vessel. (From this definition note that when the set pressure of the first safety or relief valve to open is less than the maximum allowable working pressure of the vessel the overpressure may be greater than 10 percent of the set pressure of the first safety or relief valve.)
9. Blowdown is the difference between the set pressure and the reseating pressure of a safety or relief valve, expressed as a percent of a set pressure or pounds per square inch.
10. Lift is the rise of the disc in a safety or relief valve.
11. Backpressure is the pressure developed on the discharge side of the safety valves.
12. Superimposed backpressure is the pressure in the discharge header before the safety valve opens (discharged from other valves).
13. Built-up backpressure is the pressure in the discharge header after the safety valve opens.

#### Safety Valves

Nozzle-type safety valves are available in the conventional or balanced-bellows configurations. These two types of valves are shown schematically in Figures 433 and 434. Backpressure in the piping downstream of the standard-type valve affects its set pressure, but theoretically, this backpressure does not affect the set pressure of the balanced-type valve. Owing, however, to imperfections in manufacture and limitations of practical design, the balanced valves available vary in relieving pressure when the backpressure reaches approximately 40 percent of the set pressure. The actual accumulation depends upon the manufacturer.

Until the advent of balanced valves, the general practice in the industry was to select safety valves that start relieving at the design pressure of the vessel and reach full capacity at 3 to 10 percent above the design pressure. This overpressure was defined as accumulation. With the balanced safety valves, the allowable accumulation can be retained with smaller pipe size.

Each safety valve installation is an individual problem. The required capacity of the valve depends upon the condition producing the overpressure. Some of the conditions that can cause overpressure in refinery process vessels, and the required relief capacity for each condition are given in Table 157.

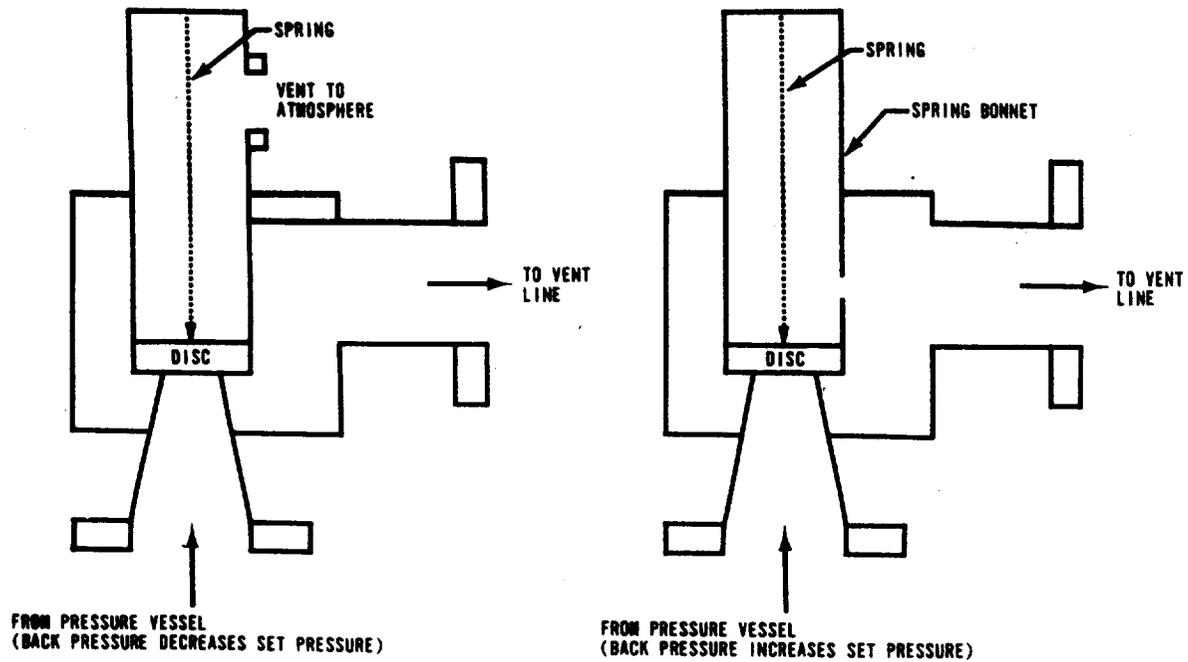


Figure 433. Schematic diagram of standard safety valves (Samans, 1955).

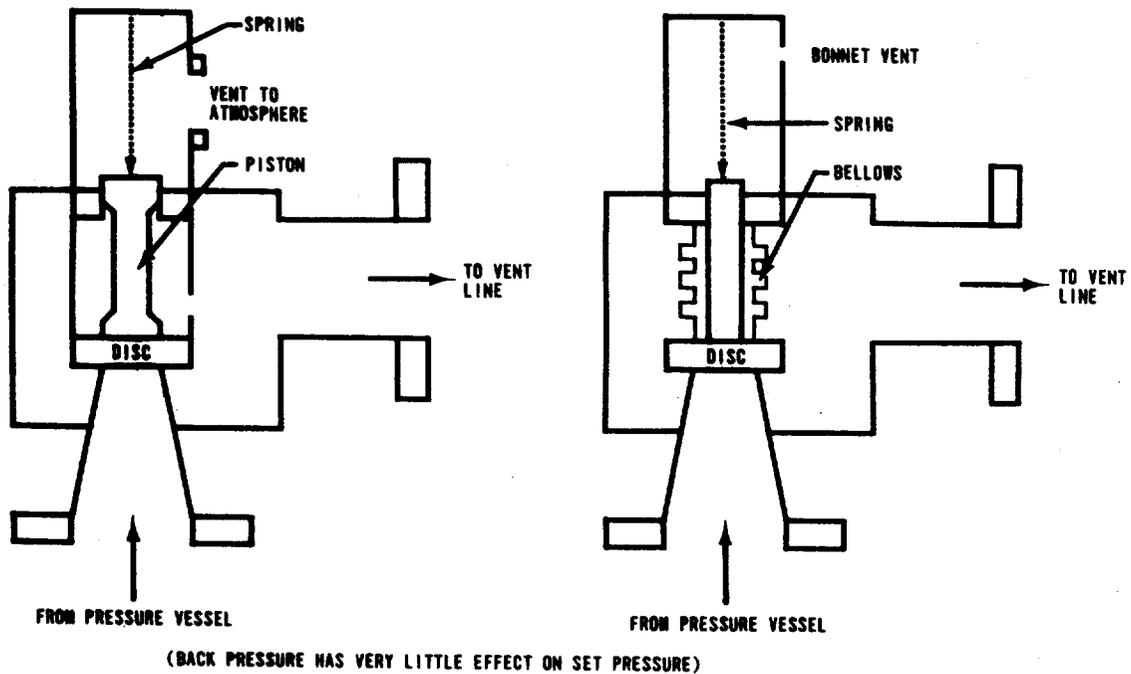


Figure 434. Schematic diagram of balanced safety valves (Samans, 1955).

#### Rupture Discs

A rupture disc is an emergency relief device consisting of a thin metal diaphragm carefully designed to rupture at a predetermined pressure.

The obvious difference between a relief or safety valve and a rupture disc is that the valve reseats and the disc does not. Rupture discs may be installed in parallel or series with a relief valve. To prevent an incorrect pressure differential

from existing, the space between the disc and the valve must be maintained at atmospheric pressure. The arrangement of a rupture disc to supplement a relief or safety valve is shown in Figure 435. In an installation such as this,

the relief or safety valve is sized by conventional methods, presented later, and the rupture disc is usually designed to relieve at 1.5 times the maximum allowable working pressure of the vessel (Bingham, 1958).

Table 157. OPERATIONAL DIFFICULTIES OF A REFINERY AND REQUIRED RELIEF CAPACITIES  
(American Petroleum Institute, 1960)

Condition	Required relief capacity	
	Relief valve for liquid relief	Safety relief valve for vapor relief
Closed outlets on vessels	Maximum liquid pump-in rate	Total incoming steam and vapor, plus that generated therein under normal operation
Cooling-water failure to condenser	--	Total incoming steam and vapor, plus that generated therein under normal operation, less vapor condensed by sidestream reflux. Consideration may be given to the suppression of vapor production as the result of the valve's relieving pressure being above operating pressure, with the assumption of constant heat input
Top-tower reflux failure	--	Total vapor to condenser
Sidestream reflux failure	--	Difference between vapor entering and leaving section
Lean-oil failure to absorber	--	None
Accumulation of noncondensables	--	Same effect in towers as for cooling-water failure or overflowing in other vessels
Entrance of highly volatile material:		
Water into hot oil	--	For towers--usually not predictable
Light hydrocarbons into hot oil	--	For heat exchangers--assume an area twice the internal cross-sectional area of one tube so as to provide for the vapor generated by the entrance of the volatile fluid
Overfilling storage or surge vessel	Maximum liquid pump-in rate	
Failure of automatic controls:		
Tower pressure controller, to closed position	--	Total normally uncondensed vapor
All valves, to closed position, except water and reflux valves	No operational requirement	No operational requirement
Abnormal heat or vapor input:		
Fired heaters or steam reboilers	--	Estimated maximum vapor generation including non-condensable from overheating
Split reboiler tube	--	Steam entering from twice the cross-sectional area of one tube
Internal explosions	--	Not controlled by conventional relief devices, but by avoidance of circumstances
Chemical reaction	--	Estimated vapor generation from both normal and uncontrolled conditions
Hydraulic expansion:		
Cold fluid shut in	Nominal size	
Lines outside process area shut in	Nominal size	
Exterior fire	--	Estimate by the method given in Sect 6 of API Manual, RP 520

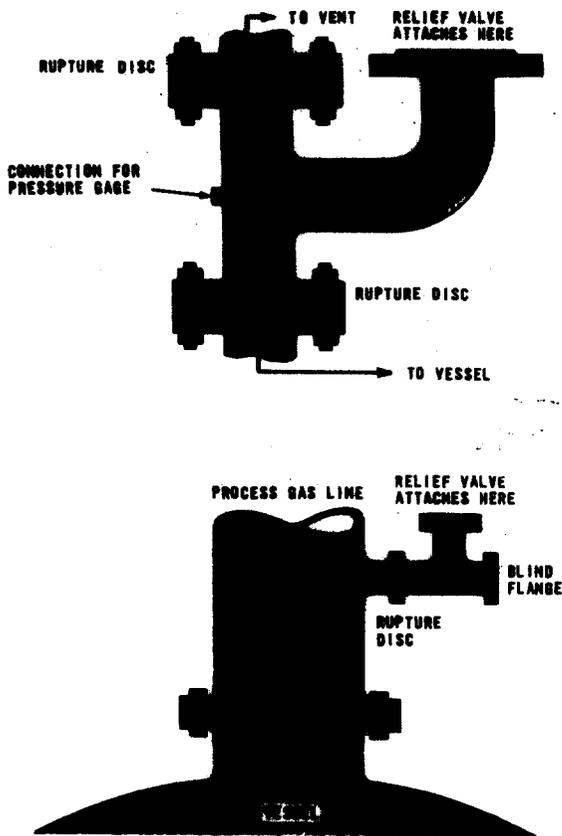


Figure 435. Rupture disc and relief valve installation: (top) How rupture disc gives secondary protection, (bottom) assembly protects relief valve from disc fragments (Bingham, 1958).

In determining the size of a disc, three important effects that must be evaluated are low rupture pressure, elevated temperatures, and corrosion. Minimum rupture pressures with maximum recommended temperatures are given in Table 158. Manufacturers can supply discs that are guaranteed to burst at plus or minus 5 percent of their rated pressures.

The corrosive effects of a system determine the type of material used in a disc. Even a slight amount of corrosion can drastically shorten disc life. Discs are available with plastic linings, or they can be made from pure carbon materials.

#### Sizing rupture discs

The causes of overpressure, and the required capacity for a disc can be determined by methods previously discussed.

The first estimate of the required rupture disc area can be made by using the formula (Bingham, 1958):

$$A = \frac{Q_a}{11.4 P} \quad (119)$$

where

$$A = \text{area of disc, in.}^2$$

Table 158. MINIMUM RUPTURE PRESSURES, psig (Puleo, 1960; Copyrighted by Gulf Publishing Co., Houston, Texas)

Disc size, in.	Aluminum	Aluminum lead lined	Copper	Copper lead lined	Silver	Platinum	Nickel	Monel	Inconel	321 or 347 stainless
1/4	310	405	500	650	485	500	950	1,085	1,550	1,600
1/2	100	160	250	330	250	250	450	530	775	820
1	55	84	120	175	125	140	230	265	410	435
1-1/2	40	60	85	120	85	120	150	180	260	280
2	33	44	50	65	50	65	95	105	150	160
3	23	31	35	50	35	45	63	74	105	115
4	15	21	28	40	28	35	51	58	82	90
6	12	17	25	25	24	26	37	43	61	70
8	9	19	35	35	27	--	30	34	48	55
10	7	16	42	42	--	--	47	28	--	45
12	6	10	55	55	--	--	--	360	--	45
16	5	8	55	55	--	--	--	270	--	33
20	3	8	70	70	--	--	--	215	--	27
24	3	8	60	60	--	--	--	178	--	65
Maximum recommended temperature	250°F 120°F	250°F 120°C	250°F 120°C	250°F 120°C	250°F 120°C	600°F 320°C	750°F 400°C	800°F 430°C	900°F 480°C	600°F 320°C

(base temperature, 72°F [20°C])

$Q_a$  = required capacity, cfm air

$P$  = relieving pressure, psia.

When the overpressure is caused by an explosion, a method of sizing discs has been presented by Lowenstein (1958). In an explosion, a relief or safety valve does not respond fast enough and a rupture disc is required.

The maximum allowable backpressure in an individual discharge line from a disc is 10 percent of the disc's bursting pressure. The maximum allowable backpressure for a manifolded blowdown header serving rupture discs and relief or safety valves should not exceed the individual allowable backpressure for the lowest rupture pressure, or 25 percent of the lowest set pressure of the included valves, whichever is less.

Sizing liquid safety valves

To calculate the required area for a relief valve handling liquid and with constant backpressure, the following formula may be used:

$$A = \frac{Q_1}{C} \left[ \frac{S}{P_1 - P_2} \right]^{0.5} \quad (120)$$

where

$A$  = effective opening of valve, in.<sup>2</sup>

$C$  = constant for relief valve and percent accumulation

$Q_1$  = required liquid flow at flowing temperature, gpm

$P_1$  = relieving pressure at inlet, psia

$P_2$  = discharge pressure at outlet, psia

$S$  = specific gravity of fluid at flowing conditions.

For one manufacturer, the valve constant is 27.2. The overpressure factor for 10 percent accumulation, or overpressure, is determined from Figure 436 to be 0.6. Equation 120 becomes, therefore, for this particular type of valve with a 10 percent accumulation:

$$A = \frac{Q_1}{16.32} \left[ \frac{S}{P_1 - P_2} \right]^{0.5} \quad (121)$$

The use of a balanced relief valve such as the bellows type permits a variable percent backpressure but introduces another variable into the valve-sizing equation. Equation 121 now becomes:

$$A = \frac{Q_1}{16.32 L_f} \left[ \frac{S}{P_1 - P_2} \right]^{0.5} \quad (122)$$

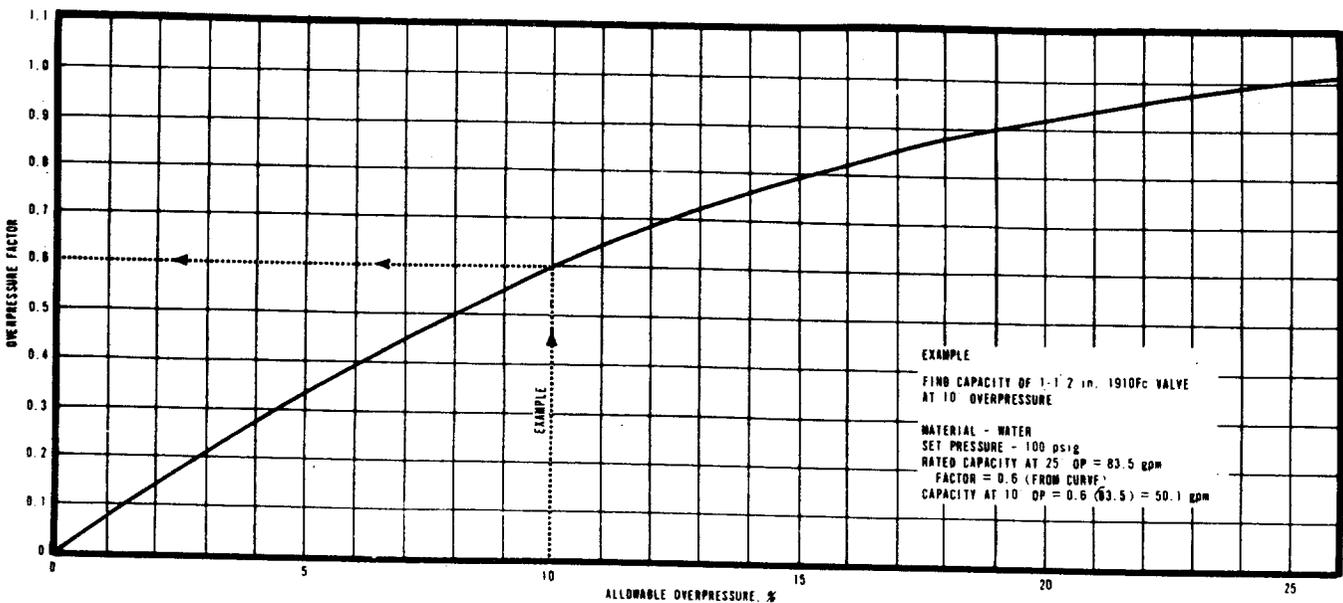


Figure 436. Overpressure sizing factor for liquid relief valves (Consolidated Safety Relief Valves, Manning, Maxwell, and Moore, Inc., Catalog 1900, Tulsa, Okla.).

where nomenclature is as before and  $L_f$  is the variable backpressure flow factor. This factor is supplied by the particular manufacturer, typified by Figure 437.

**Sizing vapor and gas relief and safety valves**

The theoretical area required to vent a given amount of gas or vapor can be calculated by assuming adiabatic reversible flow of an ideal gas through a nozzle. Based upon these assumptions, the following equation can be derived:

$$A = \frac{W}{C C_D P_1} \left[ \frac{T}{M} \right]^{0.5} \quad (123)$$

where

A = area, in.<sup>2</sup>

W = flow capacity, lb/hr

C = nozzle gas constant, which varies as the ratio of specific heats, as shown in Figure 438

$C_D$  = coefficient of discharge for nozzle or orifice

$P_1$  = inlet pressure, psia

T = inlet temperature, °R

M = average molecular weight of gas.

$$k = \frac{c_p}{c_v} = \frac{\text{specific heat at constant pressure}}{\text{specific heat at constant volume}}$$

For hydrocarbon vapors where the actual value of k is not known, the conservative value of  $k = 1.001$  has been commonly used ( $C = 315$ ). The nozzle discharge coefficient for a well-designed relief valve is about 0.97. Hydrocarbon gases can be corrected for nonideality by use of a compressibility factor. With these assumptions, equation 123 reduces to:

$$A = \frac{W}{306 P_1} \left[ \frac{Z T}{M} \right]^{0.5} \quad (124)$$

where

A = area, in.<sup>2</sup>

Z = compressibility factor. For hydrocarbons, Z may be determined from Figure 439 or is usually taken as 1.0 if unknown.

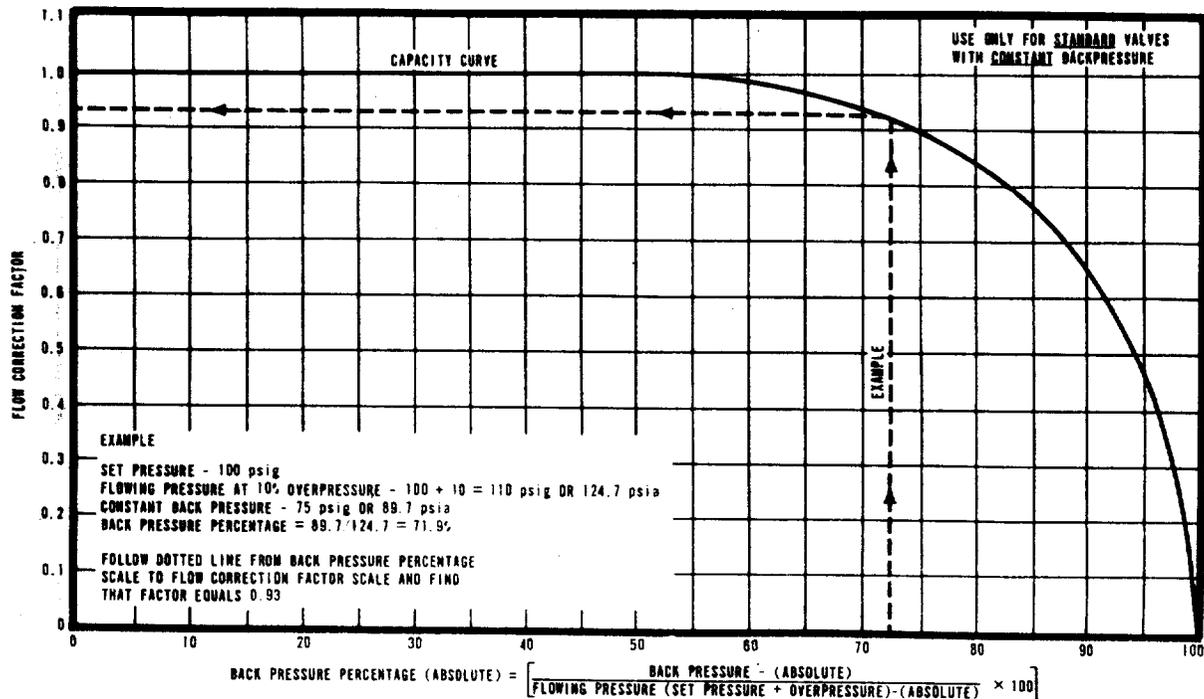


Figure 437. Overpressure sizing factor for standard vapor safety valves (Consolidated Safety Relief Valves, Manning, Maxwell, and Moore, Inc., Tulsa, Okla.).

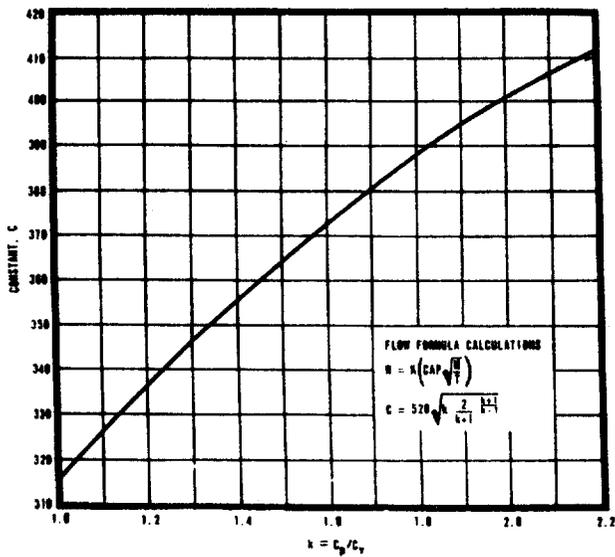


Figure 438. Nozzle gas constant (American Society of Mechanical Engineers, 1962).

Where the critical pressure ratio is such that subsonic fluid velocities are obtained, a correction factor  $K_{bp}$  as shown in Figure 440 may be applied. For more precise calculations, the following formula may be used:

$$A = \frac{W}{2,370 P_1} \left[ \frac{ZT/M}{(P_2/P_1)^{1.818} - (P_2/P_1)^{1.909}} \right]^{0.5} \quad (125)$$

An approximation of the absolute temperature at the valve outlet can be calculated under critical flow conditions from the following equation:

$$T_1 = T \left[ \frac{2}{k + 1} \right] \quad (126)$$

where

$T_1$  = temperature at valve outlet, °R

$T$  = temperature at valve inlet, °R

$k$  = ratio of specific heats,  $c_p/c_v$ .

Before 1957, capacity conversion formulas for valve sizing in petroleum service were given in the API-ASME Code (1951). Since 1957, these formulas have been incorporated in Section VIII of the ASME Unfired Pressure Vessel Code (1962).

The catalogs of relief valve manufacturers are also sources of valve-sizing methods and specific details about various types of valves.

Installing relief and safety valves and rupture discs

The same general rules for discharge piping apply equally to relief and safety valves and rupture discs. Inlet piping should be such that

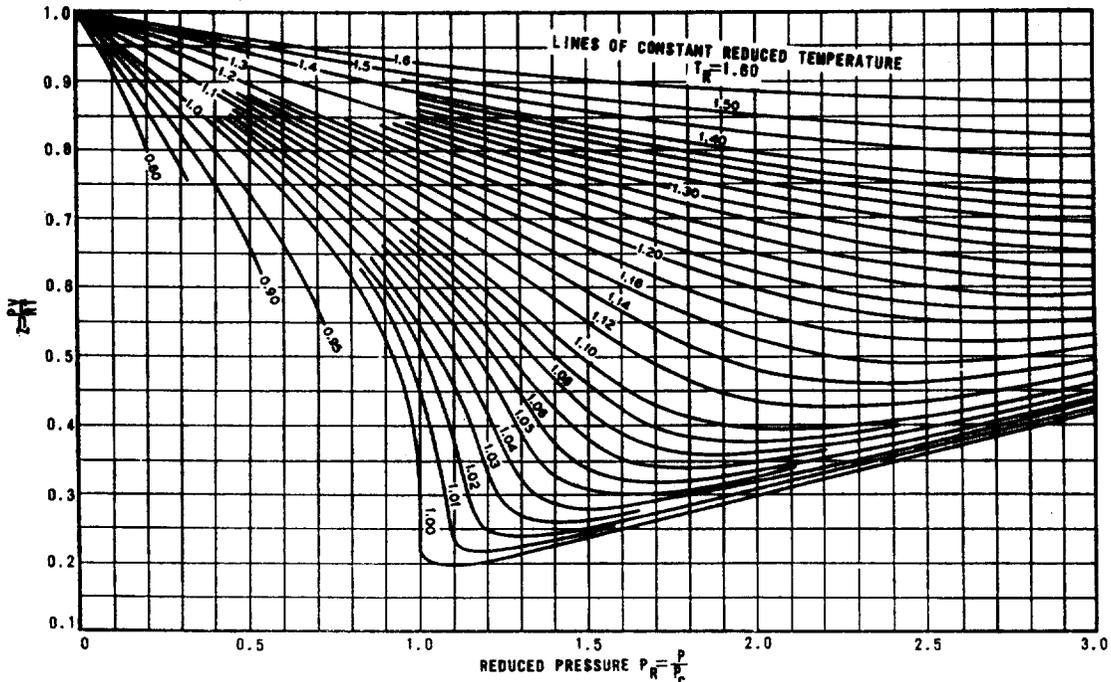


Figure 439. Compressibility constants for hydrocarbons (American Petroleum Institute, 1960).

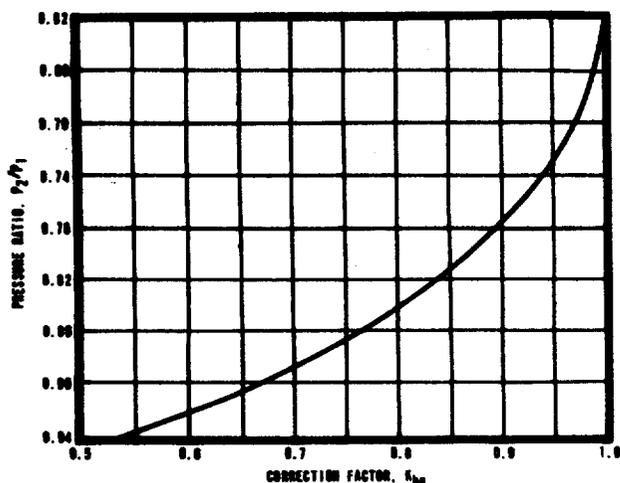


Figure 440. Correction factor ( $K_{dp}$ ) for subsonic flow (Conison, 1960).

there is direct and unobstructed flow between the vessel and the relief device. A conservative limit for the total pressure drop between the vessel and the safety valve is 2 percent of the absolute relieving pressure.

The discharge piping for relief and safety valves and rupture discs should have a minimum of fittings and bends. There should be minimum loading on the valve, and piping should be used with adequate supports and expansion joints. Suitable drains should be used to prevent liquid accumulation in the piping and valves.

Figures 441 to 444 illustrate good design of relief device piping (for further details on Figures 442 and 444, see Tables 159 and 160, respectively).

#### Knockout vessels

In a vapor blowdown system, a knockout drum is used to remove entrained liquids from the gas stream. This is particularly important if the gas is to be burned in a smokeless flare. A knockout drum can be quickly sized or checked by the use of a graphical calculation (see Figure 445; Kerns, 1960). The diameter of the drum is based on the allowable vapor velocity, which can be determined by the well-known equation:

$$u_{\max} = \phi \left[ \frac{\rho_1 - \rho_v}{\rho_v} \right]^{0.5} \quad (127)$$

where

$u_{\max}$  = maximum allowable vapor velocity, ft/sec

$\rho_1$  = liquid density, lb/ft<sup>3</sup>

$\rho_v$  = vapor density, lb/ft<sup>3</sup>

$\phi$  = a constant. Use  $\phi = 0.2$  to  $0.3$ .  
 $\phi = 0.227$  is often used for light liquid loading.

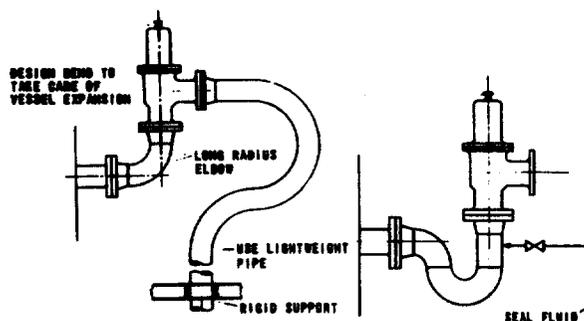


Figure 441. Inlet piping for safety valves: (left) Horizontal vessel nozzles, when used for safety valve mounting can be connected in manner illustrated; (right) valve can be isolated from process fluid in manner illustrated (Driskell, 1960; copyrighted by Gulf Publishing Co., Houston, Texas).

The maximum design velocity should be  $0.5 u_{\max}$  to allow for gas surges.

Light liquid loads indicate the use of a vertical vessel, and heavy liquid loads, a horizontal vessel. The optimum dimensions of the vessel will have a length-to-diameter ratio (L/D) of 3 for larger drums and 4 for smaller drums, and never less than 4 feet between tangents (Kerns, 1960).

When wire mesh is used in the drum as an added precaution against mist entrainment, the selected diameter should be multiplied by 0.65 for conventional mesh and 0.62 for high-capacity mesh (Neimeyer, 1961).

Surge time for most designs is 5 to 10 minutes. The graphical sizing method of Figure 445 is based on a surge time of 7-1/2 minutes.

The preliminary sizing of a knockout drum is illustrated by the following example.

Given:

Gas flow 100 ft<sup>3</sup>/sec (under flow conditions)

Vapor density,  $\rho_v$ , 0.1 lb/ft<sup>3</sup>

Liquid density,  $\rho_1$ , 50 lb/ft<sup>3</sup>.

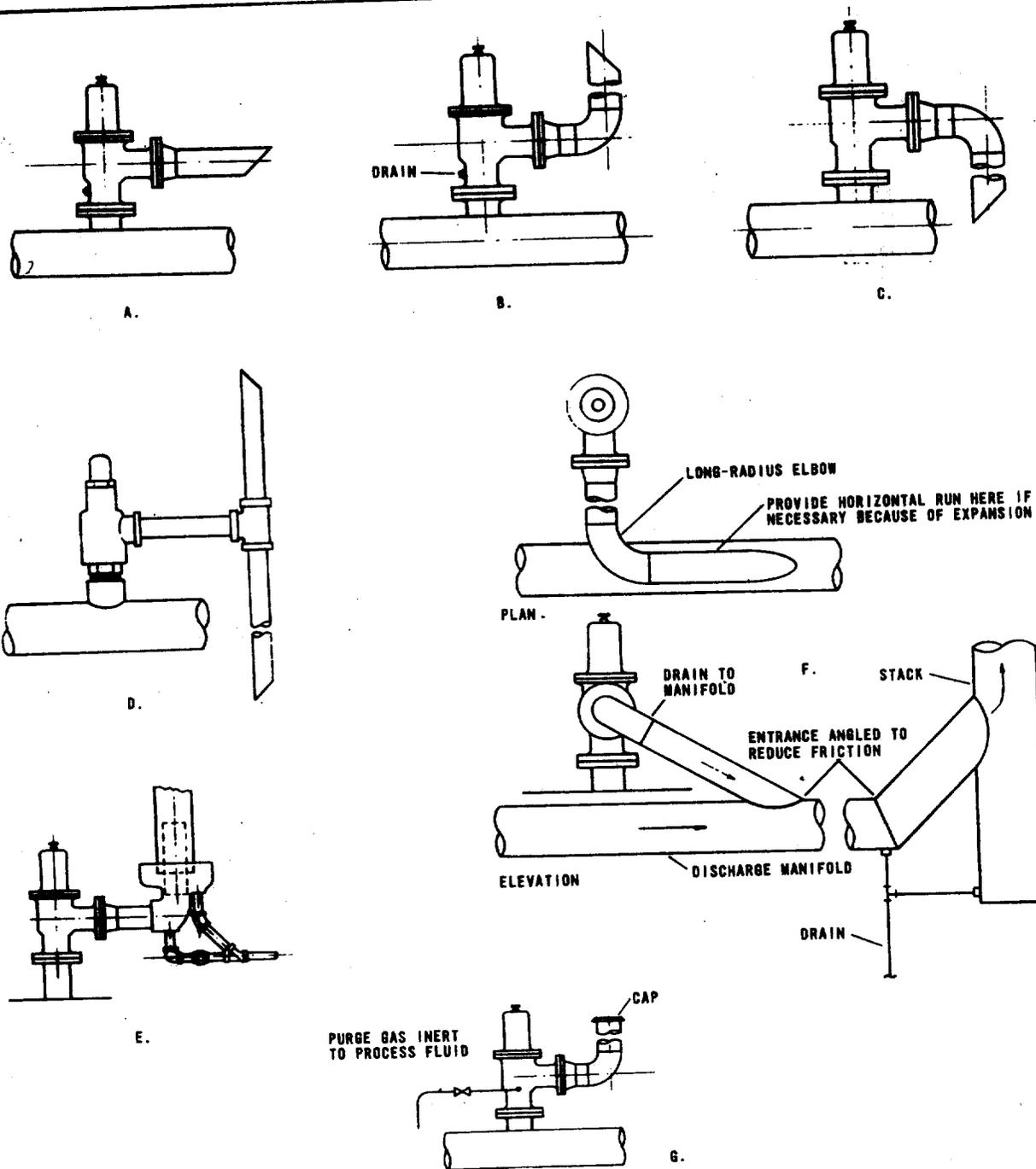


Figure 442. Discharge piping for relief and safety valves: (A) For air or gas service, (B) for air, gas, or steam service, (C) for liquid service, (D) for steam or vapor service, (E) for steam or vapor service to 3-inch pipe, (F) closed system for hazardous service, (G) open system for pyrophoric gases (Driskell, 1980; copyrighted by Gulf Publishing Co., Houston, Texas; for further details, see Table 159).

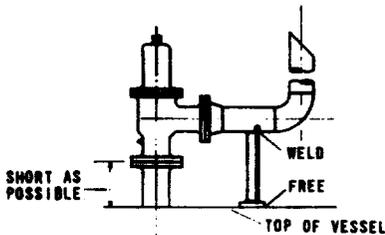
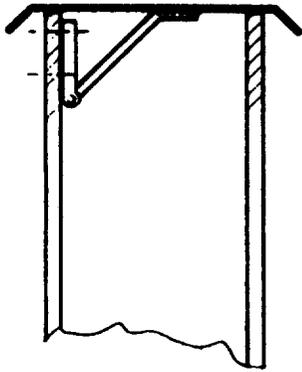


Figure 443. Discharge piping for relief and safety valves: (top) A cap like one illustrated protects discharge pipe from being plugged with snow, (bottom) piping must be adequately anchored to prevent sway or vibration while the valve is discharging (Driskell, 1960; copyrighted by Gulf Publishing Co., Houston, Texas).

#### Problem:

Determine dimensions of knockout drum.

#### Solution:

1. Maximum allowable vapor velocity,  $u_{\max}$ :

$$u_{\max} = \phi \left[ \frac{\rho_1 - \rho_v}{\rho_v} \right]^{0.5}$$

$$u_{\max} = 0.227 \left[ \frac{50 - 0.1}{0.1} \right]^{0.5}$$

$$u_{\max} = 5.06 \text{ ft/sec.}$$

2. Design vapor velocity,  $u_D$ :

$$u_D = u_{\max} \times 0.50$$

$$u_D = 5.06 \times 0.50 = 2.5 \text{ ft/sec.}$$

3. Diameter of vessel:

$$D = \left[ \frac{(4)(100)}{(\pi)(2.5)} \right]^{0.5}$$

$$D = 7.12 \text{ ft.}$$

Use 7-ft diameter.

4. Height of vessel:

Assume low liquid loading.

Use vertical drum,  $L/D = 3$ .

$$\text{Height} = 3 \times 7 \text{ ft} = 21 \text{ ft.}$$

#### Alternative solution:

The same problem can be solved graphically as follows:

1.  $\rho_1 / \rho_v = \frac{50}{0.1} = 500$

2. Enter Figure 445 at 100 cfs and proceed vertically to

$$\rho_1 / \rho_v = 500.$$

Proceed horizontally and read drum diameter as 7 feet.

3. Again assume  $L/D$  ratio = 3.
4. Therefore, drum dimensions are 7 ft in diameter x 21 ft high.

#### Sizing a blowdown line

As previously stated, the selection of a particular line capacity depends upon the following considerations: (1) Maximum expected vapor flow, (2) maximum allowable backpressure in the system, (3) type of relief device to be used, and (4) governing code.

The maximum design capacity of a blowdown line is generally based upon the operation of a group of relief and safety valves. Selection of a design capacity is based upon upsets in the process or by exterior fire. Table 157 indicates the relief requirements for various conditions.

The maximum allowable backpressure in the relieving system depends upon the vessel with the lowest operating or working pressure, the type of valve used, and the code used. In the past, the pressure drop in the relief manifold was customarily limited to 10 percent of the set

Table 159. SUPPLEMENTARY INFORMATION TO FIGURE 442  
(Driskell, 1960; copyrighted by Gulf Publishing Co., Houston, Texas)

Service	Letters keyed to caption for Figure 403	
	Valve indoors	Valve outdoors
<b>Nonhazardous service<sup>a</sup></b>		
Air or gas	A, <sup>b</sup> B, <sup>b</sup> E	A, <sup>b</sup> B <sup>b</sup>
Liquid	C	C
Steam or vapor		
Discharge pipe size to 1 in.	D	D
Discharge pipe size to 1-1/2 to 2-1/2 in.	B	B
Discharge pipe size to 3 in. and over	E	B
<b>Hazardous service<sup>a</sup></b>		
Closed system (to vent stack, burning stack, or scrubber)	F	F
Open system (to atmosphere)		
Gas <sup>c</sup>	A, B	A, B
Liquid <sup>d</sup>	C	C
Vapor <sup>c, d</sup>	A, B, D	A, B, D
Pyrophoric gases or vapor <sup>c</sup>	G	G

#### Low-temperature service

At or below ambient--design discharge pipe so that snow or ice accumulate at any point in the line where the temperature may be at or below freezing. Use A, if possible. Where necessary, B may be used with a cover.

Below 32°F--locate safety valve to avoid need for discharge piping, if possible. Discharge opening and exposed spring must be protected from the weather. A housing or local heating may be required. The discharge, if properly designed, may be sealed with a low-viscosity oil and covered with plastic to prevent the entrance of moisture.

<sup>a</sup>Flammable or toxic fluids are considered hazardous.

<sup>b</sup>Discharge pipe not required if outlet over 7 feet above walkway, or directed away from personnel, or both.

<sup>c</sup>Carry discharge outdoors to a safe elevation.

<sup>d</sup>Carry to an appropriate drain.

pressure. As previously stated, however, the development of balanced relief and safety valves has removed this restriction. In the usual refinery application, there can be considerable savings in piping and valves with balanced valves and about a 40 percent backpressure.

Where several valves discharge to a common header, the use of two separate relieving systems--high- and low-pressure--may be economically advantageous. Otherwise, a single manifold design will be limited by the lowest pressured vessel.

A reduction in the size of the manifold line may be achieved if the operating pressure of a vessel is less than the maximum working, or design, pressure. The set pressure of the relief or safety valve can be made less than the design pressure, permitting a greater backpressure in the relief line.

Another method that can be used with standard safety valves is to plug the guide and vent the bonnet, as shown in Figure 433. An increase in backpressure lowers the relieving pressure and yet does not overpressure the vessel. The arrangement can, however, upset the process if the valve setting is too close to the operating pressure. Thus, in a manifold system, an upset in one section of a process could cause additional relief or safety valves to vent.

In determining the size of a vapor relief line, the pressure drop is usually large, and this precludes the direct use of a Fanning equation. In calculations of compressible fluid flow, the following criteria are used (Crane Company, 1957):

1. If the pressure drop is less than 10 percent of the inlet pressure, reasonable accuracy is obtained if the density of the gas is based upon either inlet or outlet conditions.

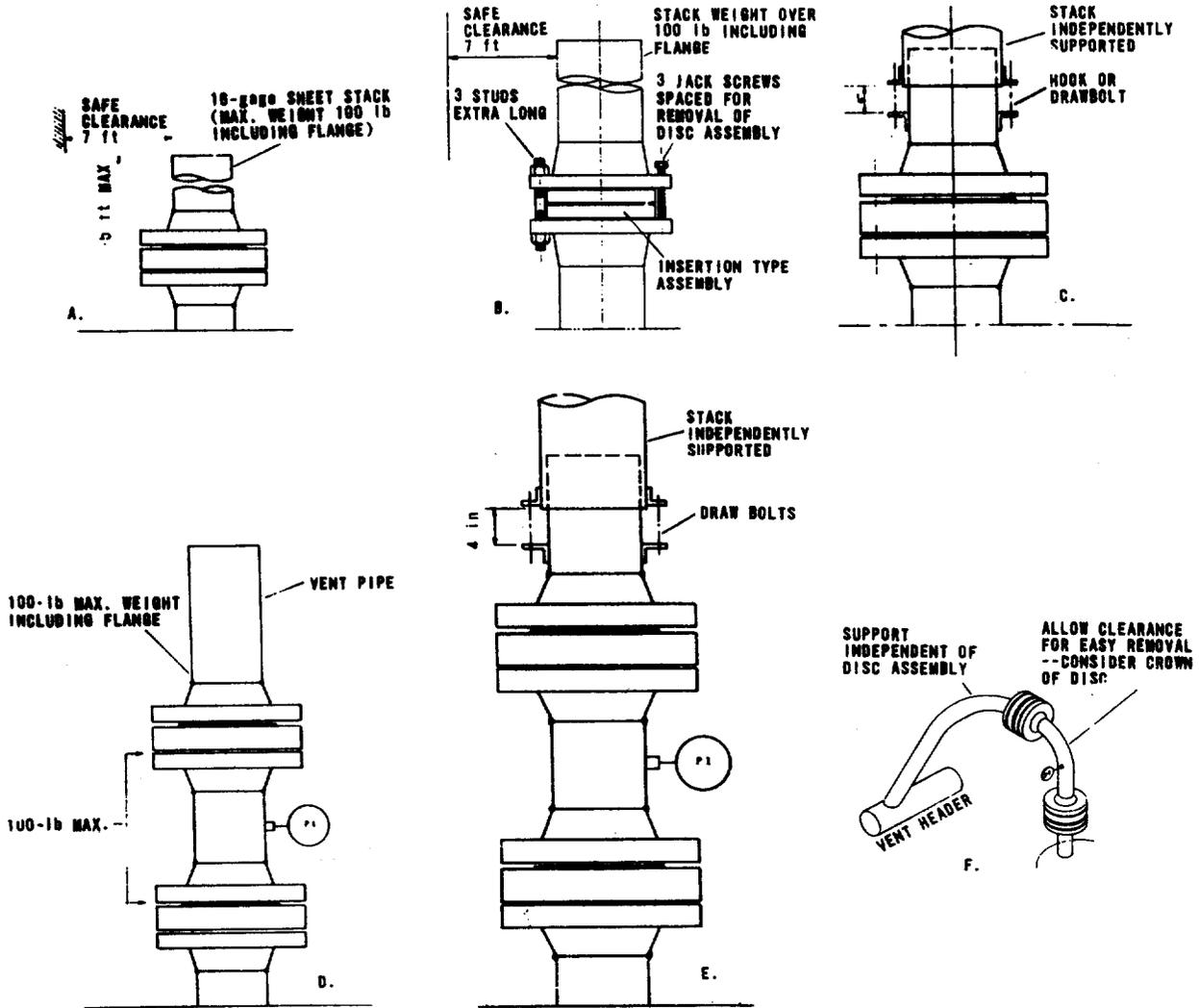


Figure 444. Discharge piping for rupture discs: (A) For lightweight assembly, (B) for heavy assembly with short stack, (C) for heavy assembly with long stack, (D) double disc with lightweight assembly, (E) double disc with heavy assembly, (F) closed system (Driskell, 1960; copyrighted by Gulf Publishing Co., Houston Texas; for further details, see Table 162).

Table 160. SUPPLEMENTARY INFORMATION TO FIGURE 444 (Driskell, 1960; copyrighted by Gulf Publishing Co., Houston, Texas)

Service	Letters keyed to caption for Figure 405	
	Single disc	Double disc
Discharge to atmosphere		
Outdoors, lightweight assembly <sup>a</sup>	A	D
Outdoors, heavy assembly <sup>b</sup>	B, C	E
Indoors <sup>c</sup>	C	E
Closed system	F	F

<sup>a</sup>Parts of assembly 100 lb or less for ease of handling.  
<sup>b</sup>Parts of assembly exceed 100 lb and require mechanical lifting.  
<sup>c</sup>Vent stack through roof.

- If the pressure drop is greater than 10 percent but less than about 40 percent of inlet pressure, the Fanning equation may be used with reasonable accuracy if an average density is used. Otherwise a method with a kinetic energy correction can be used.
- For greater pressure drops, empirical equations can be used.

API Manual RP520 presents kinetic-energy correction factors, as shown in Figure 446, that may be applied to the Fanning equation.

Another method generally used involves dividing the line into increments having pressure drops of

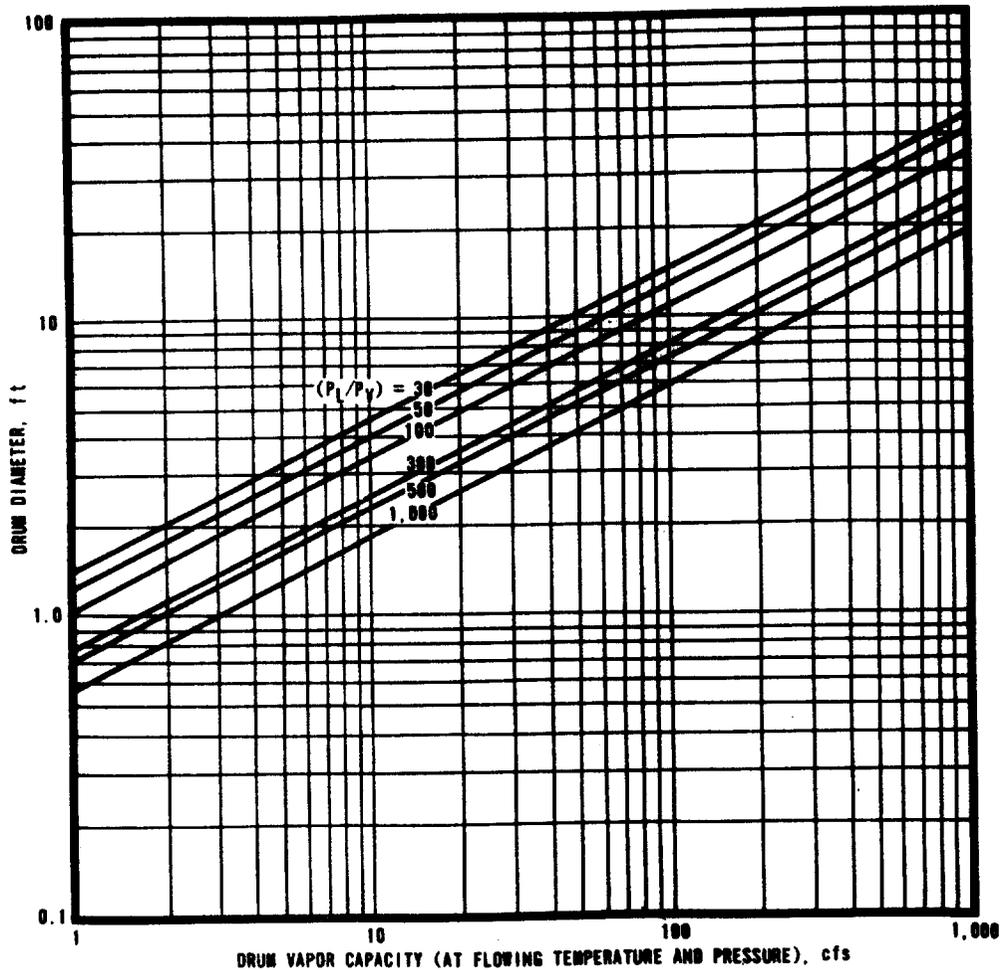


Figure 445. Knockout drum-sizing chart (Kerns, 1960; copyrighted by Gulf Publishing Co., Houston, Texas).

10 percent or less and working from the line terminus back to the relief device.

With the greater availability of computers more exact methods of calculation can be used. Machine computers can handle the tedious equations for calculating pressure drop of compressible fluids where the velocity is subsonic and the density of the vapor or gas is constantly changing.

For hand calculations, a simplified method has been proposed (Conison, 1960) that gives conservative results. The maximum carrying capacity of any line is limited by the acoustic velocity at the outlet of the pipe and in turn sets the outlet pressure. The equation developed by Crocker for solving the maximum pipe capacity for flowing gas and vapors is as follows:

$$P_2 = \frac{W}{d^2} \sqrt{\frac{RT}{k(k+1)}} \quad (128)$$

where

$P_2$  = outlet pressure, psia

$d$  = ID of pipe line, in.

$$R = \frac{1,544}{\text{mol wt of gas}}$$

$k$  = ratio of specific heats,  $c_p/c_v$

$W$  = vapor or gas, lb/hr

$T$  = outlet temperature, °R.

Equation 128 is used to determine the pressure at the pipe line outlet with  $W$  pounds of gas or vapor flowing per hour. If the vapors are discharged to the atmosphere, the outlet pressure must be equal to or greater than atmospheric pressure. If  $P_2$  calculated is less than 1 atmosphere, then  $W$  can be increased before any ef-

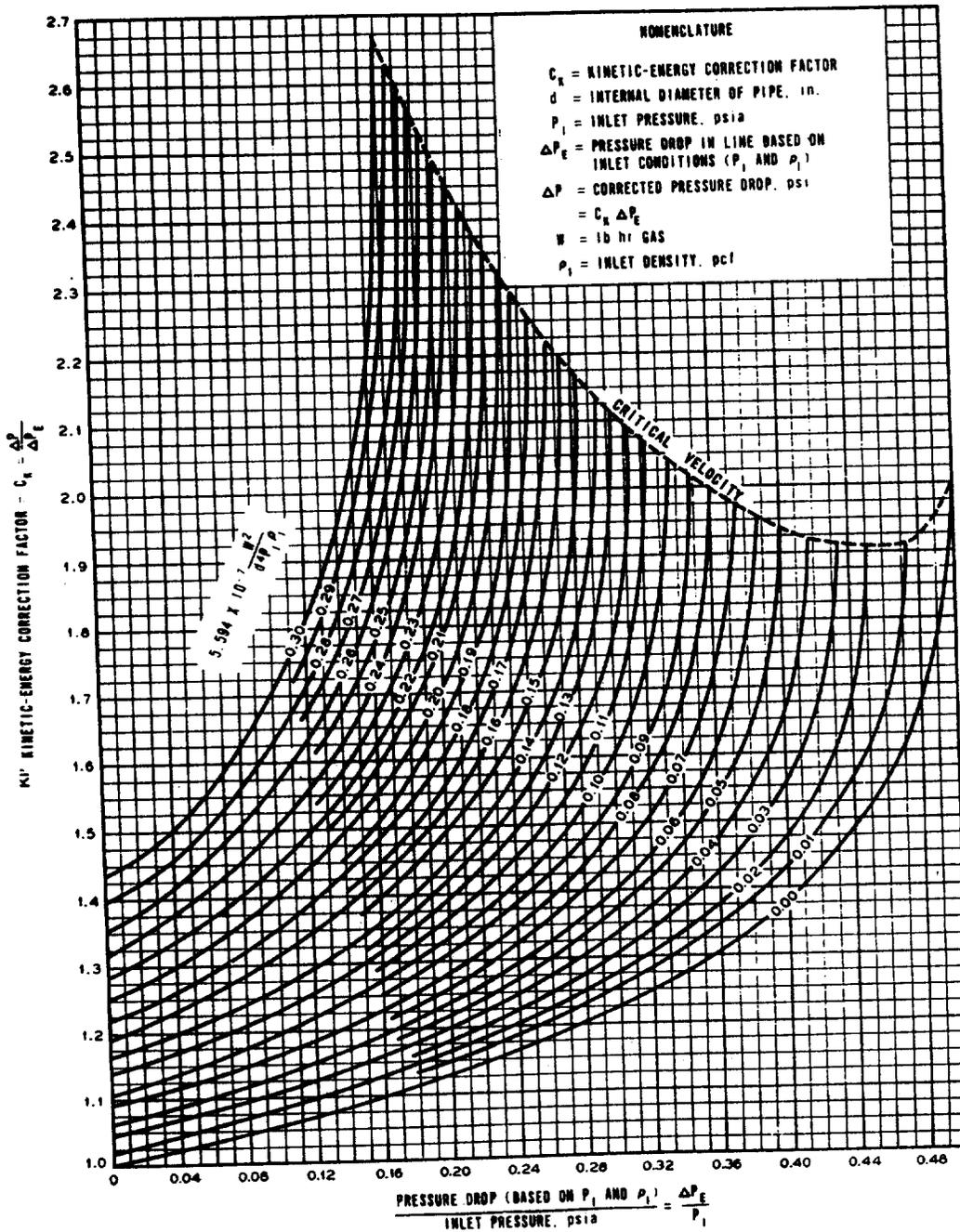


Figure 446. Kinetic energy correction for pressure drop for isothermal flow (American Petroleum Institute, 1960).

fect is made on backpressure in the line. If  $P_2$  calculated is equal to atmospheric pressure, then any increase in  $W$  increases the discharge pressure at the pipe outlet. If  $P_2$  calculated is greater than atmosphere, then it must be added to the line friction loss calculated from the relief device to the pipe outlet in order to determine the total backpressure at the relief device.

To simplify the calculation of the line pressure drop, the following equation can be used

when the line lengths are approximately 100 feet or more or velocity change is small:

$$P_1 = \left[ \left( \frac{f l \rho_{vt} \mu_t^2}{2gD 144} \right) (2 P_2) + P_2^2 \right]^{1/2} \quad (129)$$

where

$P_1$  = inlet pressure, psig

$P_2$  = outlet pressure, psig (equal to values in equation 128 when  $P_2$  = atmospheric pressure or greater)

$\rho_{vt}$  = vapor density, lb/ft<sup>3</sup>, at line terminus

$f$  = a friction factor

$l$  = line length, ft

$g$  = 32.2 ft/sec<sup>2</sup>

$D$  = line ID, ft

$\mu_t$  = velocity at line outlet, fps.

Inspection of equation 129 reveals that the quantity  $\left(\frac{f l \rho_{vt} \mu_t^2}{2gD}\right)$  is the Fanning equation for determining pressure drop in a line in pounds per square foot. This quantity is readily determined with the aid of conventional charts in handbooks and other publications.

All gas or vapor terms in the final or line outlet conditions are based on the inlet temperature  $T$ , calculated from equation 126 and  $P_2$  from equation 129. Where the line lengths are less than 100 feet, equation 129 is modified as follows:

$$P_1^2 = P_2^2 \left( \frac{f l \rho_{vt} \mu_t^2}{gD} \right) + \left( P_2^2 \right) + \left( \frac{2 \mu_t^2 \rho_{vt} P_2}{g} \log_e \frac{\mu_t}{\mu_i} \right) \quad (130)$$

where:  $\mu_i$  = inlet velocity, fps.

Equation 130 can be rearranged to facilitate trial and error solutions:

$$P_1 = \left[ P_2^2 + \left( \frac{f l}{D} + 2 \log_e \frac{\mu_t}{\mu_i} \right) \frac{\mu_t^2 P_2 \rho_{vt}}{g} \right]^{1/2} \quad (131)$$

The constant-temperature approach provides a safety factor because the line temperature is less than the relief valve outlet temperature. The degree of cooling depends upon atmospheric conditions.

The use of this method of sizing a vapor relief line is illustrated by the following example:

Given:

Expected gas flow, 25,000 lb/hr

Outlet temperature at valve, 790°R

Atmospheric pressure, 14.5 psia

Specific volume ( $\bar{v}$ ) at 14.5 psia and 790°R, 13 ft<sup>3</sup>/lb

Length of line, 600 equivalent ft

Maximum allowable pressure drop, psia

$k$  of vapor, 1.3

Molecular weight of vapor, 44

Friction factor of gas, 0.017.

Problem:

Select diameter of blowdown line for given conditions.

Solution:

1. Assume a 6-inch ID pipe and calculate terminal pressure  $P_2$ :

$$P_2 = \frac{W}{d^2} \sqrt{\frac{RT}{k(k+1)}} \quad (11,400)$$

$$P_2 = \frac{25,000}{36} \times \sqrt{\frac{(1,544)}{44} \left( \frac{790}{1.3(1.3+1)} \right)}$$

$$P_2 = 5.86 \text{ psia.}$$

Since  $P_2$  is less than atmospheric pressure, the outlet pressure  $P_2$  equals 14.5 psia.

2. Determine pressure drop in line using equation 131:

$$P_1 = \left[ P_2^2 + \left( \frac{f l}{D} + 2 \log_e \frac{\mu_t}{\mu_i} \right) \frac{\mu_t^2 P_2 \rho_{vt}}{g} \right]^{1/2}$$

$$P_1 = \left[ (14.5)^2 + \left( \frac{(0.017)(600)}{0.5} + 2 \log_e \frac{460}{\mu_i} \right) \frac{(460)^2 (14.5)(.077)}{(32.2)(144)} \right]^{1/2}$$

$$P_1 = \left[ 210 + \left( 20.4 + 2 \log_e \frac{460}{\mu_i} \right) 50.8 \right]^{1/2}$$

As a first approximation, ignore  $\log_e \frac{460}{\mu_i}$ .

Then:

$$\begin{aligned} P_1 &= [210 + (20.4)(50.8)]^{1/2} \\ &= [1,249]^{1/2} \\ &= 35.3 \text{ psia.} \end{aligned}$$

3. Correct  $P_1$  for change in velocity:

$$\bar{v}_1 = \frac{P_2 \bar{v}_2}{P_1} = \frac{(14.5)(13)}{35.3} = 5.35 \text{ ft}^3/\text{lb}$$

$$\text{Velocity} = \frac{W \bar{v}_1}{A} = \frac{(25,000)(5.35)}{(3,600)(0.2006)}$$

$$\mu_i = 185 \text{ fps}$$

$$50.8 \times 2 \log_e \frac{460}{\mu_i} = 101.6 \log_e \frac{460}{185} =$$

$$101.6 \log_e 2.49 = (101.6)(.912) = 92.6$$

And applying the correction for the log term:

$$P_1 = [1,249 + 92.6]^{1/2} = [1,342]^{1/2}$$

$$P_1 = 36.7 \text{ psia.}$$

### THE AIR POLLUTION PROBLEM

The air pollution problem associated with the uncontrolled disposal of waste gases is the venting of large volumes of hydrocarbons and other odorous gases and aerosols. The preferred control method for excess gases and vapors is to recover them in a blowdown recovery system and, failing that, to incinerate them in an elevated-type flare. Such flares introduce the possibility of smoke and other objectionable gases such as carbon monoxide, sulfur dioxide, and nitrogen oxides. Flares have been further developed to ensure that this combustion is smokeless and in some cases nonluminous. Luminosity, while not an air pollution problem, does attract attention to the refinery operation and in certain cases can cause bad public relations. Noise also can result in a nuisance problem if the refinery is located in an area zoned for residential expansion into the property surrounding the plant or if a new facility is built in close proximity to a residential area.

### Smoke From Flares

Smoke is the result of incomplete combustion. Smokeless combustion can be achieved by: (1) Adequate heat values to obtain the minimum theoretical combustion temperatures, (2) adequate combustion air, and (3) adequate mixing of the air and fuel.

An insufficient supply of air results in a smoky flame. Combustion begins around the periphery of the gas stream where the air and fuel mix, and within this flame envelope the supply of air is limited. Hydrocarbon side reactions occur with the production of smoke. In this reducing atmosphere, hydrocarbons crack to elemental hydrogen and carbon, or polymerize to form hydrocarbons. Since the carbon particles are difficult to burn, large volumes of carbon particles appear as smoke upon cooling. Side reactions become more pronounced as molecular weight and unsaturation of the fuel gas increase. Olefins, diolefins, and aromatics characteristically burn with smoky, sooty flames as compared with paraffins and naphthenes (Rupp, 1956).

A smokeless flame can be obtained when an adequate amount of combustion air is mixed with the fuel so that it burns completely and rapidly before any side reactions can take place.

### Noise From Flares

The noise produced by flares results from three distinct noise producing mechanisms. The first of these occurs in elevated flares where steam is injected into the combustion zone and noise is produced by the release of the steam from jets and injector tubes at sonic velocity. The second noise producing mechanism is present in all flares but is most noticeable in the elevated type. In this case, the noise is caused by the release of the vent gas stream itself into the atmosphere at the flare tip. The third noise source, the combustion process itself, is present in all flares.

The noise produced by release of steam from injector tubes is generally more significant than that caused by steam released through the jets and can be reduced by the use of a continuous muffler as shown in Figure 447. The noise produced by the discharge of the vent gas to the atmosphere can be reduced by ensuring that the flow is made as continuous as possible without incremental pressure increases which result in an exploding noise as the mass of gas is released and ignited. If additional noise control is required, silencers are commercially available. "Combustion" noise is not readily controlled but is not as significant as that produced by the sudden expansion of steam and gas.

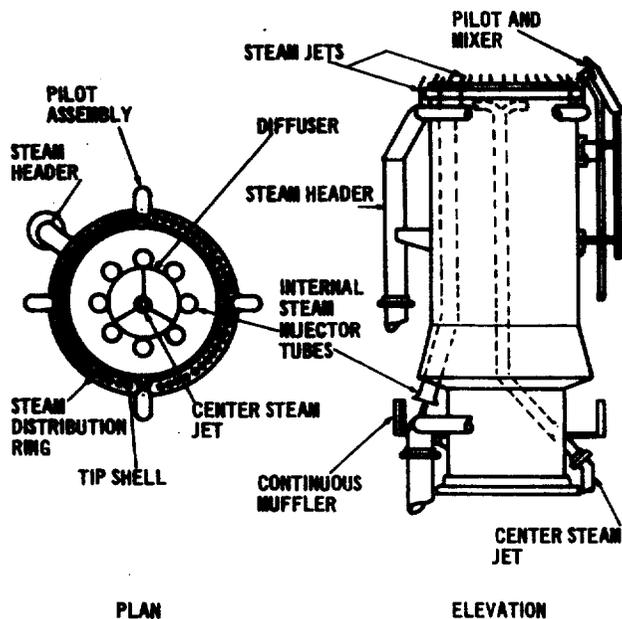


Figure 447. Detail of John Zink flare tip showing internal steam injection system (Model STF-SA; patent pending, John Zink Company, Tulsa, Okla.).

#### Other Air Contaminants From Flares

Combustion of hydrocarbons in the steam-injected-type elevated flare appears to be complete. The results of a field test (Sussman et al., 1958) on a flare unit such as this were reported in the form of ratios as follows:

CO <sub>2</sub> : hydrocarbons	2,100:1
CO <sub>2</sub> : CO	243:1

These results indicate that the hydrocarbon and carbon monoxide emissions from a flare can be much greater than those from a properly operated refinery boiler or furnace. Calculations based on these data, with the assumption of a gas with two carbon atoms and a molecular weight of 30, indicate that the flares in Los Angeles County cause an average daily emission of approximately 100 pounds of hydrocarbons per day and 840 pounds of carbon monoxide per day.

Other combustion contaminants from a flare include nitrogen oxides. The importance of these compounds to the total air pollution problem depends upon the particular conditions in a particular locality. The total emission of nitrogen oxides from the approximately 40 flares in Los Angeles County has been estimated (Chass and George, 1960) at 110 pounds per day.

Other air contaminants that can be emitted from flares depend upon the composition of the gases burned. The most commonly detected emission is sulfur dioxide, resulting from the combustion of various sulfur compounds (usually hydrogen sulfide) in the flared gas. Toxicity, combined with low odor threshold, make venting of hydrogen sulfide to a flare an unsuitable and sometimes dangerous method of disposal. In addition, burning relatively small amounts of hydrogen sulfide can create enough sulfur dioxide to cause crop damage or local nuisance.

Materials that tend to cause health hazards or nuisances should not be disposed of in flares. Compounds such as mercaptans or chlorinated hydrocarbons require special combustion devices with chemical treatment of the gas or its products of combustion.

#### AIR POLLUTION CONTROL EQUIPMENT

The ideal refinery flare, according to the American Petroleum Institute, is a simple device for safe and inconspicuous disposal of waste gases by combustion. From an air pollution viewpoint, the ideal flare is a combustion device that burns waste gases completely and smokelessly.

#### Types of Flares

There are, in general, three types of flares for the disposal of waste gases: Elevated flares, ground-level flares, and burning pits.

The burning pits are reserved for extremely large gas flows caused by catastrophic emergencies in which the capacity of the primary smokeless flares is exceeded. Ordinarily, the main gas header to the flare system has a water seal bypass to a burning pit. Excessive pressure in the header blows the water seal and permits the vapors and gases to vent a burning pit where combustion occurs.

The essential parts of a flare are the burner, stack, seal, liquid trap, controls, pilot burner, and ignition system. In some cases, vented gases flow through chemical solutions to receive treatment before combustion. As an example, gases vented from an isomerization unit that may contain small amounts of hydrochloric acid are scrubbed with caustic before being vented to the flare.

#### Elevated flares

Smokeless combustion can be obtained in an elevated flare by the injection of an inert gas to the combustion zone to provide turbulence and inspi- rate air. A mechanical air-mixing system would

be ideal but is not economical in view of the large volume of gases handled. The most commonly encountered air-inspiring material for an elevated flare is steam. Three main types of steam-injected elevated flares are in use. These types vary in the manner in which the steam is injected into the combustion zone.

In the first type, there is a commercially available multiple nozzle, as shown in Figure 448, which consists of an alloy steel tip mounted on the top of an elevated stack (Brumbaugh, 1947; Hannaman and Etingen, 1956). Steam injection is accomplished by several small jets placed concentrically around the flare tip. These jets are installed at an angle, causing the steam to discharge in a converging pattern immediately above the flare tip.

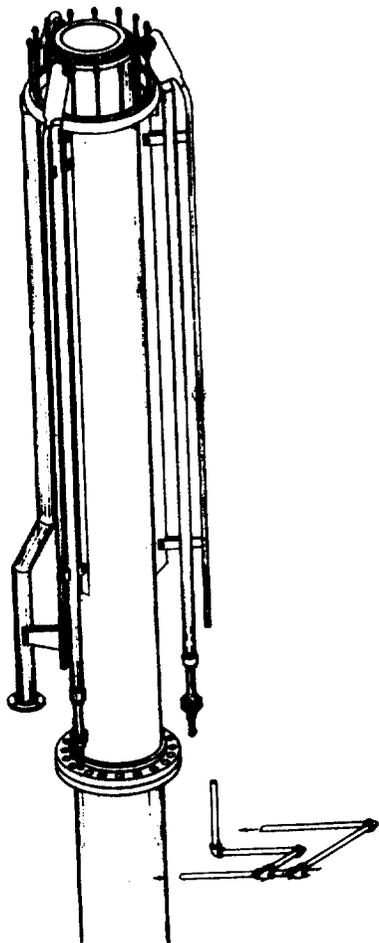


Figure 448. View of John Zink smokeless flare burner (John Zink Co., Tulsa, Okla.)

Figure 447 shows a recent modification of the multiple-nozzle type tip. Modern refining process units with large capacities and greater use of high operating pressures have increased the

mass flow rates to flares, thus requiring larger diameter tips. To ensure satisfactory operation under varied flow conditions, internal injector tubes along with a center tube have been added. The injector tubes provide additional turbulence and combustion air, while the central steam jet and attached diffuser plate provide additional steam to eliminate smoke at low flow conditions. The flare continues to employ steam jets placed concentrically around the tip as shown in Figure 448, but in a modified form. As discussed earlier, noise problems may result at the injector tubes if muffling devices are not used.

A second type of elevated flare has a flare tip with no obstruction to flow, that is, the flare tip is the same diameter as the stack. The steam is injected by a single nozzle located concentrically within the burner tip. In this type of flare, the steam is premixed with the gas before ignition and discharge.

A third type of elevated flare has been used by the Sinclair Oil Company (Decker, 1950). It is equipped with a flare tip constructed to cause the gases to flow through several tangential openings to promote turbulence. A steam ring at the top of the stack has numerous equally spaced holes about 1/8 inch in diameter for discharging steam into the gas stream.

The injection of steam in this latter flare may be automatically or manually controlled. All the flares of this type located in Los Angeles County are instrumented to the extent that steam is automatically supplied when there is a measurable gas flow. In most cases, the steam is proportioned automatically to the rate of gas flow; however, in some installations, the steam is automatically supplied at maximum rates, and manual throttling of a steam valve is required for adjusting the steam flow to the particular gas flow rate. There are many variations of instrumentation among various flares, some designs being more desirable than others. For economic reasons, all designs attempt to proportion steam flow to the gas flow rate.

Steam injection is generally believed to result in the following benefits: (1) Energy available at relatively low cost can be used to inspire air and provide turbulence within the flame, (2) steam reacts with the fuel to form oxygenated compounds that burn readily at relatively low temperatures, (3) water-gas reactions also occur with this same end result, and (4) steam reduces the partial pressure of the fuel and retards polymerization. (Inert gases such as nitrogen have also been found effective for this purpose; however, the expense of providing a diluent such as this is prohibitive.)

The effectiveness of steam injection in an elevated flare is graphically illustrated by comparing Figures 449 and 450.

*Multisteam-jet-type elevated flare*

A multisteam-jet-type elevated flare (Cleveland, 1952) is shown in Figure 451. All relief headers from process units combine into a common header that conducts the hydrocarbon gases and vapors to a large knockout drum. Any entrained liquid is dropped out and pumped to storage. The gases then flow in one of two ways. For emergency gas releases that are smaller than or equal to the design rate, the flow is directed to the main flare stack. Hydrocarbons are ignited by continuous pilot burners, and steam is injected by means of small jet fingers placed concentrically about the stack tip. The steam is injected in proportion to the gas flow. The steam control system consists of a pressure controller, having a range of 0 to 20 inches water column, that senses the pressure in the vent line and sends an air signal to a valve operator mounted on a 2-inch V-Port control valve in the steam line. If the emergency gas flow exceeds the designed capacity of the main flare, backpressure in the vent line increases, displacing the water seal and permitting gas flow to the auxiliary flare. Steam consumption of the burner at a peak flow is about 0.2 to 0.5 pound of steam per

pound of gas, depending upon the amount and composition of hydrocarbon gases being vented. In general, the amount of steam required increases with increases in molecular weight and the degree of unsaturation of the gas.

A small amount of steam (300 to 400 pounds per hour) is allowed to flow through the jet fingers at all times. This steam not only permits smokeless combustion of gas flows too small to actuate the steam control valves but also keeps the jet fingers cooled and open.

*Esso-type elevated flare*

A second type of elevated, smokeless, steam-injected flare is the Esso type. The design is based upon the original installation in the Bayway Refinery of the Standard Oil Company of New Jersey (Smolen, 1951 and 1952). A typical flare system serving a petrochemical plant using this type burner is shown in Figure 452. The type of hydrocarbon gases vented can range from a saturated to a completely unsaturated material. The injection of steam is not only proportioned by the pressure in the blowdown lines but is also regulated according to the type of material being flared. This is accomplished by the use of a ratio relay that is manually controlled. The relay is located in a central control room where



Figure 449. Refinery flare with steam injection in operation.



Figure 450. Refinery flare with steam injection not in operation.

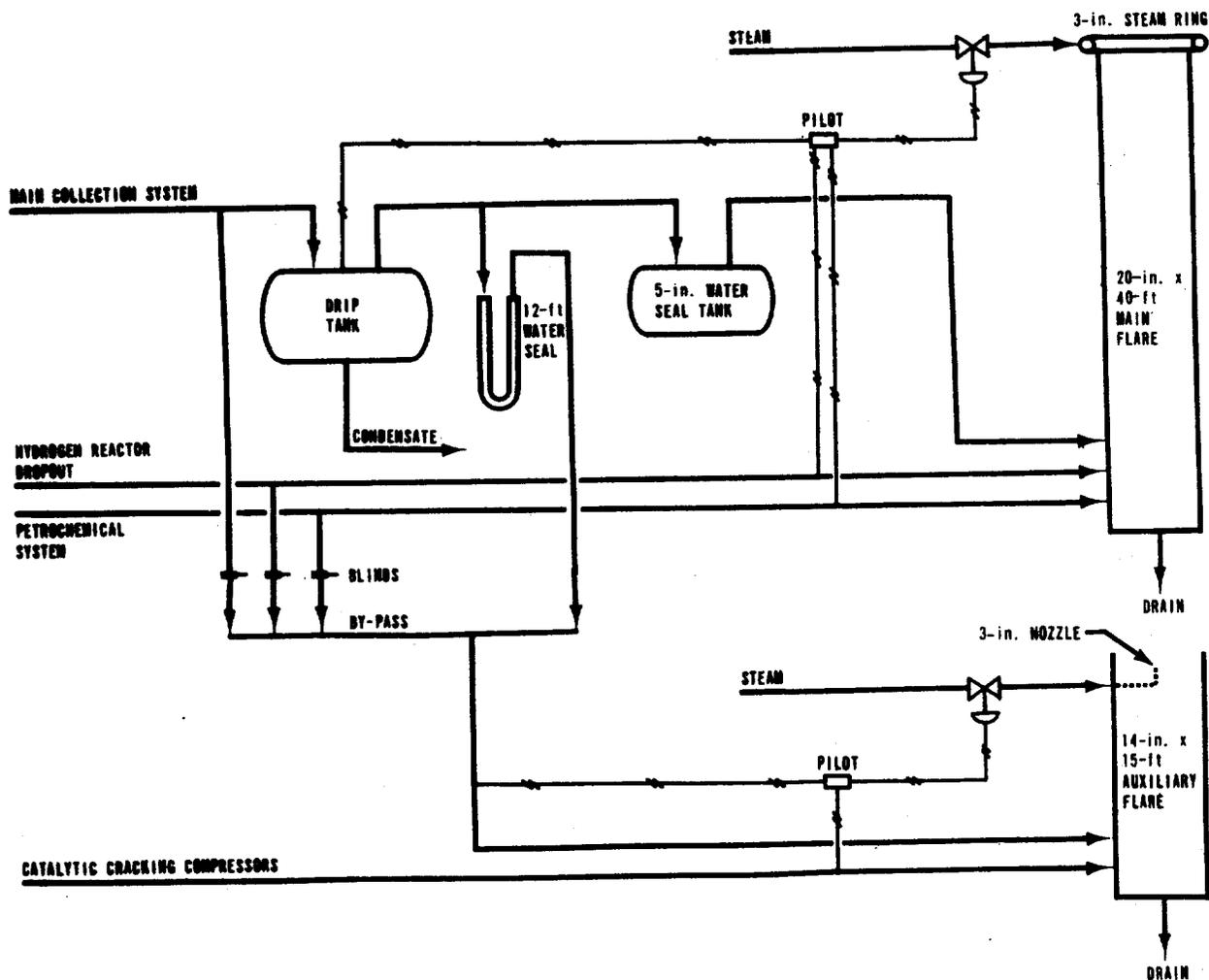


Figure 451. Waste-gas flare system using multistream-jet burner (Cleveland, 1952).

the operator has an unobstructed view of the flare tip. In normal operation the relay is set to handle feed gas, which is most common to this installation.

In this installation, a blowdown header conducts the gases to a water seal drum as shown in Figure 453. The end of the blowdown line is equipped with two slotted orifices. The flow transmitter senses the pressure differential across the seal drum and transmits an air signal to the ratio relay. The signal to this relay is either amplified or attenuated, depending upon its setting. An air signal is then transmitted to a flow controller that operates two parallel steam valves. The 1-inch steam valve begins to open at an air pressure of 3 psig and is fully open at 5 psig. The 3-inch valve starts to open at 5 psig and is fully open at 15 psig air pressure. As the gas flow increases,

the water level in the pipe becomes lower than the water level in the drum, and more of the slot is uncovered. Thus, the difference in pressure between the line and the seal drum increases. This information is transmitted as an air signal to actuate the steam valves. The slotted orifice senses flows that are too small to be indicated by a Pitot-tube-type flow meter. The water level is maintained 1-1/2 inches above the top of the orifice to take care of sudden surges of gas to the system.

A 3-inch steam nozzle is so positioned within the stack that the expansion of the steam just fills the stack and mixes with the gas to provide smokeless combustion. This type of flare is probably less efficient in the use of steam than some of the commercially available flares but is desirable from the standpoints of simpler construction and lower maintenance costs.

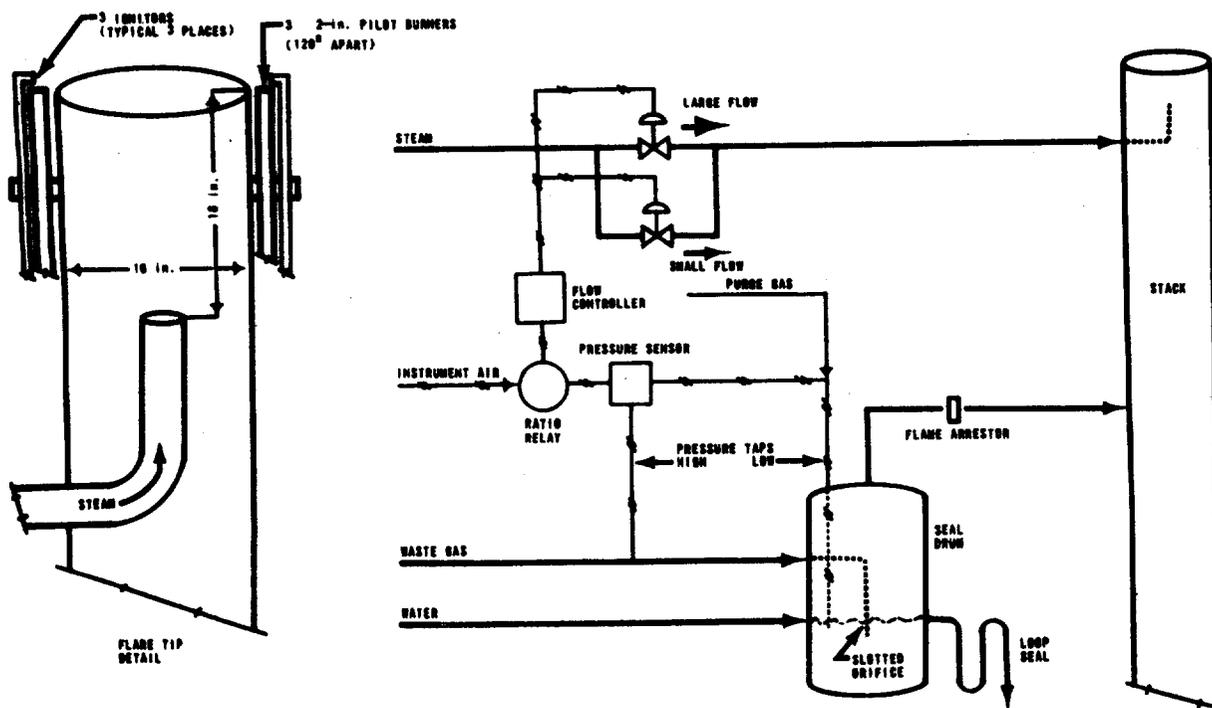


Figure 452. Waste-gas flare system using Esso-type burner.

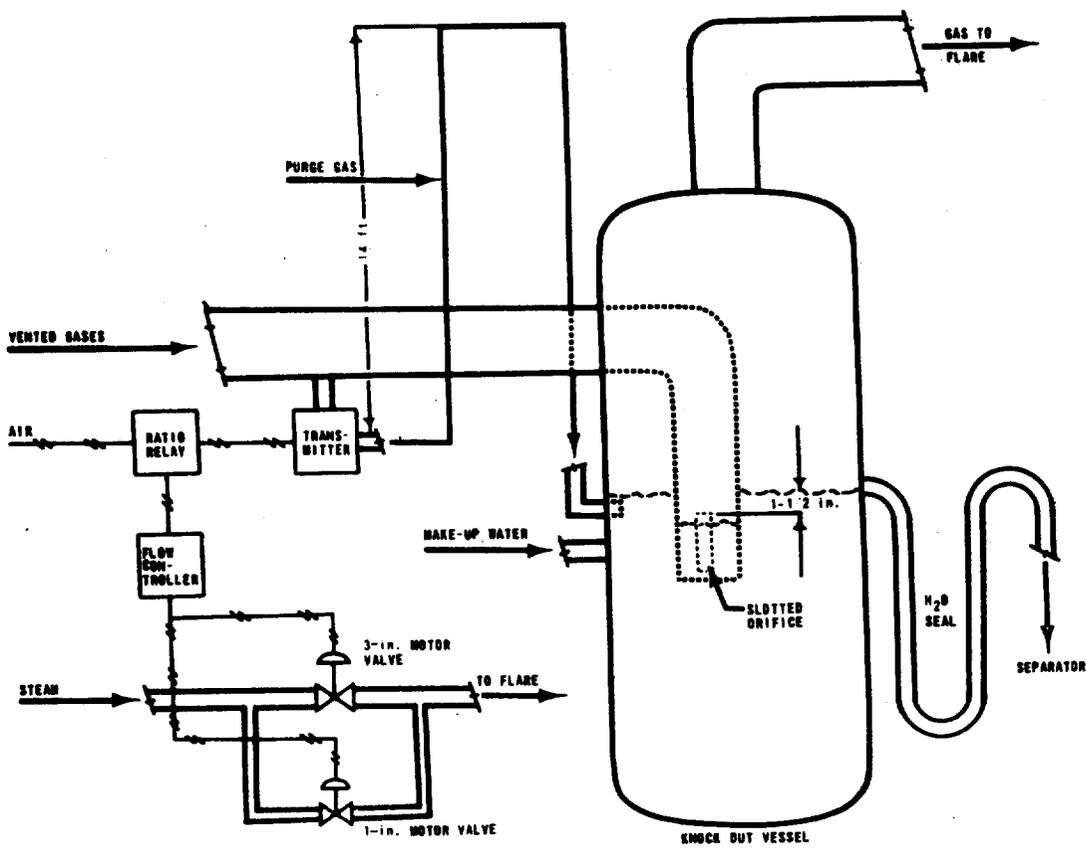


Figure 453. Water seal drum with slotted orifice for measuring gas flow to flare.

### Sinclair-type elevated flare

A diagram (Decker, 1950) of an installation using a Sinclair-type elevated flare is shown in Figure 454. A detail of the burner used for this flare is shown in Figure 455.

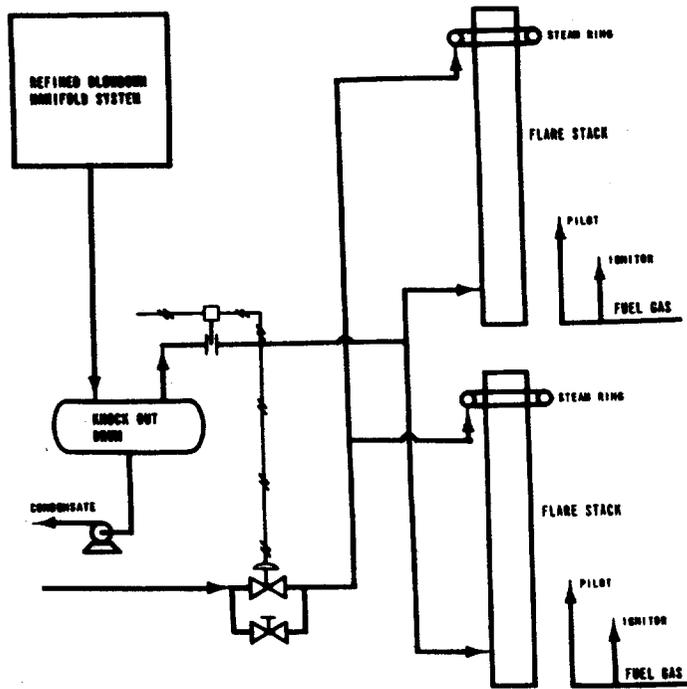


Figure 454. Diagram of waste-gas flare system using a Sinclair burner.

The flow of steam from the ring inspirates air into the combustion area, and the shroud protects the burner from wind currents and provides a partial mixing chamber for the air and gas. Steam is automatically supplied when there is gas flow. A pressure-sensing element actuates a control valve in the steam supply line. A small bypass valve permits a small, continuous flow of steam to the ring, keeping the steam ring holes open and permitting smokeless burning of small gas flows.

### Ground level flares

There are four principal types of ground level flare: Horizontal venturi, water injection, multi-jet, and vertical venturi.

#### Horizontal, venturi-type ground flare

A typical horizontal, venturi-type ground flare system is shown in Figure 456. In this system, the refinery flare header discharges

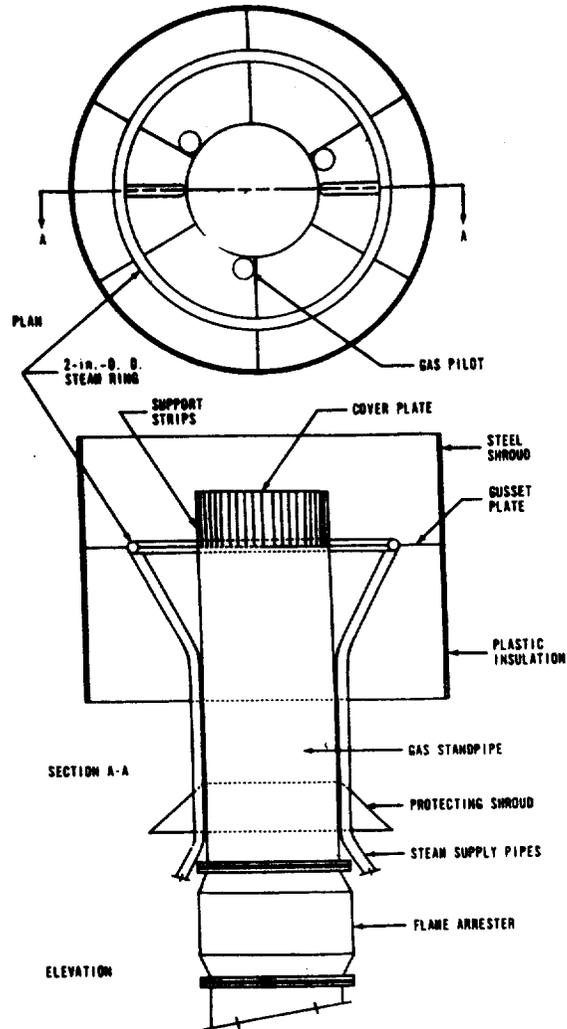


Figure 455. Detail of Sinclair flare burner, plan and elevation (Decker, 1950).

to a knockout drum where any entrained liquid is separated and pumped to storage. The gas flows to the burner header, which is connected to three separate banks of standard gas burners through automatic valves of the snap-action type that open at predetermined pressures. If any or all of the pressure valves fail, a bypass line with a liquid seal is provided (with no valves in the circuit), which discharges to the largest bank of burners.

The automatic-valve operation schedule is determined by the quantity of gas most likely to be relieved to the system. The allowable back-pressure in the refinery flare header determines the minimum pressure for the control valve on the No. 1 burner bank. On the assumption that the first valve was set at 3 psig, then the second valve for the No. 2 burner

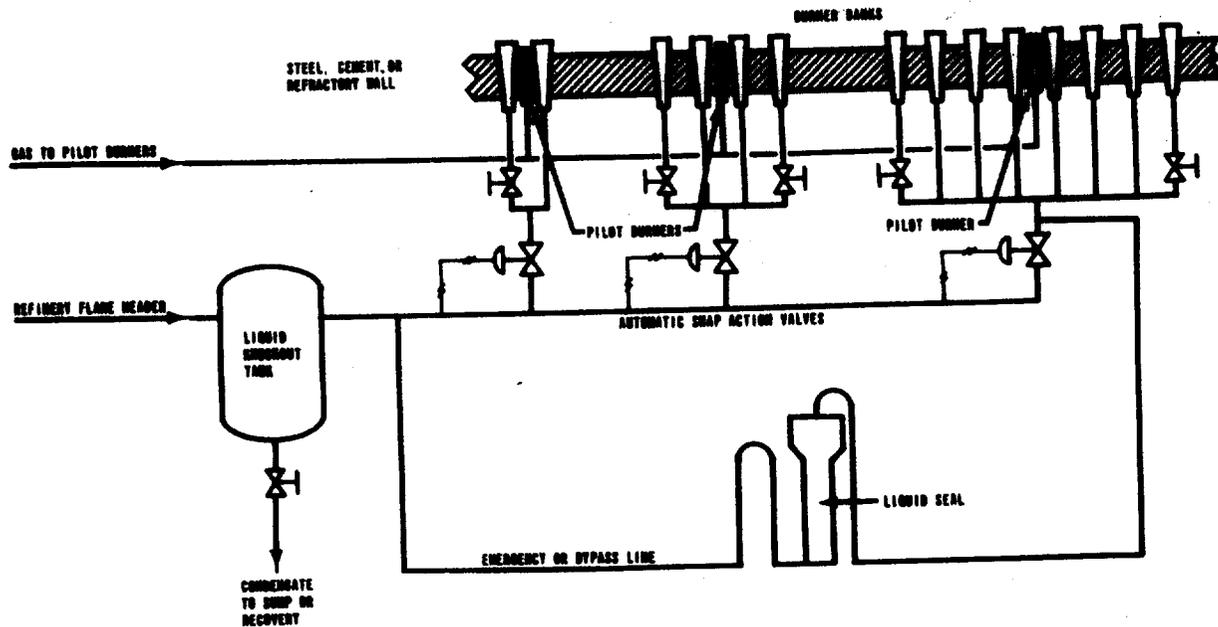


Figure 456. Typical venturi ground flare. The ignitors for pilot burners and the warning element for pilot operation are not shown (American Petroleum Institute, 1957).

bank would be set for some higher pressure, say 5 psig. The quantity of gas most likely to be released then determines the size and the number of burners for this section. Again, the third most likely quantity of gas determines the pressure setting and the size of the third control valve. Together, the burner capacity should equal the maximum expected flow rate.

The valve-operating schedule for the system pictured in Figure 456 is set up as follows:

1. When the relief header pressure reaches 3 psig, the first control valve opens and the four small venturi burners go into operation. The controller setting keeps the valve open until the pressure decreases to about 1-1/2 psig.
2. When the header pressure reaches 5 psig, the second valve opens and remains open until the pressure drops to about 3 psig.
3. When the pressure reaches 6 psig, the third valve opens and remains open until the pressure decreases to 4 psig.
4. At about 7 psig, the gas blows the liquid seal.

A small flare unit of this design, with a capacity of 2 million scf per day, reportedly cost less than \$5,000.00 in 1953 (Beychok, 1953). Another large, horizontal, venturi-type flare

that has a capacity of 14 million scfh and requires specially constructed venturi burners (throat diameter ranges from 5 to 18 inches) cost \$63,000.

#### *Water-injection-type ground flare*

Another type of ground flare used in petroleum refineries has a water spray to insipitate air and provide water vapor for the smokeless combustion of gases (Figure 457). This flare requires an adequate supply of water and a reasonable amount of open space.

The structure of the flare consists of three concentric stacks. The combustion chamber contains the burner, the pilot burner, the end of the ignitor tube, and the water spray distributor ring. The primary purpose of the intermediate stack is to confine the water spray so that it will be mixed intimately with burning gases. The outer stack confines the flame and directs it upward.

Water sprays in elevated flares are not too practical for several reasons. Difficulty is experienced in keeping the water spray in the flame zone, and scale formed in the waterline tends to plug the nozzles. In one case it was necessary to install a return system that permitted continuous waterflow to bypass the spray nozzle. Water main pressure dictates the height to which water can be injected without the use of a booster pump. For a 100- to

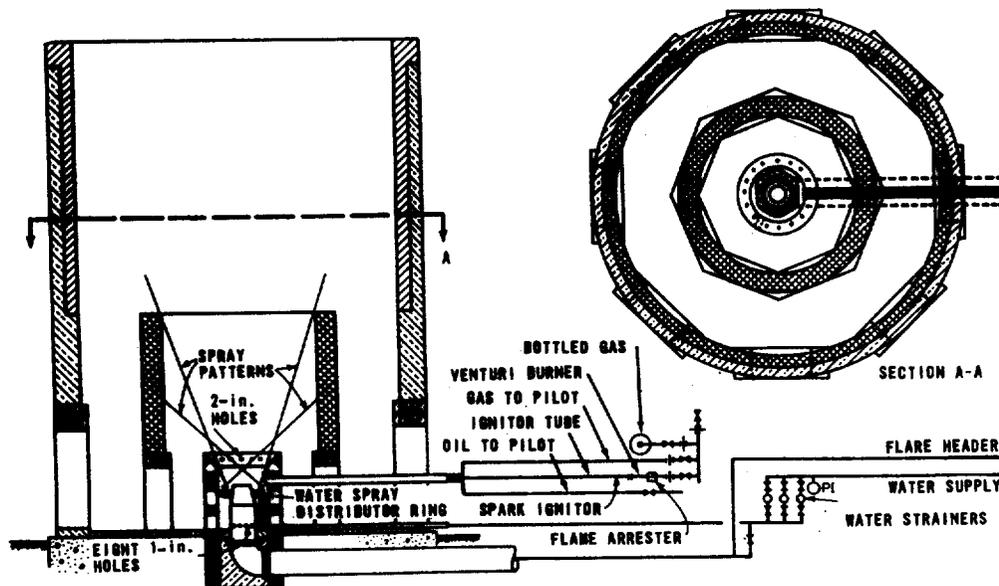


Figure 457. Typical water-spray-type ground flare. Six water sprays are shown. Two pilots and two ignitors are recommended (American Petroleum Institute, 1957).

250-foot stack, a booster pump would undoubtedly be required. Rain created by the spray from the flare stack is objectionable from the standpoint of corrosion of nearby structures and other equipment.

Water is not as effective as steam for controlling smoke with high gas flow rates, unsaturated materials, or wet gases. The water spray flare is economical when venting rates are not too high and slight smoking can be tolerated. In Los Angeles County, where restrictions on the emission of smoke from flares are very strict, a water spray smokeless flare is not acceptable.

#### *Multijet-type ground flare*

A recent type of flare developed by the refining industry is known as a multijet (Miller et al., 1956). This type of flare was designed to burn excess hydrocarbons without smoke, noise, or visible flame. It is claimed to be less expensive than the steam-injected type, on the assumption that new steam facilities must be installed to serve a steam-injected flare unit. Where the steam can be diverted from noncritical operations such as tank heating, the cost of the multijet flare and the steam-inspiring elevated flare may be similar.

A sketch of an installation of a multijet flare is shown in Figure 458. The flare uses two sets of burners; the smaller group handles normal gas leakage and small gas releases,

while both burner groups are used at higher flaring rates. This sequential operation is controlled by two water-sealed drums set to release at different pressures. In extreme emergencies, the multijet burners are bypassed by means of a water seal that directs the gases to the center of the stack. This seal blows at flaring rates higher than the design capacity of the flare. At such an excessive rate, the combustion is both luminous and smoky, but the unit is usually sized so that an overcapacity flow would be a rare occurrence. The overcapacity line may also be designed to discharge through a water seal to a nearby elevated flare rather than to the center of a multijet stack. Similar staging could be accomplished with automatic valves or backpressure regulators; however, in this case, the water seal drums are used because of reliability and ease of maintenance. The staging system is balanced by adjusting the hand control butterfly valve leading to the first-stage drum. After its initial setting, this valve is locked into position.

Design details of this installation are given in the literature reference (Miller et al., 1956).

#### *Vertical, venturi-type ground flare*

Another type of flare based upon the use of commercial-type venturi burners is shown in Figure 459. This type of flare has been used to handle vapors from gas-blanketed tanks, and vapors displaced from the depres-

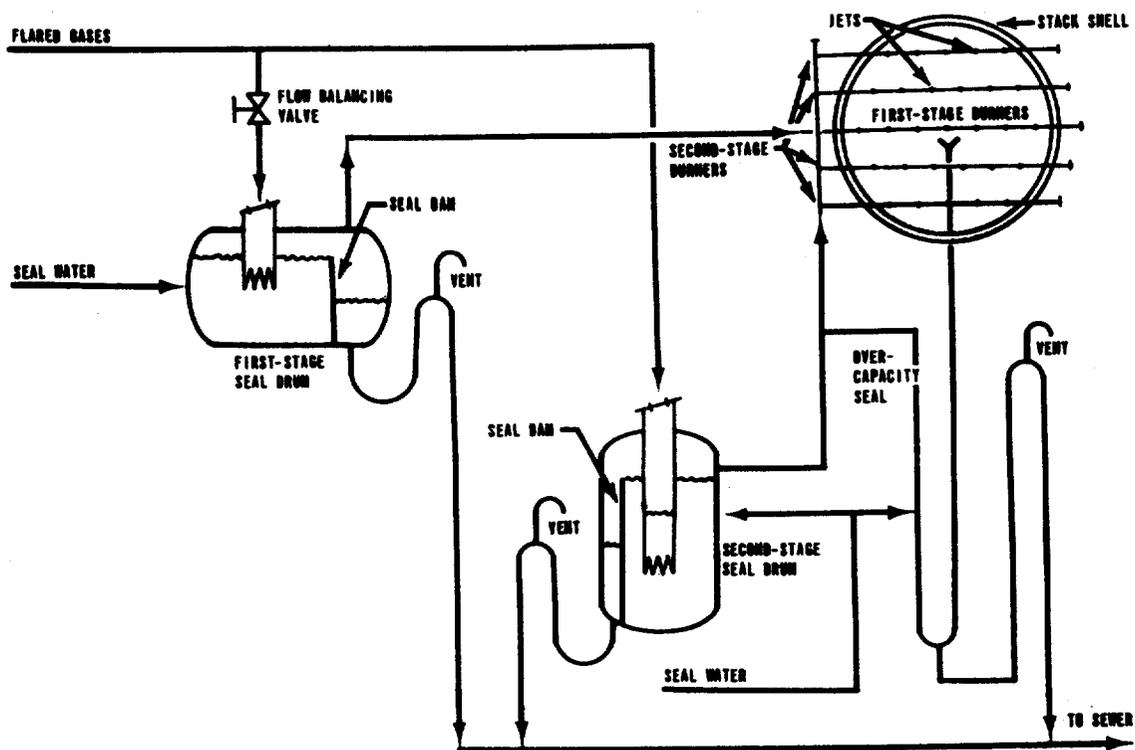


Figure 458. Flow diagram of multijet-flare system (Miller et al., 1956).

suring of butane and propane tank trucks. Since the commercial venturi burner requires a certain minimum pressure to operate efficiently, a gas blower must be provided. In the installation shown in Figure 460, two burners operate at a pressure of 1/2 to 8 psig. A compressor takes vapors from tankage and discharges them at a rate of 6,000 cfh and 7 psig through a water seal tank and a flame arrestor to the flare. This type of arrangement can readily be modified to handle different volumes of vapors by the installation of the necessary number of burners.

This type of flare is suitable for relatively small flows of gas of a constant rate. Its main application is in situations where other means of disposing of gases and vapors are not available.

#### Effect of steam injection

A flare installation that does not inspire an adequate amount of air or does not mix the air and hydrocarbons properly emits dense, black clouds of smoke that obscure the flame. The injection of steam into the zone of combustion causes a gradual decrease in the amount of smoke, and the flame becomes more visible. When trailing smoke has been eliminated, the flame is very luminous

and orange with a few wisps of black smoke around the periphery. The minimum amount of steam required produces a yellowish-orange, luminous flame with no smoke. Increasing the amount of steam injection further decreases the luminosity of the flame. As the steam rate increases, the flame becomes colorless and finally invisible during the day. At night this flame appears blue.

An injection of an excessive amount of steam causes the flame to disappear completely and be replaced with a steam plume. An excessive amount of steam may extinguish the burning gases and permit unburned hydrocarbons to discharge to the atmosphere. When the flame is out, there is a change in the sound of the flare because a steam hiss replaces the roar of combustion. The commercially available pilot burners are usually not extinguished by excessive amounts of steam, and the flame reappears as the steam injection rate is reduced. As the use of automatic instrumentation becomes more prevalent in flare installations, the use of excessive amounts of steam and the emission of unburned hydrocarbons decrease and greater steam economies can be achieved. In evaluating flare installations from an air pollution standpoint, controlling the volume of steam is important. Too little steam results in black smoke, which, obviously, is objectionable. Conversely, excessive use of steam produces a white steam plume and an invisible emission of unburned

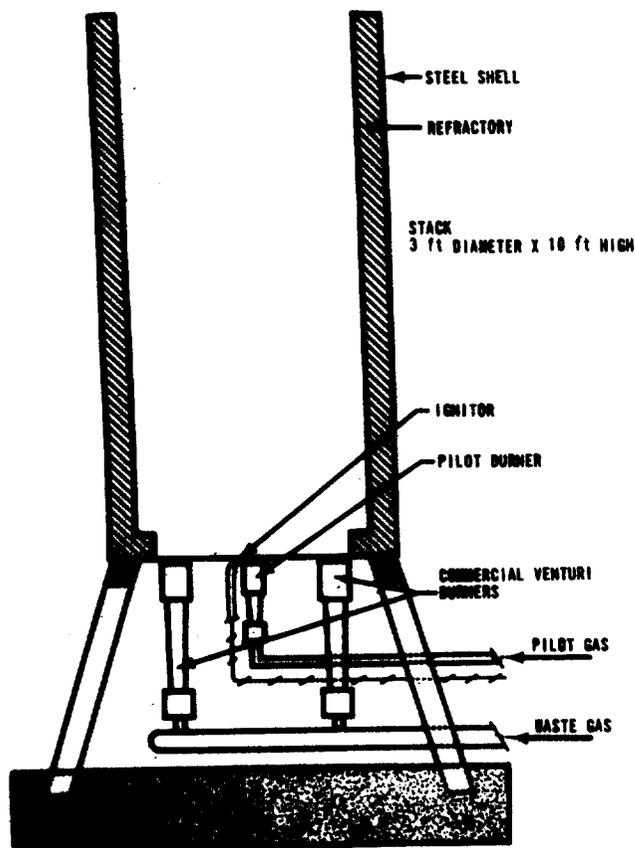


Figure 459. Vertical, venturi-type flare.

hydrocarbons. A condition such as this can also be a serious air pollution problem.

#### Design of a smokeless flare

The choice of a flare is dictated by the particular requirements of the installation. A flare may be located either at ground level or on an elevated structure. Ground flares are less expensive, but locations must be based upon considerations such as proximity of combustible materials, tanks, and refinery processing equipment. In a congested refinery area, there may be no choice but to use an elevated flare.

A method of determining the distance a stack should be from surrounding equipment and personnel has been developed (Hajek and Ludwig, 1960). The recommended equation is

$$D = \sqrt{\frac{(F)(H)}{(4)(3.14)(K)}} \quad (132)$$

where

D = minimum distance, ft from the flame to the object

F = a dimensionless constant equal to 0.20 for methane, which has a hydrogen-to-carbon weight ratio of 0.333, and equal to 0.33 for propane, which has a hydrogen-to-carbon weight ratio of 0.222. (Use 0.40 when in doubt.)

H = heat release, Btu/hr

K = a constant, Btu/hr-ft<sup>2</sup>:

K = 1,000 for objects exposed 20 minutes or more

K = 1,500 for objects exposed less than 20 minutes.

The usual flare system includes gas collection equipment, the liquid knockout tank preceding the flare stack. A water seal tank is usually located between the knockout pot and the flare stack to prevent flashbacks into the system. Flame arrestors are sometimes used in place of or in conjunction with a water seal pot. Pressure-temperature-actuated check valves have been used in small ground flares to prevent flash-back. The flare stack should be continuously purged with steam, refinery gas, or inert gas to prevent the formation of a combustible mixture that could cause an explosion in the stack (Hajek and Ludwig, 1960). The purge gas should not fall below its dew point under any condition of flare operation.

To prevent air from entering a flare stack which is used to dispose of gases that are lighter than air, a device known as a molecular seal (John Zink Company) is sometimes used in conjunction with purge gas. It is installed within the flare stack immediately below the flare tip and acts as a gas trap by preventing the lighter-than-air gas from bleeding out of the system and being displaced with air. A cross-section of a flare stack and seal is so shown in Figure 461.

The preferred method of inspirating air is injecting steam either into the stack or into the combustion zone. Water has sometimes been used in ground flares where there is an abundant supply. There is, however, less assurance of complete combustion when water is used, because the flare is limited in its operation by the type and composition of gases it can handle efficiently.

The diameter of the flare stack depends upon the expected emergency gas flow rate and the permissible backpressure in the vapor relief manifold system. The stack diameter is usually the same or greater than that of the vapor header discharging to the stack and should be the same diameter as or greater than that of the burner

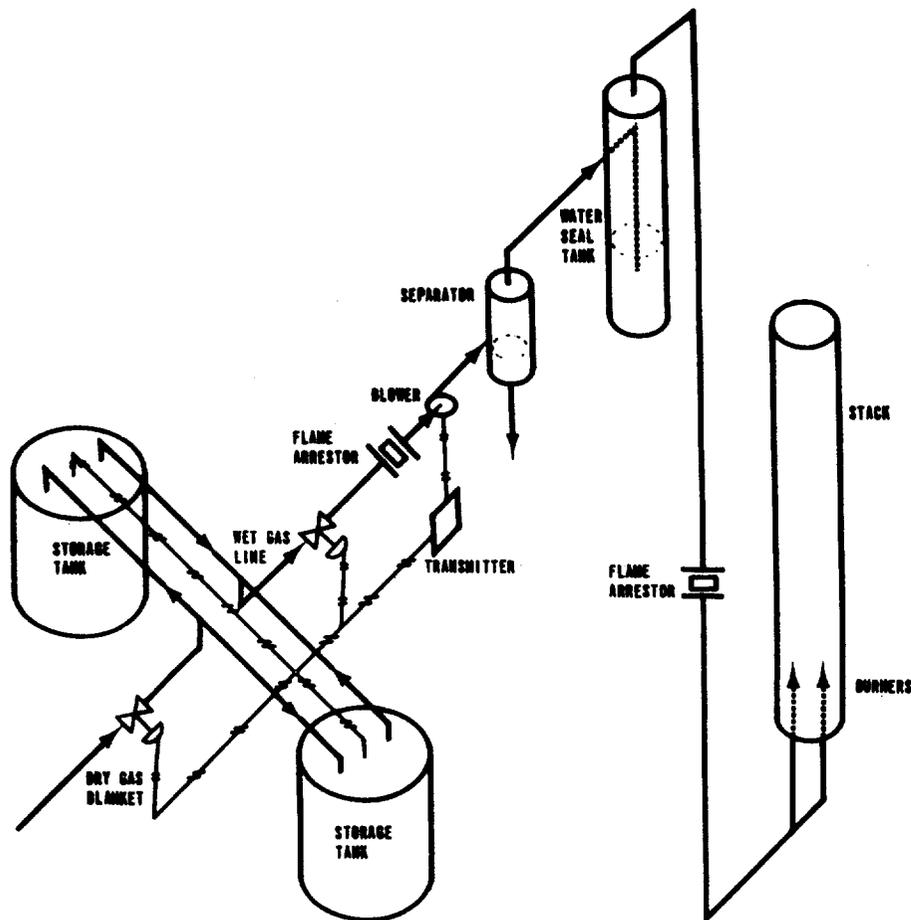


Figure 460. Flow diagram of tank-gas-blanketing system venting to a vertical, venturi flare.

section. The velocity of the gas in the stack should be as high as possible to permit use of lower stack heights, promote turbulent flow with resultant improved combustion, and prevent flashback. Stack gas velocity is limited to about 500 fps in order to prevent extinction of the flame by blowout. A discharge velocity of 300 to 400 fps based upon pressure drop considerations is the optimum design figure of a patented flare tip manufactured by the John Zink Company. The nature of the gas determines optimum discharge velocity (John Zink Company).

Adequate stack heights must be provided to permit safe dispersion of toxic or combustible material in the event of pilot burner failure. Techniques are available for calculating adequate stack heights to obtain certain ground concentrations at various distances from the stack, depending upon atmospheric conditions (Bodurtha, 1958; Gosline et al., 1956). These methods of calculation should not be generally applied to any one location, and meteorological data should be obtained for the particular location involved.

The structural support of an elevated-flare stack over 40 to 50 feet high requires the use of guy wires. A self-supporting stack over 50 feet high requires a large and expensive foundation. Stacks over 100 feet high are usually supported by a steel structure such as is shown in Figure 462.

Three burner designs for elevated flares have been discussed--the multisteam-jet, or Zink, and the Esso and Sinclair types. The choice of burner is a matter of personal preference. The Zink burner provides more efficient use of steam, which is important in a flare that is in constant use. On the other hand, the simplicity, ease of maintenance, and large capacity of the Esso burner might be important considerations in another installation.

As previously mentioned, the amount of steam required for smokeless combustion varies according to the maximum expected gas flow, the molecular weight, and the percent of unsaturated hydrocarbons in the gas. Data for steam requirements for elevated flares are shown in Figure 463. Actual tests should be run on the various materials to

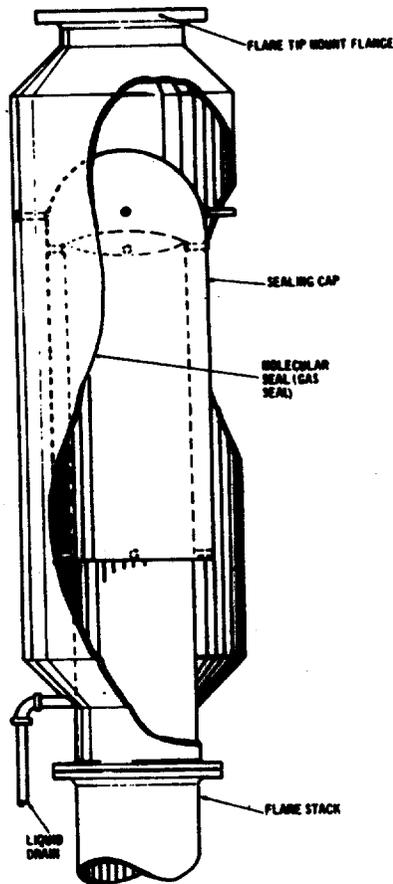


Figure 461. John Zink molecular seal (U.S. patent 3,055,417, John Zink Company, Tulsa, Okla.).

be flared in order to determine a suitable steam-to-hydrocarbon ratio. In the typical refinery, the ratio of steam to hydrocarbon varies from 0.2 to 0.5 pound of steam per pound of hydrocarbon. The John Zink Company's recommendation for their burner is 5 to 6 pounds per 1,000 cubic feet of a 30-molecular-weight gas at a pressure drop of 0.65 psig.

#### Pilot ignition system

The ignition of flare gases is normally accomplished with one of three pilot burners. A separate system must be provided for the ignition of the pilot burner to safeguard against flame failure. In this system, an easily ignited flame with stable combustion and low fuel usage must be provided. In addition, the system must be protected from the weather.

One good arrangement for a pilot ignitor is shown in Figure 464. To obtain the proper fuel-air ratio for ignition in this system, the two plug valves are opened and adjustments are made with the globe valves, or pressure regulator valves. After the mixing, the fuel-air mixture is lit in an igni-

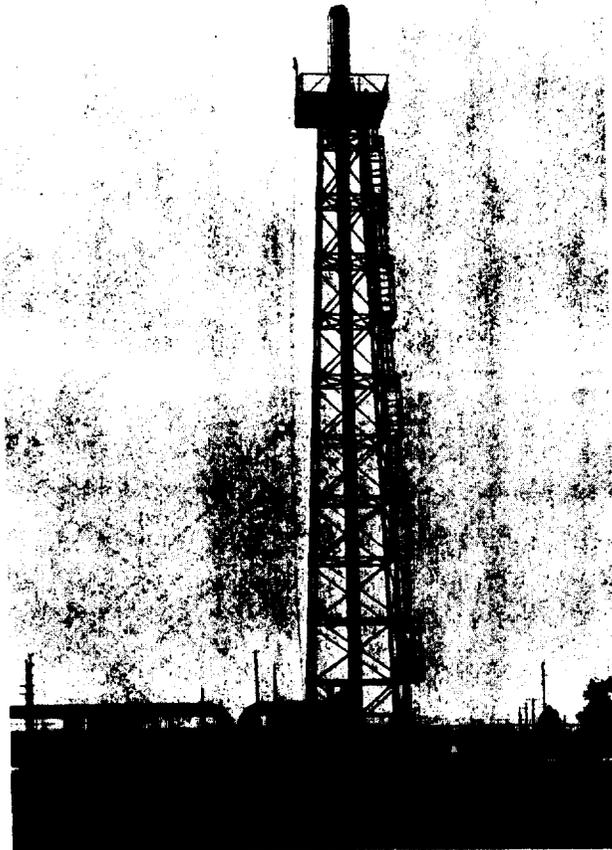


Figure 462. A 200-ft flare stack supported by a steel tower (Atlantic-Richfield Co., Wilmington, Calif.).

tion chamber by an automotive spark plug controlled by a momentary-contact switch. The ignition chamber is equipped with a heavy Pyrex glass window through which both the spark and ignition flame can be observed. The flame front travels through the ignitor pipe to the top of the pilot burner. The mixing of fuel gas and air in the supply lines is prevented by the use of double check valves in both the fuel and air line. The collection of water in the ignitor tube can be prevented by the installation of an automatic drain in the lower end of the tube at the base of the flare. After the pilot burner has been lit, the flame front generator is turned off by closing the plug cocks in the fuel and air lines. This prevents the collection of condensate and the overheating of the ignitor tube.

On elevated flares, the pilot flame is usually not visible, and an alarm system to indicate flame failure is desirable. This is usually accomplished by installing thermocouples in the pilot burner flame. In the event of flame failure, the temperature drops to a preset level, and an alarm sounds.

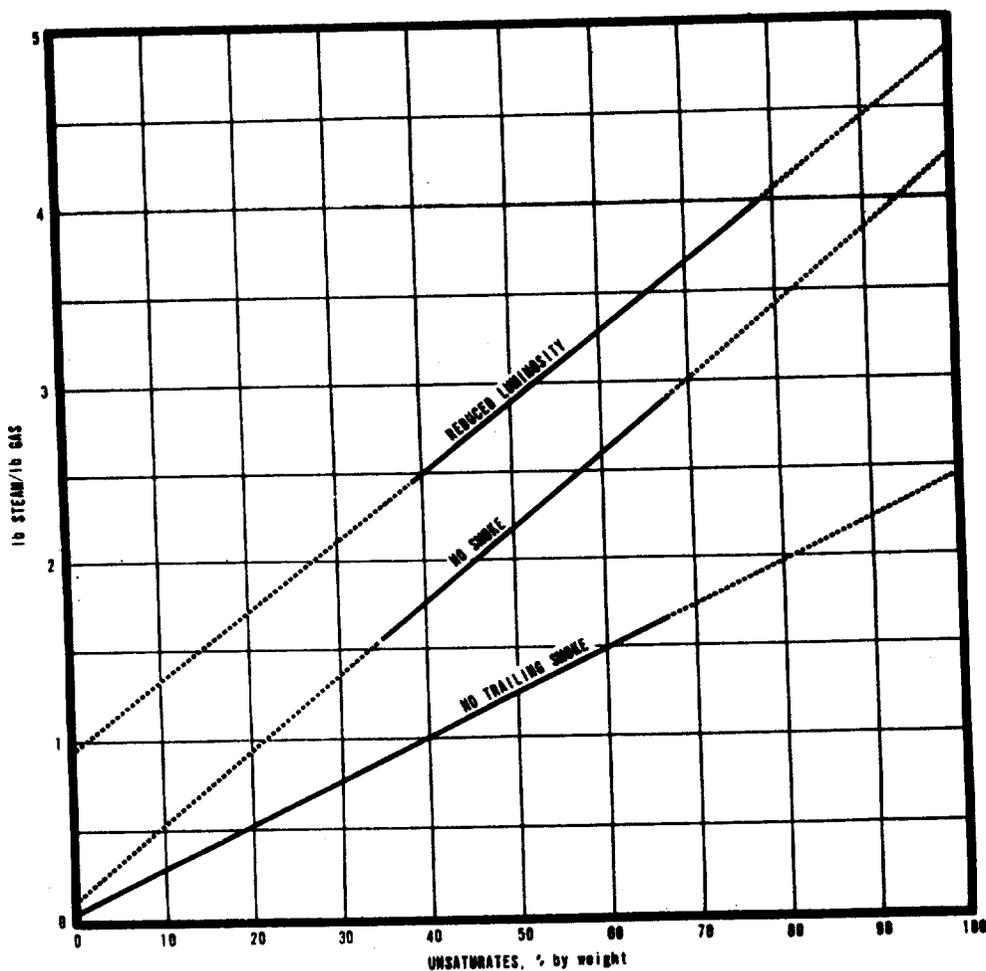


Figure 463. Steam requirements for smokeless burning of unsaturated hydrocarbon vapor (American Petroleum Institute, 1957).

#### Instrumentation and control of steam and gas

For adequate prevention of smoke emission and possible violations of air pollution regulations, an elevated, smokeless flare should be equipped to provide steam automatically and in proportion to the emergency gas flow.

Basically, the instrumentation required for a flare is a flow-sensing element, such as a Pitot tube, and a flow transmitter that sends a signal (usually pneumatic) to a control valve in the steam line. Although the Pitot tube has been used extensively in flare systems, it is limited by the minimum linear velocity required to produce a measurable velocity head. Thus, small gas flows will not actuate the steam control valves. This problem is usually overcome by installing a small bypass valve to permit a constant flow of steam to the flame burner.

A more sensitive type of flow-measuring device is the inverted weir. A typical installation is

shown in Figure 465. A variation of the inverted weir is the slotted orifice previously shown in Figure 453. The operation of this installation has already been described.

The hot-wire flow meter has also been used in flare systems (Huebner, 1959). The sensing element is basically a heat loss anemometer consisting of an electrically heated wire exposed to the gas stream to measure the velocity. The gas flow is perpendicular to the axis of the hot wire. A conventional recorder is used with this probe, modified for the resistance bridge circuit of the gas flow meter. As the flow of gas past the probe varies, the heat loss from the hot wire varies and causes an imbalance of the bridge circuit. The recorder then adjusts for the imbalance in the bridge and indicates the gas flow. This type of installation provides sensitivity at low velocities, and the gas flow measurement can be made without causing an appreciable pressure drop. This is an important advantage in a system using constant backpressure-

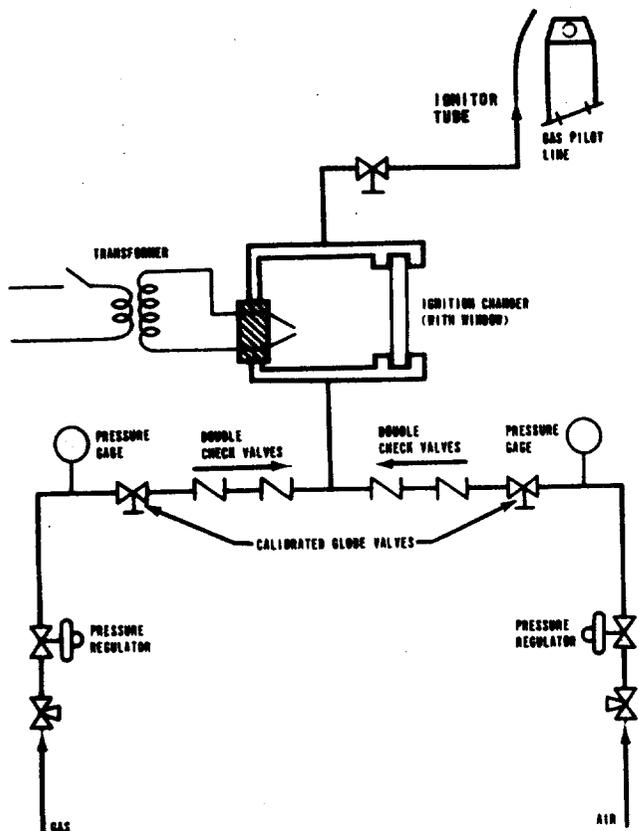


Figure 464, Remote-control system for igniting flare pilot burners (American Petroleum Institute, 1957).

type relief valves. One flow meter of this type in use has a velocity range of 0 to 6,000 fpm. The hot-wire flow meter can be used as a primary flow-sensing element or as a leak detector in laterals connected to the main flare header.

Another system using a venturi tube as the primary element for measuring the rate of gas flow to a flare is shown in Figure 466.

Supply and control of steam

After the amount of steam required for maximum design gas flow rates is determined, the size of the steam supply line can be estimated by conventional methods of calculation, such as shown in Figure 467. The following example illustrates the calculations for sizing the steam supply line.

Given:

- 200 psig (215 psia) saturated steam
- 9,000 lb/hr propane
- 1,000 lb/hr propylene
- 10% (by weight) unsaturated material.

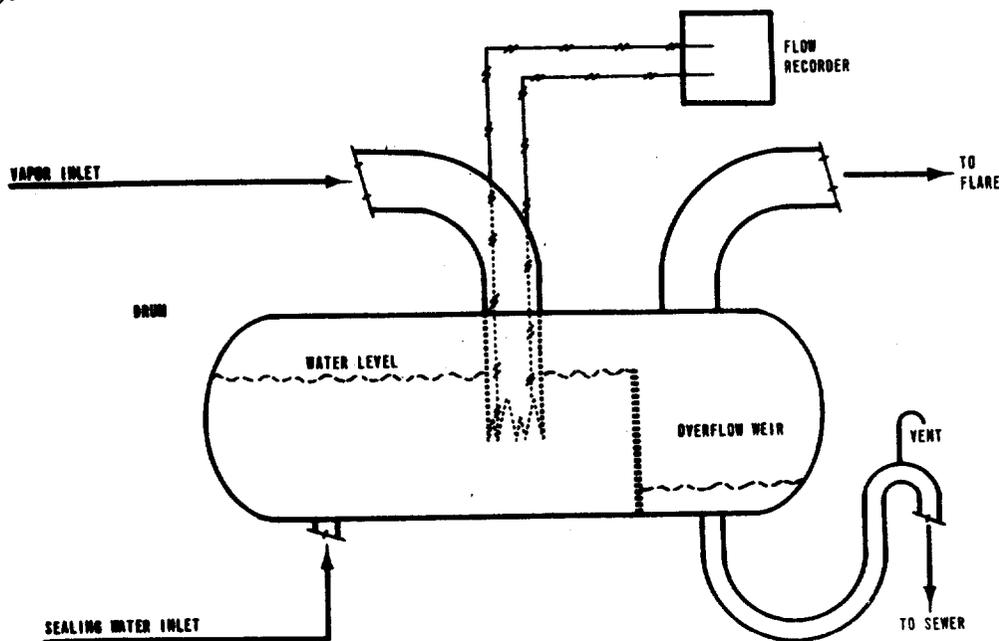


Figure 465. Inverted weir for measuring gas flow to a flare. The end of the low-pressure line to the flow recorder should be at the same level as the tops of the slots in the inverted weir. The end of the high-pressure line to the recorder should be at the same level as the bottoms of the weir slots (American Petroleum Institute, 1957).

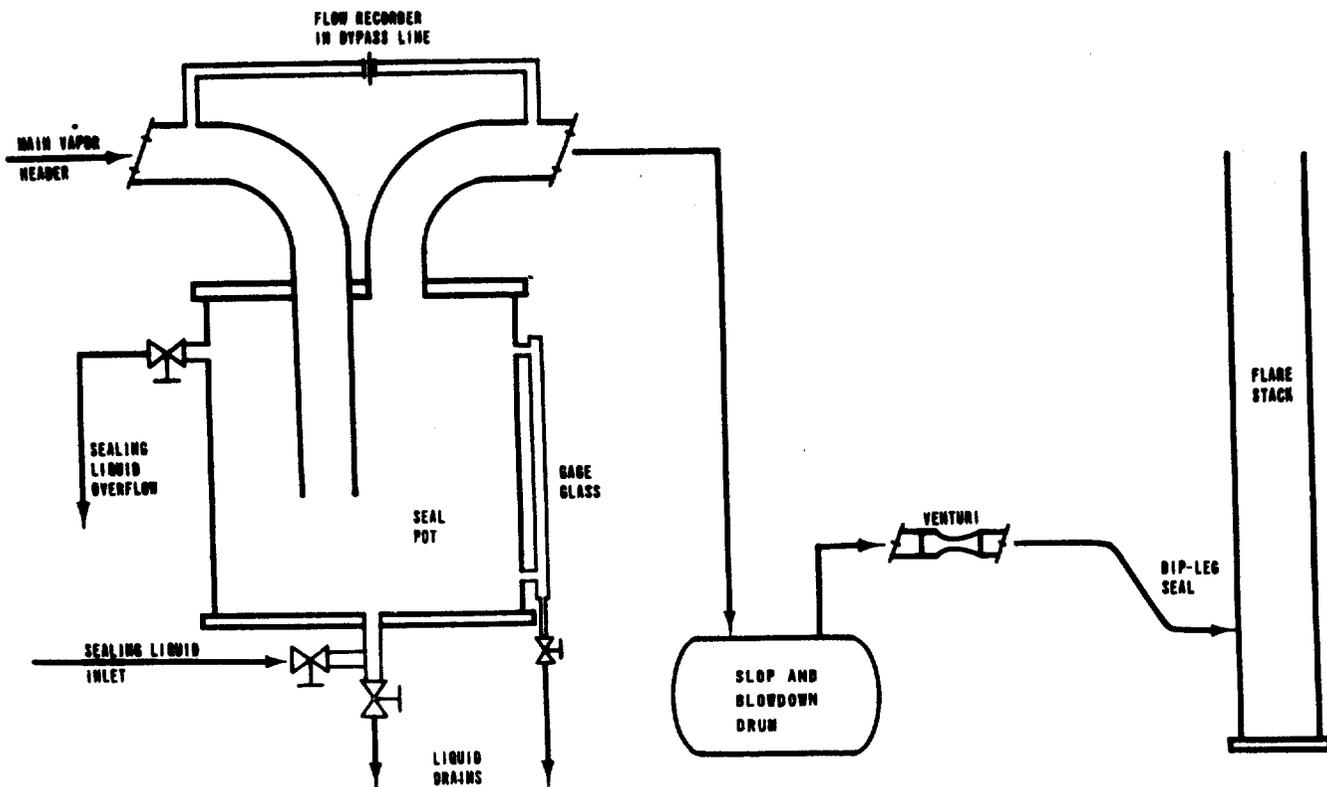


Figure 466. System for measuring flare gas. Small flows of gas are measured by the flow recorder in the bypass line. When a blow occurs that is large enough to overcome the static head of the sealing liquid in the seal pot, the liquid is blown to the sloop and blowdown drum. The gas flow is measured by the venturi in the main line to the flare (American Petroleum Institute, 1957).

**Problem:**

Determine the size of the steam supply line required.

**Solution:**

From Figure 463, the steam-to-hydrocarbon ratio should be 0.55.

Steam required = (10,000 lb/hr)(0.55) = 5,500 lb/hr

With allowance for a future increase in steam requirements, the steam line should be designed to provide 7,000 lb/hr at a velocity of 6,000 fpm. From Figure 467, the pipe diameter is found to be 3 inches.

The number and size of steam jets can be estimated by the following empirical equation (Marks, 1951) for steam flow through a small nozzle:

$$W = 0.0165 A P_1^{0.97} \quad (133)$$

where

W = steam flow, lb/sec

A = nozzle area, in.<sup>2</sup>

P<sub>1</sub> = upstream pressure, psia.

Commercial burners use 1/8- to 1/2-inch-diameter stainless steel pipe for the steam jets with orifices of 1/8 to 7/16 inch in diameter. The number of jets depends upon the gas flow rates and the steam to be delivered into the combustion zone.

Figure 468 is a plot of steam flow versus upstream pressure for various sizes of jet orifices. This chart may be used for preliminary design or for checking an existing installation as shown in the following example.

**Given:**

Steam flow, 5,500 lb/hr

Available pressure upstream of jets, 80 psia

Assume jet orifice diameter, 3/8 in..

**Problem:**

Determine minimum number of steam jets required.

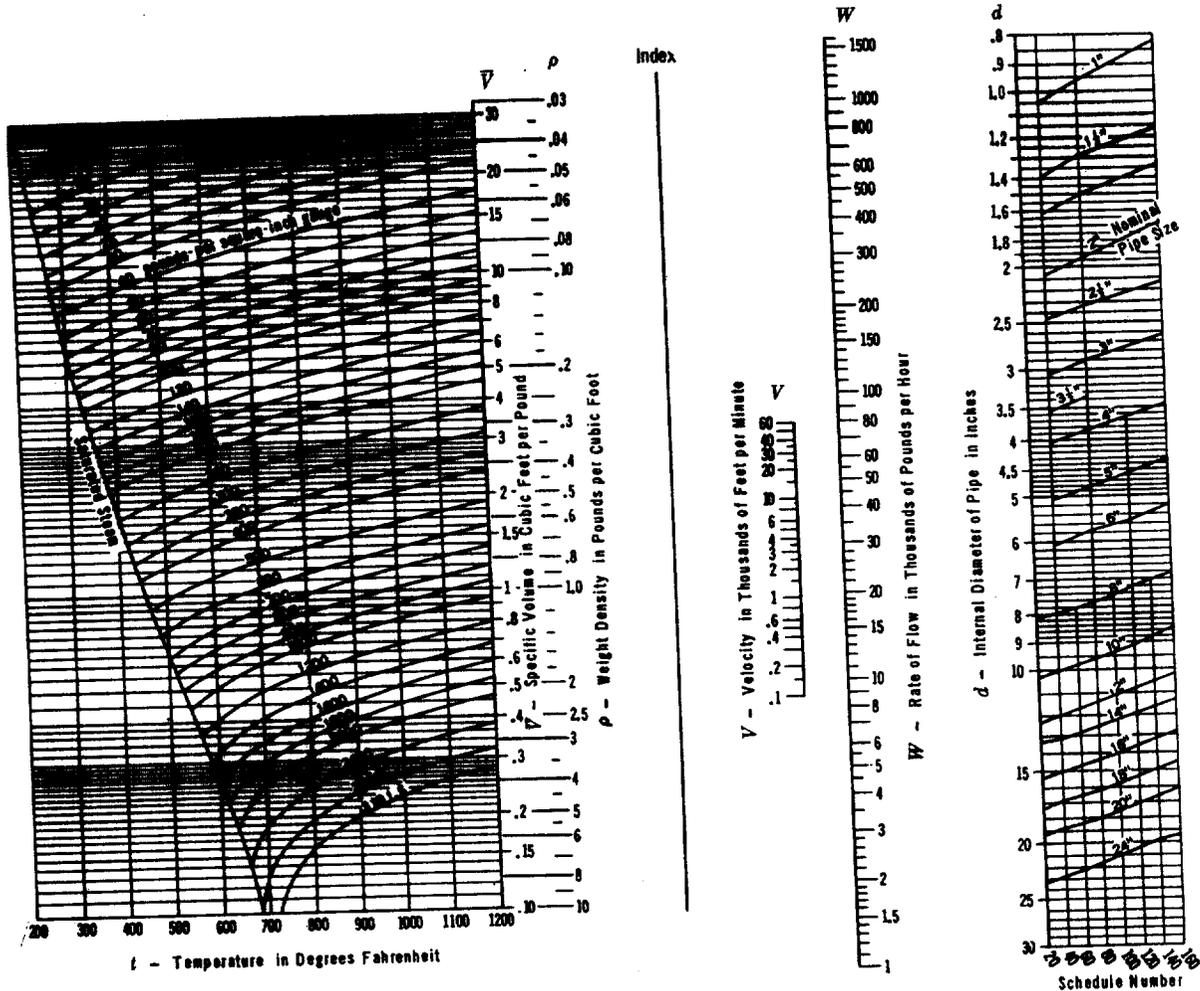


Figure 467, Steam pipe sizing chart. Establish the steam pressure and temperature intersection. Draw a horizontal line to specific volume scale V. Draw a line from V to the expected rate of flow, W. Mark the intersect with the index line. Using either known quantity, pipe size, d; or velocity, V; find the unknown by drawing a line from the index to the known quantity (Crane Company, 1957).

Solution:

From Figure 468, the steam flow per jet = 460 lb/hr

$$\text{Number of jets required} = \frac{5,500 \text{ lb/hr}}{460 \text{ lb/hr}} = 11.97$$

Use 12 steam jets with 3/8-inch orifices.

As shown in Figure 469, a jet located at an acute angle to the direction of a gas flow improves the mixing of the gas with air or steam. Commercial flare burners usually have steam jets placed at angles of 15 to 60 degrees with the gas flow.

A steam control system is provided to ensure correct proportions of gas and steam flow. A control valve with equal percentage characteristics is often used in this application. A diagram

of this type of valve is shown in Figure 470. Flow curves for valves with various characteristics are shown in Figure 471. The manufacturer's literature should be consulted for specific valves.

Accurate selection of the size of steam control valve requires a full knowledge of the actual flowing conditions. In most cases, the pressure across the valve must be estimated. A conservative working rule is that one-third of the total system pressure drop, including all fittings and equipment, should be absorbed by the control valve. The pressure drop across valves in long lines or high-pressure drop lines may be somewhat lower. In these cases the pressure drop should be at least 15 to 25 percent of the total system drop, provided the variations in flow rates are small. A control valve can regulate flow only by absorbing energy and giving a pressure drop to the system.

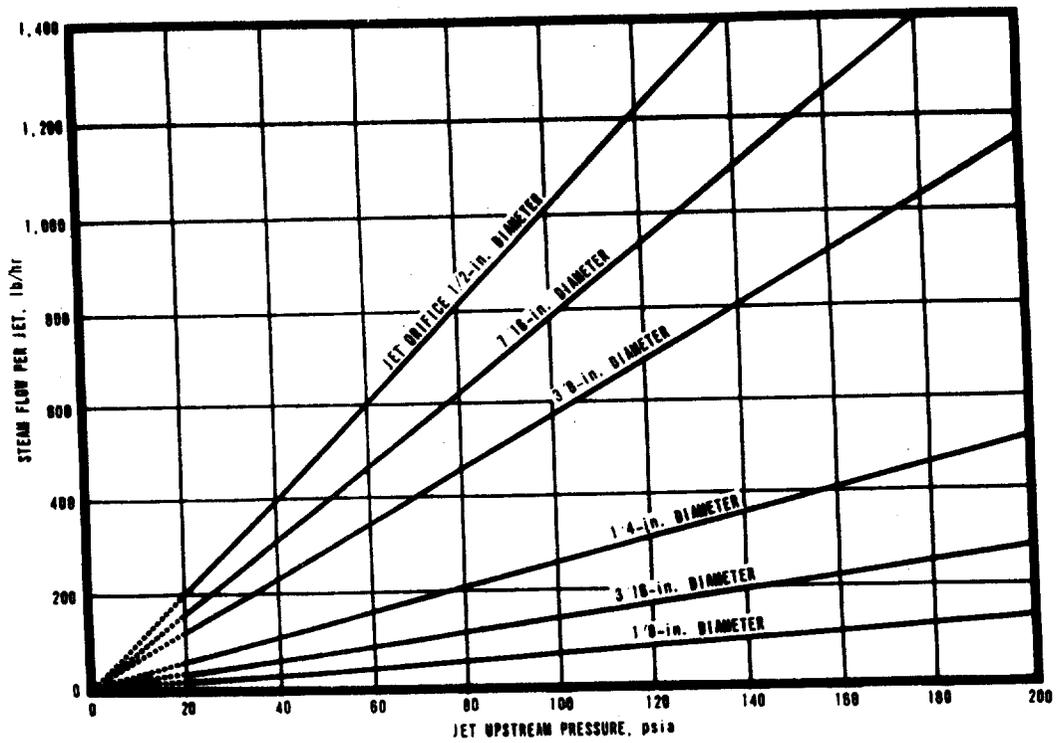


Figure 468. Jet upstream pressure versus jet capacity (based on equation  $W = 0.0165 AP$  where  $P < 0.575 P_{atm}$ ).

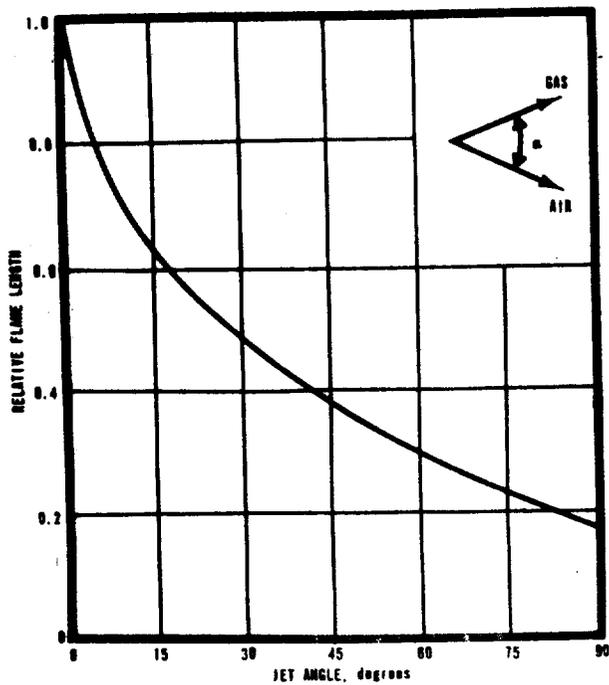


Figure 469. Relationship between flame length and jet angle (Gumz, 1950).

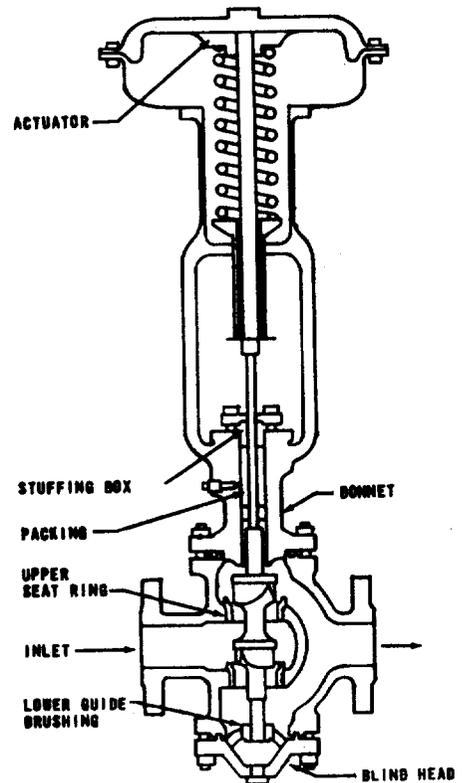


Figure 470. Diagram of double-seated, V-port control valve and valve power unit (Holzbock, 1959).

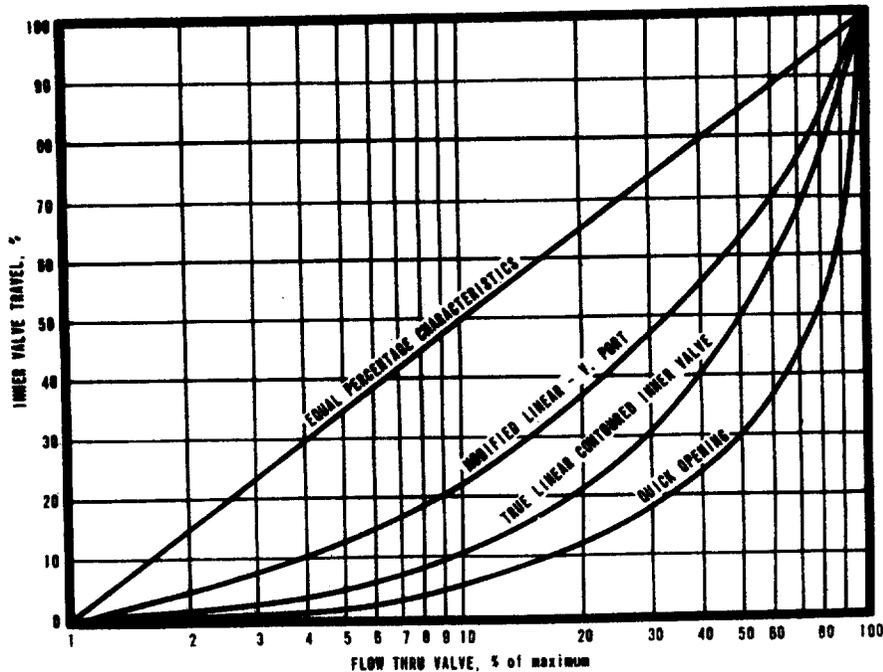


Figure 471. Flow curves for control valves with characterized plugs (Lieblich, 1953).

The most convenient method of sizing control valves involves the use of the flow coefficient,  $C_v$ . This flow coefficient is essentially a capacity index of the valve and can be obtained from the manufacturer's literature.

By using the basic conversion formulas shown in Table 161, the flow coefficient for any restriction can be determined. Under special conditions, such as a high pressure drop or use of special designs, deviation from the simple fundamental law can be substantial. For most practical valve-sizing problems, the use of the simplified formulas is adequate.

A brief method of selection of a control valve is explained in the following example.

Given:

Gas flow, 10,000 lb/hr

Steam-to-hydrocarbon ratio, 0.55 (by wt)

Maximum steam flow, 5,500 lb/hr

$P_1$ , upstream pressure, 160 psig

$P_2$ , downstream pressure, 100 psig

Steam density, downstream,  $0.226 \text{ lb/ft}^3$ .

Problem:

Select a control valve for this system.

Solution:

Determine  $C_v$  from the formula as shown in Table 161:

$$\begin{aligned}
 C_v &= \frac{W}{2.1 [(P_1 - P_2)(P_1 + P_2)]^{1/2}} & (134) \\
 &= \frac{5,500}{2.1 [(174.7 - 114.7)(174.7 + 114.7)]^{1/2}} \\
 &= 19.8
 \end{aligned}$$

A valve with a  $C_v$  of 19.8 is indicated. Since an equal percentage characteristic is desired in this application, a correction factor should be applied. This adjustment is necessary because of the flow characteristics of this type of valve. It is suggested by the manufacturer that a 20 percent increase in the  $C_v$  be taken to compensate for this adjustment. Thus the  $C_v$  for the equal percentage valve would be 23.8.

Other items to consider in the selection of control valves are the valve actuator, valve positioners, and future steam requirements. The control valve actuator supplies the power for operating the valve. In flare applications the power unit is usually a pneumatic-spring-diaphragm-type actuator of the type shown in Figure 464, operated by 3 to 15 psig air pressure. These units are designed to open the valve if

Table 161. EQUATIONS FOR CONTROL VALVE SIZING  
(Mason-Neilan Division, 1963)

NOMENCLATURE FOR C<sub>v</sub> FORMULAS

- V = flow in U.S. gpm
- Q = cfm @ 14.7 psia and 60°F
- W = lb/hr
- P<sub>1</sub> = inlet pressure - psia (14.7 + psi gauge)
- P<sub>2</sub> = outlet pressure - psia (14.7 + psi gauge)
- C = gas sp. gr. (air = 1.0)
- G<sub>r</sub> = sp. gr. @ flowing temperature
- T<sub>r</sub> = flowing temperature - °F abs. (460 + °F)
- T<sub>sa</sub> = superheat in °F

Desired	Known	Liquid		Gas		Saturated Steam ① lb/hr	Superheated Steam ① lb/hr
		U.S. gpm	lb/hr	① cfm	① lb/hr		
C <sub>v</sub>	V, Q or W G, P <sub>1</sub> & P <sub>2</sub> G <sub>r</sub>	$\frac{V\sqrt{G_r}}{\sqrt{P_1 - P_2}}$	$\frac{W}{500\sqrt{(P_1 - P_2)G_r}}$	$\frac{Q\sqrt{G_r}}{48.3\sqrt{(P_1 - P_2)(P_1 + P_2)}}$	$\frac{W}{3.22\sqrt{(P_1 - P_2)(P_1 + P_2)G_r}}$	$\frac{W}{2.1\sqrt{(P_1 - P_2)(P_1 + P_2)}}$	$\frac{(1 + 0.0007T_{sa})W}{2.1\sqrt{(P_1 - P_2)(P_1 + P_2)}}$
C <sub>v</sub> Temp. Corrected	Q G, P <sub>1</sub> & P <sub>2</sub> T <sub>r</sub>			$\frac{Q\sqrt{G_r T_r}}{949\sqrt{(P_1 - P_2)(P_1 + P_2)}}$			
W (lb/hr) V (U.S. gpm) Q (cfm)	C <sub>v</sub> G, P <sub>1</sub> & P <sub>2</sub> G <sub>r</sub>	$\frac{C_v\sqrt{P_1 - P_2}}{\sqrt{G_r}}$	$500C_v\sqrt{(P_1 - P_2)G_r}$	$\frac{48.3C_v\sqrt{(P_1 - P_2)(P_1 + P_2)}}{\sqrt{G_r}}$	$3.22C_v\sqrt{(P_1 - P_2)(P_1 + P_2)G_r}$	$2.1C_v\sqrt{(P_1 - P_2)(P_1 + P_2)}$	$\frac{2.1C_v\sqrt{(P_1 - P_2)(P_1 + P_2)}}{(1 + 0.0007T_{sa})}$
Q (scfm) Temp. Corrected	C <sub>v</sub> G, P <sub>1</sub> & P <sub>2</sub> T <sub>r</sub>			$\frac{949C_v\sqrt{(P_1 - P_2)(P_1 + P_2)}}{\sqrt{G_r T_r}}$			

- ① When P<sub>2</sub> is less than  $\frac{P_1}{2}$  the expression  $\sqrt{(P_1 - P_2)(P_1 + P_2)}$  becomes 0.87P<sub>1</sub>.
- ② On gas flow the effect of flowing temperatures may be neglected for all temperatures between 30°F and 150°F. For higher or lower temperatures a correction should be included.

the air pressure fails. Selection of valve actuators can be made by referring to manufacturer's literature.

Control valve positioners are devices that position the valve stem to match the controller's output signal. The valve plug is thus moved to the desired position, overcoming the packing friction and unbalanced forces in the system. Positioners are also used when split-range valves are operated by one controller. In most elevated-flare installations, the range of gas flow is such that one steam valve does not properly proportion the steam flow, and two parallel steam valves are required. This means that one valve moves from closed to open when the controller output changes from 3 to 9 psig, and the other valve is operated when the controller output is 9 to 15 psig.

Where future steam requirements may be expected to increase, the steam supply line and control valves can be sized for the expected larger capacity. Smaller inner-valve plugs can then be used in the control valves to supply the necessary reduced capacity while the larger body size is retained. The smaller plugs have the same flow characteristics as the standard size plugs, but flow can be reduced as low as 40 percent of nominal capacity.

Design of water-injection-type ground flares

Designing a typical water injection flare consists of sizing the stack structure and combustion air-ports, and determining the water required to ob-

tain smokeless combustion (American Petroleum Institute, 1957).

With the three-concentric-stack-type flare as previously discussed, the air ports in the intermediate and outer stacks should be designed to admit 150 percent of the theoretical air for complete combustion. The draft for these stacks can be calculated from the equation

$$h = H \frac{\rho_a \rho_v}{\rho_w} \tag{135}$$

where

- h = draft, in. of water
- H = height of stack, ft
- $\rho_a$  = density of cold air, lb/ft<sup>3</sup>
- $\rho_v$  = density of hot gas in stack, lb/ft<sup>3</sup>
- $\rho_w$  = density of water, lb/ft<sup>3</sup>.

The area of the stack's arches can be calculated according to the formula

$$A = \frac{W}{457 \text{ CY } \left(\frac{h}{w}\right) (\rho_a)} \tag{136}$$

where

$$A = \text{area of orifice, ft}^2$$

- W = rate of flow, lb/hr
- C = orifice discharge coefficient, dimensionless
- Y = expansion factor, dimensionless
- $h_w$  = differential pressure across orifice, in. of water at 60°F
- $\rho_a$  = density of air at upstream tap conditions, lb/ft<sup>3</sup>.

In this case  $\rho_a$  is the density of air at 60°F, Y is assumed to be 1.0, and C is assigned the value of 0.6. Equation 136 can now be reduced to

$$A = \frac{W}{20.9 h_w} \quad (137)$$

Test data indicate that water pressure is more important in achieving smokeless burning than the amount of water delivered to the flare. In general, a high water pressure results in better mixing of gas. Higher water pressure is required as the molecular weight and unsaturated content of the gas increase. Table 162 lists water spray pressures required for smokeless burning.

Table 162. WATER SPRAY PRESSURES REQUIRED FOR SMOKELESS BURNING<sup>a</sup>  
(American Petroleum Institute, 1957)

Gas rate, scfh	Unsaturation, % by vol	Molecular weight	Water pressure, psig	Water rate, gpm
200,000	0 to 20	28	30 to 40	31 to 35
150,000	30	33	80	45
125,000	40	37	120	51

<sup>a</sup>The data in this table were obtained with a 1-1/2-inch-diameter spray nozzle in a ground flare with the following dimensions:

	Height, ft	Diameter, ft
Outer stack	30	14
Intermediate stack	12	6
Inner stack	4	2.5

Satisfactory proportioning of the flow of water to the flow of gas is difficult to achieve because the pressure drop required for proper spray nozzle operation is high. Where the opacity of smoke emission is limited, some type of remote manual or automatic control is necessary.

#### Design of venturi-type ground flares

The venturi-type ground flare, as previously discussed, consists of burners, pilots, igniters, and control valves.

The total pressure drop permitted in a given installation depends upon the characteristics of

the particular blowdown system. In general, the allowable pressure drop through the relief valve headers, liquid traps, burners, and so forth, must not exceed one-half the internal unit's relieving pressure. The burner cut-in schedule is based upon a knowledge of the source, frequency, and quantity of the release gases. Pressure downstream of the control valves must be adequate to provide stable burner operation.

Flare installations designed for relatively small gas flows can use clusters of commercially available venturi burners. For large gas releases, special venturi burners must be constructed. The venturi (air-inspiring) burners are installed in clusters with a small venturi-type pilot burner in the center. This burner should be connected to an independent gas source. The burners may be mounted vertically or horizontally. The burners should fire through a refractory wall to provide protection for personnel and equipment. Controls can be installed to give remote indication of the pilot burner's operation.

For large-capacity venturi burners, field tests are necessary to obtain the proper throat-to-orifice ratio and the minimum pressure for stable burner operation. The design of one flare system using special venturi burners has been reported (Brumbaugh, 1947). An analysis of the burner limitations and the pressure relief system in this installation yielded the design data set forth in Table 163.

Table 163. DESIGN DATA FOR A FLARE SYSTEM USING SPECIAL VENTURI BURNERS  
(Brumbaugh, 1947)

Burner No.	Cut-in pressure, psi	Cut-out pressure, psi	Gas orifice diameter, in.	Venturi throat dia, in.	Ratio of throat-to-orifice area
1	2-1/4	1/4	1.61	5	9.6
2	2-3/4	1/2	2.90	8	7.8
3	3-1/4	3/4	4.03	11.5	8.1
4	3-3/4	1	7	18	6.6

After 5 years, this flare was reported to be satisfactory and had required relatively few changes (Green, 1952).

The selection of the control valves and burners for a small-capacity ground flare is indicated by the following example:

Given:

Range of gas flow, 2,000 to 30,000 cfh

Most frequently expected gas flow, 12,000 cfh

Blowdown line size, 4-in. dia

Specific gravity of gas, 1.2

Calorific value of gas, 1,300 Btu/ft<sup>3</sup>  
 Flowing temperature of gas, 100°F.

**Problem:**

Select control valves and determine the number and size of standard air-inspiring burners to permit smokeless burning of all expected gas flows.

**Solution:**

On the basis of the range of expected gas flow, try three banks of burners with a water seal bypass to the largest bank to handle gas flows in excess of flare capacity. The maximum allowable pressure at the burners has been set at 5 psig. Various intermediate pressures for the control valves will be arbitrarily selected. The intermediate pressures, which indicate stable operations of the different burner banks relative to the gas flows, will be used as the operating points for the valves.

1. Valve selection and capacity data:

Try two 1-inch and one 2-inch single-seated, quick-opening valves.

Valve size, in.	Capacity index, C <sub>v</sub>	Pressure, psi	Capacity, cfh
1	14	0.5	2,070
		1.0	2,940
		3.0	5,080
		5.0	6,580
2	46	3.0	15,000
		5.0	20,000

2. Burner selection--No. 1 bank:

No. 1 bank of burners to handle a minimum flow of 2,000 cfh at 0.5 psig.

Try a No. 16X NGE burner with a 1/2-in. orifice.

From Table 164, capacity of a No. 16X burner at 0.5 psig (1,000 Btu/ft<sup>3</sup> gas) is 1,360 cfh.

Capacity of 1,300 Btu/ft<sup>3</sup> gas:

$$\frac{1,000}{1,300} \times 1,360 \text{ cfh} = 1,047 \text{ cfh/burner}$$

Number of burners required:

$$\frac{2,000 \text{ cfh}}{1,047 \text{ cfh/burner}} = 1.91 \text{ burners}$$

Table 164. VENTURI BURNER CAPACITIES, ft<sup>3</sup>/hr (Natural Gas Equipment, Inc., 1955)<sup>a</sup>

Gas pressure, in. H <sub>2</sub> O	Type 14 3/16-in. orifice	Type 16 7/16-in. orifice	Type 16X 1/2-in. orifice
2	70		
4	100		
6	123		
8	142		
10	160		
1/2 psig	210	1,042	1,360
1 psig	273	1,488	1,900
2 psig	385	2,157	2,640
3 psig		2,654	3,200
4 psig		3,065	3,680
5 psig		3,407	4,080
6 psig		3,742	4,480
7 psig		4,040	4,800
8 psig		4,320	5,160

<sup>a</sup>Basis: 1,000 Btu/ft<sup>3</sup> natural gas.

Use two burners.

No. 1 bank capacity at other operating pressures:

No. of burners	Capacity, cfh			
	0.5 psig	1.0 psig	3.0 psig	5 psig
2	2,094	2,930	4,920	6,270

Range of No. 1 bank burners is 2,000 to 6,000 cfh, with valve capacity range from 2,000 to 7,000 cfh.

3. Burner selection--No. 2 bank:

No. 2 bank of burners to be sized such that capacity of the 1 and 2 banks will equal the most frequently expected flow of 12,000 cfh. Use 6,000 cfh as approximate capacity of No. 1 bank.

$$12,000 \text{ cfh} - 6,000 \text{ cfh} = 6,000 \text{ cfh}$$

Size and capacity of No. 2 bank burners and valves will be the same as those of No. 1 bank.

4. Burner selection--No. 3 bank:

No. 3 bank capacity must equal the difference between 30,000 cfh and 12,000 cfh.

$$30,000 \text{ cfh} - 12,000 \text{ cfh} = 18,000 \text{ cfh}$$

From Table 166, capacity of No. 16X burner at 5 psig is 4,080 cfh (1,000 Btu/ft<sup>3</sup> gas).

Capacity for 1,300 Btu/ft<sup>3</sup> gas:

$$\frac{1,000}{1,300} \times 4,080 = 3,140 \text{ cfh/burner}$$

Number of burners required:

$$\frac{18,000/\text{cfh}}{3,140 \text{ cfh/burner}} = 5.7 \text{ burners}$$

Use six No. 16X NGE burners.

No. 3 bank capacity at other pressures:

No. of burners	Capacity, cfh	
	3.0 psig	5.0 psig
6	14,760	18,830

Range of No. 3 bank burners, 14,760 to 18,300 cfh, with 2-inch valve range of 15,500 to 20,000 cfh.

#### 5. Safety seal:

Basis: Seal pressure	6 psig
Sealing liquid	Water
Temperature	70°F

ft of water =

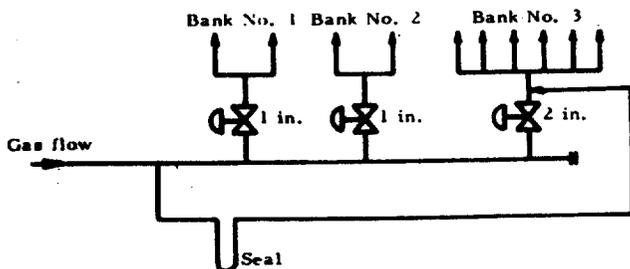
$$\frac{(6 + 14.7) \text{ lb/in.}^2 (144) \text{ in.}^2/\text{ft}^2}{62.3 \text{ lb/ft}^3} = 47.8 \text{ ft}$$

#### 6. Summary of flare operation:

Valve No.	Valve action			Burner capacity at 5 psig	Valve capacity at 5 psig
	Open, psig	Closed, psig	Range, psi		
1	1.0	0.5	0.5-5	6,270	6,580
2	3.0	1.0	1-5	6,270	6,580
3	5.0	3.0	5-6	18,830	20,000
				31,370	33,160

The bypass seal is set to open to No. 3 burner bank at 6 psig.

#### 7. Sketch of flare:



#### Maintenance of flares

Most refineries and petrochemical plants have a fixed schedule for inspection and maintenance of processing units and their auxiliaries. The flare system should not be exempted from this practice. Removal of a flare from service for

maintenance requires some type of standby equipment to disperse emergency gas vents during the shutdown. A simple stack with pilot burner should suffice for a standby. Coordinating this inspection to take place at time when the major processing units are also shut down is good practice.

Flare instrumentation requires scheduled maintenance to ensure proper operation. Most of the costs and problems of flare maintenance arise from the instrumentation.

Maintenance expenses for flare burners can be reduced by constructing them of chrome-nickel alloy. Because of the inaccessibility of elevated flares, the use of alloy construction is recommended.

## STORAGE VESSELS

### TYPES OF STORAGE VESSELS

Even in the most modern petroleum refineries and petrochemical plants, storage facilities must be provided for large volumes of liquids and gases. These facilities can be classified as closed-storage or open-storage vessels. Closed-storage vessels include fixed-roof tanks, pressure tanks, floating-roof tanks and conservation tanks. Open-storage vessels include open tanks, reservoirs, pits, and ponds.

Closed-storage vessels are constructed in a variety of shapes, but most commonly as cylinders, spheres, or spheroids. Steel plate is the usual material of construction though concrete, wood, and other materials are sometimes used. Before modern welding methods, the sections of the tank shell were joined by rivets or bolts. Welded joints are now used almost universally except for the small bolted tank found in production fields. The definition of a welded shell tank is given by API Standard 12 C entitled "Welded Oil Storage Tanks." Capacities of storage vessels range from a few gallons up to 500,000 barrels, but tanks with capacities in excess of 150,000 barrels are relatively rare.

Open-storage vessels are also found in a variety of shapes and materials of construction. Open tanks generally have cylindrical or rectangular shells of steel, wood, or concrete. Reservoirs, pits, ponds, and sumps are usually oval, circular, or rectangular depressions in the ground. The sides and bottom may be the earth itself or may be covered with an asphalt-like material or concrete. Any roofs or covers are usually of wood with asphalt or tar protection. Capacities of the larger reservoirs may be as much as 3 million barrels.

Vapors, gases, aerosols, and odors are examples of air contaminants emitted from storage facilities. In most cases, practical and feasible air pollution control measures are available to reduce the emissions.

#### Pressure Tanks and Fixed-Roof Tanks

Pressure tanks and fixed-roof tanks are grouped together because, in a sense, pressure tanks are special examples of fixed-roof tanks designed to operate at greater than atmospheric pressure. A horizontal, cylindrical (bullet) pressure tank is shown in Figure 472. Other



Figure 472. Horizontal, cylindrical pressure tank (Graver Tank and Manufacturing Company, Division Union Tank Car Co., East Chicago, Indiana).

types of pressure tanks--spheres, plain and noded spheroids, and noded hemispheroids--are illustrated in Figure 473. Maximum capacities of these pressure tanks are as much as 30,000 barrels for spheres and hemispheroids, and 120,000 barrels for noded spheroids. Spheres can be operated at pressures up to 217 psi; spheroids, up to 50 psi; noded spheroids, up to 20 psi; and plain or noded hemispheroids, up to 15 and 2-1/2 psi respectively. Horizontal, cylindrical pressure tanks are constructed with various capacities and pressures.

The ordinary vertical, cylindrical, fixed-roof tank is shown in Figure 474. This type of storage facility operates at or within a few ounces of pressure and may have a flat, recessed flat, conical, or domed roof. The term gastight, often applied to welded tanks, is misleading. Many of the roofs of the welded tanks have free vents open to the atmosphere. Others are equipped with conservation vents that open at very slight positive pressures. A tank also has many standard appurtenances including gaging hatches, sample hatches, relief vents, and foam mixers. Any of these accessories may fail in service and result in vapor leaks.

The operating pressure of a tank is limited by the thickness (weight) of the roof, as noted in Table 165. A cone roof tank may be operated at higher pressures, if necessary, by structural reinforcement or weighting of the roof. Safe operating pressures up to 4 ounces can be realized by this added expense. Use of unsupported dome-shaped roofs is another method of increasing the allowable operating pressure of the fixed-roof tank.

#### Floating-Roof Tanks

Floating-roof storage tanks are used for storing volatile material with vapor pressures in the low-

Table 165. ROOF PROPERTIES OF STEEL TANKS (Bussard, 1956)

Thickness, in. (gage)	Wt, lb/ft <sup>2</sup>	Operating pressure, oz/in. <sup>2</sup>
1/16 (16)	2.553	0.284
5/64 (14)	3.187	0.354
7/64 (12)	4.473	0.497
1/8 (11)	5.107	0.568
9/64 (10)	5.740	0.638
5/32 (9)	6.374	0.708
11/64 (8)	7.000	0.778
3/16 (7) <sup>a</sup>	7.650	0.850
1/4 (3)	10.200	1.333

<sup>a</sup>Minimum thickness specified by API Std 12C.

er explosive range, to minimize potential fire or explosion hazards. These vessels also economically store volatile products that do not boil at atmospheric pressures or less and at storage temperatures or below. These tanks are subclassified by the type of floating-roof section as pan, pontoon, or double-deck floating-roof tanks (Figure 475).

Pan-type floating-roof tanks were placed in service more than 40 years ago. These roofs require considerable support or trussing to prevent the flat metal plate used as the roof from buckling (Figure 475, lower right). These roofs are seldom used on new tanks because extreme tilting and holes in the roof have caused more than one-fifth of installed pan roofs to sink, and because their use results in high vaporization losses. Solar heat falling on the metal roof in contact with the liquid surface results in higher than normal liquid surface temperatures. Hydrocarbons boil away more rapidly at the higher temperatures and escape from the opening around the periphery of the roof.

To overcome these disadvantages, pontoon sections were added to the top of the exposed deck. Better stability of the roof was obtained, and a center drain with hinged or flexible connections solved the drainage problem. Center-weighted

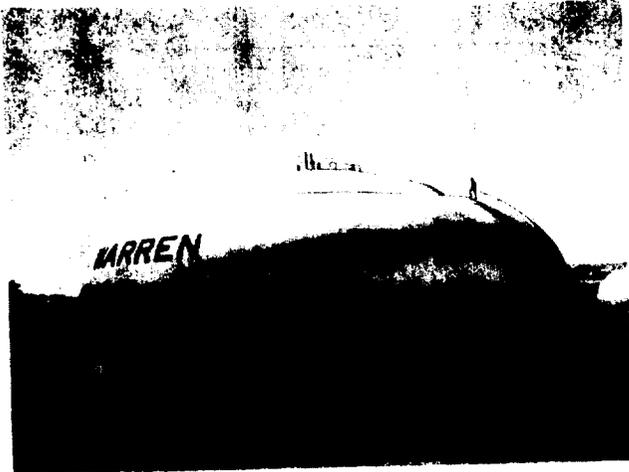
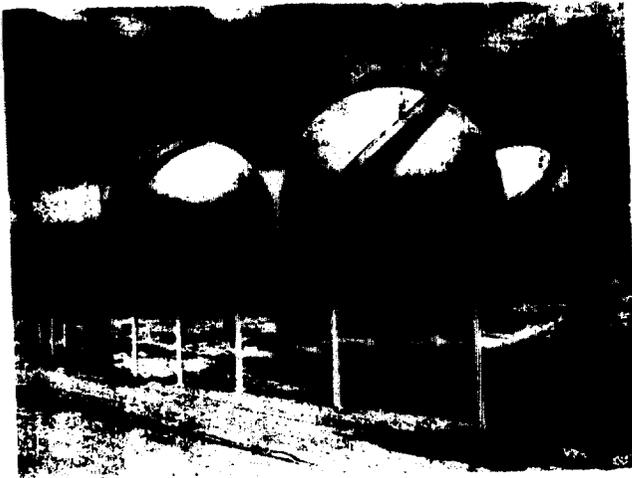


Figure 473. Types of pressure vessels: (upper left) 51-foot-diameter spheres (Butane is stored in these spheres at a petroleum refinery in California. Capacity of each is 15,000 barrels, diameter is 54 feet 9 inches and design working pressure is 35 pounds per square inch.); (upper right) two 5,000-barrel spheroids designed for 20-psi pressure; (lower left) large noded spheroids, each designed for 100,000-barrel capacity and 15-psi pressure; (lower right) a 20,000-barrel noded hemispheroid designed for 2-1/2-psi pressure (Chicago Bridge and Iron Company (1959).

pontoons, double pontoons, and high- and low-deck-pontoon floating-roof tanks are available today. Current practice is to use the pontoon roof on tanks with very large diameters. Included with some pontoon roof designs is a vapor trap or dam installed on the underside of the roof. This trap helps retain any vapors formed as a result of localized boiling and converts the dead vapor space into an insulation medium. This dead vapor space tends to retard additional boiling.

The more expensive double-deck floating roof was eventually introduced to reduce the effect of solar boiling and to gain roof rigidity. The final design generally incorporates compartmented dead-air spaces more than 12 inches deep over the entire liquid surface. The top deck is generally sloped toward the center or to a drainage area. Any liquid forming or falling on the roof top is drained

away through a flexible roof drain to prevent the roof from sinking. The bottom deck is normally coned upwards. This traps under the roof any vapors entrained with incoming liquid or any vapors that might form in storage. A vertical dam similar to those used on pan or pontoon floating roofs can also be added to retain these vapors.

#### Conservation Tanks

Storage vessels classified as conservation tanks include lifter-roof tanks and tanks with internal, flexible diaphragms or internal, plastic, floating blankets. The lifter roof or, as more commonly known, gas holder, is used for low-pressure gaseous products or for low-volatility liquids. This type of vessel can be employed as a vapor surge tank when manifolded to vapor spaces of fixed-roof tanks.

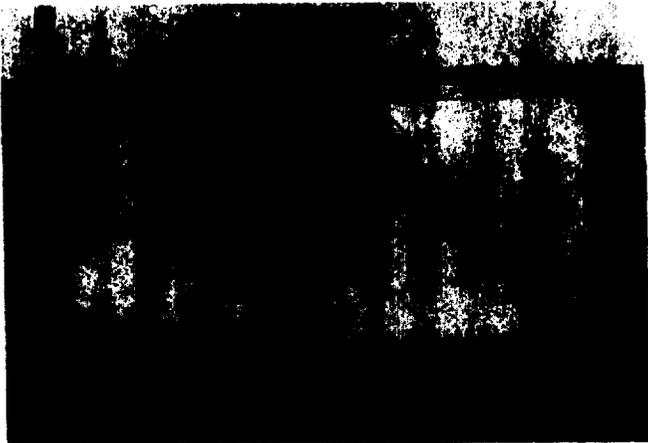


Figure 474. Vertical, cylindrical, fixed-roof storage tank.

Two types of lifter-roof tanks are available, as shown in Figure 476. One type has a dry seal consisting of a gastight, flexible fabric; the other type employs a liquid seal. The sealing liquid can be fuel oil, kerosene, or water. Water should not be employed as a sealing liquid where there is danger of freezing.

The physical weight of the roof itself floating on vapor maintains a slight positive pressure in the lifter-roof tank. When the roof has reached its maximum height, the vapor is vented to prevent overpressure and damage to tank.

The conservation tank classification also includes fixed-roof tanks with an internal coated-fabric diaphragm, as shown in Figure 477. The diaphragm is flexible and rises and falls to balance changes in vapor volume. Normal operating

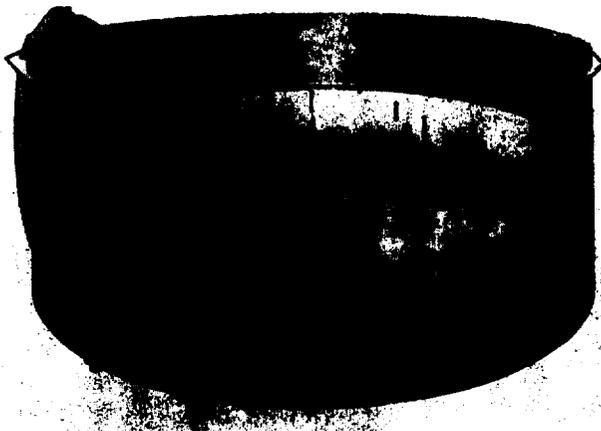


Figure 475. Types of floating-roof tanks: (upper left) Sectional view of single-deck, center-weighted (pan-type) floating roof; (upper right) sectional view of pontoon deck floating roof; (lower left) cutaway view of double-deck floating roof; (lower right) cutaway view of trussed-pan floating roof (Graver Tank and Manufacturing Company, East Chicago, Ind.).

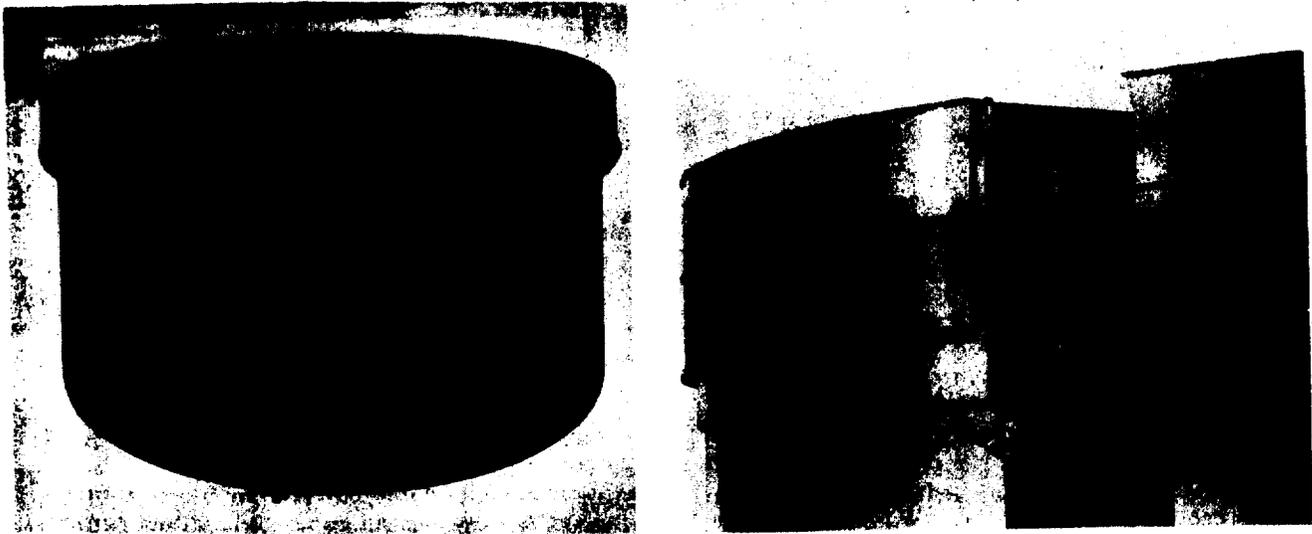


Figure 476. Types of lifter-roof tanks: (left) Sectional view of expansion roof tank with a liquid seal, (right) closeup view of liquid seal and vapor piping (Graver Tank and Manufacturing Co., Division of Union Tank Car Co., East Chicago, Indiana).

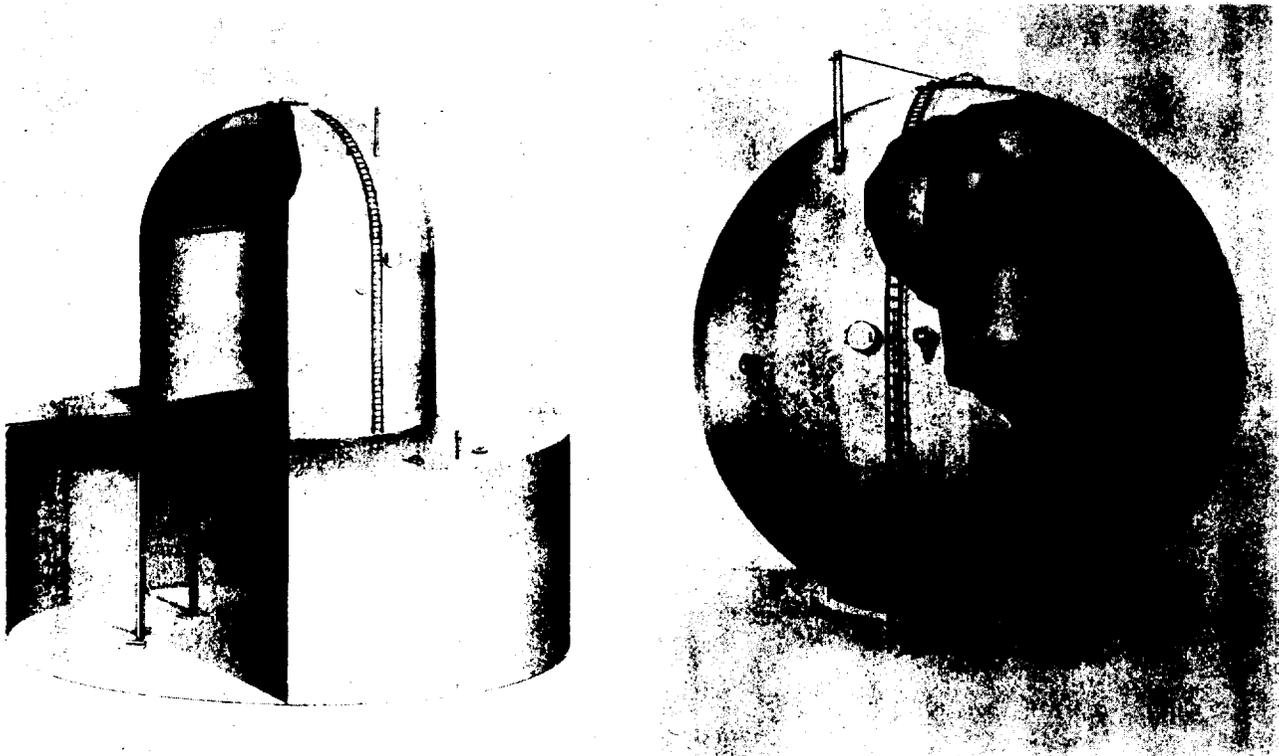


Figure 477. Conservation tanks; (left) Sectional view of integrated conservation tank with internal, flexible diaphragm; (right) cutaway view of a vapor conservation tank showing flexible membrane (Chicago Bridge and Iron Co., Chicago, Ill.).

pressure is 1/2 ounce per square inch, which is approximately one-eighth the operating pressure possible with most gas holders. Two basic types of diaphragm tanks are the integrated tank, which stores both liquid and vapor, and the separate tank, which stores only vapor. Common trade names for integrated tanks are "diaflote," "di-lift," and "vapor-mizer" tanks (Bussard, 1956), or they may be referred to as vapor spheres or vapor tanks. The separate type of tank offers more flexibility and does not require extensive alteration of existing tanks.

#### Open-Top Tanks, Reservoirs, Pits, and Ponds

The open-top tank is not used as extensively as in the past. Safety, conservation, and house-keeping are factors effecting the elimination of open vessels. Even tanks that require full access can and should be equipped with removable covers. The open vessels generally have a cylindrical shell, but some have a rectangular shell.

Reservoirs were devised to store the large quantities of residual oils, fuel oils, and, sometimes, crude oils resulting from petroleum production and refining. Safety considerations, larger fixed-roof tanks, and controlled crude oil production have reduced the number of reservoirs in use today. Even when covered, reservoirs have open vents, which maintain atmospheric pressures in the reservoir. Windbreaks divert the windflow pattern over a large roof area and prevent the roof from raising and buckling.

Open ponds or earthen pits were created by diking low areas or by excavation. These storage facilities served for holding waste products, refinery effluent water, or inexpensive oil products for considerable periods of time. In these, oils "weathered" extensively, leaving viscous, tar-like materials, and water seeped into the lower ground levels. As the pond filled with solids and semisolids, the contents were removed by mechanical means, covered in place, or the pond was simply abandoned. The use of these ponds has diminished, and the remaining ponds are usually reserved for emergency service.

Smaller ponds or sumps were once used extensively in the crude oil production fields. This use was primarily for drilling muds though oil-water emulsions and crude oil were also stored by this method. Their use is gradually disappearing because unattended or abandoned sumps cause nuisance problems to a community.

#### THE AIR POLLUTION PROBLEM

Different types and quantities of air pollution can be associated with the storage vessel. The types of

pollution can be separated into three categories-- vapors, aerosols or mists, and odors. Of these pollutants, the largest in quantity and concentration are hydrocarbon vapors.

#### Factors Affecting Hydrocarbon Vapor Emissions

Emissions of hydrocarbon vapors result from the volatility of the materials being stored. They are effected by physical actions on the material stored or on the storage itself. Changes in heat or pressure change the rate of evaporation. Heat is a prime factor and can cause unlimited vaporization of a volatile liquid. Heat is received from direct solar radiation or contact with the warm ambient air, or is introduced during processing. The rate of evaporation is correlated with atmospheric temperature, weather conditions, tank shell temperature, vapor space temperature, and liquid body and surface temperatures.

The vapor space of a tank can contain any degree of saturation of air with vapor of the liquid up to the degree corresponding to the total vapor pressure exerted by the liquid at storage temperatures. Since the pressure in this vapor space increases with temperature increase, some of the air-vapor mixture may have to be discharged or "breathed out" to prevent the safe operating pressure of the tank from being exceeded. These emissions are continually promoted by the diurnal change in atmospheric temperatures, referred to as the tank's breathing cycle.

When the air temperature cools, as at night, the vapor space within the tank cools and the vapors contract. Fresh air is drawn in through tank vacuum vents to compensate for the decrease in vapor volume. As this fresh air upsets any existing equilibrium of saturation by diluting the vapor concentration, more volatile hydrocarbons evaporate from the liquid to restore the equilibrium. When the atmospheric temperature increases, as occurs with daylight, the vapor space warms, and the volume of rich vapors and the pressure in the tank increase. In freely vented tanks, or when the pressure settings of the relief vents have been exceeded, the vapors are forced out of the tank. This cycle is repeated each day and night. Variation in vapor space temperature also results from cloudiness, wind, or rain.

Filling operations also result in expulsion of part or all of the vapors from the tank. The rate and quantity of vapor emissions from filling are directly proportional to the amount and the rate at which liquid is charged to the vessel. Moreover, as the liquid contents are withdrawn from the tank, air replaces the empty space. This fresh air allows more evaporation to take place.

Another emission of vapors caused by atmospheric conditions is termed a windage emission. This emission results from wind's blowing through a free-vented tank and entraining or educting some of the saturated vapors. The windage emission is not as large as that occurring during breathing or filling cycles. Other variables affecting emissions include: Volume of vapor space, frequency of filling, and vapor tightness of the vessel. Tanks that can be kept completely full of liquid limit the volume of the vapor space into which volatile hydrocarbons can vaporize and eventually be emitted to the atmosphere. The frequency of filling and emptying a tank influences the overall vapor emissions. When extensive periods of time elapse between pumping operations, the vapor space of a tank becomes more nearly fully saturated with vapor from the liquid. Then, during filling of the tank or during breathing cycles, a larger concentration of vapors exists in the air-vapor mixture vented to the atmosphere. Vapor tightness of the tank can influence the evaporation rate. The moving molecule in the vapor state tends to keep going if there is no restraining force such as a tight shell or roof.

Different causes of emissions are associated with a floating-roof tank. These causes are known as wicking and wetting. Wicking emissions are caused by the capillary flow of the liquid between the outer side of the sealing ring and the inner side of the tank wall. The wetting emission results when the floating roof moves towards the bottom of the tank during emptying and leaves the inner tank shell covered with a film of liquid, which evaporates when exposed to the atmosphere.

#### Hydrocarbon Emissions From Floating-Roof Tanks

The American Petroleum Institute (1962b) has published a method of determining the standing (wicking) and withdrawal (wetting) evaporation emissions associated with floating roof-tanks. The method is applicable to tanks in crude oil as well as gasoline service. It is based upon field test data for the standing emission, and laboratory data for the withdrawal emission. The correlation presents factors under many combinations of tank construction, type and condition of roof seal, and color of tank paint. Parameters include range of vapor pressure from 2 to 11 psia true vapor pressure, 4 to 16 mph average wind velocity, and 20- to 200-foot-diameter tanks.

The standing storage emission is determined from Table 166 and Figure 478. It is the product of emission factor  $L_f$  obtained from the graph and corresponding factors obtained from the table. One must know the following factors to find the value of the standing storage emissions: (1) Type

of product stored, (2) Reid vapor pressure, (3) average storage temperature, (4) type of shell construction, (5) tank diameter, (6) color of tank paint, (7) type of floating roof, (8) type and condition of seal, and (9) average wind velocity in area.

The standing storage emission formula is given as

$$L_y = k_t D^{1.5} \left( \frac{P}{14.7 - P} \right)^{0.7} V_w^{0.7} k_s k_c k_p \quad (138)$$

where  $L_y$  = standing storage evaporation emission, bbl/yr

$k_t$  = tank factor with values as follows:

0.045 for welded tank with pan or pontoon roof, single or double seal;

0.11 for riveted tank with pontoon roof, double seal;

0.13 for riveted tank with pontoon roof, single seal;

0.13 for riveted tank with pan roof, double seal;

0.14 for riveted tank with pan roof, single seal (double deck roof is similar to a pontoon roof);

$D$  = tank diameter, ft [for tanks larger than 150 ft in diameter use  $150^{1.5} (D/150)$ ]

$P$  = true vapor pressure of stock at its average storage temperature, psia

$V_w$  = average wind velocity, mph

$k_s$  = seal factor:

1.00 for tight-fitting seals (typical of modern metallic or tube seals)

1.33 for loose-fitting seals

$k_c$  = stock factor:

1.00 for gasoline stocks

0.75 for crude oils

$k_p$  = paint factor for color of shell and roof:

1.00 for aluminum or light grey

0.90 for white.

Actual standing storage emissions of petroleum hydrocarbons from tanks equipped with seals in good operation should not deviate from the estimated emissions determined by this equation by more than  $\pm 25$  percent. The actual emissions, however, can exceed the calculated amount by two or three times for a seal in poor condition.

The seal length can be expressed in terms of tank diameter because the two are directly proportional to each other. The actual emission is not di-

Table 166. STANDING STORAGE EVAPORATION EMISSIONS FROM FLOATING-ROOF TANKS:  
 $L_y$  (LOSS IN bbl/yr) =  $L_f$  (LOSS FACTOR FROM FIGURE 478) TIMES MULTIPLYING FACTOR  
 (FROM THIS TABLE; American Petroleum Institute, 1962b)

Multiplying factors apply to $L_f$	Welded tanks				Riveted tanks															
	Pan or pontoon roof				Pan roof								Pontoon roof							
	Single or double seal				Single seal				Double seal				Single seal				Double seal			
	Modern		Old <sup>a</sup>		Modern		Old <sup>a</sup>		Modern		Old <sup>a</sup>		Modern		Old <sup>a</sup>		Modern		Old <sup>a</sup>	
	Tank paint <sup>b</sup>		Tank paint		Tank paint		Tank paint		Tank paint		Tank paint		Tank paint		Tank paint		Tank paint		Tank paint	
	Lt grey	White	Lt grey	White	Lt grey	White	Lt grey	White	Lt grey	White	Lt grey	White	Lt grey	White	Lt grey	White	Lt grey	White	Lt grey	White
Gasoline	1.0	0.90	1.33	1.20	3.2	2.9	4.2	3.8	2.8	2.5	3.8	3.4	2.8	2.5	3.8	3.4	2.5	2.2	3.3	3.0
Crude oil	0.75	0.68	1.0	0.90	2.4	2.2	3.1	2.8	2.1	1.9	2.8	2.5	2.1	1.9	2.8	2.5	1.9	1.7	2.5	2.2

<sup>a</sup>Seals installed before 1942 are classed as old seals.  
<sup>b</sup>Aluminum paint is considered light grey in loss estimation.

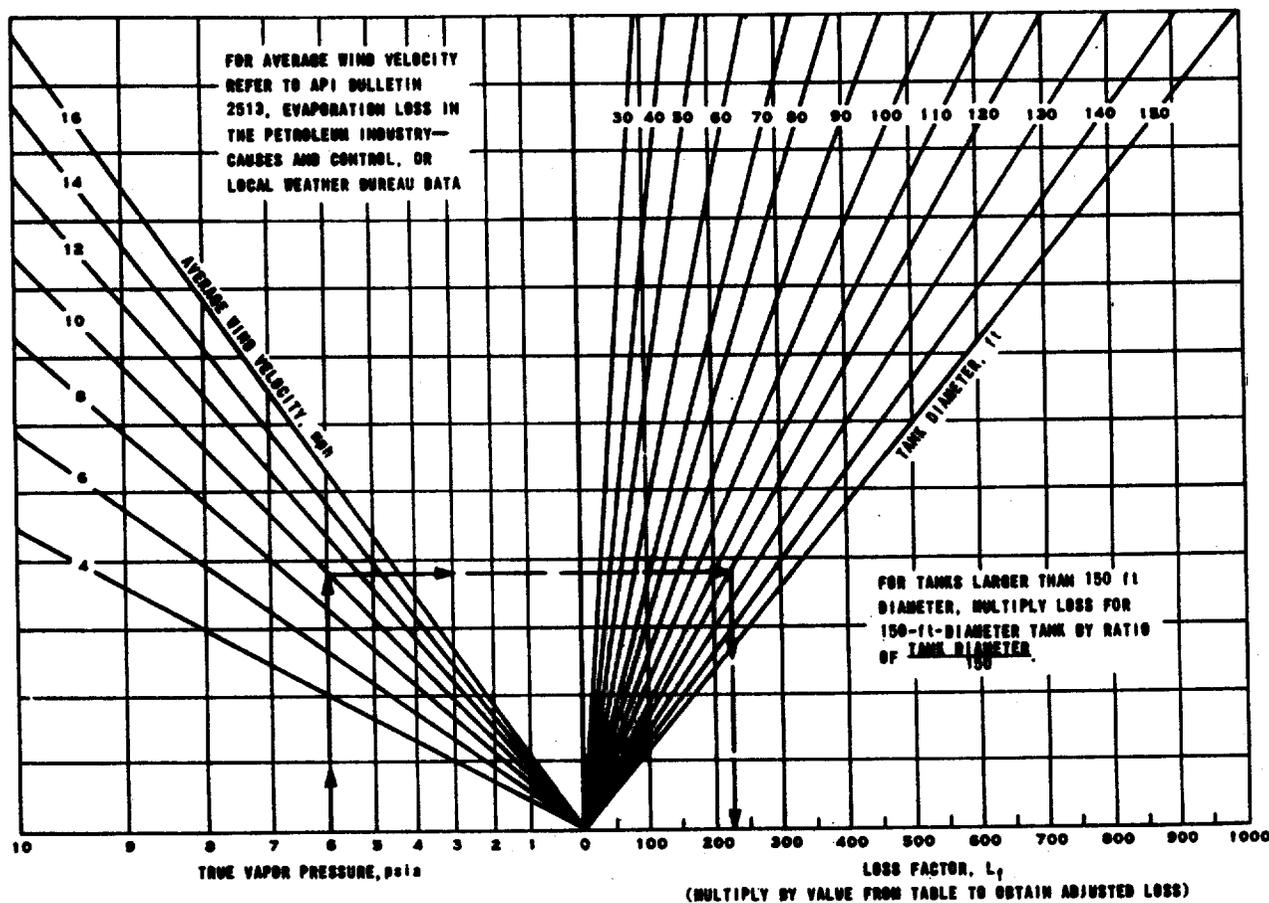


Figure 478. Calculation of emission factor,  $L_f$ , for standing storage evaporation emissions from floating-roof tanks (see Table 166).

rectly proportional to the diameter because several other variables are involved. Items such as wind velocity and the decreased shading effect of the shell on the roof of large-diameter tanks are examples.

Emissions increase, but not directly, as the vapor pressure increases. The relationship  $P/(14.7 - P)$  correctly identifies this phenomenon, and no substantial error exists within the valid range of this correlation.

Standing storage emissions increase but do not double when the average wind velocity doubles. The 0.7 exponent applied to the wind factor fits data for average wind velocities exceeding 4 mph. No localities were recorded as having less than this 4 mph average wind velocity.

#### Withdrawal emissions

As product is withdrawn from a floating-roof tank, the wetted inner shell is exposed to the atmosphere. Part of the stock clinging to the inner surface drains down the shell. The remainder evaporates to the atmosphere. Tests made determined the amount of gasoline clinging to a rusty steel surface as ranging from 0.02 to 0.10 barrel of gasoline per 1,000 square feet of surface.

The withdrawal emissions are represented by the equation

$$W = 22,400 \left( \frac{C}{D} \right) \quad (139)$$

where

W = withdrawal emissions, bbl per million bbl throughout

C = 0.02 (based on barrels of clingage per 1,000 ft<sup>2</sup> of shell surface)

D = tank diameter, ft

Withdrawal emissions for gunited tanks can be significant. Laboratory data indicated a factor of C = 2.0. Since withdrawal emissions counter standing storage emissions, a factor C = 1.0 is recommended for gunite-lined tanks storing gasoline.

#### Application of results

The emissions from floating-roof tanks can be estimated from Table 166. Necessary data include: Tank diameter; color of tank paint; type of tank shell, roof, and seal; Reid vapor pressure and average temperature of stored product; and the average wind velocity at tank site.

The true vapor pressure, P, can be obtained from vapor pressure charts by the use of data in Figures 479 and 480. To use these charts, one must know the Reid vapor pressure of the stock. Figure 479 is used for gasoline or other finished stocks. The value of S (slope of the ASTM distillation curve at 10 percent evaporated) can be estimated by using suggested values given in a note of the chart. The value of S is zero for a single component stock. The vapor pressure chart, Figure 480, should be used for crude oils.

This chart is intended for stabilized crudes that have not been subjected to extreme weathering or mixed with light oils.

The average stock temperatures should be used in these vapor pressure determinations.

Withdrawal emissions should be added to the standing storage emissions when gunited tanks are encountered.

#### Hydrocarbon Emissions From Low-Pressure Tanks

Low-pressure tanks are used to store petroleum stocks of up to 30 pounds RVP\* with relief valve settings of 15 psig. The American Petroleum Institute's Evaporation Loss Committee (1962c) recommends a theoretical approach to emission calculations from tanks such as these. Insufficient data are available to establish any accurate correlation with actual field conditions.

Application of the following equation indicates the theoretical pressure (P<sub>2</sub>) required to prevent breathing losses:

$$P_2 = 1.1 (P_a + P_1 - p_1) - (P_a - p_2) \quad (140)$$

where

P<sub>2</sub> = gage pressure at which pressure vent opens, psig

P<sub>a</sub> = atmospheric pressure

P<sub>1</sub> = gage pressure at which vacuum vent opens, psig

p<sub>1</sub> = true vapor pressure at 90°F minimum liquid surface temperature, psia

p<sub>2</sub> = true vapor pressure at 100°F maximum liquid surface temperature, psia.

This equation is applicable only when the vapor pressure at minimum surface temperature (P<sub>1</sub>) is less than the absolute pressure (P<sub>1</sub> + P<sub>a</sub>) at which the vacuum vent opens. Air always exists in the vapor space under a condition such as this. Figure 481 is a plot of equation 140. The pressure required to eliminate breathing emissions from products ranging up to 17.5 psia TVP† at 100°F storage temperature and 14.7 atmospheric pressure can be determined from this curve. The gage pressure at which the vacuum vent opens

\*RVP refers to Reid vapor pressure as measured by ASTM D 323-5b Standard Method of Test for Vapor Pressure of Petroleum Products (Reid Method).

†TVP refers to true vapor pressure.

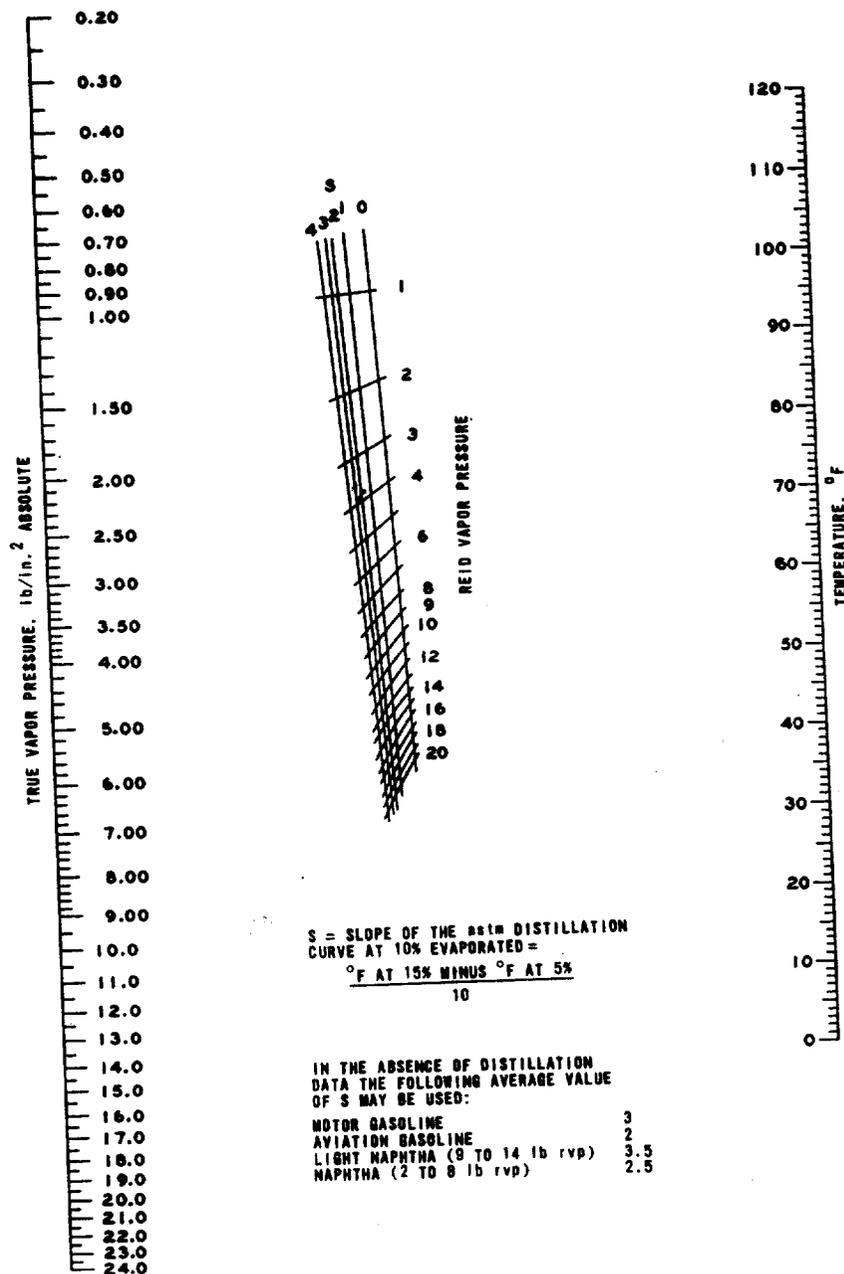


Figure 479. Vapor pressures of gasolines and finished petroleum products, 1 lb to 20 lb RVP. Nomograph drawn from data of the National Bureau of Standards (American Petroleum Institute, 1962b).

( $P_1$ ) is zero for this curve. The values of  $p_1$  and  $P_2$  were obtained from Figure 479. Since higher vapor pressure stocks have a smaller distillation slope ( $s$ ), a range of distillation slopes was used.

The altitude of the storage vessel's location affects the required storage pressure. Proper adjustments for various altitudes can be made by substituting the proper atmospheric pressure ( $P_a$ ) in equation 140. Table 167 lists atmospheric pressures at various altitudes.

Some pressure tanks must be operated at relatively low pressures--some by design, others because of corroded tank conditions. Pressure settings from zero to 2.5 psig are believed to decrease the breathing emissions from 100 percent to zero percent, depending upon the vapor pressure of the material stored. This is shown in Figure 482. Each additional increment of pressure reduces the breathing emissions by a progressively smaller amount. Boiling emissions occur when the true vapor pressure of the liquid exceeds the pressure

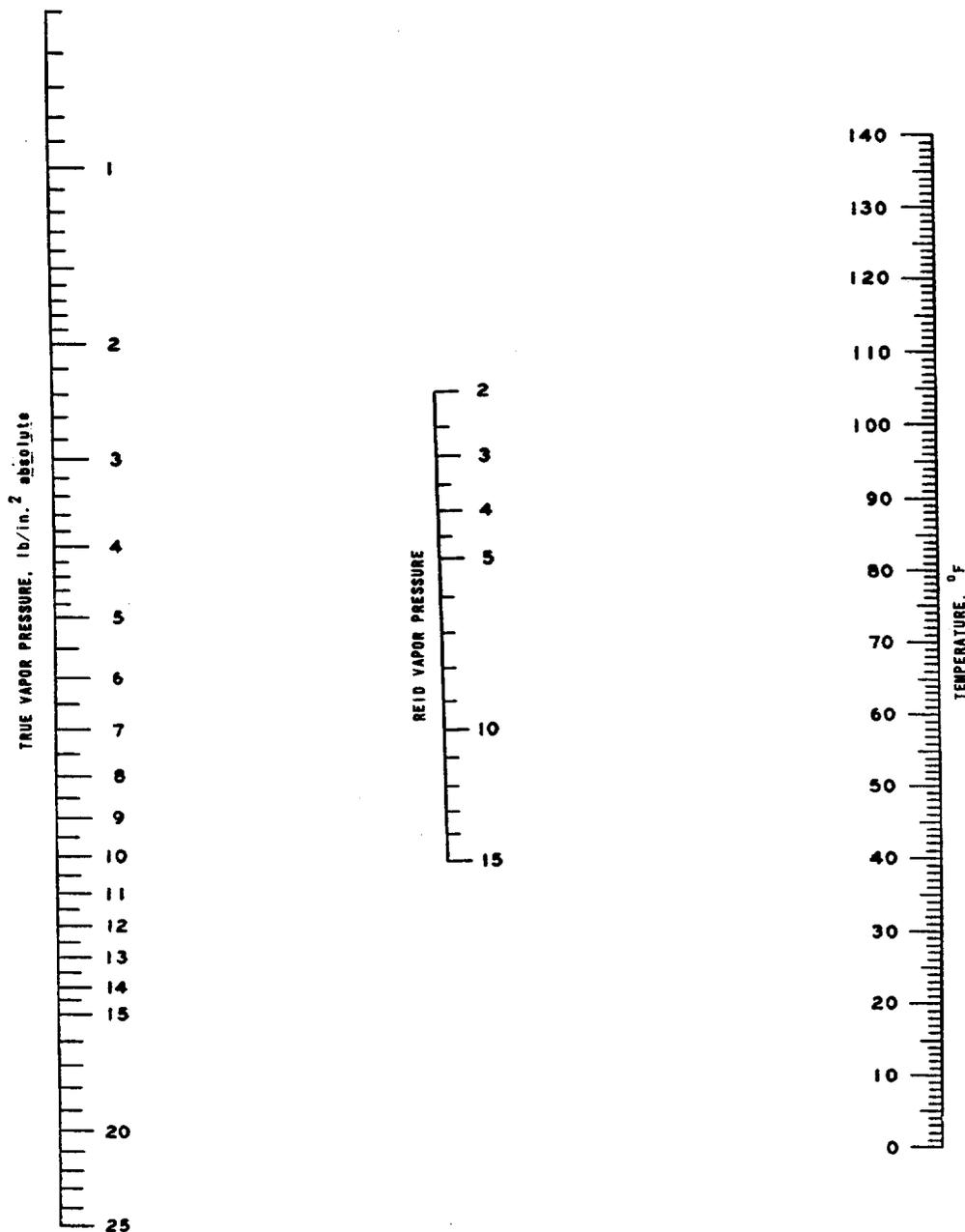


Figure 480. Vapor pressures of crude oil (American Petroleum Institute, 1962b).

Table 167. ATMOSPHERIC PRESSURE AT ALTITUDES ABOVE SEA LEVEL (American Petroleum Institute, 1962c)

Altitude, ft	Pressure, psia
1,000	14.17
2,000	13.66
3,000	13.17
4,000	12.69
5,000	12.23

vent setting. If this vapor pressure equals or exceeds the absolute pressure ( $P_1 + P_a$ ) at which the tank vent opens, air is kept out of the tank. The absolute tank pressure then equals the vapor pressure of the liquid at the liquid surface temperature. The storage pressure required to prevent boiling is

$$P_2 = P_2 - P_a \quad (141)$$

This equation is also indicated in Figure 481. These minimum pressure requirements have

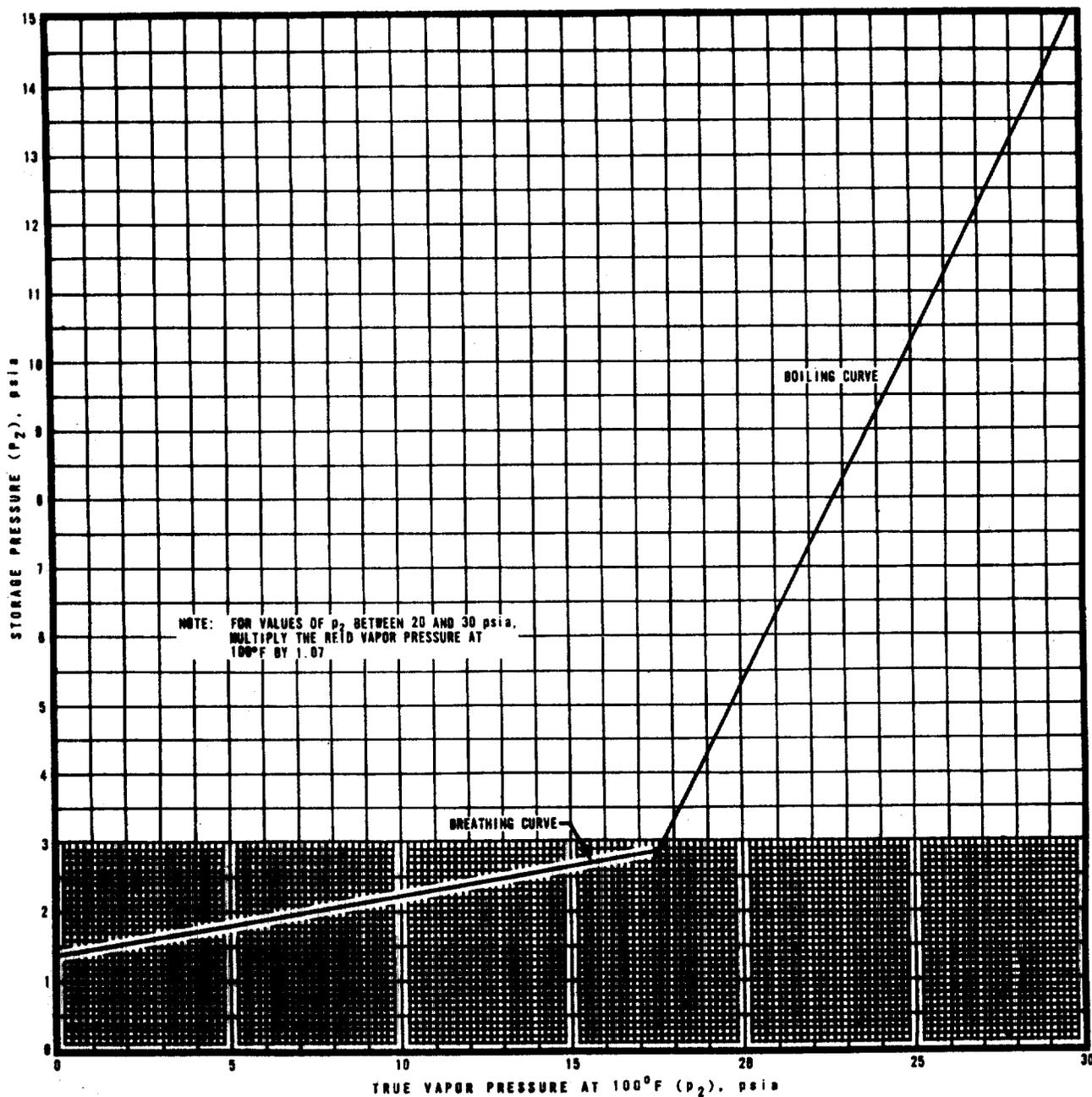


Figure 481. Storage pressure required to eliminate breathing and boiling losses. For values of  $p_2$  between 20 and 30 psia, multiply the Reid vapor pressure at 100°F by 1.07 (American Petroleum Institute, 1962c).

proved adequate to prevent boiling emissions under usual storage conditions. The true vapor pressure at 100°F can be obtained from Figure 479 up to 20 pounds RVP. In the range of 20 to 30 RVP,  $P_2$  is approximately 7 percent higher than the RVP at 100°F.

A filling or working emission occurs if the tank pressure exceeds the vent setting. During the initial stage of filling, compression of the air-hydrocarbon mixture with some condensation of

vapor takes place if the tank pressure is less than the pressure vent setting. This condensation maintains a fairly constant hydrocarbon partial pressure. Thus, a certain fraction of the vapor space can be filled with a liquid before the tank pressure increases above the vent setting. As filling continues, the total pressure increases to the pressure at which the relief valve opens. Venting to the atmosphere occurs beyond this point. If there is no change in temperature of the liquid or vapor during the filling

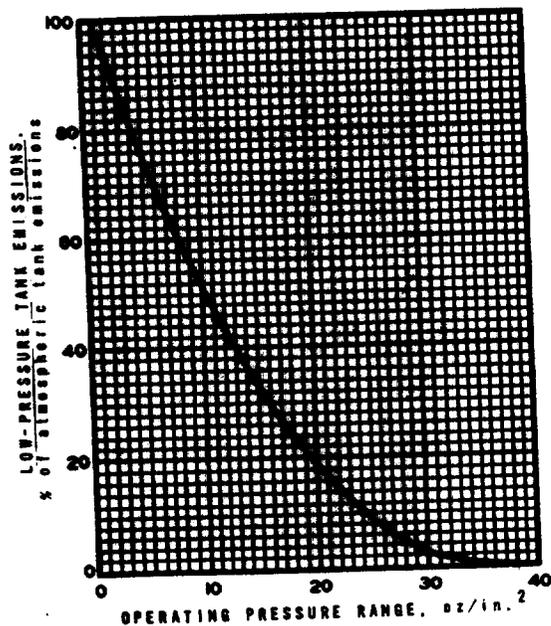


Figure 482. Relationship for estimating motor gasoline breathing emissions from tanks operating at less than the recommended 2.5-psig vent setting (American Petroleum Institute, 1962c).

period, the liquid entering the tank displaces to the atmosphere an equal volume of vapors.

The total emissions depend upon the capacity of the vapor space of the tank. Since the temperature changes as condensation occurs, the rates of filling and emptying can also affect the vapor emissions. These variables increase the difficulty of determining the actual emissions. In order that theoretical emissions can be calculated, two assumptions are made:

1. Equilibrium exists between the hydrocarbon content in the vapor and liquid phases under given temperature and pressure conditions.
2. Filling begins at slightly below atmospheric pressure.

The following equation can then be derived:

$$F_v = \frac{3 P_v (P_a - P_1 - P_v)}{100 (P_a + P_2 - P_v)} \quad (142)$$

where

- $F_v$  = working emissions, % of volume pump
- $P_v$  = true vapor pressure at liquid temperature, psia
- $P_a$  = atmospheric pressure, psia

$P_1$  = gage pressure at which vacuum vent opens, psig

$P_2$  = gage pressure at which pressure vent opens, psig.

This calculated emission is correct on the assumption that the vapor pressure of the liquid at its surface temperature and the vapor space temperature are the same at the start and end of filling. The emissions, expressed as a percentage, are reduced to the extent that the tank is not completely filled.

Obtaining the true liquid-surface temperature is difficult. Thus, the value of  $p_v$  is based upon the average main body temperature of the liquid. As a result of possible variables, the required pressure to prevent breathing emissions from low-pressure tanks, as found by Figure 481, should be considered to have no pressure rise available to decrease the working emissions. The working emissions can be found in the same manner as for an atmospheric tank.

Figure 483 is based upon equation 142, except that the emission values are plotted for various vapor pressures and pressure vent settings greater than atmospheric pressure. The straight line gives theoretical filling emissions from tanks with vents set at only slightly greater than atmospheric pressure. The values are representative for 12 turnovers per year normally experienced with this type of low-pressure storage.

#### Hydrocarbon Emissions From Fixed-Roof Tanks

A revised method of determining hydrocarbon emissions from fixed-roof tanks has been published by the American Petroleum Institute (1962a). Various test data were evaluated and correlated to obtain methods of estimating breathing emissions and filling and emptying (working) emissions from fixed-roof storage tanks. The method is applicable to the full range of petroleum products, from crude oil to finished gasoline. Data were considered only for tanks with tight bottoms, shells, and roofs. All tank connections were assumed to be vapor tight and liquid tight. Of 256 separate tests recorded and screened, 178 were found acceptable for correlation. A limited number of factors were definitely found to establish a correlation. The following factors were applied in the correlation:

1. True vapor pressure,  $P$ , at storage conditions, in pounds per square inch absolute (if temperature of the liquid was not available, a temperature 5°F above average atmospheric temperature was selected);
2. tank diameter,  $D$ , in feet;

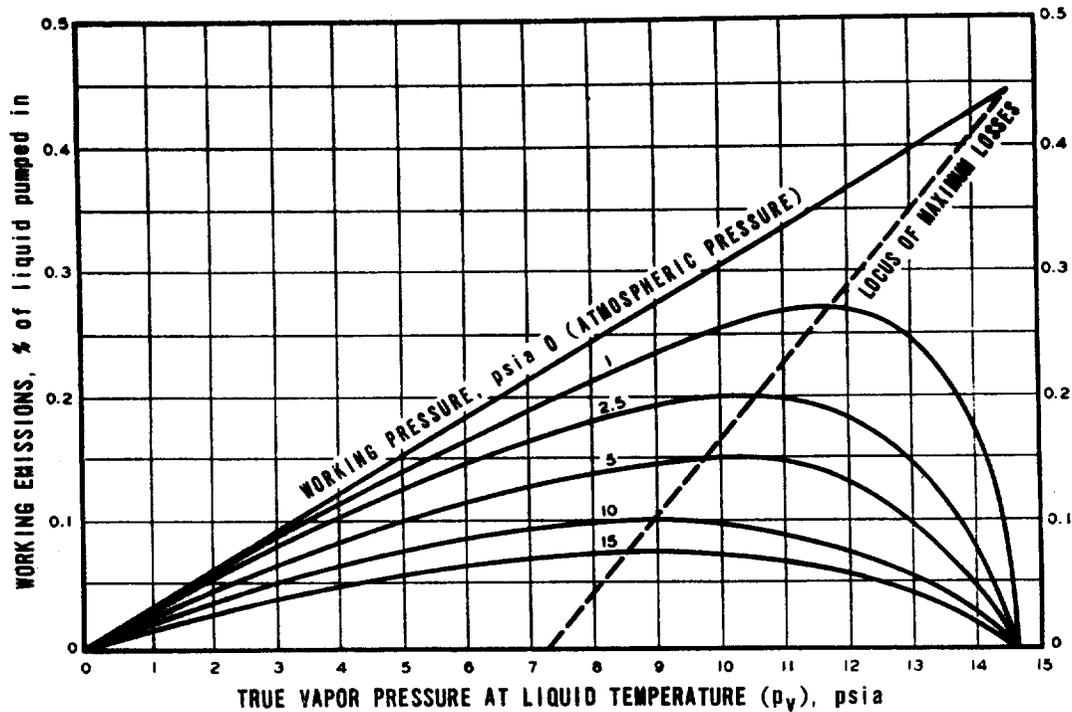


Figure 483. Emissions, % volume pumped into tank for various vent settings.  $\Delta P$  is the difference between the pressure vent setting and the pressure required to prevent breathing loss (American Petroleum Institute, 1962c).

3. average tank outage,  $H$ , in feet (outage involves height of the vapor space and includes an allowance for the roof);
4. average daily ambient temperature change,  $T$ , in degrees Fahrenheit, as reported by the U.S. Weather Bureau for area where tank is located;
5. paint factor  $F_p$  (vessels with white paint in good condition have a factor of unity).

A correlation applicable to tanks with diameters of 20 feet or larger was developed:

$$L_y = \frac{24}{1,000} \left( \frac{P}{14.7 - P} \right)^{0.68} D^{1.73} H^{0.51} T^{0.50} F_p \quad (143)$$

where

- $L_y$  = breathing emissions, bbl/yr  
 $P$  = true vapor pressure at bulk liquid temperature, psia, from Figure 479. If the average liquid body temperature is not available, it may be estimated at 5°F above average ambient temperature  
 $D$  = tank diameter, ft

$H$  = average outage, ft. This value includes correction for roof volume. A cone roof is equal in volume to a cylinder with the same base diameter of the cone and one-third the height of the cone

$T$  = average daily ambient temperature change, °F

$F_p$  = paint factor (see Table 168).

Smaller diameter tanks require a modification of equation 143. Observed emissions were less than calculated emissions for tanks of less than 30 feet diameter. If an adjustment factor, as indicated in Figure 484, is applied to the calculated emissions from equation 143, the correlation between observed and calculated data becomes more exact. By combining the adjustment factor with the tank diameter factor, a final equation is

$$L_y = \frac{24}{1,000} \left( \frac{P}{14.7 - P} \right)^{0.68} D^{1.73} H^{0.51} T^{0.50} F_p C \quad (144)$$

where

$C$  = an adjustment factor for small-diameter tanks, determined from Figure 484. For

Table 168. PAINT FACTORS FOR DETERMINING  
EVAPORATION EMISSION FROM FIXED-ROOF TANKS  
(American Petroleum Institute, 1962a)

Tank color		Paint factor	
Roof	Shell	Paint in good condition	Paint in poor condition
White	White	1.00	1.15
Aluminum <sup>a</sup>	White	1.04	1.18
White	Aluminum <sup>a</sup>	1.16	1.24
Aluminum <sup>a</sup>	Aluminum <sup>a</sup>	1.20	1.29
White	Aluminum <sup>b</sup>	1.30	1.38
Aluminum <sup>b</sup>	Aluminum <sup>b</sup>	1.39	1.46
White	Gray	1.30	1.38
Light gray	Light gray	1.33	1.38
Medium gray	Medium gray	1.46	1.38

<sup>a</sup>Specular.

<sup>b</sup>Diffuse.

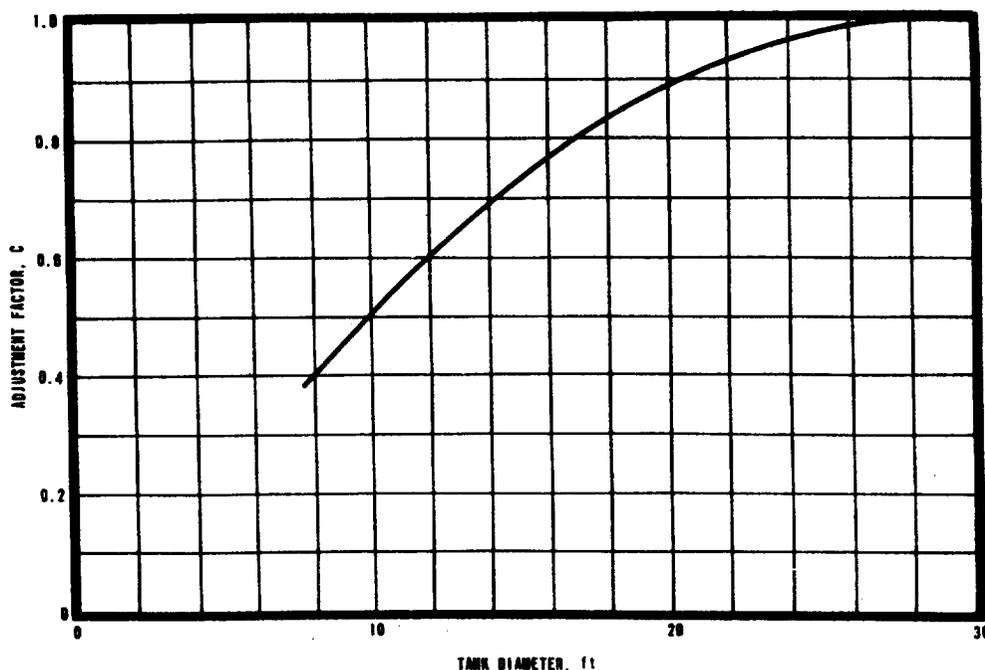


Figure 484. Adjustment factor for small-diameter tanks  
(American Petroleum Institute, 1962a).

tanks 30 feet or more in diameter, use a factor = 1. The breathing emissions from fixed-roof tanks can also be estimated from Figure 485, as well as from equation 144.

The working emissions include two phases of storage: (1) The filling emissions under which vapors are displaced by incoming liquid, and (2) the emptying emissions, which draw in fresh air and thus allow additional vaporization to take place.

Variables considered in determining this loss are true vapor pressure, throughput, and tank turnovers, which yield the equation:

$$F = \left( \frac{3 PV}{10,000} \right) K_t \quad (145)$$

where

F = working loss, bbl



$P$  = true vapor pressure at storage temperatures, psia (if these temperature data are not available, estimation of 5°F above average ambient temperature is satisfactory)

$V$  = volume of liquid pumped into tank, bbl

$K_t$  = turnover factor determined from Figure 486.

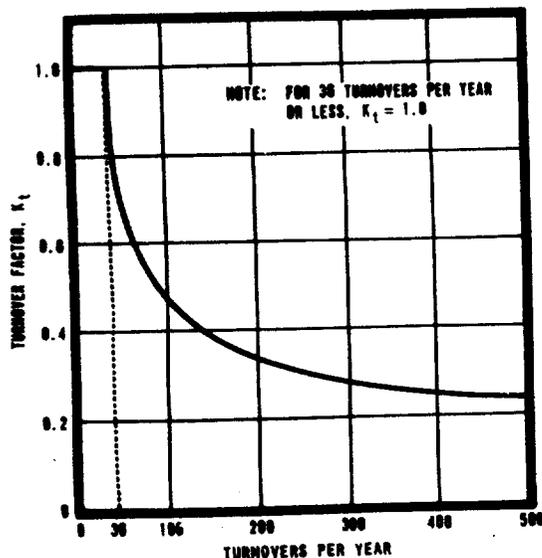


Figure 486. Effect of turnover on working emissions. For 36 or less turnovers per year,  $K_t = 1.0$  (American Petroleum Institute, 1962a).

By using equation 145, a nomograph has been developed in Figure 487 showing the working emissions of gasoline and crude oil from fixed-roof tanks. Limited data resulted in the committee's using the same formula for crude oil breathing emissions as for gasoline breathing emissions with an applied adjustment factor  $K_c$ . This approach is based upon an assumption that the emissions from crude oil storage vary in the same manner as the emissions from gasoline storage, calculated from variables in equation 143. The adjustment factor,  $K_c$ , represents the ratio between the respective emissions. The true vapor pressure of crude oil must be determined from Figure 480. This figure applies to stabilized crude oil only. The breathing emission factor of 0.58 results in part from slower convective movement. This is true in the case of a liquid surface less volatile than the body of the liquid. In considering the working emissions from crude oil storage, however, filling cycles are normally less frequent than daily breathing cycles are. Thus more crude oil evaporates between cycles, creating a more saturated vapor space. The action of

filling causes fresh liquid to move to the surface. A factor somewhere between 0.58 and unity appears feasible. A review of the scattered data available supports a factor of 0.75. Equation 145 then becomes

$$F_{co} = \left( \frac{2.25 PV}{10,000} \right) K_t \quad (146)$$

where

$F_{co}$  = working emissions for crude oil, bbl

$P$  = true vapor pressure, psia, determined from Figure 439 (again this may be estimated at 5°F higher than average ambient temperature in lieu of better data)

$V$  = volume pumped into tank, bbl

$K_t$  = turnover factor, determined from Figure 486.

#### Aerosol Emissions

Storage equipment can also cause air pollution in the form of aerosols or mists. An aerosol-type discharge is associated with storage of heated asphalt. This discharge is more predominant during filling operations. The reasons for this emission, other than basic displacement, are not thoroughly understood. Continued oxidation of the asphalt followed by condensation, or condensation of any moisture in the hot gases upon their entering the cooler atmosphere, are believed to be the primary causes of the mists. An analysis conducted during the filling operation found essentially air and water as the main components of the displaced vapor. Table 169 shows the results of this analysis. These vapors are frequently highly odoriferous.

Whenever live steam or air is added to a vessel for mixing, heating, oxidizing, or brightening, droplets or aerosols can be entrained with the discharge gases. Visible discharges, product loss, and odors can result.

#### Odors

The release of odors is closely related to evaporation and filling operations associated with the storage vessel. The concentration of odors is not, however, directly proportional to the amount of material released. Some relatively heavy compounds are very noticeable at dilutions of 1 to 5 ppm. These compounds are often toxic or highly malodorous and generally contain sulfur or nitrogen compounds.

Agitation, especially by means of air or live steam, will increase the release of odors to the atmosphere.

**AIR POLLUTION CONTROL EQUIPMENT**

Control of air pollution originating from storage vessels serves a three-fold purpose: (1) Elimina-

tion or reduction of air contaminants, (2) elimination or reduction of fire hazards, and (3) economic savings through recovery of valuable products. Methods of control include use of floating roofs, plastic blankets, spheres, variable vapor space systems, various recovery systems, and altered pumping and storage operations.

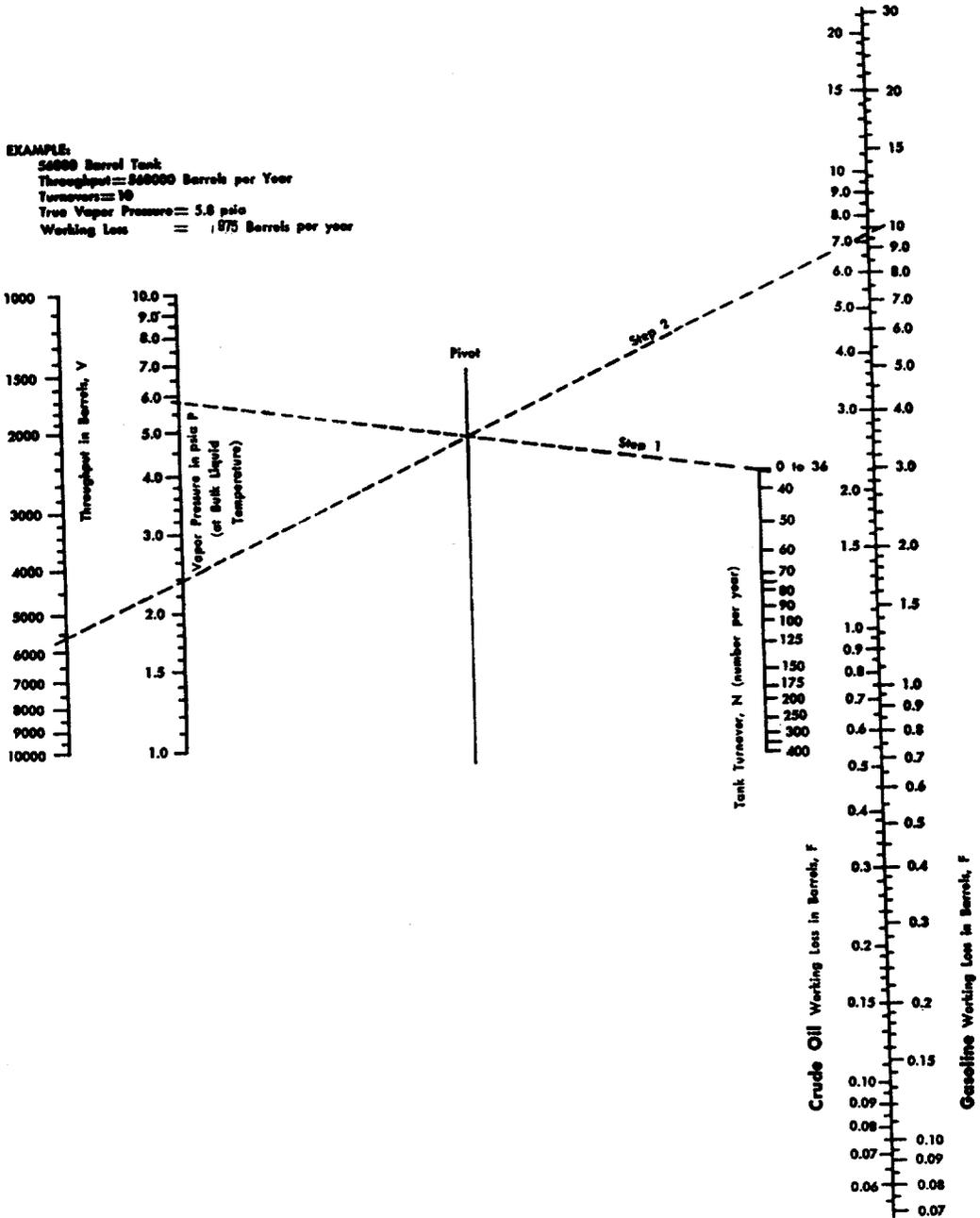


Figure 487. Working emissions of gasoline and crude oil from fixed-roof tanks. The throughput is divided by a number (1,10,100,1,000) to bring it into the range of the scale. The working emission, read from the scale, must then be multiplied by the same number (American Petroleum Institute, 1962a).

Table 169. ANALYSIS OF VAPORS DISPLACED DURING FILLING 85/100 PAVING-GRADE ASPHALT INTO A FIXED-ROOF TANK<sup>a</sup>

Component	Volume %
Methane	Trace
Ethane	Trace
Heavy hydrocarbons (28° API gravity)	0.1
Nitrogen	67.3
Oxygen	13.0
Carbon dioxide	1.4
Water	18.2
Argon	Trace

<sup>a</sup>Sample was collected over 3-1/2-hour filling period, the noncondensables were analyzed by mass spectrometer. Condensable hydrocarbons were separated from the steam, and gravity and distillation curves were determined.

### Seals for Floating-Roof Tanks

The principle by which a floating roof controls emissions from a volatile liquid is that of eliminating the vapor space so that the liquid cannot evaporate and later be vented. To be successful the floating roof must completely seal off the liquid surface from the atmosphere (Chicago Bridge and Iron Company, 1959). The seal for the floating roof is therefore very important. A sectional view of the sealing mechanism is shown in Figure 488. The floating section is customarily constructed about 8 inches less in diameter than the tank shell. A sealing mechanism must be provided for the remaining open annular gap. The seal also helps keep the roof centered.

Conventional seals generally consist of vertical metal plates or shoes connected by braces or pantograph devices to the floating roof. The shoes are suspended in such a way that they are forced outward against the inner tank wall. An impervious fabric bridges the annular area between the tops of the shoes contacting the tank wall and the circumference of the floating roof. To reduce emissions, a secondary seal or wiper blade has been added to the floating-roof design by extending the fabric seal or by adding a second section of fabric as shown in Figure 489. This seal remains in contact with the tank wall. Its flexibility allows it to make contact even in rivet head areas of the inner shell or in places where the shell might be slightly out of round. This improvement lowers hydrocarbon emissions further by reducing the effect of wetting and wicking associated with floating-roof tanks.

Recently, other types of sealing devices to close the annular gap have been marketed, as shown in Figure 490. These devices consist of a fabric tube that rests on the surface of liquid exposed



Figure 488. Sectional view of double-deck floating-roof's sealing mechanism (Chicago Bridge and Iron Co., Chicago, Ill.).

in the annular space. The fabric tube is filled with air, liquid or plastic material. The pneumatic, inflated seal is provided with uniform air pressure by means of a small expansion chamber and control valves. The sides of the tube remain in contact with the roof and inner shell. The liquid-filled tube holds a ribbed scuff band against the tank wall. The ribbed band acts as a series of wiper blades as well as a closure. All tubes are protected by some type of weather covering.

A weather covering can also be added to protect the sealing fabric of the conventional seals. The covering includes flat metal sections held in place by a metal band. The metal protects the fabric seal from the elements. When floating-roof sections are added to older tanks constructed of riveted sections, better contact of the shoes with the shell can be ensured by guniting or plastic coating the inner shell. The wetting condition of guniting walls may, however, offset the gain of better contact.

### Floating Plastic Blankets

A floating plastic blanket, operates on the same principle of control as a floating roof. It is also

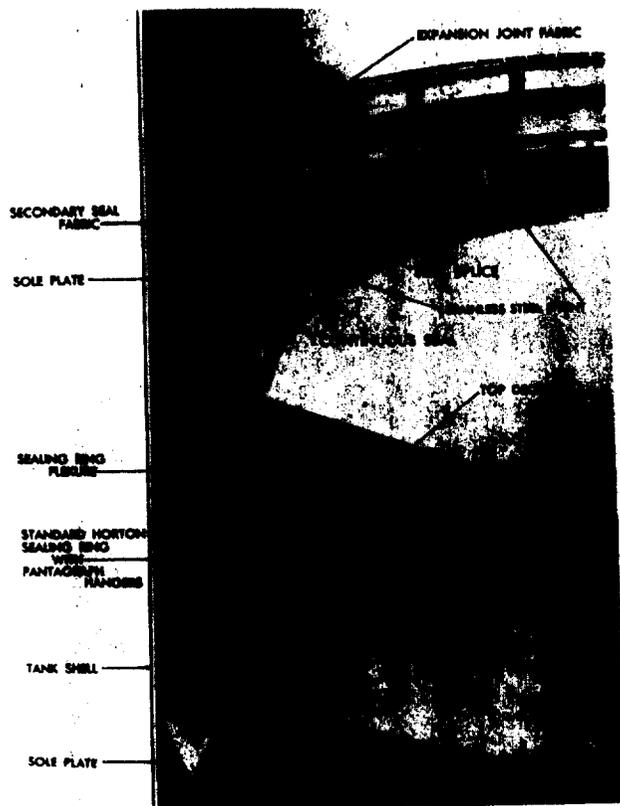


Figure 489. Secondary seals stop vapor loss from high winds on riveted tanks by sealing off the space between the tank shell and the sealing ring sole plate (Chicago Bridge and Iron Co., Chicago, Ill.).

available as a surface cover, as depicted in Figure 491. It was developed in France and has been tried principally in foreign markets (Laroche Bouvier and Company). Recent applications have been made in the United States. The blanket is usually made of polyvinyl chloride but can be made of other plastics such as polyvinyl alcohol, superpolyamides, polyesters, fluoride hydrocarbons, and so forth. The blanket's underside is constructed of a large number of floats of the same plastic material. The blanket is custom manufactured so that only a 1-inch gap remains around the periphery. A vertical raised skirt is provided at the edge of the blanket to serve as a vapor seal over the annular area. Once this area is saturated, further evaporation diminishes. The only remaining loss is gaseous diffusion. The seal is made as effective as possible by using an elastic, Z-shaped skirt.

Provisions are made in the blanket for openings fitted with vertical sleeves for measuring and sampling operations. These openings have a crosscut, flexible inner diaphragm to minimize exposure of the liquid surface. Small holes with downspouts to effect a liquid seal are used to provide drainage of any condensate from the

top of the blanket. Another feature includes a stainless steel cable grid to prevent a buildup of static charges. The grid is closely attached just under the blanket in parallel lines and connected to the tank shell by a flexible conductor cable. Installation of a plastic blanket is convenient for both new and existing tanks. The blanket is made in sections and can be introduced into a tank through a manhole.

A rigid foam-plastic cover constructed of polyisocyanate foam is also available to equip small fixed-roof tanks with a floating cover. The cover is manufactured in radial sections, each equipped with a flexible neoprene seal attached on the outer edge. The sections are easily installed through roof manholes and assembled with slip-fit joints.

### Plastic Microspheres

An outgrowth of application of plastic material provides another type of control mechanism. This type of control is also similar to the floating roof. A phenolic or urea resin in the shape of tiny, hollow, spherical particles has been developed by Standard Oil Company of Ohio (American Petroleum Institute, 1962d). This material has the physical properties necessary to form a foam covering over the denser petroleum products. The fluidity of the layer enables it to flow around any internal tank parts while keeping the liquid surface sealed throughout any level changes. These plastic spheres are known under their trademark names of microballoons or Microspheres. These coverings have proved to be effective controls for fixed-roof crude oil tanks. Excessive amounts of condensation or high turbulence should be avoided. The plastic foam has not proved as satisfactory for one-component liquid or gasoline products.

A 1/2-inch layer of foam has been found sufficient for crude oil where pumping rates do not exceed 4,000 barrels per hour. A layer 1 inch thick is recommended for pumping rates up to 10,000 barrels per hour. In order to overcome wall holdup in smaller tanks, it is suggested that a 1-inch layer be used regardless of pumping rates. For tanks storing gasoline, the recommended foam thickness is 2 inches for tanks up to 40 feet in diameter, and 1 inch for all larger diameter vessels.

Various methods can be used to put the foam covering on the crude oil. One method is to inject the plastic spheres with the crude oil as it is charged to the tank. Spheres are added by means of an aspirator and hopper similar to equipment used in fire-fighting foam systems. The spheres can also be added by placing the desired quantity

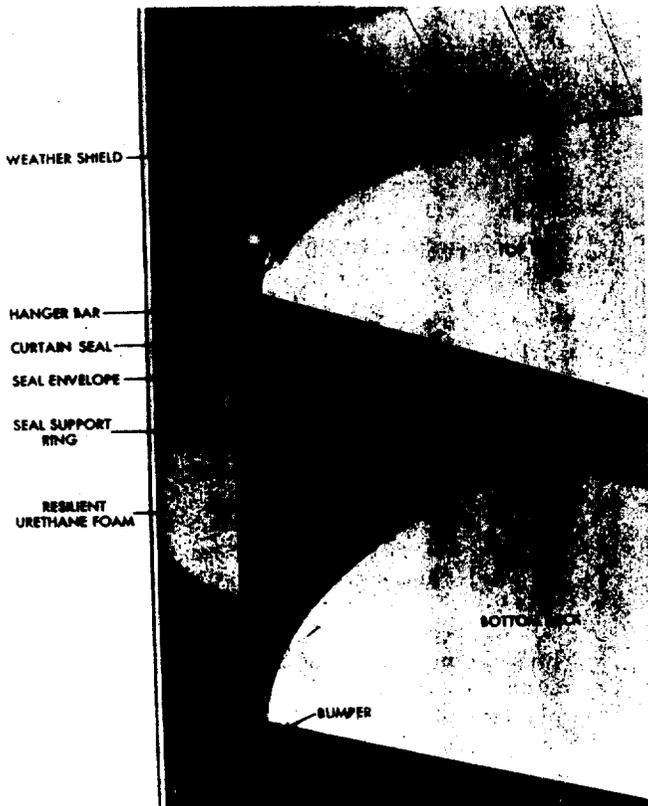
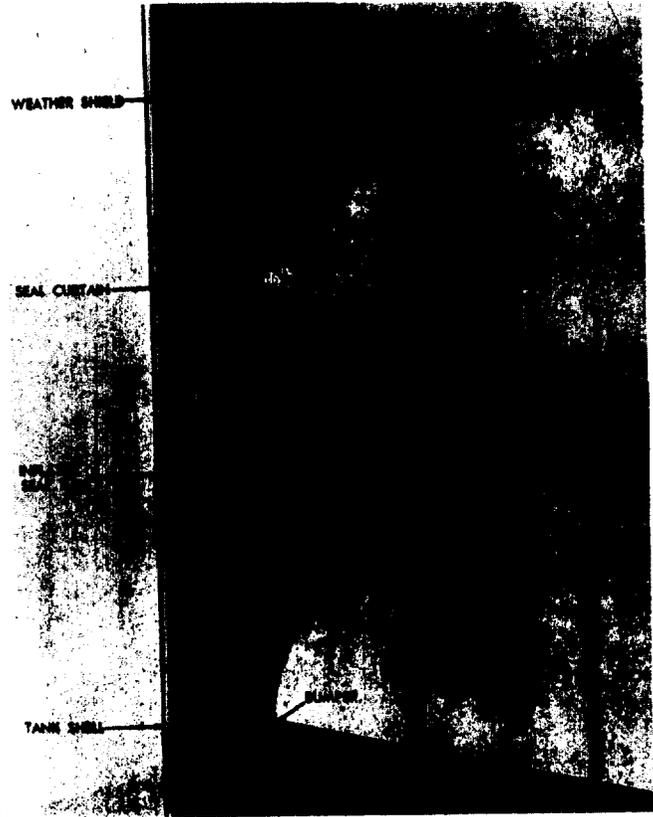
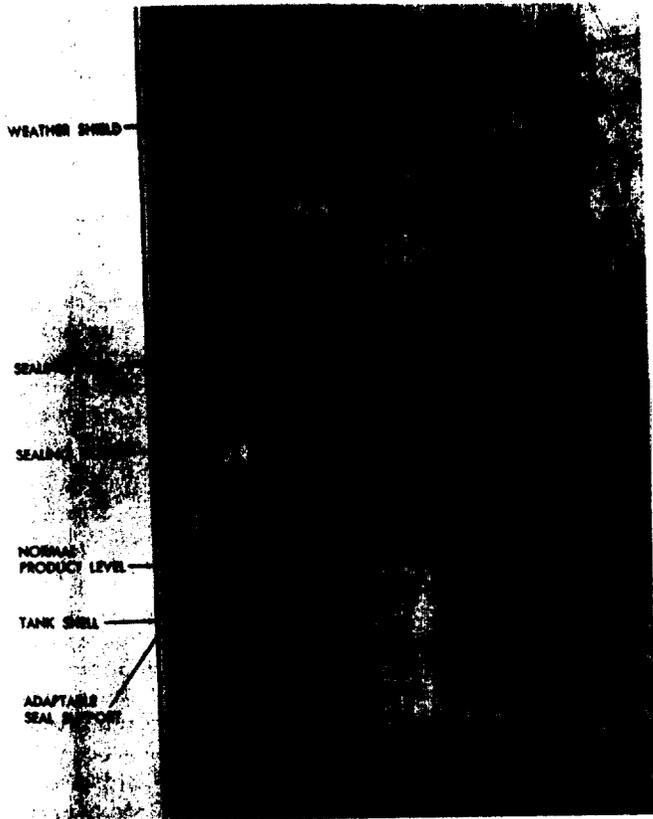


Figure 490. Sealing devices for floating-roof tanks: (upper left) Liquid-filled tube seal, (upper right) inflated tube seal, (lower left) foam-filled tube seal (Chicago Bridge and Iron Co., Chicago, Ill.)

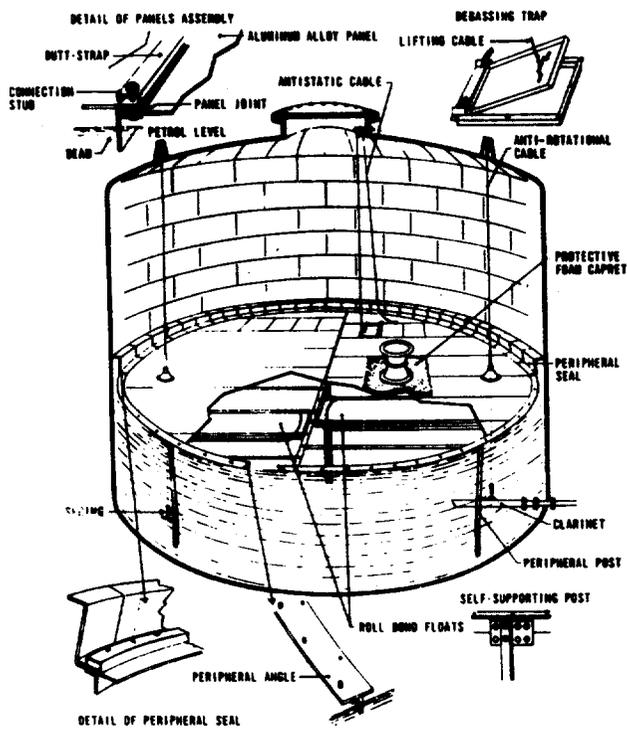


Figure 491. Fixed-roof tank with internal plastic floating blanket (Laroche Bouvier and Company, 5, Boulevard Edgar-Quinet, Colombes (Seine), France).

on the clean, dry floor of the tank just before the crude oil is charged. A wetting agent must be used when the foam covering is to be used on gasoline products. This is accomplished by slurring the plastic spheres, wetting agent, and gasoline in a separate container. The slurry is then injected into the tank. Changes in tank operation are not necessary except for gaging or sampling. A floating-type well attached to a common-type gaging tape allows accurate measurement of the tank's contents. A sample thief with a piercing-type bottom is needed for sampling.

Protection against excessive loss of the plastic spheres is necessary because of the relative value of the foam covering. Precaution must be taken against overfilling and pumping the tank too low. Standard precautions against air entrainment in pipelines normally safeguard against the latter. Overfilling can be prevented by automatic shutoff valves or preset shutoff operations. Low-level shutoff should prevent vortices created during tank emptying. Other than loss of the foam, no trouble should be encountered if the spheres escape into process lines. The plastic material is not as abrasive as the sand particles normally found entrained in crude oil. Excessive pressures crush the spheres and the plastic settles

in the water or sediment. At high temperatures, the thermo-setting resins soften, liquefy, and mix with the fuel oil, asphalt, or coke.

### Vapor Balance Systems

Variable vapor space or vapor balance systems are designed to contain the vapors produced in storage. They do not achieve as great a reduction in emissions as an appropriately designed vapor recovery system does. A well-planned unit includes storage of similar or related products, and uses the advantage of in-balance pumping situations. Only the vapor space of the tanks is manifolded together in these systems. Other systems include a vapor reservoir tank that is either a lifter-roof type or a vessel with an internal diaphragm. The latter vessel can be an integrated vapor-liquid tank or a separate vaporsphere. The manifold system includes various sizes of lightweight lines installed to effect a balanced pressure drop in all the branches while not exceeding allowable pressure drops. Providing isolating valves for each tank so that each tank can be removed from the vapor balance system during gaging or sampling operations is also good practice. Excessive vapors that exceed the capacity of the balance system should be incinerated in a smokeless flare or used as fuel.

### Vapor Recovery Systems

The vapor recovery system is in many ways similar to and yet superior to a vapor balance system in terms of emissions prevented. The service of this type of vapor recovery system is more flexible as to the number of tanks and products being stored. The recovery unit is designed to handle vapors originating from filling operations as well as from breathing. The recovered vapors are compressed and charged to an absorption unit for recovery of condensable hydrocarbons. Noncondensable vapors are piped to the fuel gas system or to a smokeless flare. When absorption of the condensable vapors is not practical from an economic standpoint, these vapors, too, are sent directly to the fuel system or incinerated in a smokeless flare.

The recovery system, like the vapor balance system, includes vapor lines interconnecting the vapor space of the tanks that the system serves. Each tank should be capable of being isolated from the system. This enables the tanks to be sampled or gaged without a resulting loss of vapors from the entire system. The branches are usually isolated by providing a butterfly-type valve, a regulator, or a check valve. Since the valves offer more line resistance, their use is sometimes restricted. Small

vessels or knockout pots should be installed at low points on the vapor manifold lines to remove any condensate.

In some vapor recovery systems, certain tanks must be blanketed with an inert atmosphere in order to prevent explosive mixtures and product contamination. In other, larger systems, the entire manifolded section is maintained under a vacuum. Each tank is isolated by a regulator-control valve. The valves operate from pressure changes occurring in the tank vapor space.

Because the vapor-gathering system is based upon positive net vapor flow to the terminus (suction of compressors), the proper size of the vapor lines is important. Sizing of the line, as well as that of the compressors, absorption unit, or flare, is based upon the anticipated amount of vapors. These vapors are the result of filling operations and breathing. The distance through which the vapors must be moved is also important.

#### Miscellaneous Control Measures

Recent tests have shown that breathing emissions from fixed-roof tanks can be reduced by increasing the storage pressure. An increase of 1 ounce per square inch was found to result in an 8 percent decrease in emissions due to breathing. Tanks operated at 2-1/2 psig or higher were found to have little or no breathing emissions. The pressure setting, however, should not exceed the weight of the roof.

A major supplier (Shand and Jurs Co.) of tank accessories offers another method of reducing breathing losses. The method is based upon the degree of saturation in the vapor space. A baffle located in a horizontal position immediately below the vent, as shown in Figure 492, directs entering atmospheric air into a stratified layer next to the top of the tank. Since this air is lighter, it tends to remain in the top area; thus, there is less mixing of the free air and any of the rich vapor immediately above the liquid surface. The top stratified layer is first expelled during the outbreathing cycle. Test data indicate a reduced surface evaporation of 25 to 50 percent.

Hydrocarbon emissions can be minimized further by the proper selection of paint for the tank shell and roof. The protective coating applied to the outside of shell and roof influences the vapor space and liquid temperatures. Reflectivity and glossiness of a paint determine the quantity of heat a vessel can receive via radiation. A cooler roof and shell also allows any heat retained in the stored material to dissipate. Weathering of the paint also influences its effectiveness. The rela-

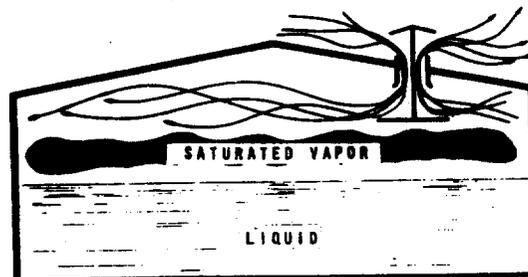
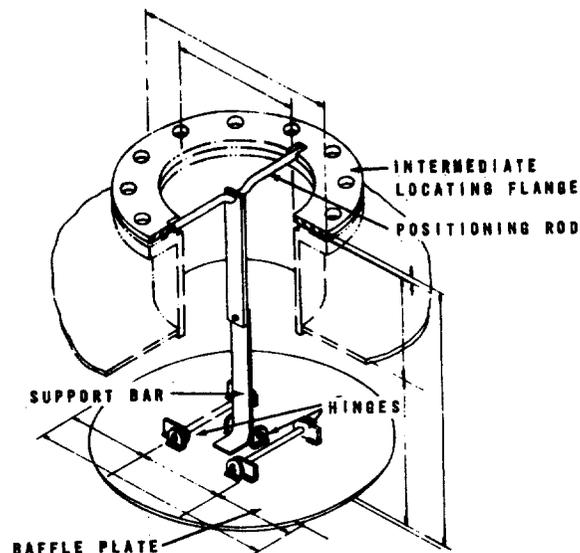


Figure 492. Air baffle (Shand and Jurs Co., Berkeley, Calif.).

tionship of paints in keeping tanks from warming in the sun is indicated in Table 170. Vapor space temperature reductions of 60°F have been reported. Similarly, liquid-surface temperature reductions of 3 to 11 degrees have been achieved. Data gathered by the American Petroleum Institute on hydrocarbon emissions indicate breathing emission reductions of 25 percent for aluminum over black paint and 25 percent for white over aluminum paint. All paints revert to "black body" heat absorption media in a corrosive or dirt-laden atmosphere.

Table 170. RELATIVE EFFECTIVENESS OF PAINTS IN KEEPING TANKS FROM WARMING IN THE SUN (Nelson, 1953)

Color	Relative effectiveness as reflector or rejector of heat, %
Black	0
No paint	10.0
Red (bright)	17.2
Red (dark)	21.3
Green (dark)	21.3
Red	27.6
Aluminum (weathered)	35.5
Green (dark chrome)	40.4
Green	40.8
Blue	45.5
Gray	47.0
Blue (dark Prussian)	49.5
Yellow	56.5
Gray (light)	57.0
Aluminum	59.2
Tan	64.5
Aluminum (new)	67.0
Red iron oxide	69.5
Cream or pale blue	72.8
Green (light)	78.5
Gray (glossy)	81.0
Blue (light)	85.0
Pink (light)	86.5
Cream (light)	88.5
White	90.0
Tin plate	97.5
Mirror or sun shaded	100.0

Insulation applied to the outside of the tank is one method of reducing the heat energy normally conducted through the wall and roof of the vessel. Another method of controlling tank temperatures is the use of water. The water can be sprayed or retained on the roof surface. The evaporation of the water results in cooling of the tank vapors. Increased maintenance and corrosion problems may, however, be encountered.

Storage temperatures may be reduced by external refrigeration or autorefrigeration. External refrigeration units require the circulation of the refrigerant or of the tank contents. Autorefrigeration is practical in one-component liquid hydrocarbon storage where high vapor pressure material is involved. The pressure in the tank is reduced by removing a portion of the vapor. Additional vapor is immediately formed. This flash vaporization results in lowering the temperature of the main liquid body.

Routine operations can be conducted in such a manner as to minimize other emissions associated with storage tanks. Use of remote-level

reading gages and sampling devices reduces emissions by eliminating the need to open tank gage hatches. Emissions can be further reduced by proper production scheduling to (1) maintain a minimum of vapor space, (2) pump liquid to the storage tank during cool hours and withdraw during hotter periods, and (3) maintain short periods between pumping operations.

Using wet scrubbers as control equipment for certain stored materials that are sufficiently soluble in the scrubbing media employed is both possible and practical. The scrubbers can be located over the vent when the scrubbing medium, for example, a water scrubber for aqua ammonia storage, can be tolerated in the product. In other cases, the vent of one or more tanks can be manifolded so that any displaced gas is passed through a scrubbing unit before being discharged to the atmosphere. A typical example is a scrubber packed with plastic spirals that serves ketone storage vessels. The scrubbing liquid is water, which is drained to a closed waste effluent disposal system.

Properly designed condensers can be used to reduce the vapor load from tank vents in order that smaller control devices can be employed.

#### Masking Agents

Masking agents do not afford any degree of control of the emissions from storage equipment. The agent is employed to make the vapor or gas less objectionable. On the basis of local experience, the use of these agents is impractical, and in the long run, proper control equipment is necessary.

#### Costs of Storage Vessels

The installed costs of various storage vessels are indicated in Figures 493 through 500. Included are standard tank accessories such as manholes, vents, ladders, stairways, drains, gage hatches, and flanged connections.

## LOADING FACILITIES

### INTRODUCTION

Gasoline and other petroleum products are distributed from the manufacturing facility to the consumer by a network of pipelines, tank vehicle routes, railroad tank cars, and ocean-going tankers, as shown in Figure 501.

As integral parts of the network, intermediate storage and loading stations receive products from refineries by either pipelines or tank ve-

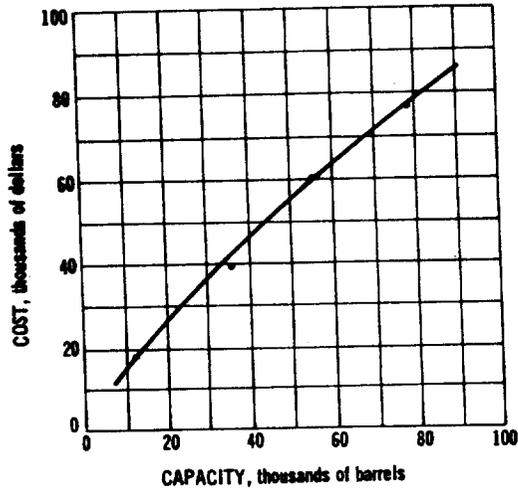


Figure 493. Installed costs of cone roof tanks.\*

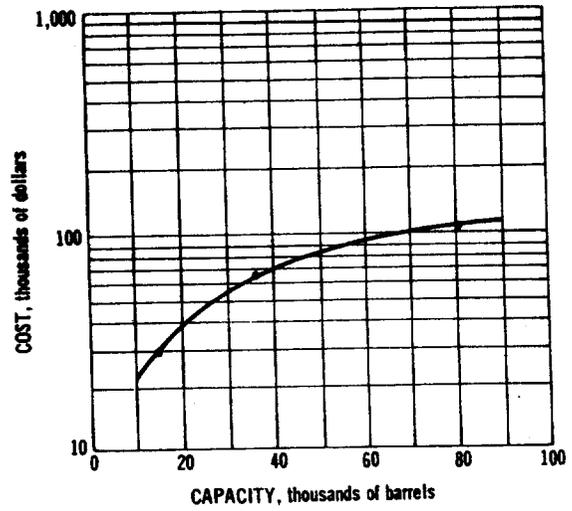


Figure 494. Installed costs of double-deck floating-roof tanks.\*

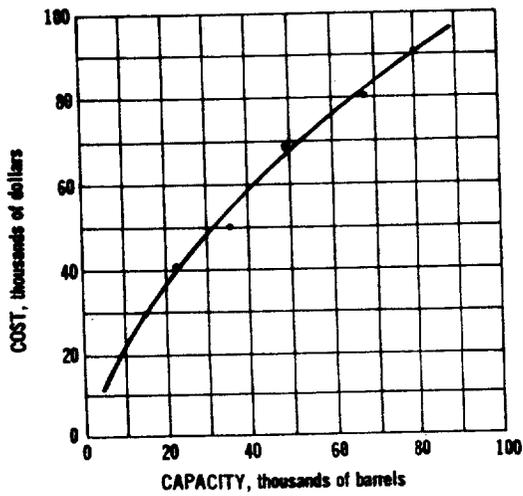


Figure 495. Installed costs of pontoon floating-roof tanks.\*

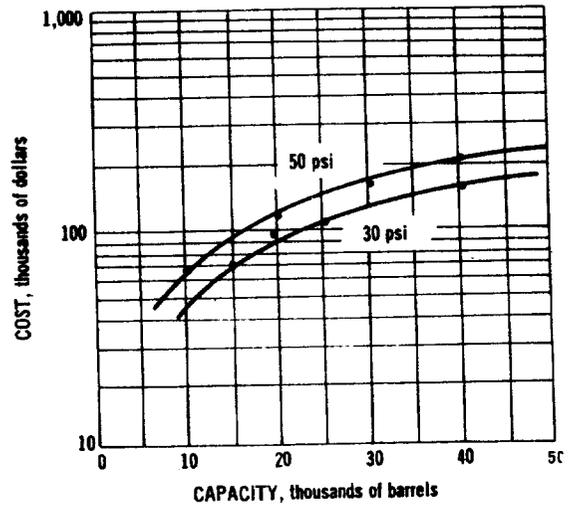


Figure 496. Installed costs of spherical pressure storage tanks.\*

\*Including accessories, delivered and erected (Prater and Mylo 1961; copyrighted by Gulf Publishing Co., Houston, Texas).

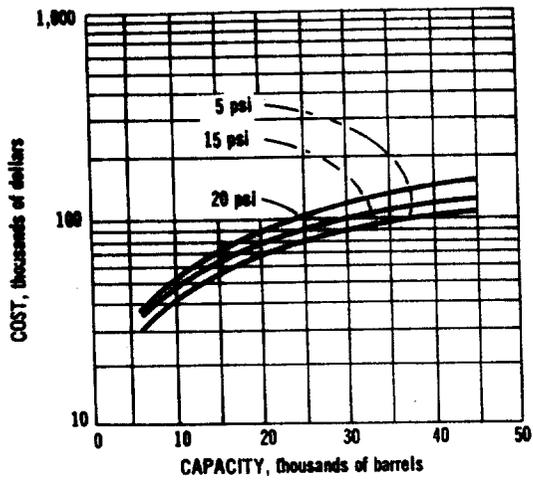


Figure 497. Installed costs of spheroids.\*

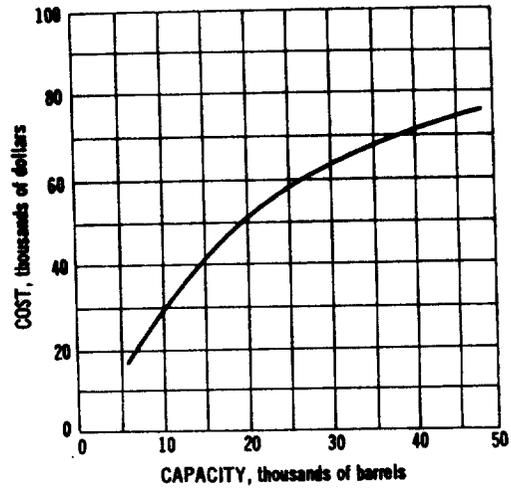


Figure 498. Installed costs of basic hemispheroids.\*

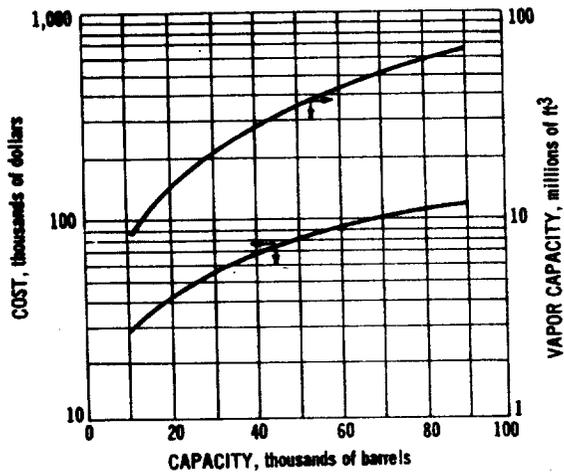


Figure 499. Installed costs of 5-ft lift expansion roof storage tanks.\*

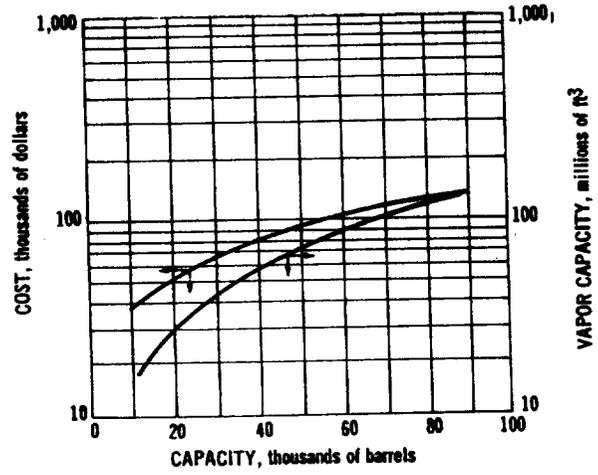


Figure 500. Installed costs of 10-ft lift expansion roof storage tanks.\*

\*Including accessories, delivered and erected (Prater and Mylo, 1961; copyrighted by Gulf Publishing Co., Houston, Texas).

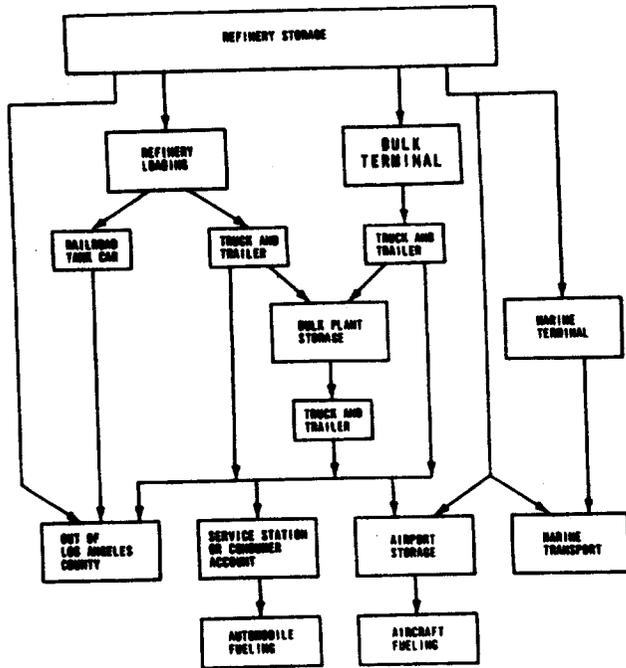


Figure 501. Representation of gasoline distribution system in Los Angeles County, showing flow of gasoline from refinery to consumer.

hicles. If the intermediate station is supplied by pipeline, it is called a bulk terminal, to distinguish it from the station supplied by tank vehicle, which is called a bulk plant. Retail service stations fueling motor vehicles for the public are, as a general rule, supplied by tank vehicle from bulk terminals or bulk plants. Consumer accounts, which are privately owned facilities operated, for example, to fuel vehicles of a company fleet, are supplied by tank vehicles from intermediate bulk installations or directly from refineries.

Gasoline and other petroleum products are loaded into tank trucks, trailers, or tank cars at bulk installations and refineries by means of loading racks. Bulk products are also delivered into tankers at bulk marine terminals.

### Loading Racks

Loading racks are facilities containing equipment to meter and deliver the various products into tank vehicles from storage. Sizes of loading racks vary in accordance with the number of products to be loaded and the number of trucks or railroad tank cars to be accommodated. The loading platform may be an elevated structure for overhead filling of vehicles, that is, through the top hatches in the tank vehicle, or a ground-level facility for

bottom filling. The elevated-platform structure employed for overhead filling, shown in Figures 502 and 503, is generally constructed with hinged side platforms attached to the sides of a central walkway in such a way that they can be raised when not in use. Thus, when a vehicle is positioned adjacent to the central walkway for loading, the hinged side platforms can be lowered to rest upon the top of the vehicle to provide an access to the compartment hatches. The meters, valves, loading tubes or spouts, motor switches, and similar necessary loading equipment are located on the central walkway. Bottom-loading installations are less elaborate, since the tank vehicle is filled through easily accessible fittings on the underside of the vehicles.

### Marine Terminals

Marine terminals have storage facilities for crude oil, gasoline, and other petroleum products, and facilities for loading and unloading these products to and from oceangoing tankers or barges. The loading equipment is on the dock and, in modern terminals, is similar to elevated-tank vehicle-loading facilities except for size (see Figure 504). A pipeline manifold with flexible hoses is used for loading at older terminals. Marine installations are considerably larger and operate at much greater loading rates than inland loading installations.

### Loading Arm Assemblies

The term loading arm assembly refers to the equipment and appurtenances at the discharge end of a product pipeline that are necessary to the filling of an individual tank vehicle or tanker compartment. Component parts may include piping, valves, meters, swivel joints, fill spouts, and vapor collection adapters. These installations are commonly called loading arms. A loading arm without provisions to control vapors displaced from the compartment during filling is shown in Figure 505.

Overhead loading arms employed for filling of tank trucks or railroad tank cars may be classified in accordance with the manner in which vertical movement of the arm is achieved, such as pneumatic, counterweighted, or torsion spring. The pneumatically operated arm is a successor to the common spring-loaded, automatic-locking arm in which the spring-loaded cylinder has been replaced by an air cylinder (see Figure 506). Bottom loading employs a flexible hose or a non-flexible, swing-type arm connected to the vehicle from ground-level pipeline termini.

Loading arms at modern marine terminals are similar in design to those used for overhead loading of tank vehicles. The tanker loading

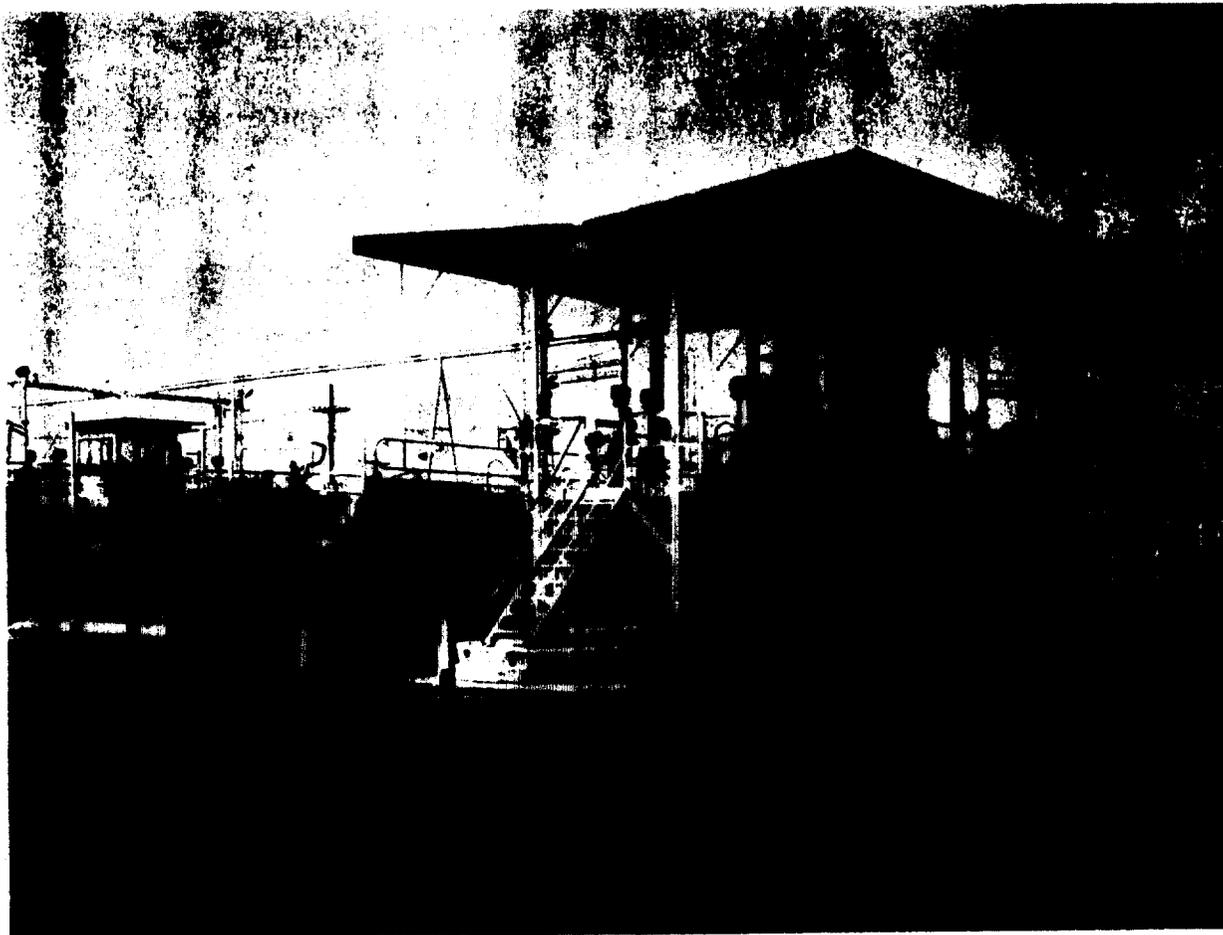


Figure 502. An overhead-controlled loading rack (Phillips Petroleum, Los Angeles, Calif.).

arms are too large for manual operation, requiring a hydraulic system to effect arm motion. Older installations use reinforced, flexible hoses to convey products from pipeline discharge manifolds to the tanker. The hoses are positioned by means of a winch or crane.

#### THE AIR POLLUTION PROBLEM

When a compartment of a tank vehicle or tanker is filled through an open overhead hatch or bottom connection, the incoming liquid displaces the vapors in the compartment to the atmosphere. Except in rare instances, where a tank vehicle or tanker is free of hydrocarbon vapor, as when being used for the first time, the displaced vapors consist of a mixture of air and hydrocarbon concentration, depending upon the product being loaded, the temperature of the product and of the tank compartment, and the type of loading. Ordinarily, but not always, when gasoline is loaded, the hydrocarbon concen-

tration of the vapors is from 30 to 50 percent by volume and consists of gasoline fractions ranging from methane through hexane (Deckert et al., 1958). Table 171 shows a typical analysis of the vapors emitted during the loading of motor gasoline into tank vehicles.

The volume of vapors produced during the loading operation, as well as their composition, is greatly influenced by the type of loading or filling employed. The types in use throughout the industry may be classified under two general headings, overhead loading and bottom loading.

Overhead loading, presently the most widely used method, may be further divided into splash and submerged filling. In splash filling, the outlet of the delivery tube is above the liquid surface during all or most of the loading. In submerged filling the outlet of the delivery tube is extended to within 6 inches of the bottom and is submerged beneath the liquid during most of the loading. Splash filling generates more turbulence and therefore more hydrocarbon vapors

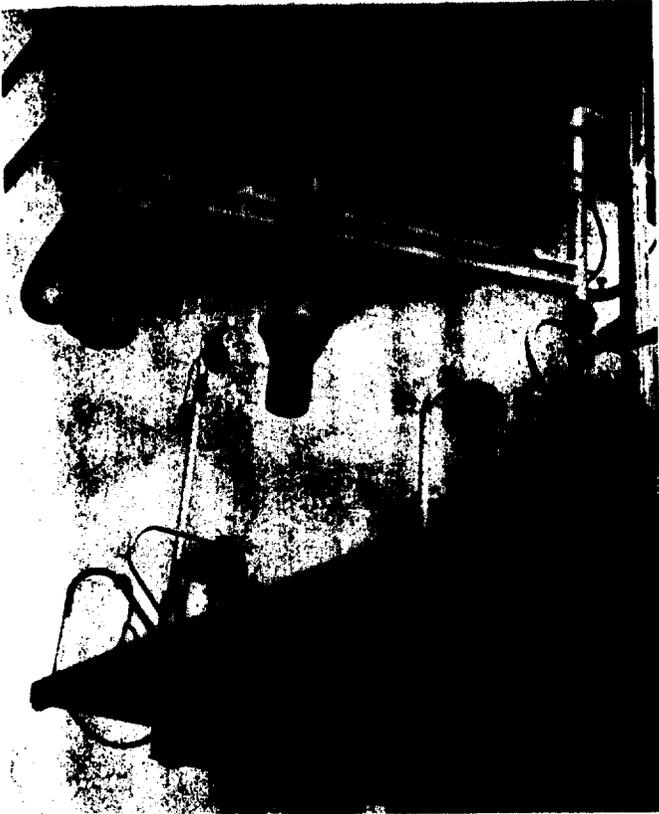


Figure 503. A closeup view of a controlled loading arm with the access platform in a lowered position (Phillips Petroleum, Los Angeles, Calif.).

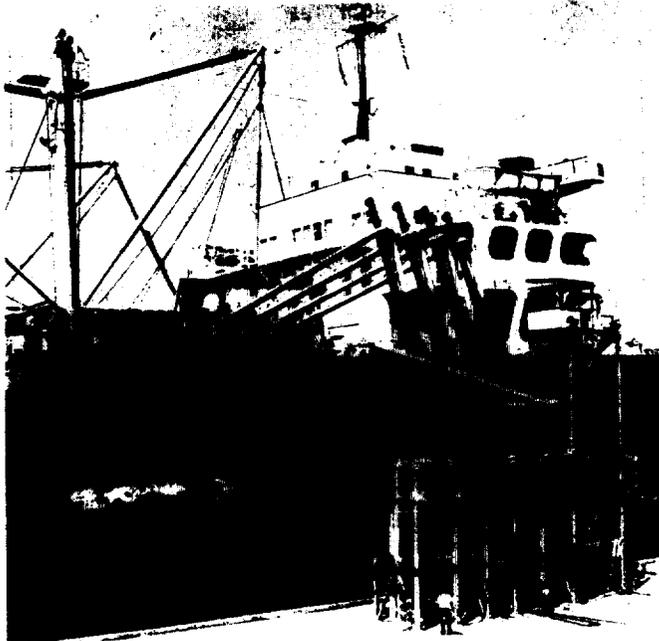


Figure 504. Marine terminal loading station (Chiksian Company, Brea, Calif.).

than submerged filling does, other conditions being equal. On the basis of a typical 50 percent splash filling operation, vapor losses from the overhead filling of tank vehicles with gasoline have been determined empirically to amount to 0.1 to 0.3 percent of the volume loaded (Duckert et al., 1958). Figure 507 presents a correlation of loading losses with gasoline vapor pressures.

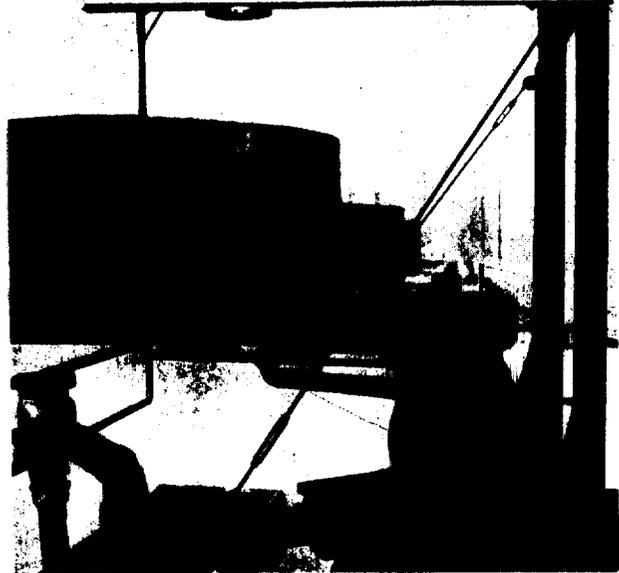


Figure 505. View of uncontrolled loading arm.

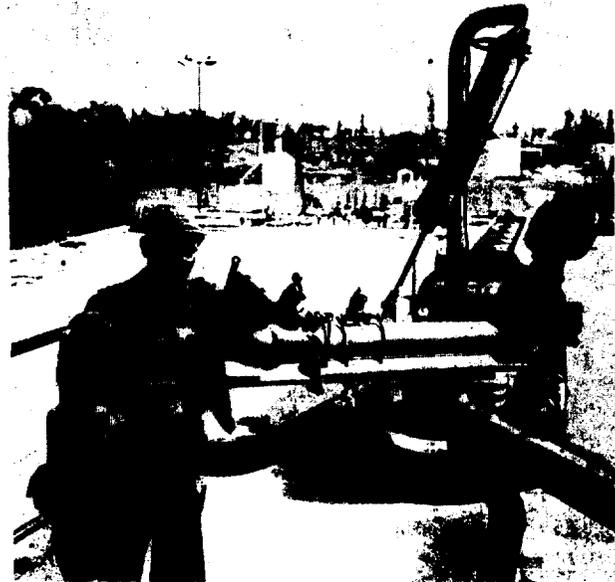


Figure 506. View of a pneumatically operated loading arm (Union Oil Company of California, Los Angeles, Calif.).

Table 171. TYPICAL ANALYSIS OF VAPORS FROM THE BULK LOADING OF GASOLINE INTO TANK TRUCKS (Deckert et al., 1958)

Fraction	Vol %	Wt %
Air	58.1	37.6
Hydrocarbon		
Propane	0.6	0.6
Iso-Butane	2.9	3.8
Butene	3.2	4.0
N-Butane	17.4	22.5
Iso-Pentane	7.7	12.4
Pentene	5.1	8.0
N-Pentane	2.0	3.1
Hexane	3.0	8.0
	100.0	100.0

Bottom loading has been introduced by a few oil companies and found practical for loading trucks (Hunter, 1959). The equipment required is simpler than that used for overhead loading. Loading by this method is accomplished by connecting a swing-type loading arm or hose at ground level, as shown in Figure 508, to a matching fitting on the underside of the tank vehicles. Aircraft-type, quick-coupling valves are used to ensure a fast, positive shutoff and prevent liquid spills. Several companies experienced in aircraft-fueling operations have developed fully automatic bottom-loading systems. All the loading is submerged and under a slight pressure; thus, turbulence and resultant production of vapors are minimized.

The method employed for loading marine tankers is essentially a bottom-loading operation. Liquid is delivered to the various compartments through lines that discharge at the bottom of each compartment. The vapors displaced during loading are vented through a manifold line to the top of the ship's mast for discharge to the atmosphere.

In addition to the emissions resulting from the displacement of hydrocarbon vapors from the tank vehicles, additional emissions during loading result from evaporation of spillage, drainage, and leakage of product.

#### AIR POLLUTION CONTROL EQUIPMENT

An effective system for control of vapor emissions from loading must include a device to collect the vapors at the tank vehicle hatch and a means for disposal of these vapors.

#### Types of Vapor Collection Devices for Overhead Loading

Four types of vapor collectors or closures, fitting the loading tube, have been developed for use during overhead-loading operations of trucks: The General Petroleum Corporation unit, the Vernon Tool Company or Greenwood unit, the SOCO unit, and the Chiksan unit. All are essentially plug-shaped devices that fit into the hatch openings and have a central channel through which gasoline can flow into the tank vehicle compartment. This central channel, actually a section of the loading tube, is surrounded by an annular vapor space. Entry into this vapor space is achieved through openings on the bottom of the closure that are below the point of contact of the external closure surface with the sides of the hatch opening. Thus, vapors are prevented from passing around the closure and out of the hatch, and must flow in-

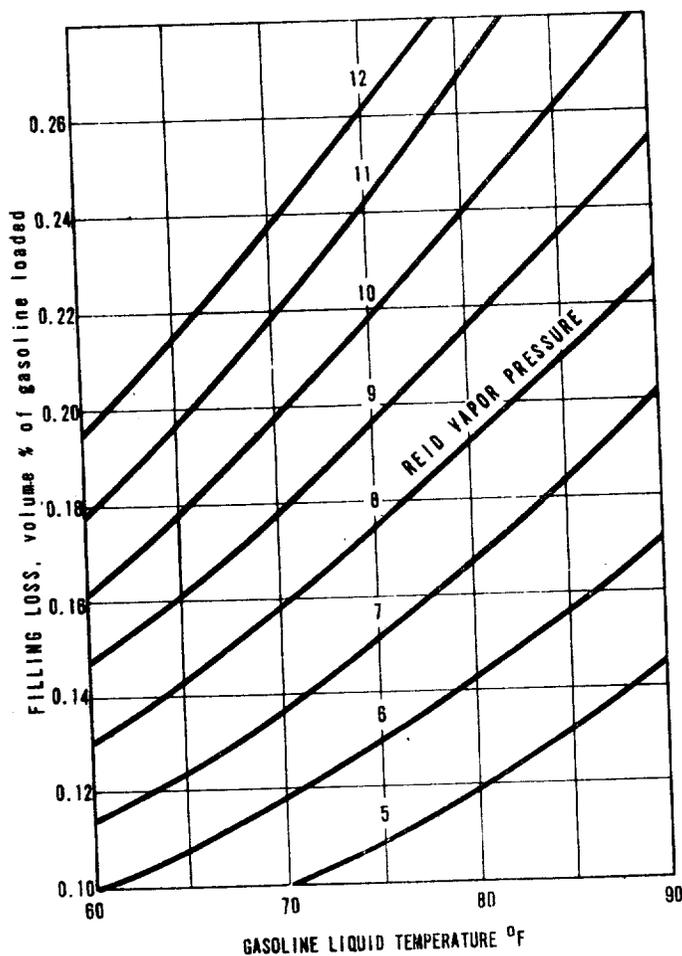


Figure 507. Correlation of tank vehicle-loading losses (50% submerged filling) with Reid vapor pressure and liquid temperatures of the motor gasoline.



Figure 508. View of a bottom-loading station (Standard Oil Company of California, Western Operations Inc., Los Angeles, Calif.).

stead into the annular space, which in turn, is connected to a hose or pipe leading to a vapor disposal system.

The vapor closure device developed by the General Petroleum Corporation (now Mobil Oil Corp.) has the annular vapor space connected to an auxiliary, transparent, plexiglas vapor chamber section above the closure to allow the operator to observe the calibrated capacity markers.\* A typical Mobil Oil Corporation vapor closure is shown in Figure 509. A neoprene rubber bellows above the plexiglas chamber compensates for vertical misalignment of the closure in the hatch opening. The closure is aluminum and is cast in the shape of a truncated cone. The lateral surface of the closure is faced with a neoprene rubber gasket in the shape of a spherical section so as to give a vaportight seal between the closure and the hatch when the closure is positioned in the hatch for loading. The top of the closure has openings for the loading tube and the vapor takeoff line. An adjustable slipring serves as a positioner enabling the loading operators to slide the closure to the proper height on the loading tube for various depths of tank vehicle compartments. This closure requires a constant downward force to keep it in contact with the hatch opening's sides at all times during filling and is built to fit only hatches 8 to 10 inches in diameter.

\*These markers are gages located within the tank compartment and positioned at a calibrated volume to indicate visually the amount of liquid loaded.

The second type of closure, the Greenwood Unit, (Figures 510 and 511), which also requires a downward force during the filling operation, was developed by the Vernon Tool Company. This closure is also cast aluminum in the shape of a plug similar to the Mobil Oil Corporation closure and with a neoprene rubber gasket. This closure has no auxiliary, transparent, vapor chamber section, though some versions of this closure do have auxiliary, metal vapor chambers or a transparent, light well. The closure fits tank truck compartments with hatches from 8 to 10 inches in diameter. Since compartments with hatches of larger diameters are sometimes encountered, an adapter has been provided. The adapter consists of a flat, gasketed plate with an 8-inch-diameter hole in the center through which the closure can be inserted.

The third type of vapor closure, referred to as SOCO, was developed by Standard Oil Company of California (Figures 512, 513, and 514). It consists of an aluminum cast plug of more complicated design. This closure is locked into the hatch opening by a cam lever that forces a floating, internal, cylindrical section to move upward and squeeze a neoprene rubber collar out against the sides of the hatch opening, which effects a vaportight seal during all phases of loading. As the floating, internal, cylindrical section is rolled upward by the action of the cam lever device, it exposes the vapor entry opening. A piston-type, internal filling valve, similar to an aircraft-fueling valve, was developed for this closure. A safety shutoff float operates a needle



Figure 509. View of General Petroleum Corporation Vapor closure (Mobil Oil Corporation, Los Angeles, Calif.).

pilot valve that controls the internal valve to prevent overfilling. The cam lever must be released to remove the vapor closure. The floating cylinder is returned to the closed position at the same time. Thus, the vapor side is sealed off to prevent any leakage from the vapor-gathering lines. At the same time the internal valve is locked in the closed position. SOCO closures fit only hatches 8 inches in diameter, though adapters have been developed for hatches of greater diameter. This adapter is a circular casting with an 8-inch opening and is placed over the hatch opening. When the SOCO unit is inserted, spring-loaded arms act to clamp and seal the adapter against the top of the hatch.

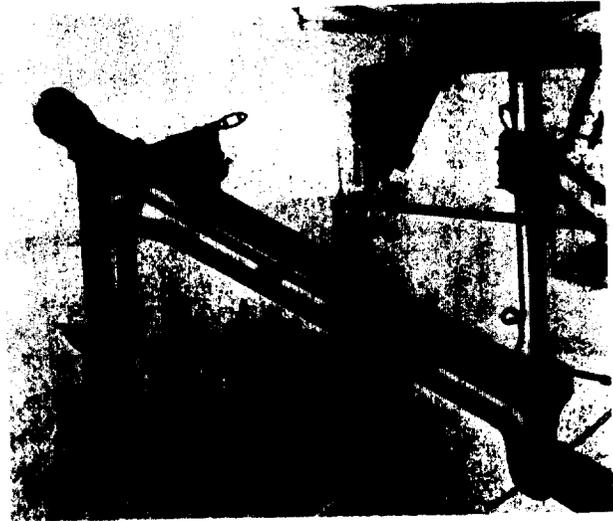


Figure 510. View of the Greenwood vapor closure (Atlantic-Richfield Oil Corporation, Los Angeles, Calif.).



Figure 511. Closeup view of Greenwood vapor closure (Atlantic-Richfield Oil Corporation, Los Angeles, Calif.).

The Chiksan Company has recently offered a fourth system, a modern loading arm that incorporates the hatch closure, the vapor return line, and the fill line as an assembled unit (Figure 515). This unit incorporates features to prevent overfills, topping off, or filling unless



Figure 512. Closeup view of SOCO vapor closure, withdrawn position (American Airlines, Los Angeles, Calif.).

the assembly is properly seated in the truck hatch. A pneumatic system ensures contact with the tank truck as the gasoline is added and provides a delay at the end of the loading cycle to achieve adequate drainage of the arm before it is withdrawn from the truck hatch.

The slide positioner of the Mobil Oil Corporation vapor closure, though permitting adjustments for submerged loading, can be a source of vapor leaks and requires proper attention by the operator. SOCO closures with inner valves are considerably heavier than other types, and the inner valve involves added pressure drops, which slow the loading rates. Both the Greenwood and the Mobil Oil Corporation closures require vapor check valves in the vapor-gathering lines to prevent the vapor from discharging back to the atmosphere when the loading assembly is withdrawn. In addition, inspections have shown that the Mobil Oil Corporation and Greenwood closures require nearly vertical entry of the loading tube into the compartment hatch opening in order to provide a tight seal against vapor leaks. A connecting rod between the riser and filling stem has been added to some assemblies, as shown

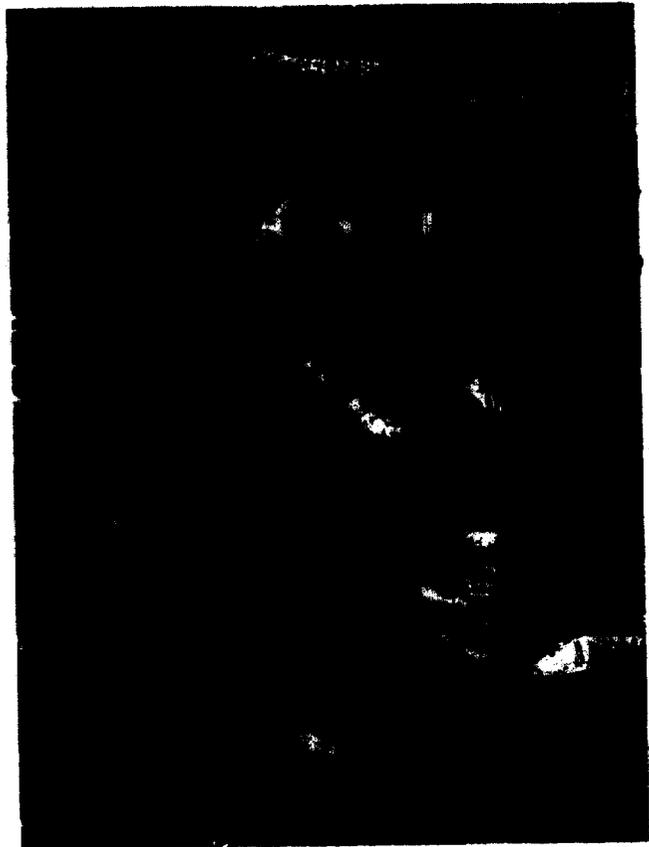


Figure 513. Closeup view of SOCO vapor closure, filling position (American Airlines, Los Angeles, Calif.).

in Figure 516, to form a pantograph arrangement to maintain the filling stem of the loading arm in the vertical position at all times. The loading operator is thus able to obtain good sealing contact more quickly between the vapor collector and the hatch opening.

#### Collection of Vapors From Bottom Loading

Vapors displaced from tank vehicles during the bottom-loading operation are more easily collected than those are that result from overhead loading. The filling line and the vapor collection line are independent of each other with resultant simplification of the design (see Figure 517). The vapor collection line is usually similar to the loading line, consisting of a flexible hose or swing-type arm connected to a quick-acting valve fitting on the dome of the vehicle. This fitting could be placed at ground level to simplify the operation further.

A check valve must be installed on the vapor collection line to prevent backflow of vapors to the atmosphere when the connection to the tank vehicle is broken.

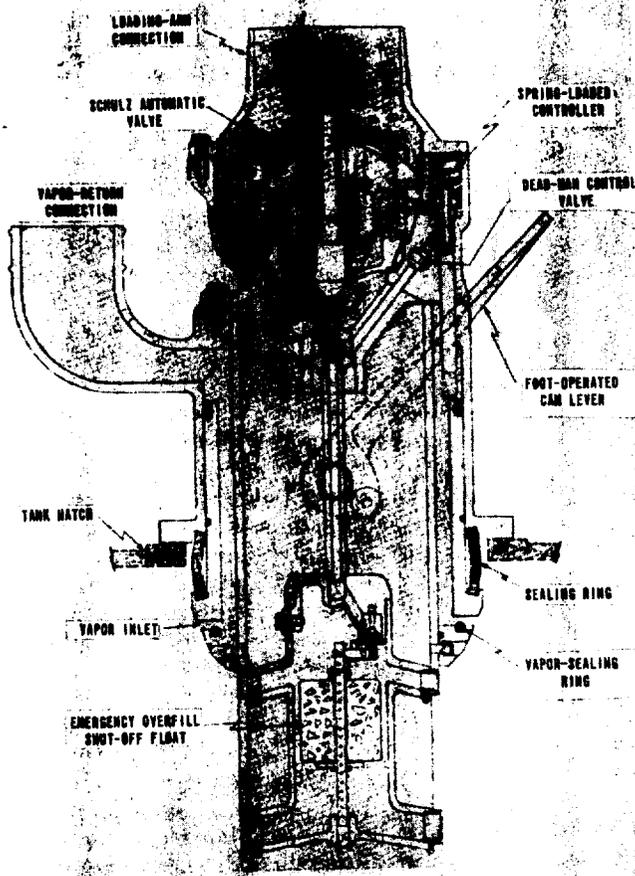


Figure 514. Schematic drawing of SOCO vapor closure used to collect displaced vapors during loading (Standard Oil Company of California, Western Operations, Inc., Los Angeles, Calif.).

#### Factors Affecting Design of Vapor Collection Apparatus

In designing for complete vapor pickup at the tank vehicle hatch, several factors, including tank settling, liquid drainage, and topping off must be considered.

The settling of a tank vehicle due to the weight of product being added requires that provision be made for vertical travel of the loading arm to follow the motion of the vehicle so that the vapor collector remains sealed in the tank hatch during the entire loading cycle. Two solutions to the problem of settling have been used. The first, applicable to pneumatically operated arms, includes the continuous application of air pressure to the piston in the air cylinder acting on the arm. The arm is thus forced to follow the motion of the vehicle without need for clamping or fastening the vapor collector to the tank ve-

hicle. The second solution, employed on counterweighted and torsion spring loading arms, provides for locking the vapor collector to the tank vehicle hatch. The arm then necessarily follows the motion of the vehicle. The second solution is also applicable to vapor collection arms or hoses that are connected to the top of a tank vehicle during bottom loading.

The second problem, that of preventing considerable liquid drainage from a loading arm as it is withdrawn after completion of filling operations, has been adequately solved. The air valve that operates the air cylinder of pneumatically operated loading arms may be modified by addition of an orifice on the discharge side of the valve. The orifice allows 30 to 45 seconds to elapse before the loading assembly clears the hatch compartment. This time interval is suffi-



Figure 515. View of a pneumatically operated loading assembly with an integrated vapor closure and return line (Chiksan Co., Brea, Calif.).

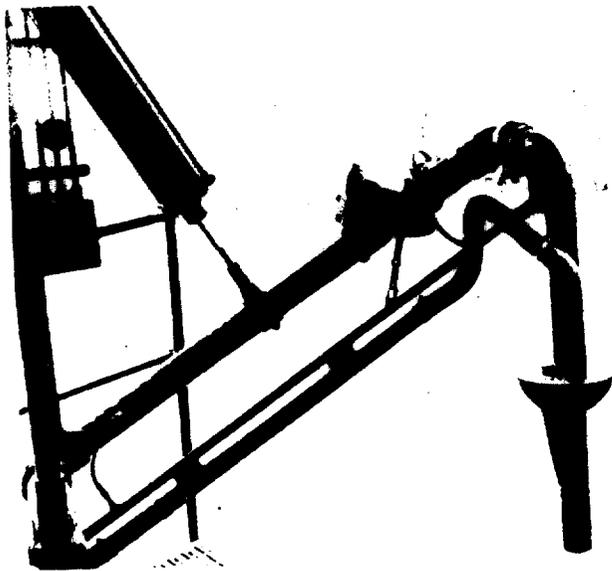


Figure 516. View of a pneumatically operated loading arm showing pantograph linkage (Atlantic-Richfield Oil Corporation, Los Angeles, Calif.).



Figure 517. Bottom loading of tank trucks provides one way to collect vapor during loading in conjunction with the use of return line to storage tanks (Standard Oil Company of California, Western Operations, Inc., Los Angeles, Calif.).

cient to permit complete draining of liquid into tank compartments from arms fitted with loading valves located in an outboard position. Loading arms with inboard valves require additional drainage time and present the problem of gasoline retention in the horizontal section of the arm. To prevent drainage the SOCO vapor collection closure is fitted with an internal shutoff valve that

is closed before the loading arm is withdrawn from the tank hatch. Providing for thermal expansion has been found necessary when an inboard valve and a SOCO vapor closure are used. This has been accomplished by installing a small expansion chamber at the normal position of the loading arm's vacuum breaker. In bottom loading, the valve coupling at the end of the loading arm or hose, as well as the mating portion of the valve on the trucks, is self-sealing to prevent drainage of product when the connection is made or broken.

The third factor to be considered in the design of an effective vapor collection system is topping off. Topping off is the term applied to the loading operation during which the liquid level is adjusted to the capacity marker inside the tank vehicle compartment. Since the loading arm is out of the compartment hatch during the topping operation, vapor pickup by the collector is nil. Metering the desired volumes during loading is one solution to the problem. Metered loading must, however, be restricted to empty trucks or to trucks prechecked for loading volume available. Accuracy of certain totalizing meters or preset stop meters is satisfactory for loading without the need for subsequent open topping. An interlock device for the pneumatic-type loading arms, consisting of pneumatic control or mechanical linkage, prevents opening of the loading valve unless the air cylinder valve is in the down position. Thus, open topping is theoretically impossible.

Topping off is not a problem when bottom loading is employed. Metered loading, or installation of a sensing device in the vehicle compartments that actuates a shutoff valve located either on the truck or the loading island, eliminates the need for topping off.

#### Methods of Vapor Disposal

The methods of disposing of vapors collected during loading operations may be considered under three headings: Using the vapors as fuel, processing the vapors for recovery of hydrocarbons, or effecting a vapor balance system in conjunction with submerged loading.

The first method of disposal, using the vapors directly as fuel, may be employed when the loading facilities are located in or near a facility that includes fired heaters or boilers. In a typical disposal system, the displaced vapors flow through a drip pot to a small vapor holder that is gas blanketed to prevent forming of explosive mixtures. The vapors are drawn from the holder by a compressor and are discharged to the fuel gas system.

The second method of disposal uses equipment designed to recover the hydrocarbon vapors. Vapors have been successfully absorbed in a liquid such as gasoline or kerosine. If the loading facility is located near a refinery or gas absorption plant, the vapor line can be connected from the loading facility to an existing vapor recovery system through a regulator valve.

Vapors are recovered from loading installations distant from existing processing facilities by use of package units. One such unit (Figures 518 and 519) that absorbs hydrocarbon vapors in gasoline has been developed by the Superior Tank and Construction Company. This unit includes a vaporsphere or tank equipped with flexible membrane diaphragm, saturator, absorber, compressor, pumps, and instrumentation. Units are available to fit any size operation at any desired loading location since they use the gasoline product as the absorbent.

Explosive mixtures must be prevented from existing in this unit. This is accomplished by passing the vapors displaced at the loading rack through a saturator countercurrently to gasoline pumped

from storage. The saturated vapors then flow to the vaporsphere. Position of the diaphragm in the vaporsphere automatically actuates a compressor that draws the vapors from the sphere and injects them at about 200 psig into the absorber. Countercurrent flow of stripped gasoline from the saturator or of fresh gasoline from storage is used to absorb the hydrocarbon vapors. Gasoline from the absorber bottoms is returned to storage while the tail gases, essentially air, are released to the atmosphere through a back-pressure regulator. Some difficulty has been experienced with air entrained or dissolved in the sponge gasoline returning to storage. Any air released in the storage tank is discharged to the atmosphere saturated with hydrocarbon vapors. A considerable portion of the air can be removed by flashing the liquid gasoline from the absorber in one or more additional vessels operating at successively lower pressures.

Another type of package unit adsorbs the hydrocarbon vapors on activated carbon, but no installation of this kind has been observed in Los Angeles County. The application of this type of unit is presently restricted to loading installations

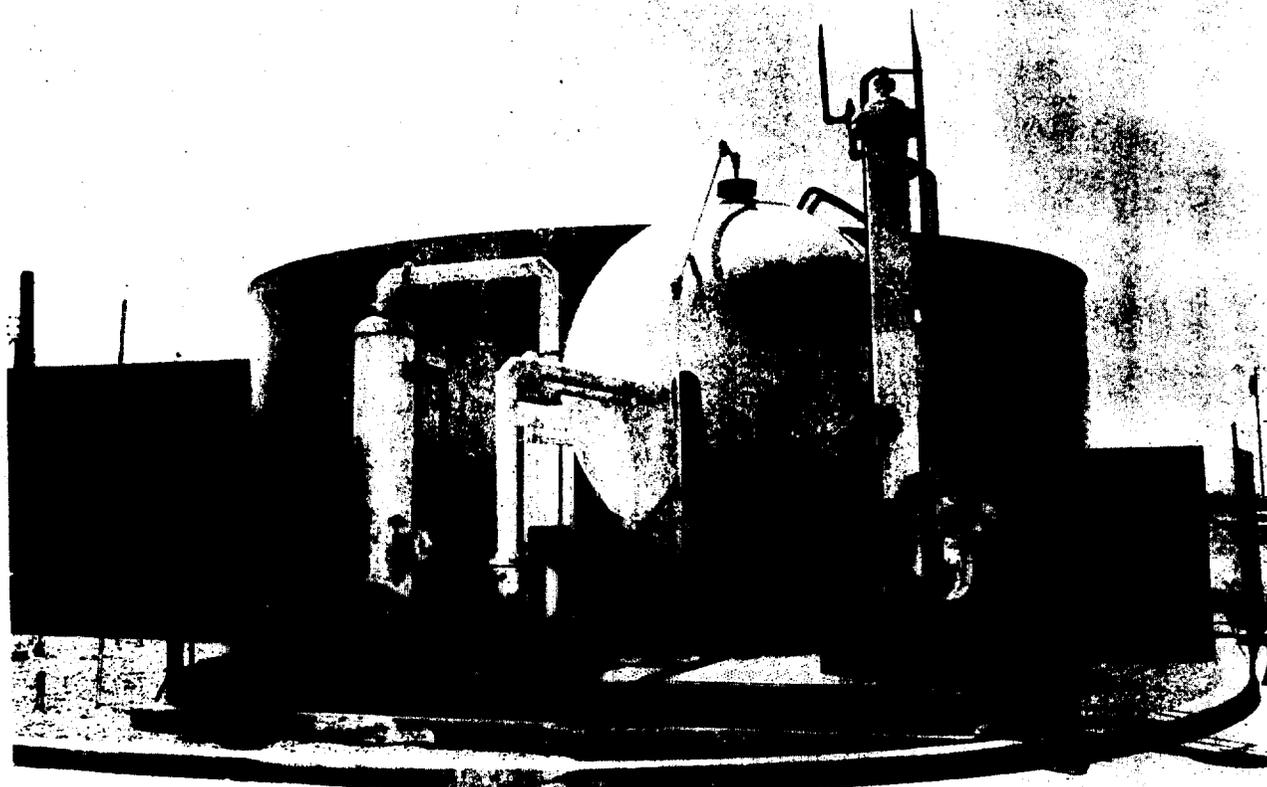


Figure 518. View of small-capacity vaporsaver gasoline absorption unit (American Airlines, Los Angeles, Calif.).

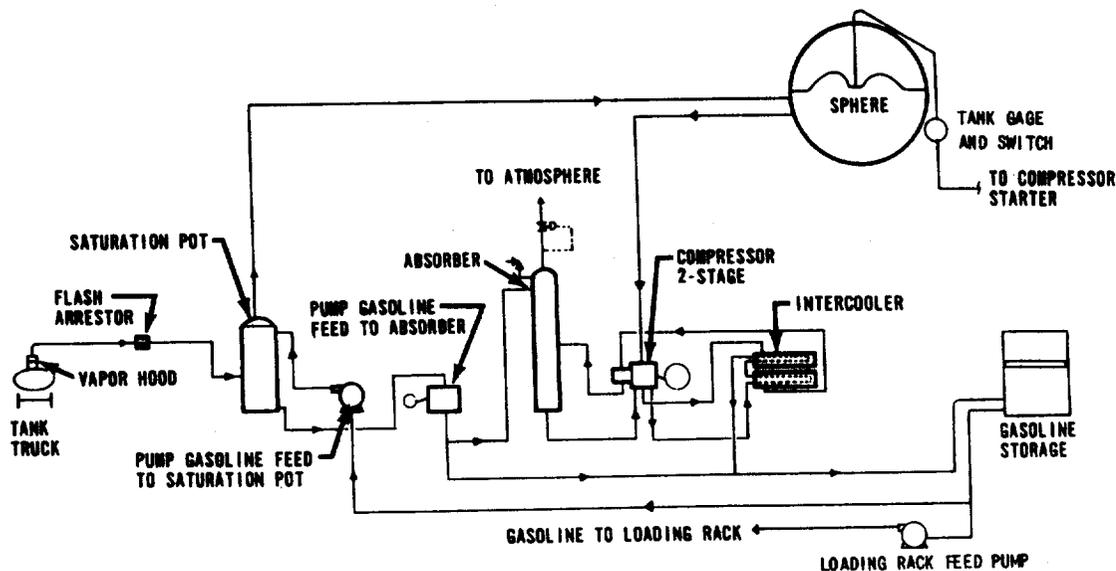


Figure 519. Schematic flow diagram of a vaporsaver unit used for recovery of loading rack vapors at a bulk terminal.

that have low throughputs of gasoline, since the adsorbing capacity and the life of the carbon are limited. Units of this type find application in control of vapors resulting from fueling of jet aircraft.

The vapors displaced during bottom filling are minimal. Data indicate a volume displacement ratio of vapor to liquid of nearly 1:1. A closed system can then be employed by returning all the displaced vapors to a storage tank. The storage tank should be connected to a vapor recovery system.

## CATALYST REGENERATION

Modern petroleum processes of cracking, reforming, hydrotreating, alkylation, polymerization, isomerization, and hydrocracking are commercially feasible because of materials called catalysts. Catalysts have the ability, when in contact with a reactant or mixture of reactants, to accelerate preferentially or retard the rate of specific reactions and to do this, with few exceptions, without being chemically altered themselves. Different catalysts vary in their effects. One might, for example, increase oxidation rates while another might change the rate of dehydrogenation or alkylation.

Contact between the catalyst and reactants is achieved in some processes by passing the reactants through fixed beds or layers of catalysts contained in a reactor vessel. Contact in other processes involves simultaneous charging of

catalyst and reactants to a reactor vessel and withdrawal of used catalyst in one stream, and products and unreacted materials in another stream. The first process may be termed a fixed-bed system and the latter a moving-bed system. Moving-bed systems may be further subclassified by the type of catalyst and method of transporting it through the process. Examples are the use of vaporized charge material to fluidize powdered catalyst, as in fluid catalytic cracking units (FCC), and the use of bucket elevators, screws, airlifts, and so forth, to move the catalyst pellets or beads, as in Thermoform catalytic cracking units (TCC) (see Figures 520, 521, and 522).

## TYPES OF CATALYSTS

Generally, the catalysts are used in the form of solids at process temperatures, though some liquid catalysts are used alone or impregnated into inert solid carriers. Pellets, beads, and powders are the common physical shapes. Cracking catalysts are usually beads or powders of synthetic silica-alumina compositions, including acid-treated bentonite clay, Fuller's earth, aluminum hydrosilicates, and bauxite. Little-used synthetic catalysts include silica-magnesia, alumina-boria, and silica-zirconia (Nelson, 1958). Bead or pelleted catalyst, noted for ease of handling and freedom from plugging, is used in TCC units while powdered catalyst is used in FCC units. Natural catalysts are softer and fail more rapidly at high temperatures than most synthetic

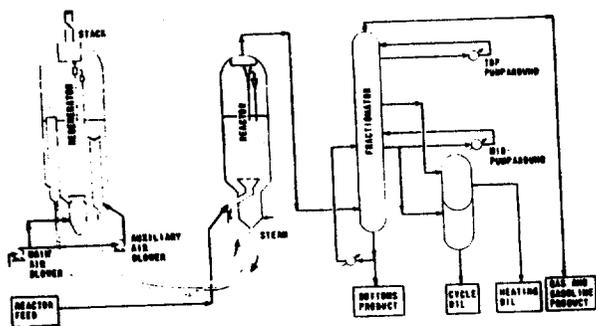


Figure 520. Simplified flow diagram of a Model IV fluid catalytic cracking unit (Oil and Gas Journal, 1957).

catalysts do. The cost of natural catalysts, however, is under \$100 per ton while synthetic types cost \$300 or more per ton.

Catalysts employed in catalytic reforming include the platinum-containing catalysts used in modern fixed-bed reformers, except for the bauxite pellet catalyst for Cycloversion used at 950° to 1,000°F and 50 to 57 psig, and the molybdena-alumina catalysts used for fluid hydroforming. Fixed-bed reactors operate at 825° to 1,000°F and 200 to 1,000 psig with catalyst pellets about 1/8 inch in diameter. These catalysts contain less than 1 percent platinum and are supported on a base of either alumina or silica-alumina. Acid-type catalyst required for reforming processes may be provided by one of the oxides as the catalyst base. The acid may be a halogen compound add-

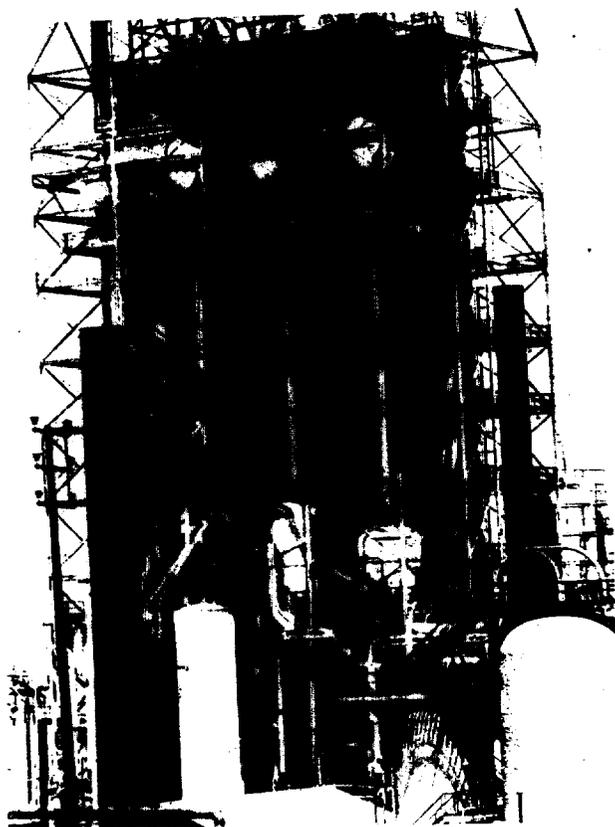


Figure 521. Thermoform catalytic cracking unit (Union Oil Company of California, Los Angeles, Calif.).

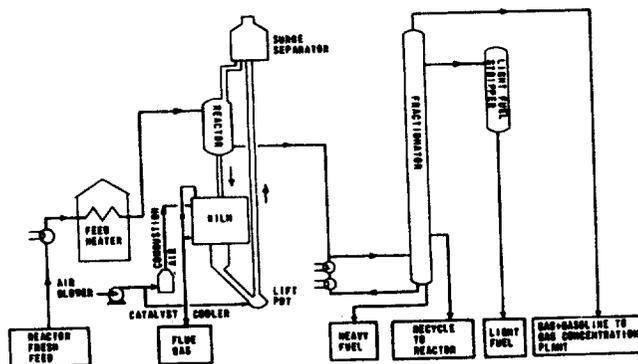


Figure 522. Simplified flow diagram of Thermoform catalytic cracking unit with modern catalyst air-lift (Oil and Gas Journal, 1957).

ed to the catalyst, or may be directly added to the reformer charge. The flow diagram of a platforming process is shown in Figure 523.

The major desulfurization processes—Autofining, Dieselforming, HDS, Hydrofining, Ultrafining, Unifining, and so forth—employ a cobalt-molybdenum catalyst supported on bauxite and operate within a range of 450° to 850°F and 50 to 1,500 psig.

Commercial alkylation processes employ as catalysts either sulfuric acid, hydrogen fluoride, or aluminum chloride with a hydrogen chloride promoter.

Commercial polymerization catalysts consist of a thin film of phosphoric acid on fine-mesh quartz, copper pyrophosphate, or a calcined mixture of phosphoric acid.

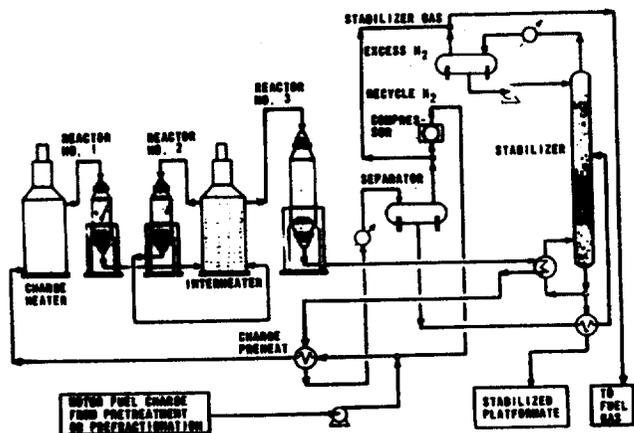


Figure 523. Simplified flow diagram of platforming process (Oil and Gas Journal, 1957).

Isomerization processes such as Butamer, Iso-ikel, Isomerate, Penex, and Pentafining employ a noble metal, usually platinum, as the catalyst in a hydrogen atmosphere. Liquid-phase isomerization is accomplished with aluminum chloride in molten antimony chloride with a hydrogen chloride activator.

#### Loss of Catalyst Activity

The activity of a catalyst, or its effectiveness in changing rates of specific reactions decreases with on-stream time. The rate of decrease is related to composition of reactants contacted, throughput rate, and operating conditions. Loss of activity results from metal contamination and poisoning or deposits that coat the catalyst surfaces and thus reduce the catalytic area available for contact with the reactants. Frequently carbon from the coking of organic materials is the main deposit. To continue in successful operation, catalyst activity must be restored. One procedure consists of replacing the spent catalyst with fresh catalyst. A second procedure consists of treating the spent catalyst for removal of contaminants. This latter procedure, called catalyst regeneration, is the more significant from the standpoint of air pollution, since combustion is frequently the method of regeneration.

In fixed-bed systems, catalysts are regenerated periodically in the reactor or removed and returned to the manufacturer for regeneration. In moving-bed systems, catalysts are continuously removed from the reactor, regenerated in a special regenerator vessel, and returned to the reactor.

#### REGENERATION PROCESSES

Catalysts for the catalytic cracking and reforming processes are regenerated to restore activity

by burning off the carbon (coke) and other deposits from the catalyst surface at controlled temperature and regeneration air rates. Actually, the so-called "carbon" on the catalyst is not all pure carbon but contains other compounds. Moreover, the catalyst is not entirely freed of the carbon deposits during regeneration, though an effort is made to keep the residual carbon below 0.9 percent by weight on the regenerated catalyst. FCC units, all of which have continuous catalyst regeneration, have a coke burnoff rate 5 to 10 times higher than TCC unit regenerators have. Since fixed-bed reformer units, which incorporate catalyst regeneration, have a very small coke laydown on the catalyst surface, they require regeneration only once or twice a year, as the desulfurizer reactors do, which have both a coke and sulfur laydown.

#### FCC Catalyst Regenerators

Catalyst regenerators for FCC units may be located alongside, above, or below the reactor. Regenerators normally have a vertical, cylindrical shape with a domed top. The inside shell of the regenerator is insulated with 4 to 6 inches of refractory lining. This lining may also be extended into the regenerator's discharge line and the regenerator's catalyst charge line.

The upper section of the regenerator is equipped with internal cyclone separators to separate the catalyst dust from the regeneration combustion gases. The number of cyclone separators varies from a single-stage or two-stage separator to as many as 12 sets of three-stage cyclone separators. External size of the regenerator varies from 20 feet in diameter by 40 feet high to 50 feet in diameter by 85 feet high. In Los Angeles County, regenerator flue gases pass through additional equipment, consisting of electrical precipitators or cyclone separators and electrical precipitators for final dust removal, before discharging to the atmosphere. Carbon monoxide waste-heat boilers are employed before or following the electrical precipitators.

In a typical FCC unit, as shown in Figure 520, the spent catalyst from the base of the reactor is steam stripped to remove residual hydrocarbons and then transferred to the regenerator by injecting preheated air into the transfer line. Burning off of the carbon starts when the hot, spent catalyst contacts the air, and continues as the catalyst flows up through the regenerator to the overflow well. Additional combustion air is furnished by the main blower. The amount of air supplied is controlled to prevent glazing the catalyst. This results in the formation of considerable amounts of carbon monoxide. The depth of the fluidized catalyst bed is usually limited to

15 feet to prevent the load on the cyclones from being excessive. Regenerated catalyst flows down through the overflow well to the reactor as a result of a slight pressure differential.

The flue gases pass through the regenerator's cyclone separators, for removal of most of the catalyst more than 10 microns in size; through a steam generator, where process steam is made; through a pressure-reducing chamber to air pollution control units; and then to the atmosphere. The pressure-reducing chamber serves as a noise suppressor. Final dust cleanup is accomplished by passing the effluent gases from the cyclone separators through an electric precipitator. The gases from the precipitator are introduced into a carbon monoxide boiler where the sensible heat and the heat content of the CO is used to produce steam in some flow schemes. Other operations place the waste-heat boiler before the precipitator.

According to Brown and Wainwright (1952), the weight of dust per cubic foot of exit gas remains constant at about 0.002 pound at bed velocities up to a critical velocity of 1.5 fps, whereupon it rises rapidly with higher velocities, for example, to 0.01 pound at 1.8 fps. The pressures in FCC unit regenerators are always low, between 1 and 10 psig. Regeneration temperatures are usually between 1,050° and 1,150°F. Other general operating data for large and small FCC unit regenerators are as follows:

	<u>Small unit</u>	<u>Large unit</u>
Catalyst circulation rate, tons/min	10	60
Coke burnoff rate, lb/hr	5,000	34,000
Regeneration air rate, scfm	13,000	102,000

#### TCC Catalyst Regenerators

TCC (and Houdry unit) catalyst regenerators, referred to as kilns, are usually vertical structures with horizontal, rectangular, or square cross sections. A regenerator that has a catalyst circulation rate of 150 tons per hour would have an outside dimension of about 11 feet square by 43 feet high. This size regenerator, or kiln, has approximately 10 regeneration zones and a topside kiln hopper. Each zone is equipped with a flue gas duct, air distributors, and steam- or water-cooling coils. The carbon steel shell of the regenerator is lined with about 4 inches of firebrick, which is, in turn, covered with alloy steel. The discharge flue gases from the regeneration kilns are usually vented through dry-type, centrifugal dust collectors.

In a TCC unit, Figure 521, spent catalyst (beads) from the base of the reactor is steam purged for

removal of hydrocarbons and lifted by a bucket elevator to a hopper above the regeneration kiln. Catalyst fines at this point in the process are separated from catalyst beads in an elutriator vessel using up-flowing gases and are collected from these gases in a cyclone separator discharging to a fines bin. Spent catalyst beads drop through a series of combustion zones, each of which contains flue gas collectors, combustion air distributors, and cooling coils. The catalyst is regenerated as it flows downward through the kiln zones countercurrent to preheated air (400° to 900°F). The pressure is essentially atmospheric in the kiln. Water is circulated through cooling coils in each kiln zone to control the rate of coke combustion. The regeneration temperatures at the top of the kiln are between 800° and 900°F, while the bottom section of the kiln operates between 1,000° and 1,100°F. A minimum temperature of 900°F is required for catalyst regeneration. An average-size TCC unit regenerator with a catalyst circulation of 2.5 tons per minute has a coke burnoff rate of 3,500 pounds per hour and a regeneration air rate of 24,000 scfm.

Regenerated catalyst from the bottom of the kiln is then transferred by bucket elevator to the catalyst bin for reuse in the reactor. The more modern TCC units use a catalyst airlift (Figure 522) rather than bucket elevators for returning regenerated catalyst to the reactor, and gravity flow for moving spent catalyst to the regenerator. The elevators of those units must be vented through wet centrifugal collectors or scrubbers to the atmosphere.

#### Catalyst Regeneration in Catalytic Reformer Units

Some types of catalytic reformer units are shut down once or twice each year for regeneration of the catalyst in the desulfurizer reactor. Reforming units using Sinclair-Baker catalyst are in this category. Before the regenerating, the reformer system is depressured, first to the fuel gas system and then to vapor recovery. A steam jet discharging to vapor recovery is then used to evacuate the reformer further to 100 millimeters of mercury absolute pressure. An inert gas such as nitrogen is introduced to purge and then repressure the system to 50 psig. The nitrogen is circulated by the recycle gas compressor through the heaters, reactors, heat exchangers, flash drum, and regeneration gas drier. Inert gas circulation is continued while combustion air for burning off the coke is introduced into the top of the first reactor by the regeneration air compressor. The rate of air is controlled to maintain catalyst bed temperatures below 850°F. Pressure is controlled to 150 psig by releasing products of combustion to the fire-

box of the reformer heater. After burning is completed in the first reactor, as indicated by the rise in oxygen content in the effluent, the air supply is then switched to the second reactor. The same procedure is repeated for the other reactors.

In the regeneration cycle, circulation of approximately 15,000 scfm flue gas is maintained by using the reformer recycle gas compressor, and approximately 500 scfm regeneration air is added for burning off the coke. About 24 to 30 hours is required for regeneration, based upon a coke content of 5 percent by weight in the catalyst. The coke may run about 90 percent carbon and 10 percent hydrogen.

Desulfurization reactors are depressured in the same manner as the catalytic reformer described. During catalyst regeneration, however, superheated steam is added along with inert air containing about 1.4 mol percent oxygen to effect temperature control. In addition to coke, there are also sulfur deposits that are burned to sulfur dioxide. In some installations the regeneration gases are passed through packed scrubbers that use water or caustic for partial absorption of sulfur dioxide. These reactors are also regenerated for a period of approximately 24 hours about once or twice a year.

Regeneration of fluid hydroforming catalyst, a white powder consisting of molybdena-coated alumina, is accomplished by continuously withdrawing a portion of the catalyst recirculating in the reactor and burning the carbon off in a separate regenerator using fresh air with no preheat. The regeneration temperature is 1,100° to 1,150°F at 200 to 250 psig with 100 percent carbon removal. Molybdenum sulfide, formed by the reaction of catalyst molybdenum oxide and feed stock sulfur, is reoxidized to molybdenum oxide with the release of sulfur dioxide during regeneration.

In alkylation units using hydrogen fluoride as catalyst, the acid strength is restored by removing the water of dilution by distillation. The effectiveness of alkylation units using sulfuric acid as the catalyst is maintained by adding fresh acid as spent acid is withdrawn. The spent acid may be reconcentrated or used as is for other purposes.

Phosphoric acid catalyst used in polymerization units is regenerated by water washing, steaming, and drying the fine-mesh quartz carrier, and adding fresh phosphoric acid. After the excess acid is drained, the reactor is ready to go back on stream.

Many of the remaining catalytic processes require only infrequent catalyst replacement or

regeneration (Unicracking and Isomax). In the H-Oil process, however, catalyst is continuously replaced.

### THE AIR POLLUTION PROBLEM

Air contaminants are invariably released to the atmosphere from regeneration operations, especially from operations involving combustion. The variety of air contaminants released is broad and may include catalyst dust and other particulate matter, oil mists, hydrocarbons, ammonia, sulfur oxides, chlorides, cyanides, nitrogen oxides, carbon monoxide, and aerosols. The contaminants evolved by any one type of regenerator are a function of the compositions of the catalyst and reactant, and operating conditions.

Tables 172 through 177 show stack emissions for regeneration of both FCC and TCC units. The data in these tables are the results of a testing program (Sussman, 1957) to establish the magnitude of the listed components in the catalyst regeneration gases.

The largest quantities of air pollution from catalyst-regenerating operations are experienced in FCC units. The pollutants include carbon monoxide, hydrocarbons, catalyst fines dust, oxides of nitrogen and sulfur, ammonia, aldehydes, and cyanide. Typical losses from fluid catalytic cracking regenerators, based upon Tables 173 through 176, include:

<u>Pollutant</u>	<u>Loss to atmosphere, lb/hr</u>
Carbon monoxide	24,300
Sulfur dioxide	545
Hydrocarbons	231
NO <sub>x</sub> as nitrogen dioxide	80.2
Particulate matter	65.5
Ammonia	57.4
Sulfur trioxide	32.7
Aldehydes as formaldehyde	21.6
Cyanides as hydrogen cyanide	0.27

TCC catalyst regeneration produces air contaminants similar to those from FCC catalyst regeneration. Quantities produced, however, are considerably less, as can be seen from Tables 173 through 176. The bead-type catalyst used in TCC units does not result in the large amount of catalyst fines that are encountered in FCC units.

Air pollution problems are not as severe from catalyst regeneration of reforming and desulfurization reactors as those from FCC and TCC units. These reactors are regenerated only once or twice a year for a period of about 24 hours. The burning-off of the coke and sulfur deposits on the

Table 172. OPERATING CHARACTERISTICS OF FLUID AND THERMOFOR CATALYTIC CRACKING UNITS (Sussman, 1957)

Type <sup>a</sup>	Date tested, 1956	Feed rate		Catalyst circulation rate, tons/hr	Regenerator air rate, scfm	Coke burn-off rate, lb/hr	Avg gas temp, °F
		Fresh, bpd	Recycle, bpd				
FCC	10/4	40,000	10,000	4,500	112,000	38,000	820
FCC	12/4	29,500	2,045	1,560	28,000	23,000	510
FCC	8/30	24,000	0	1,380	22,200	21,300	520
FCC	11/27	32,610	13,680	2,532	97,500	36,416	485
TCC	11/1	9,525	1,500	180	27,000	4,715	840
TCC	11/1	8,525	7,400	150	27,000	2,610	700
FCC	10/9	25,000	9,000	3,240	64,000	21,600	530
TCC	10/18	10,000	0	165	22,000	5,655	660
TCC	10/18	8,000	3,000	150	27,600	4,620	610
TCC	9/19	7,071	5,538	150	24,000	4,410	850
TCC	9/19	6,506	5,602	150	25,000	5,020	740
TCC	9/12	7,099	6,004	150	27,000	3,420	810
TCC	9/12	6,053	6,013	120	23,000	3,000	710
FCC	11/8	6,462	606	390	13,300	5,400	610
TCC	12/19	8,000	3,000	200	16,800	3,760	680

<sup>a</sup>All fluid catalytic cracking units are equipped with electrical precipitators; all Thermoform catalytic cracking units are equipped with cyclone collectors.

Table 173. PARTICULATE LOSS FROM FLUID AND THERMOFOR CATALYTIC CRACKING UNIT STACKS (Sussman, 1957)

Type	Total particulate, <sup>a</sup> lb/hr
FCC	57.50
FCC	61.00
FCC	181.00
FCC	58.70
TCC	1.36
TCC	1.64
FCC	28.30
TCC	13.80
TCC	8.06
TCC	3.44
TCC	2.22
TCC	9.53
TCC	10.01
FCC	6.42
TCC	4.30

<sup>a</sup>The total particulate loss includes weight of insoluble solids in the water, and HCL impinger solution added to the alundum thimble catch.

catalyst surface produces hydrocarbons, sulfur dioxide, and carbon monoxide, in addition to carbon dioxide and water.

#### AIR POLLUTION CONTROL EQUIPMENT

Dust from FCC catalyst regenerators is collected by centrifugal collectors or centrifugal collectors and electrical precipitators. General design features of these collectors are discussed in Chapter 4. Carbon monoxide waste-heat boilers eliminate carbon monoxide and hydrocarbon emissions in FCC regeneration gases. Dry-type, centrifugal dust collectors are used to collect the catalyst fines from TCC regeneration gas. Dust emissions from TCC unit reactors and regenerator catalyst elevators can be adequately controlled by wet- or dry-type, centrifugal collectors. Presently, no TCC units are equipped with carbon monoxide waste-heat boilers. Manifolding several TCC units could possibly result in a quantity of flue gas large enough to improve economic justification for a CO boiler.

The carbon monoxide and hydrocarbons in reforming and desulfurization catalyst regeneration gases can be efficiently incinerated by passing the regeneration gases through a heater firebox. In some installations the sulfur dioxide is scrubbed by passing the regeneration gases through a packed water or caustic tower.

#### Wet- and Dry-Type, Centrifugal Dust Collectors

Cyclone separators are widely used for catalyst dust collection systems in refineries. They are located in the upper sections of both FCC unit

Table 174. TOTAL HYDROCARBON EMISSIONS FROM FLUID AND THERMOFOR CATALYTIC CRACKING UNIT STACKS<sup>a</sup> (Sussman, 1957)

Type	Mass spectrometer				Infrared spectrophotometer	
	Hydrocarbons	Hydrocarbons	Wt % C <sub>1</sub> and C <sub>2</sub>	Vol % C <sub>1</sub> and C <sub>2</sub>	Hydrocarbons (as hexane), tons/day	Hydrocarbons (as hexane), ppm
FCC	7.4	1,213	67.7	87.4	2.80	142
FCC	3.1	1,150	84.1	94.6	0.89	78
FCC	2.1	760	68.3	85.5	0.60	65
FCC <sup>c</sup>	1	98	42.3	54.1	0.30	12
TCC <sup>e</sup>	-	-	-	-	0.02	8
TCC <sup>e</sup>	-	-	-	-	0.02 <sup>h</sup>	-
FCC <sup>d, e</sup>	-	-	-	-	1.20	116
TCC <sup>d</sup>	0.4	308	40.9	70.8	0.04	13
TCC <sup>d</sup>	0.5	4,484	55.1	81.4	0.15	43
TCC <sup>b, c</sup>					g	-
TCC <sup>b, c</sup>	0.1	87	79.5	77	0.02	14
TCC	0.5	121	67.4	67.8	f	-
TCC					0.02	9
FCC	0.3	328	51.2	75.3	-	Trace
TCC	1.4	1,655	61.9	18.8	0.30	108

<sup>a</sup>All concentrations are reported on a dry basis.

<sup>b</sup>Only the mass spectrometer results for Units F-2T and F-4T were reliable. Since Units F-1T and F-2T and Units F-3T and F-4T are twin units, the data shown result from combining the twin units.

<sup>c</sup>No methane present as determined by mass spectrometer.

<sup>d</sup>Mass spectrometer determinations include oxygenated C<sub>4</sub> and C<sub>5</sub> hydrocarbons.

<sup>e</sup>The mass spectrometer results were not reliable.

<sup>f</sup>The infrared spectrophotometer results were not reliable.

<sup>g</sup>Concentrations of hydrocarbons are below limit of accuracy of the infrared spectrophotometer.

<sup>h</sup>Infrared spectrophotometric determinations were made on Unit D-1T only. The results shown were obtained by assuming that twin Unit D-1T and D-2T emit the same quantity of hydrocarbons.

reactors and regenerators for collecting entrained catalyst. Some TCC units also use cyclones for catalyst fines collection from kiln regeneration gases. The cyclones are employed as a single unit or in multiple two-stage or three-stage series systems. Large FCC unit regenerators may have as many as 12 three-stage cyclones, while smaller units may have only 1 two-stage cyclone. In general, high-efficiency cyclones have dust collection efficiencies of over 90 percent for particle sizes of more than 15 microns. The efficiency drops off rapidly for particles of less than 10 microns.

Multiple cyclones are used in some cases for catalyst fines collection catalyst regeneration gases in TCC units. Dust collection efficiencies are in the same range as those for high-efficiency cyclones. Wet-type, centrifugal collectors or scrubbers adequately clean the gas streams from the catalyst elevators, and part of the regeneration gases from the kilns. Untreated water in the

wet collector, however, can cause a carbonate deposit on the impeller, which is responsible for excessive wear on the collector bearings. This can and has resulted in excessive shutdown time for repairs. Table 178 shows particulate emissions from two wet-type, centrifugal catalyst dust collectors.

#### Electrical Precipitators

Many FCC units incorporate electrical precipitators for final collection of catalyst dust from catalyst regeneration gases. Electrical precipitators (see Figure 524) are normally installed in parallel systems because of the large volume of regeneration gases involved in FCC unit regenerators. Power requirements for these precipitators may range from 35 kva for small FCC units to 140 kva for the larger installations. The hot gases from the regenerator must be cooled from approximately 1,100° to below 500°F before entering the precipitator. This is accom-

Table 175. EMISSIONS OF SULFUR OXIDES, AMMONIA, AND CYANIDES FROM STACKS OF FLUID AND THERMOFOR CATALYTIC CRACKING UNITS<sup>a</sup> (Sussman, 1957)

Type	SO <sub>3</sub> lb/hr	SO <sub>2</sub>			Totals as SO <sub>2</sub> , vol %	Wt % SO <sub>3</sub> in total oxides of sulfur	NH <sub>3</sub>		Cyanides as HCN,		
		Chemical anal.		MS, <sup>b</sup> ppm			lb/hr	ppm	Chemical anal.		MS, <sup>b</sup> ppm
		lb/hr	ppm						lb/hr	ppm	
FCC	164	535	438	47	0.055	23.5	130	401	0.250	0.48	430
FCC	12.0	362	512	220	0.540	3.2	27.0	140	0.280	0.94	360
FCC	1.20	1,260	2,190	1,850	0.220	0.1	20.5	134	Trace	Trace	240
FCC	8.90	453	308	20	0.031	1.8	26.0	67	0.291	0.47	170
TCC	1.25	17.5	114	-	0.011	6.7	1.20	29	0.010	0.15	-
TCC	-	-	-	-	-	-	-	-	-	-	-
FCC	6.90	648	984	-	0.098	1.1	118	675	0.054	0.19	-
TCC	5.10	15.1	86	15	0.011	25.0	4.60	99	0.005	0.07	370
TCC	2.0	14.0	65	10	0.008	13.0	3.40	60	0.060	0.70	230
TCC	1.60	18.7	151	-	0.016	7.9	2.20	67	Trace	Trace	-
TCC	2.70	13.2	136	91	0.016	17.0	1.90	74	Trace	Trace	90
TCC	5.74	13.0	105	-	0.015	30.6	1.56	47	Trace	Trace	-
TCC	7.77	11.1	97	60	0.015	41.2	3.12	103	Trace	Trace	180
FCC	3.07	205	1,310	360	0.130	1.4	23.0	550	0.018	0.27	190
TCC	0.62	24.4	141	15	0.014	2.5	2.80	61	0.039	0.54	220

<sup>a</sup>All concentrations are reported on a dry basis.<sup>b</sup>MS = mass spectrophotometer.Table 176. EMISSIONS OF ALDEHYDES, OXIDES OF NITROGEN, CO<sub>2</sub>, O<sub>2</sub>, CO, AND N<sub>2</sub> FROM STACKS OF FLUID AND THERMOFOR CATALYTIC CRACKING UNITS<sup>a</sup> (Sussman, 1957)

Type	Aldehydes as HCHO,		NO <sub>x</sub> as NO <sub>2</sub> ,		NO by MS, ppm	CO <sub>2</sub> , vol %,		O <sub>2</sub> , vol %,		CO, vol %, ORSAT	N <sub>2</sub> , vol % by diff, ORSAT
	lb/hr	ppm	lb/hr	ppm		ORSAT	MS	ORSAT	MS		
FCC	77.0	130	26.0	29	250	8.7	11.1	5.1	2.2	4.9	81.0
FCC	18.0	53	4.2	8	-	8.5	8.8	3.5	4.1	7.8	80.2
FCC	25.9	96	163	394	160	10.0	11.8	2.3	2.3	6.1	81.6
FCC	4.0	5	202	191	11	13.4	13.4	2.0	2.3	0	84.6
TCC	3.5	49	5.7	51	-	8.2	-	7.9	-	1.4	82.5
TCC	-	-	-	-	-	-	-	-	-	-	-
FCC	0.9	3	5.9	12	-	9.5	-	2.7	-	6.8	81.0
TCC	2.2	26	0	0	200	9.2	12.1	6.6	-	3.2	81.0
TCC	1.2	12	0	0	170	4.7	9.0	13.5	-	0.7	81.1
TCC	0.6	12	3.1	34	-	9.6	-	8.3	-	1.5	80.6
TCC	0.4	9	2.2	32	190	12.8	13.3	2.5	2.5	3.6	81.1
TCC	2.6	44	2.7	30	-	8.4	-	9.8	-	0	81.6
TCC	3.4	63	0.6	7	130	8.8	9.2	7.8	11.1	2.6	80.8
FCC	1.5	20	-	-	310	7.8	7.8	5.1	5.5	6.1	81.0
TCC	14.3	177	7.7	62	230	9.0	9.0	6.9	7.3	4.1	80.0

<sup>a</sup>All concentrations are reported on a dry basis.

plished by a waste-heat boiler. The electrical conductivity of the gas stream may be increased by injecting ammonia upstream of the precipitator.

The inlet ducting is designed to effect a uniform gas distribution through the precipitator cross section. A perforated-plate inlet or vane section assists in accomplishing the desired distribution.

The precipitators usually employ either a continuous-type electrode-rapping and plate-vibrating sequence or an intermittent hourly rapping cycle. A dust plume up to 90 percent opacity arises for a period of 1 to 2 minutes from the precipitator's discharge stack during the intermittent hourly rapping cycle. This high-opacity, short-interval plume is not normally encountered with the continuous rapping sequence.

Table 177. MOISTURE AND FLUE GAS VOLUMES, %, FROM STACKS OF FLUID AND THERMOFOR CATALYTIC CRACKING UNITS (Sussman, 1957)

Type	Vol % H <sub>2</sub> O as determined from sampling trains	Vol % H <sub>2</sub> O in MS <sup>a</sup> sample	Rate of flow of flue gases (wet basis), scfm	Rate of flow of flue gases (dry basis), scfm
FCC	19.7	0.480	151,000	121,300
FCC	19.2	0.470	86,300	69,700
FCC	26.3	0.186	77,200	56,900
FCC	18.7	0.229	178,800	145,400
TCC	12.1	-	17,300	15,200
TCC	-	-	20,800	-
FCC	18	-	80,900	65,000
TCC	16.5	0.626	20,700	17,280
TCC	11.1	2.448	23,600	20,980
TCC	12.2	-	13,970	12,270
TCC	19	0.885	11,660	9,600
TCC	11	-	13,800	12,300
TCC	11	0.600	12,700	11,300
FCC	25.3	0.458	20,800	15,540
TCC	7.5	1.762	18,400	17,000

<sup>a</sup>MS = mass spectrophotometer.



Figure 524. Top of fluid catalytic cracking unit's Cottrell precipitator. Electrode terminals and 36-inch-diameter flue gasline between precipitator and silencer are shown (Union Oil Company of California, Los Angeles, Calif.).

#### Carbon Monoxide Waste-Heat Boilers

Large amounts of carbon monoxide gases are discharged to the atmosphere with the regeneration flue gases of an FCC unit. The carbon monoxide waste-heat boiler is a means of using the heat of combustion of carbon monoxide and other combustible, and the sensible heat of the regeneration gases. From the air pollution viewpoint, the CO boiler oxidizes the carbon monoxide and other combustibles, mainly hydrocarbons, to carbon dioxide and water.

In most cases, auxiliary fuel is required in addition to the carbon monoxide and may be either fuel oil, refinery process gas, or natural gas. The CO boiler may be a vertical structure with either a rectangular or circular cross section with water-cooled walls, as shown in Figure 525. The outer dimensions of a typical rectangular boiler are 32 feet wide by 44 feet deep by 64 feet high, with a 200-foot-high stack. The boiler is equipped with a forced-draft fan and four sets of fixed, tangential-type burners (one set for each corner). A typical set of burners includes two carbon monoxide gas compartments, four fuel gas nozzles, and two steam-atomized oil burners, as shown in Figure 526. The burners are approximately 1-1/2 feet wide by 6 feet high. A tangential-type mixing of the gases for more nearly complete combustion is achieved by arranging the burners slightly off center.

Table 178. EMISSIONS FROM WET-TYPE, CENTRIFUGAL CATALYST DUST COLLECTORS (THERMOFOR CATALYTIC CRACKING UNIT)<sup>a</sup>

	Collector No. 1 with two inlet streams		Collector No. 2 with two inlet streams	
	TCC No. 1	TCC No. 2	TCC No. 3	TCC No. 4
Inlet gas volume, scfm	1,780	2,090	2,350	1,680
Inlet gas temperature, °F	720	690	740	650
Inlet gas H <sub>2</sub> O content, vol %	38.8	39.3	27.6	22.1
Particulate matter, lb/hr	31.7	40.1	23.2	52.0
	Collector No. 1 discharge		Collector No. 2 discharge	
Outlet gas volume, scfm	4,230		5,090	
Outlet gas temperature, °F	210		210	
Outlet gas H <sub>2</sub> O content, vol %	41.2		30.4	
Particulate loss, lb/hr	10.2		8.6	
Collection efficiency, %	85.8		88.6	

<sup>a</sup>The inlet of each collector is connected by ductwork to the reactor elevator and the Thermoform kiln of two Thermoform catalytic cracking units.

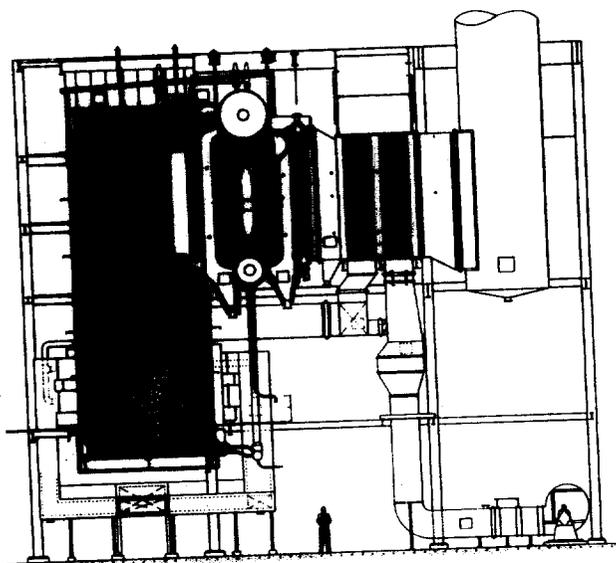


Figure 525. Cylindrical, water-cooled, carbon monoxide waste-heat boiler (Combustion Engineering, Inc., Windsor, Conn.).

Regeneration gases from the FCC unit are normally delivered to the inlet of the CO boiler ductwork at about 1,100°F and 2 psig. Whenever the overhead regenerator gases first pass through an electrical precipitator, the inlet gas to the precipitator must be cooled below 500°F. The CO boiler would then receive regeneration flue gas between 450° and 500°F.

The main reactions of the CO boiler's firebox include burning the refinery gas or fuel oil to carbon dioxide and water and completing the oxidation of the carbon monoxide. Other reactions in-

clude oxidation of the sulfur compounds in the fuel oil or refinery gas to sulfur dioxide. The small amount of ammonia in the regeneration flue gas is primarily converted to oxides of nitrogen at the firebox temperature of between 1,800° and 2,000°F. Table 179 shows the emissions from an FCC unit's CO boiler.

#### Economic Considerations

The economics of a CO boiler installation can be generalized sufficiently to determine a range of catalytic cracking unit sizes that can pay out a boiler (Alexander and Bradley, 1958). The main variable used in determining the size of the catalytic cracking unit is coke-burning rate. Other variables that affect payout include the following in the order of decreasing importance: (1) Fuel value, (2) CO<sub>2</sub>/CO ratio, (3) flue gas temperatures, (4) excess oxygen in CO gas, (5) hydrogen content of regenerator coke.

On the assumption that additional steam is required in the refinery, a coke burnoff rate of 10,000 pounds per hour or more can be economically attractive for installation of a CO boiler when the fuel has a value of 20 cents per million Btu. If, however, additional steam is not required, the minimum coke-burning rate to provide a reasonable payout for a CO boiler is about 18,000 pounds per hour. A payout of 6 years after taxes is assumed to be an attractive investment. In some areas, the reduction in the air contaminants is sufficiently important to justify a payout longer than 6 years.

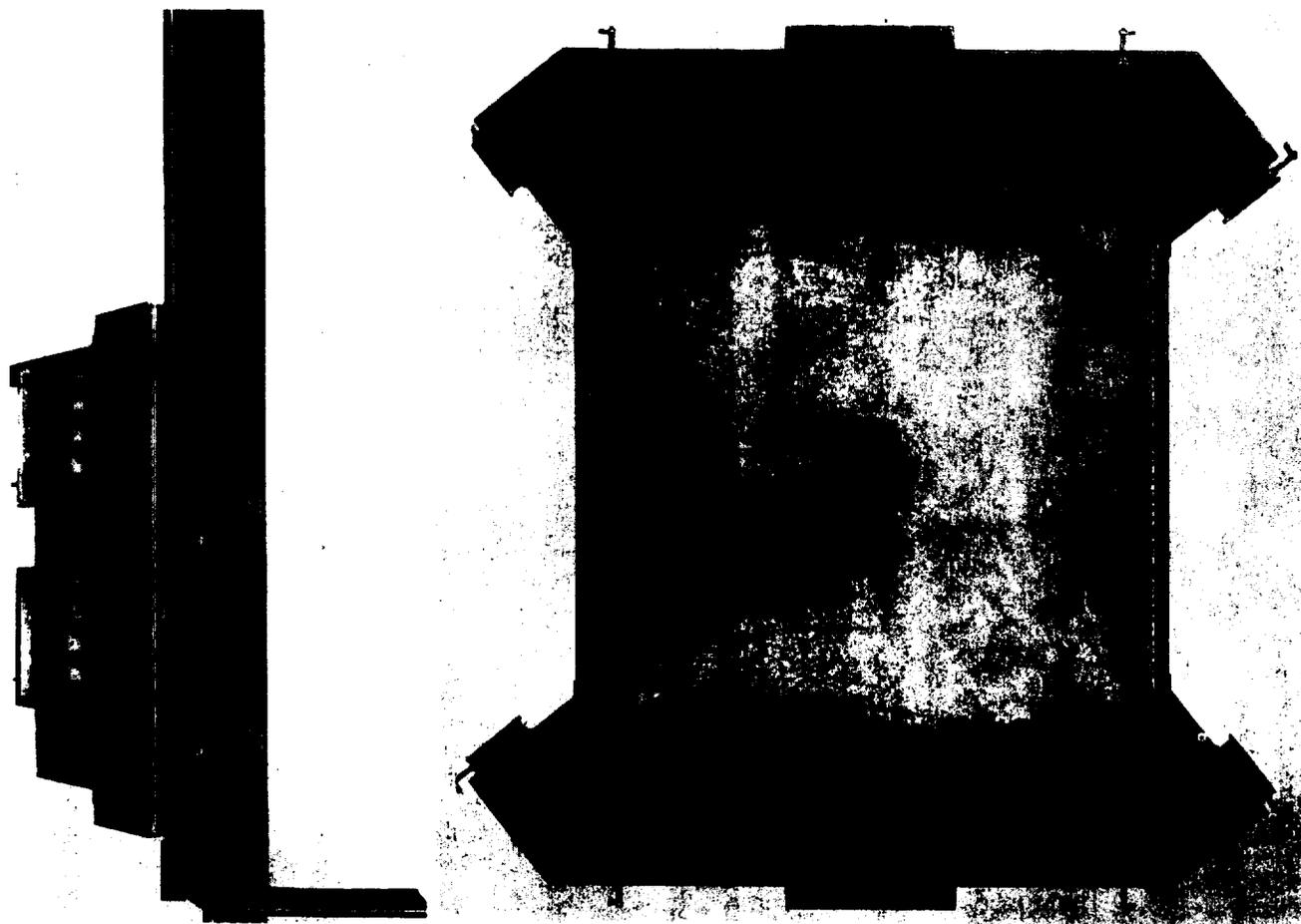


Figure 526. Corner-fired burners of a carbon monoxide waste-heat boiler: (left) Elevation view showing a typical set of burners for one corner; (right) plan view of firebox showing location of the four sets of burners (Combustion Engineering, Inc., Windsor, Conn.).

Table 179. EMISSIONS FROM THE STACKS OF FLUID CATALYTIC CRACKING UNITS' CARBON MONOXIDE WASTE-HEAT BOILERS<sup>a</sup>

	Unit I		Unit II
	East stack	West stack	
Gas volume, scfm	96,800	97,200	60,700
Gas temperature, °F	470	450	570
Dust loss, lb/hr	44	33	34.9
NO <sub>x</sub> as NO <sub>2</sub> , ppm	173	190	67
Aldehydes as HCHO, ppm	15	11	5
NH <sub>3</sub> , lb/hr	19.8	22.5	None <sup>b</sup>
SO <sub>2</sub> , lb/hr	269	282	265
SO <sub>3</sub> , lb/hr	0.16	0.4	1.61
Organic acids as acetic, ppm	-	-	11.7
Hydrocarbons as C <sub>6</sub> , ppm	None	None	< 8
CO <sub>2</sub> , vol % dry basis	14	14.4	8.8
CO, vol % dry basis	0	0	0
O, vol % dry basis	3	2.6	3.5
H <sub>2</sub> O, ol %	22.4	22.7	23.9

<sup>a</sup>Both FCC Units I and II are equipped with electrostatic precipitators.

<sup>b</sup>FCC Unit II does not use NH<sub>3</sub> injection for precipitator conditioning.

## OIL-WATER EFFLUENT SYSTEMS

### FUNCTIONS OF SYSTEMS

Oil-water effluent systems are found in the three phases of the petroleum industry--production, refining, and marketing. The systems vary in size and complexity though their basic function remains the same, that is, to collect and separate wastes, to recover valuable oils, and to remove undesirable contaminants before discharge of the water to ocean, rivers, or channels.

### Handling of Crude-Oil Production Effluents

In the production of crude oil, wastes such as oily brine, drilling muds, tank bottoms, and free oil are generated. Of these, the oilfield brines present the most difficult disposal problem because of the large volume encountered

(Rudolfs, 1953). Community disposal facilities capable of processing the brines to meet local water pollution standards are often set up to handle the treatment of brines. The most effective method of disposal of brines has been injection into underground formations.

A typical collection system associated with the crude-oil production phase of the industry usually includes a number of small gathering lines or channels transmitting waste water from wash tanks, leaky equipment, and treaters to an earthen pit, a concrete-lined sump, or a steel waste-water tank. A pump decants waste water from these containers to water-treating facilities before injection into underground formations or disposal to sewer systems. Any oil accumulating on the surface of the water is skimmed off to storage tanks.

#### Handling of Refinery Effluents

The effluent disposal systems found in refineries are larger and more elaborate than those in the production phase. A typical modern refinery gathering system usually includes gathering lines, drain seals, junction boxes, and channels of vitrified clay or concrete for transmitting waste water from processing units to large basins or ponds used as oil-water separators. These basins are sized to receive all effluent water, sometimes even including rain runoff, and may be earthen pits, concrete-lined basins, or steel tanks.

Liquid wastes discharging to these systems originate at a wide variety of sources such as pump glands, accumulators, spills, cleanouts, sampling lines, relief valves, and many others. The types of liquid wastes may be classified as waste water with:

1. Oil present as free oil, emulsified oil, or as oil coating on suspended matter;
2. chemicals present as suspensoids, emulsoids, or solutes. These chemicals include acids, alkalis, phenols, sulfur compounds, clay, and others.

Emissions from these varied liquid wastes can best be controlled by properly maintaining, isolating, and treating the wastes at their source; by using efficient oil-water separators; and by minimizing the formation of emulsions. Recovery of some of the wastes as valuable byproducts is growing in importance.

#### Treatment of Effluents by Oil-Water Separators

The waste water from the process facilities and treating units just discussed flows to the oil-

water separator for recovery of free oil and settleable solids.

The American Petroleum Institute is recognized as an authoritative source of information on the design of oil-water separators, and its recommended methods are used generally by refineries in Los Angeles County. The basis for design of a separator is the difference in gravity of oil and water. A drawing of a typical separator is shown in Figure 527.

Factors affecting the efficiency of separation include temperature of water, particle size, density, and amounts and characteristics of suspended matter. Stable emulsions are not affected by gravity-type separators and must be treated separately.

The oil-water separator design must provide for efficient inlet and outlet construction, sediment collection mechanisms, and oil skimmers. Reinforced concrete construction has been found most desirable for reasons of economy, maintenance, and efficiency.

#### Clarification of Final-Effluent Water Streams

The effluent water from the oil-water separator may require further treatment before final discharge to municipal sewer systems, channels, rivers, or streams. The type and extent of treatment depend upon the nature of the contaminants present, and on the local water pollution ordinances governing the concentration and amounts of contaminants to be discharged in refinery effluent waters. The methods of final-effluent clarification to be briefly discussed here include (1) filtration, (2) chemical flocculation, and (3) biological treatment.

Several different types of filters may be used to clarify the separator effluent. Hay-type filters, sand filters, and vacuum precoat filters are the most common. The selection of any one type depends upon the properties of the effluent stream and upon economic considerations.

The application of chemical flocculation to the treatment of separator effluent water is a relatively recent development (Reno et al., 1958; Castler et al., 1956). Methods of treatment are either by sedimentation or flotation. In sedimentation processes, chemicals such as copper sulfate, activated silica, alum, and lime are added to the waste-water stream before it is fed to the clarifiers. The chemicals cause the suspended particles to agglomerate and settle out. Sediment is removed from the bottom of the clarifiers by mechanical scrapers.

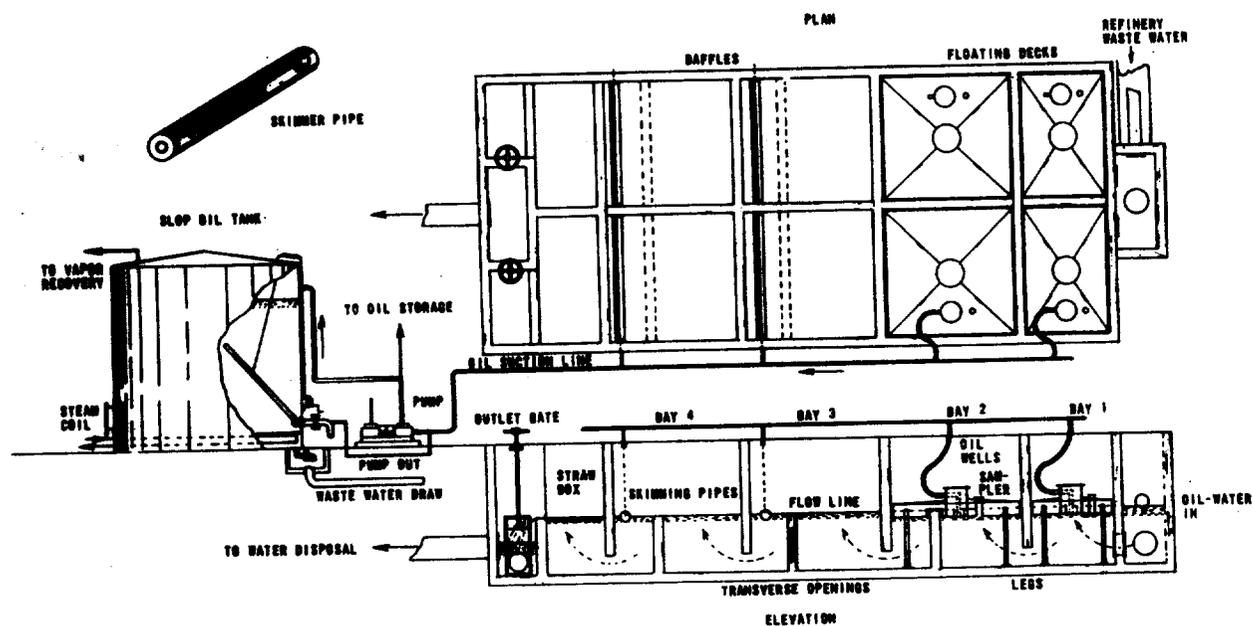


Figure 527. A modern oil-water separator.

Effectiveness of the sedimentation techniques in the treatment of separator effluents is limited by the small oil particles contained in the waste water. These particles, being lighter than water, do not settle out easily. They may also become attached to particles of suspended solids and thereby increase in buoyancy.

In the flotation process a colloidal floc and air under pressure are injected into the waste water. The stream is then fed to a clarifier through a backpressure valve that reduces the pressure to atmospheric. The dissolved air is suddenly released in the form of tiny bubbles that carry the particles of oil and coalesced solids to the surface where they are skimmed off by mechanical flight scrapers. Of the two, the flotation process has the potential to become the more efficient and economical.

Biological treating units such as trickling filters, activated-sludge basins, and stabilization basins have been incorporated into modern refinery waste disposal systems. By combining adsorption and oxidation, these units are capable of reducing oil, biological oxygen demand, and phenolic content from effluent water streams. To prevent the release of air pollutants to the atmosphere, certain pieces of equipment, such as clarifiers, digesters, and filters, used in biological treatment should be covered and vented to recovery facilities or incinerated.

#### Effluent Wastes From Marketing Operations

In the marketing and transportation phase of the industry, waste water containing oil may be discharged during the cleaning of ballast tanks or ships, tank trucks, and tank cars. Leaky valves and connections and flushing of pipelines are other sources of effluents. The methods used for treatment and disposal of these waters are similar to those used in the other phases of the industry.

#### THE AIR POLLUTION PROBLEM

From an air pollution standpoint the most objectionable contaminants emitted from liquid waste streams are hydrocarbons, sulfur compounds, and other malodorous materials.

The effect of hydrocarbons in smog-producing reactions is well known, and sulfur compounds such as mercaptans and sulfides produce very objectionable odors, even in high dilution. These contaminants can escape to the atmosphere from openings in the sewer system, open channels, open vessels, and open oil-water separators. The large exposed surface area of these separators requires that effective means of control be instituted to minimize hydrocarbon losses to the atmosphere from this source. A method (Jones and Viles, 1952) developed by personnel of Humble Oil and Refining Company may be used to estimate the hydrocarbon losses from

open oil-water separators. In the development of this method the principal variables that influence evaporation rates were assumed to be vapor pressure of the oil, and wind velocity. Experimental work was done to observe and correlate the effects of these factors on evaporation rates. From the data compiled, a procedure for calculation of losses was devised. Essentially, this procedure is as follows:

1. Obtain a representative sample of oil at the surface of the separator.
2. Obtain the vapor pressure of the sample and the average wind velocity at the surface of the separator.
3. Using Figure 528, find the loss in bbl/day per ft<sup>2</sup>.
4. Since the data compiled were collected under ideal conditions, a correlation factor is needed to correct the value obtained from Figure 487 to actual separator conditions. This correlation factor may be found by measuring the evaporation rate of a weighted sample of a constantly boiling hydrocarbon from a shallow vessel placed on the surface of the separator. The correlation factor is then calculated as the ratio of the measured rate of evaporation to the theoretical evaporation rate from Figure 487.
5. The product of the theoretical separator loss, the correlation factor, and the separator area represents the total evaporation loss.

## AIR POLLUTION CONTROL EQUIPMENT

### Hydrocarbons From Oil-Water Separators

The most effective means of control of hydrocarbon emissions from oil-water separators has been the covering of forebays or primary separator sections. Either fixed roofs or floating roofs (Brown and Sublett, 1957) are acceptable covers. Separation and skimming of over 80 percent of the floatable oil layer is effected in the covered sections. Thus, only a minimum of oil is contained in the effluent water, which flows under concrete curtains to the open afterbays or secondary separator sections.

Satisfactory fixed roofs have been constructed by using wooden beams for structural support, and asbestos paper as a cover. A mastic-type sealing compound is then used to seal all joints and cracks. Although this form of roof is acceptable for the control of pollutants, in practice, making the roof completely vaportight is difficult. The resultant leakage of air into the vapor space,

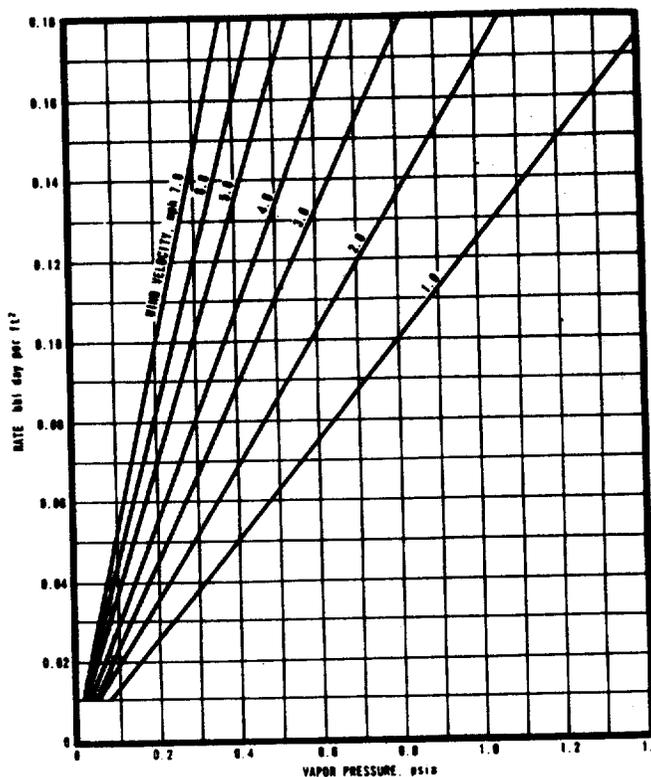


Figure 528. Relationship of laboratory evaporation rates for various wind velocities to vapor pressure of oil (Jones and Viles, 1952).

and vapor leakage into the atmosphere are not desirable from standpoints of air pollution or safety. For example, an explosive mixture resulting from leakage of air from gaging operations into the vapor space of a fixed-roof separator at a Los Angeles refinery was ignited by a static electric spark. The destruction of the wooden roof has emphasized the need for elimination of the vapor space. Another type of enclosed separator with a concrete cover and gas blanketing of the vapor space has proved satisfactory. The effluent vapors from this system are vented to vapor recovery.

The explosion hazard associated with fixed roofs is not present in a floating-roof installation. These roofs are similar to those developed for storage tanks. The floating covers are built to fit into bays with about 1 inch of clearance around the perimeter. Fabric or rubber may be used to seal the gap between the roof edge and the container wall. The roofs are fitted with access manholes, skimmers, gage hatches, and supporting legs. Floating roofs on refinery separators are shown in Figures 529 and 530. In operation, skimmed oil flows through lines from the skimmers to a covered tank (floating roof or connected to vapor recovery) or sump and then is pumped to de-

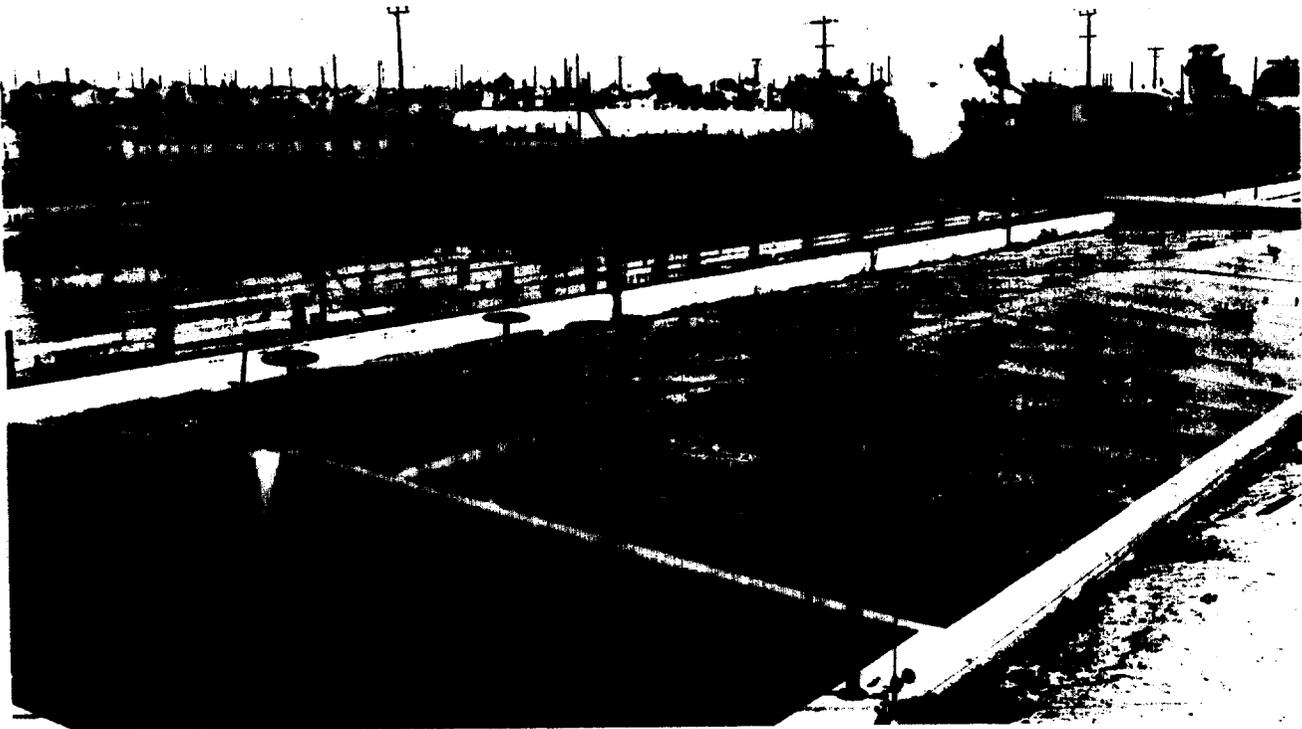


Figure 529. Floating-roof cover on refinery oil-water separator (Union Oil Company of California, Los Angeles, Calif.).

emulsifying processing facilities. Effluent water from the oil-water separator is handled in the manner described previously.

In addition to covering the separator, open sewer lines that may carry volatile products are converted to closed, underground lines with water-seal-type vents. Junction boxes are vented to vapor recovery facilities, and steam is used to blanket the sewer lines to inhibit formation of explosive mixtures.

Accurate calculation of the hydrocarbon losses from separators fitted with fixed roofs is difficult because of the many variables of weather and refinery operations involved. One empirical equation that has been used with reasonable success to calculate losses from separators is

$$w = \frac{AdHm}{(12)(379)} \quad (147)$$

where

- w = weight of hydrocarbon loss, lb/hr
- A = area of covered separator, ft<sup>2</sup>
- d = depth of vapor space, in.

H = vol % of hydrocarbons as hexane in the vapor space

m = molecular weight of hexane.

In using this equation, assume that the density of condensed vapors (C<sub>6</sub>H<sub>14</sub>) equals 5.5 pounds per gallon and that the vapor in the separator is displaced once per hour. The vapor concentration is determined by using the average of readings from a calibrated explosion meter over the entire covered area. The assumption that the vapors are displaced once every hour was determined by using data from work done by the Pacific Coast Gas Association (Powell, 1950).

The previously discussed methods of obtaining emissions from uncovered separators may also be applied to sections covered with fixed roofs. Use of more than one method and a number of tests of one source over a considerable period of time are necessary to ensure an acceptable estimate of emissions.

Emissions from separators fitted with floating-roof covers may be assumed to be almost negligible. A rough approximation of the magnitude of the emission can be made by assuming the emission to be from a floating-roof storage tank of



Figure 530. Floating roof on refinery oil-water separator (Atlantic-Richfield Oil Company, Los Angeles, Calif.).

equivalent perimeter. The API method of calculating losses from storage tanks can then be applied.

#### Treatment of Refinery Liquid Wastes at Their Source

Isolation of certain odor- and chemical-bearing liquid wastes at their source for treatment before discharge of the water to the refinery wastewater-gathering system has been found to be the most effective and economical means of minimizing odor and chemicals problems. The unit that is the source of wastes must be studied for possible changes in the operating process to reduce wastes. In some cases the wastes from one process may be used to treat the wastes from another. Among the principal streams that are treated separately are oil-in-water emulsions, sulfur-bearing waters, acid sludge, and spent caustic wastes.

#### Oil-in-water emulsions

Oil-in-water emulsions are types of wastes that can be treated at their source. An oil-in-water emulsion may be defined as a suspension of oil

particles in water that cannot be divided effectively by means of gravity alone. Gravity-type oil-water separators are, in most cases, ineffective in breaking the emulsions, and means are provided for separate treatment where the problem is serious.

Oil-in-water emulsions are objectionable in the drainage system since the separation of otherwise recoverable oil may be impaired by their presence. Moreover, when emulsions of this type are discharged into large bodies of water, the oil is released by the effect of dilution, and serious pollution of the water may result.

Formation of emulsions may be minimized by proper design of process equipment and piping. Several methods, both physical and chemical, are available for use in breaking emulsions. Physical methods of separation include direct application of heat, distillation, centrifuging, filtration, and use of an electric field. The effectiveness of any one method depends upon the type of emulsion to be treated. Chemical methods of separation are many and varied. During recent years the treatment of waste water containing emulsions with coagulating chemicals has become increasingly popular.

Variations of this form of treatment include air flotation systems, and biological treatment of the waste water, as discussed previously in this section.

#### Sulfur-bearing waters

Sulfides and mercaptans are removed from wastewater streams by various methods. Some refineries strip the waste water in a column with live steam. The overhead vapors from the column are condensed and collected in an accumulator from which the noncondensables flow to sulfur-recovery facilities or are incinerated. One Los Angeles refinery removes all the hydrogen sulfide and about 90 percent of the ammonia from a waste stream by this method. Flue gas has also been used successfully as the stripping medium in pilot-plant studies. Bottoms water from steam-stripping towers, being essentially sulfide free, can then be drained to the refinery's sewer system.

Oxidation of sulfides in waste water is also an effective means of treatment (Smith, 1956a). Air and heat are used to convert sulfides and mercaptans to thiosulfates, which are water soluble and not objectionable. Figure 531 depicts the flow through an air oxidation unit. Experience has shown that, under certain conditions, the thiosulfates may be reduced by the action of Vibrio desulfuricans bacteria, which results in

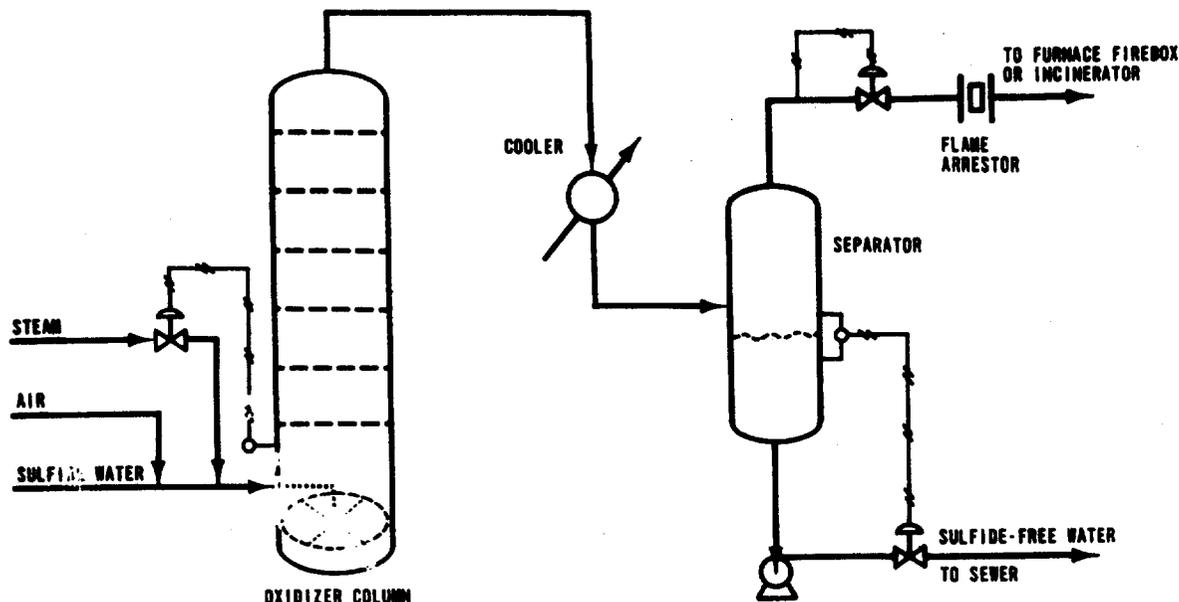


Figure 531. Flow diagram of air oxidation process (Smith, 1956b).

the release of hydrogen sulfide. The reduction takes place only in the absence of dissolved oxygen. Care must be used to keep this water from entering retention sumps or pits subject to this bacterial attack.

Chlorine is also used as an oxidizing agent for sulfides. It is added in stoichiometric quantities proportional to the waste water. This method is limited by the high cost of chlorine. Water containing dissolved sulfur dioxide has been used to reduce sulfide concentration in waste waters. For removing small amounts of hydrogen sulfide, copper sulfate and zinc chloride have been used to react and precipitate the sulfur as copper and zinc sulfides. Hydrogen sulfide may be released, however, if the water treated with these compounds contacts an acid stream.

#### Acid sludge

The acid sludge produced from treating operations varies with the stock treated and the conditions of treatment. The sludge may vary from a low-viscosity liquid to a solid. Methods of disposal of this sludge are many and varied. Basically, they may be considered under three general headings:

1. Disposal by burning as fuel, or dumping in the ground or at sea;
2. processing to produce byproducts such as ammonium sulfate, metallic sulfates, oils, tars, and other materials;
3. processing for recovery of acid.

The burning of sludge results in discharge to the atmosphere of excessive amounts of sulfur dioxide and sulfur trioxide from furnace stacks. This latter consideration has caused the discontinuance of this method of disposal in Los Angeles County. If sludge is solid or semisolid it may be buried in specially constructed pits. This method of disposal, however, creates the problem of acid leaching out to adjacent waters. Dumping in designated sea areas eliminates pollution of the potable waters and atmosphere of populated areas.

Recovery of sulfuric acid from sludge is accomplished essentially by either hydrolysis or thermal decomposition processes. Sulfuric acid sludge is hydrolyzed by heating it with live steam in the presence of water. The resulting product separates into two distinct phases. One phase consists of diluted sulfuric acid with a small amount of suspended carbonaceous material, and the second phase, of a viscous acid-oil layer. The dilute sulfuric acid may be (1) neutralized by alkaline wastes, (2) reacted chemically with ammonia-water solution to produce ammonium sulfate for fertilizer, or (3) concentrated by heating.

Acid sludge may be decomposed by heating to 300°F to form coke, sulfur dioxide, oil, water, and lighter boiling hydrocarbons as a gas. Several commercial decomposition processes have been developed to use the sulfur present in the sludge. In all these processes a kiln is used wherein the sludge is mixed with hot coke or some other carrying agent and heated to the required temperature. Another process allows the acid sludge to be burned directly. The sulfur dioxide gases from the reaction are purified and then either converted to sulfuric acid (contact process) or to free elemental sulfur. The tail gases emitted from these decomposition processes may create an odor nuisance as well as cause damage to vegetation in the surrounding area. Because of this, the tail gases may require additional treatment to preclude the possibility of a nuisance.

Of all the methods discussed, hydrolysis and decomposition are the most desirable from the standpoint of air pollution control, though they are not the most economical when the volume of acid is small.

#### Spent caustic wastes

Caustic soda is widely used in the industry to neutralize acidic materials found in crude oil and its fractions. It is also used to remove mercaptans, naphthenates, or cresols from gas, gasoline, kerosene, and other product streams. The resulting spent caustic is imbued with the odors of the compounds that have been extracted in the various treating processes (American Petroleum Institute, 1960). This spent caustic can be a source of intense objectionable odors and can result in nuisance complaints.

Spent caustic is treated by direct methods or chemical processing, or both. Direct methods of disposal include ponding, dilution, disposal wells, and sale. Of these, ponding is not recommended, since the pond could become a source of air pollutants as well as a possible source of contamination of underground water through seepage. Dilution of spent caustic in large bodies of water is a commonly used method of disposal. The ocean and brackish waters are the only desirable areas for this disposal, to preclude pollution of fresh-water streams.

Disposal wells afford another convenient means of disposing of spent-caustic solutions, provided that local conditions are favorable. The method consists of pumping the liquid wastes into underground formations that contain saline or nonpotable

water. Spent caustics that contain phenolates, cresolates, and sulfides may be sold outside the industry for recovery of these materials.

In addition to these direct methods of disposal, chemical processing methods are available. These include neutralization, combination of neutralization and oxidation, and combination of oxidation and chemical separation.

Neutralization of high-alkaline caustic wastes may be effected by means of spent acids from other refinery operations. After neutralization, the resulting salt solution may be suitable for discharge into the refinery's drainage system. In some cases odorous or oily materials may have to be stripped from the product before discharge. In these instances effluent gases should be incinerated.

Spent-caustic solutions can also be neutralized with acid gases such as flue gases (Fisher and Moriarty, 1953). Oxygen contained in the flue gas tends to oxidize sulfides and mercaptides as a secondary reaction. Effluent gases from this reaction must be properly incinerated to prevent odor problems. The resulting treated solution contains carbonates, bicarbonates, thiosulfates, sulfates, and sulfites and may be suitable for discharge into the drainage system.

A recently developed method of treating caustic wastes involves the addition of pickling acid. The acid is mixed with caustic and is airblown. The resulting solution is filtered and naphtha is added to extract organic acids for recovery. Fumes from the airblowing operation must be incinerated. The treated salt solution is discharged to a drainage system.

## PUMPS

### TYPES OF PUMPS

Pumps are used in every phase of the petroleum industry. Their applications range from the lifting of crude oil from the depths of a well to the dispensing of fuel to automobile engines. Leakage from pumps can cause air pollution wherever organic liquids are handled.

Pumps are available in a wide variety of models and sizes. Their capacities may range from several milliliters per hour, required for some laboratory pumps, to 3/4 million gallons per minute, required of each of the new pumps at Grand Coulee Dam (Dolman, 1952).

Materials used for construction of pumps are also many and varied. All the common machinable metals and alloys, as well as plastics, rubber,

and ceramics, are used. Pumps may be classified under two general headings, positive displacement and centrifugal.

### Positive-Displacement Pumps

Positive-displacement pumps have as their principle of operation the displacement of the liquid from the pump case by reciprocating action of a piston or diaphragm, or rotating action of a gear, cam, vane, or screw. The type of action may be used to classify positive-displacement pumps as reciprocating or rotary. Figures 532 and 533 de-

pic some typical pumps of each type. When a positive-displacement pump is stopped, it serves as a check valve to prevent backflow.

### Centrifugal Pumps

Centrifugal pumps operate by the principle of converting velocity pressure generated by centrifugal force to static pressure. Velocity is imparted to the fluid by an impeller that is rotated at high speeds. The fluid enters at the center of the impeller and is discharged from its periphery. Unlike positive-displacement pumps, when the cen-

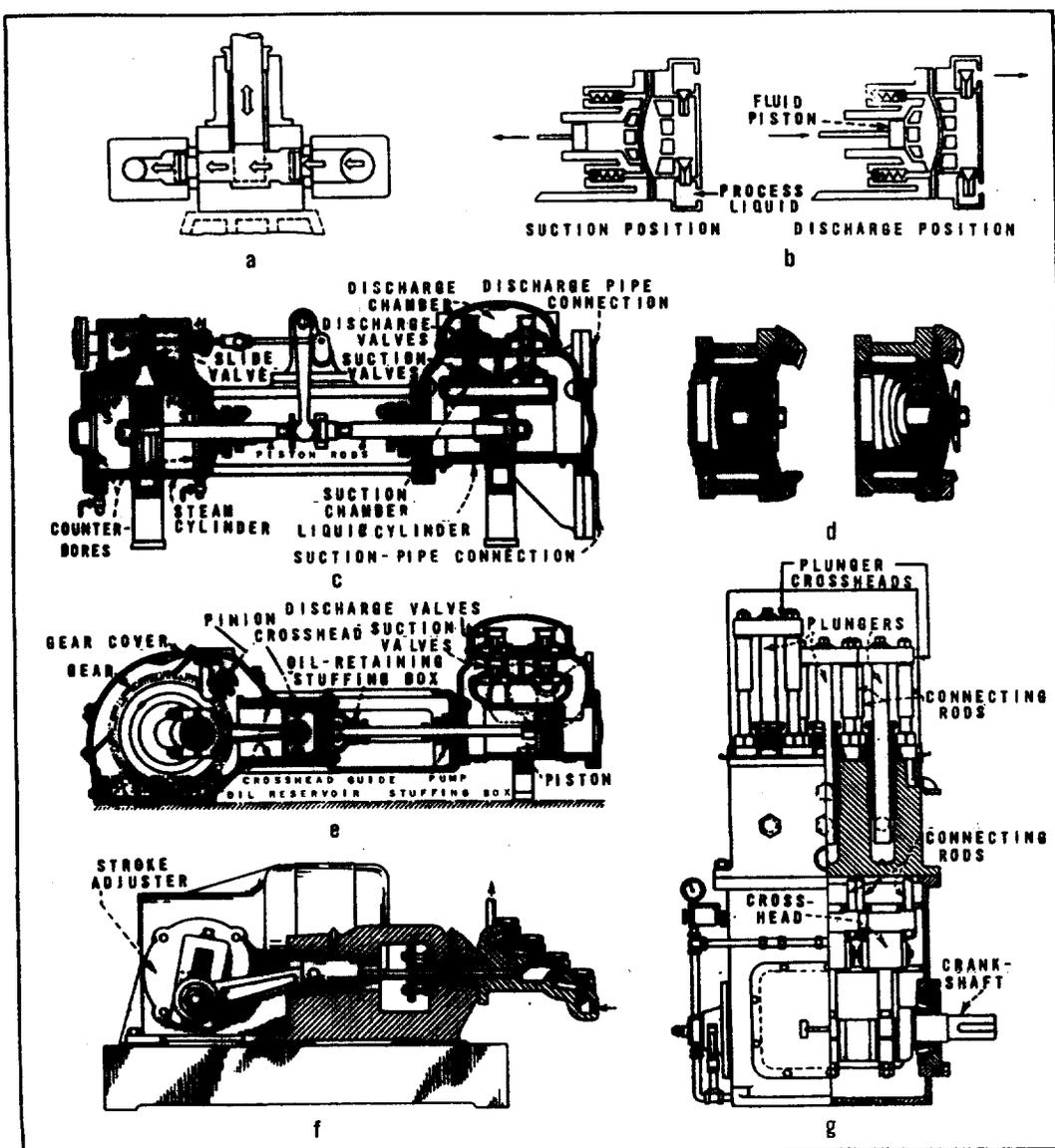


Figure 532. Reciprocating pumps: (a) Principle of reciprocating pump, (b) principle of fluid-operated diaphragm pump, (c) direct-acting steam pump, (d) principle of mechanical diaphragm pump, (e) piston-type power pump, (f) plunger-type power pump with adjustable stroke, (g) inverted, vertical, triplex power pump (Dolman, 1952).

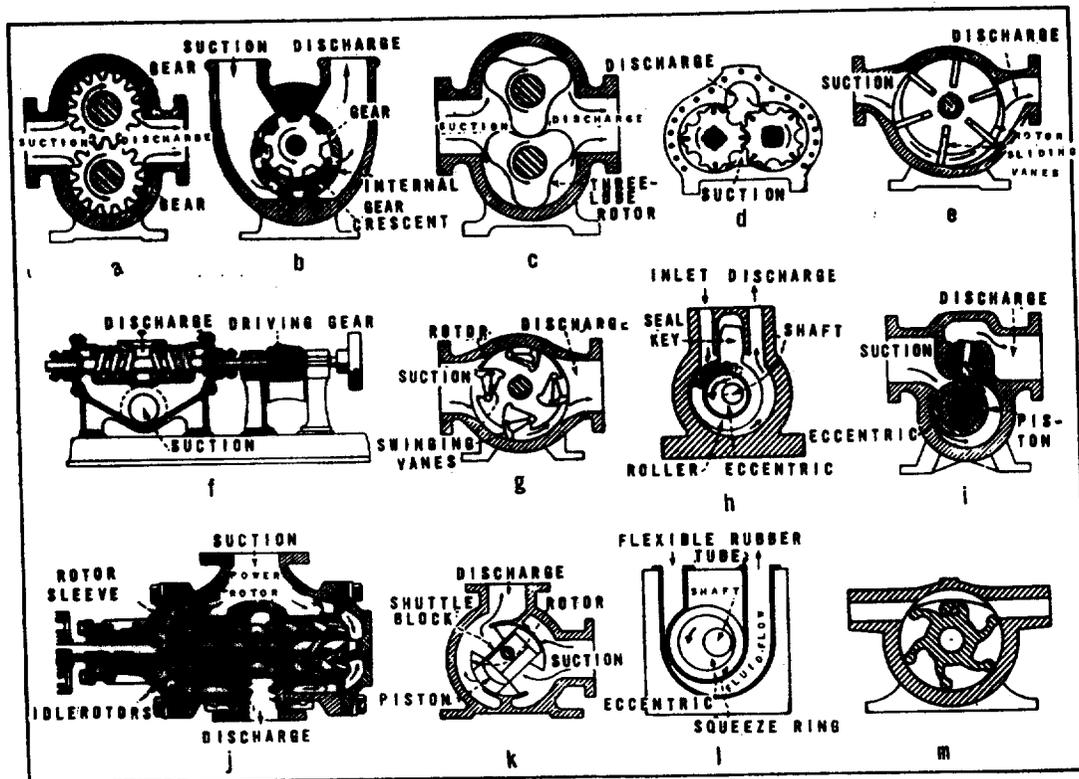


Figure 533. Rotary pumps: (a) External-gear pump, (b) internal-gear pump, (c) three-lobe pump, (d) four-lobe pump, (e) sliding-vane pump, (f) single-screw pump, (g) swinging-vane pump, (h) cam or roller pump, (i) cam-and-piston pump, (j) three-screw pump; (k) shuttle-block pump, (l) squeegee pump, (m) neoprene vane pump (DoIman, 1952).

trifugal type of pump is stopped there is a tendency for the fluid to backflow. Figures 534 and 535 depict some centrifugal pumps.

Other specialized types of pumps are available, but, generally, the pumps used by the petroleum industry fall into the two categories discussed.

Power for driving the various types of pumps is usually derived from electric motors, internal combustion engines, or steam drives. Any one of these sources may be adapted for use with either reciprocating pumps or centrifugal pumps. Most rotary pumps are driven by electric motor.

#### THE AIR POLLUTION PROBLEM

Operation of various pumps in the handling of fluids in petroleum process units can result in the release of air contaminants. Volatile materials such as hydrocarbons, and odorous substances such as hydrogen sulfide or mercaptans are of particular concern because of the large volumes handled. Both reciprocating and centrifugal pumps can be sources of emissions.

The opening in the cylinder or fluid end through which the connecting rod actuates the piston is the major potential source of contaminants from a reciprocating pump. In centrifugal pumps, normally the only potential source of leakage occurs where the drive shaft passes through the impeller casing.

#### AIR POLLUTION CONTROL EQUIPMENT

Several means have been devised for sealing the annular clearance between pump shafts and fluid casings to retard leakage. For most refinery applications, packed seals and mechanical seals are widely used.

Packed seals can be used on both positive displacement and centrifugal type pumps (Elonka, 1956). Typical packed seals, as shown in Figure 536, generally consist of a stuffing box filled with sealing material that encases the moving shaft. The stuffing box is fitted with a takeup ring that is made to compress the packing and cause it to tighten around the shaft. Materials used for packing vary with the product temperature, physical and chemical properties, pres-

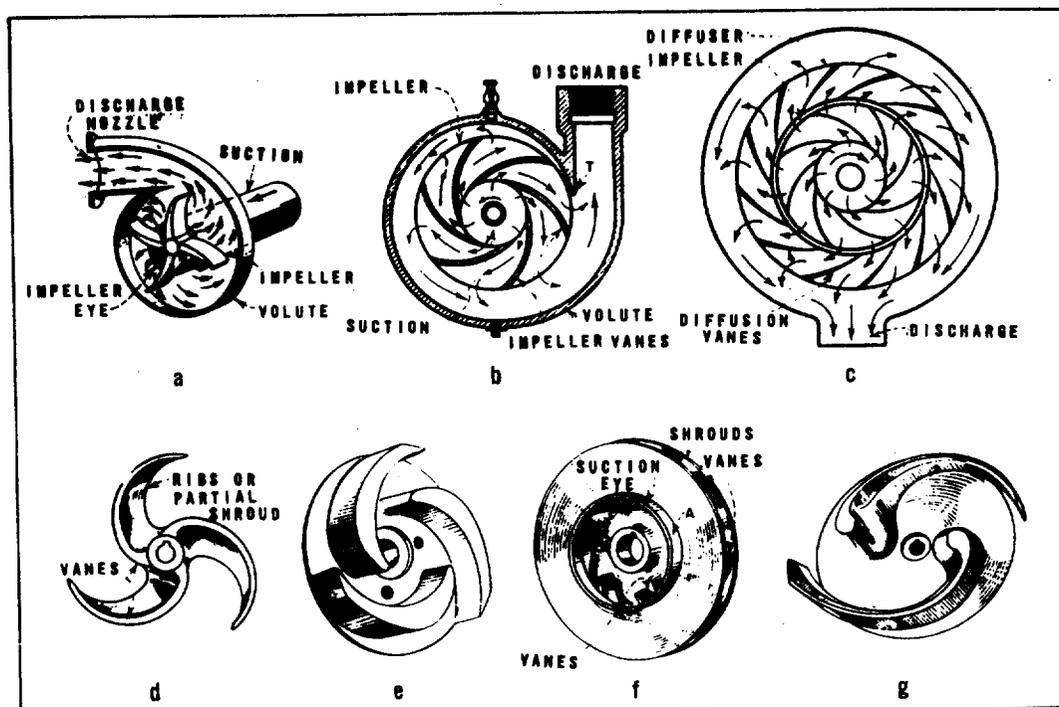


Figure 534. Centrifugal pumps: (a) Principle of centrifugal-type pump, (b) radial section through volute-type pump, (c) radial section through diffuser-type pump, (d) open impeller, (e) semi-enclosed impeller, (f) closed impeller, (g) nonclog impeller (Dolman, 1952).

sure, and pump type. Some commonly used materials are metal, rubber, leather, wood, and plastics.

Lubrication of the contact surfaces of the packing and shaft is effected by a controlled amount of product leakage to the atmosphere. This feature makes packing seals undesirable in applications where the product can cause a pollution problem. The packing itself may also be saturated with some material such as graphite or oil that acts as a lubricant. In some cases cooling or quench water is used to cool the impeller shaft and the bearings.

The second commonly used means of sealing is the mechanical seal (Elonka, 1956), which was developed over a period of years as a means of reducing leakage from pump glands. This type of seal can be used only in pumps that have a rotary shaft motion. A simple mechanical seal consists of two rings with wearing surfaces at right angles to the shaft (see Figure 537). One ring is stationary while the other is attached to the shaft and rotates with it. A spring and the action of fluid pressure keep the two faces in contact. Lubrication of the wearing faces is effected by a thin film of the material being pumped. The wearing faces are precisely finished to ensure perfectly flat surfaces. Materials used in

the manufacture of the sealing rings are many and varied. Choice of materials depends primarily upon properties of fluid being pumped, pressure, temperature, and speed of rotation. The vast majority of rotating faces in commercial use are made of carbon (Woodhouse, 1957).

Emissions to the atmosphere from centrifugal pumps may be controlled in some cases by use of the described mechanical-type seals instead of packing glands. For cases not feasible to control with mechanical seals, specialized types of pumps, such as canned, diaphragm, or electromagnetic, are required.

The canned-type pump is totally enclosed, with its motor built as an integral part of the pump. Seals and attendant leakage are eliminated. The diaphragm pump is another type devoid of seals. A diaphragm is actuated hydraulically, mechanically, or pneumatically to effect a pumping action. The electromagnetic pumps use an electric current passed through the fluid, which is in the presence of a strong magnetic field, to cause motion.

A pressure-seal-type application can reduce packing gland leakage. A liquid, less volatile or dangerous than the product being pumped, is

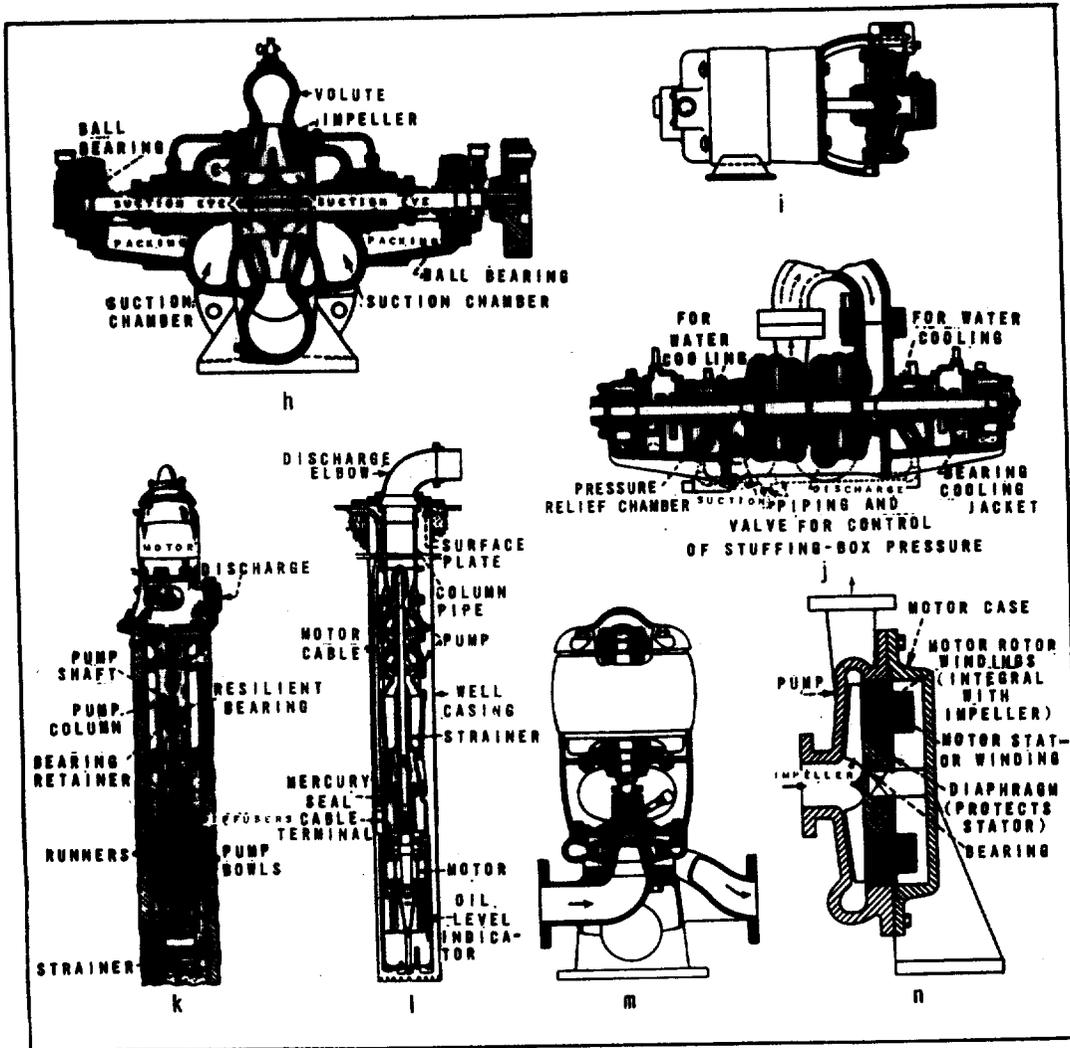


Figure 535. Centrifugal pumps: (h) single-stage, double-suction, split-case, centrifugal pump; (i) close-coupled water pump; (j) four-stage pump with opposed impellers; (k) turbine-type, deep-well pump; (l) submersible-motor, deep-well pump; (m) close-coupled, vertical, turret-type pump; (n) pump with integral motor (Dolman, 1952).

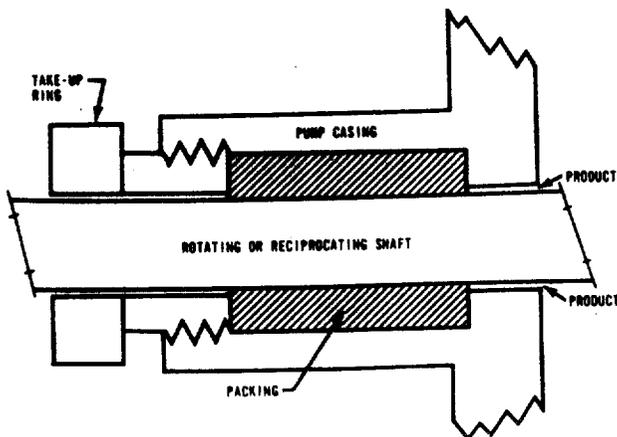


Figure 536. Diagram of simple uncooled packed seal.

introduced between two sets of packing. This sealing liquid must also be compatible with the product. Since this liquid is maintained at a higher pressure than the product, some of it passes by the packing into the product. The pressure differential prevents the product from leaking outward, and the sealing liquid provides the necessary lubricant for the packing gland. Some of the sealing liquid passes the outer packing (hence the necessity of low volatility), and a means should be provided for its disposal.

This application is also adaptable to pumps with mechanical seals. A dual set of mechanical seals similar to the two sets of packing is used.

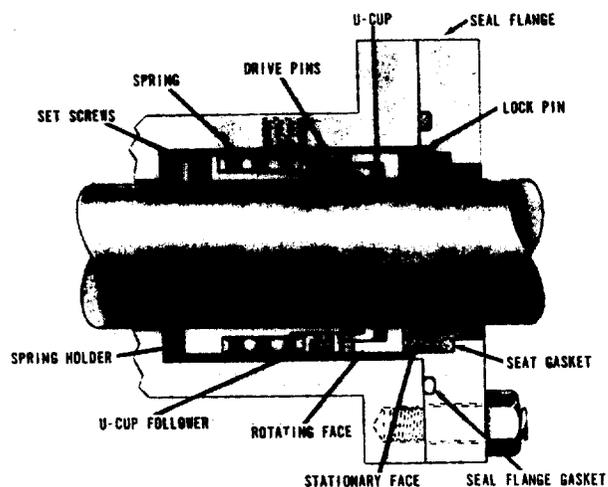


Figure 537. Diagram of simple mechanical seal (Borg-Warner Mechanical Seals, A Division of Borg-Warner Corporation, Vernon, Calif.).

Volatile vapors that leak past a main seal may be vented to vapor recovery by using dual seals and a shaft housing.

Other than the direct methods used to control leakage, operational changes may minimize re-lease of contaminants to the atmosphere. One desirable change is to bleed off pump casings during shutdown to the fuel gas system, vapor recovery facilities, or a flare instead of directly to the atmosphere.

#### Results of Study to Measure Losses From Pumps

The results of a testing program (Steigerwald, 1958) to establish the magnitude of hydrocarbon losses from pumps are presented in Tables 180 through 183. The data collected during the study are presented in Table 182 as a comparison of the effectiveness of packing glands and mechanical seals in preventing leakage.

Table 180. SCOPE AND RESULTS OF FIELD TESTS ON PUMP SEALS (Steigerwald, 1958)

Group No. <sup>a</sup>	Total number of seals	Seals inspected		Measured leaks		Small leaks		Hydrocarbon loss from inspected pumps, lb/day
		Number	% of total	Number	Hydrocarbon loss, lb/day	Number	Hydrocarbon loss, lb/day <sup>b</sup>	
1	76	14	18	2	60	2	2	62
2	82	13	16	0	0	2	2	2
3	66	12	18	0	0	2	2	2
4	127	21	17	6	294	7	7	301
5	266	59	22	3	19	13	13	32
6	56	16	28	0	0	5	5	5
7	163	34	21	13	262	6	6	268
8	191	35	18	2	23	4	4	27
9	150	19	13	2	7	2	2	9
Subtotal	1,177	223	19	28	665	43	43	708
10	92	15	16	5	26	2	2	28
11	78	9	12	1	4	2	2	6
12	68	9	13	0	0	3	3	3
13	49	0	0	0	0	0	0	0
14	179	21	12	12	83	5	5	88
15	103	18	18	0	0	3	3	3
16	100	15	15	6	280	4	4	284
17	175	26	15	6	226	11	11	237
18	124	25	20	2	16	0	0	16
Subtotal	968	138	14	32	635	30	30	665
19	26	6	23	1	23	3	3	26
20	32	5	16	0	0	0	0	0
21	38	8	21	0	0	3	3	3
22	72	13	18	6	383	3	3	386
23	173	29	17	1	71	7	7	78
24	150	17	11	0	0	0	0	0
25	60	7	12	4	19	2	2	21
26	40	7	18	3	82	3	3	85
27	50	20	40	0	0	1	1	1
Subtotal	641	112	17	15	578	22	22	600
Totals	2,786	473	17	75	1,878	95	95	1,973

<sup>a</sup>Group numbers represent a specific combination of pump type, seal type, pump operation, and product.

<sup>b</sup>A value of 1 pound per day was assigned to a small leak on a pump seal.

Table 181. EXTRAPOLATION OF FIELD DATA BY SAMPLING GROUPS TO OBTAIN A TOTAL LOSS FIGURE (Steigerwald, 1958)

1	2	3	4	5	6
Group No. <sup>a</sup>	Total number of seals	Number of seals inspected	Hydrocarbon loss from inspected seal, lb/day	Avg hydrocarbon loss per inspected seal, lb/day <sup>b</sup>	Total hydrocarbon loss, lb/day <sup>c</sup>
1	76	14	62	4.4	335
2	82	13	2	0.2	16
3	66	12	2	0.2	13
4	127	21	301	14.4	1,830
5	266	59	32	0.6	160
6	56	16	5	0.3	17
7	163	34	268	7.9	1,289
8	191	35	27	0.8	153
9	150	19	9	0.5	75
10	92	15	28	1.8	166
11	78	9	6	0.7	55
12	68	9	3	0.3	20
13	49	0	--	--	--
14	179	21	88	4.2	752
15	103	18	3	0.2	21
16	100	15	284	18.8	1,880
17	175	26	237	9.1	1,592
18	124	25	16	0.6	74
19	26	6	26	4.3	112
20	32	5	0	0	0
21	38	8	3	0.4	15
22	72	13	386	29.6	2,131
23	173	29	78	2.7	467
24	150	17	0	0	0
25	60	7	21	3.0	180
26	40	7	85	12.1	484
27	50	20	1	0.1	5
Totals	2,786	473	1,973	4.2	11,842 or 6 tons per day

<sup>a</sup>Group numbers represent a specific combination of pump type, seal type, pump operation, and product.

<sup>b</sup>Divide hydrocarbon loss from inspected seal, lb/day, by number of seals inspected.

<sup>c</sup>Multiply average hydrocarbon loss per inspected seal, lb/day, by total number of seals.

The slight difference between the average losses from mechanical seals and packed glands during handling of highly volatile hydrocarbons needs further clarification. Pumps in continuous service show an average loss per seal of 18.3 and 7.9 pounds per day for packed and mechanical seals, respectively, indicating that mechanical seals are far more efficient when running continuously. On spare or standby service the packed seals are more effective, losing 1.8 pounds per day to an average loss of 4.4 pounds from mechanical seals. Reciprocating pumps handling light products are the worst offenders both in incidence of leak and magnitude of average emissions. The largest leak encountered in the study, 266 pounds per day, was from a

reciprocating pump on intermittent service handling liquefied petroleum gas.

## AIRBLOWN ASPHALT

Asphalt is a dark brown to black, solid or semi-solid material found in naturally occurring deposits or as a colloidal suspension in crude oil. Analytical methods have been used to separate asphalt into three component groups--asphaltenes, resins, and oils. A particular grade of asphalt may be characterized by the amounts of each group it contains. The asphaltene particle provides a nucleus about which the resin forms a protective coating. The particles are suspended

Table 182. EFFECTIVENESS OF MECHANICAL AND PACKED SEALS ON VARIOUS TYPES OF HYDROCARBONS (Steigerwald, 1958)

Seal type	Pump type	Type hydrocarbon being pumped, lb Reid	Avg hydrocarbon loss per inspected seal, lb/day	Leak incidence	
				Small leaks, <sup>a</sup> % of total inspected	Large leaks, % of total inspected
Mechanical	Centrifugal	> 26	9.2	19	21
		5 to 26	0.6	18	5
		0.5 to 5	0.3	19	4
		Avg	> 0.5	3.2	19
Packed	Centrifugal	> 26	10.3	20	37
		5 to 26	5.9	32	34
		0.5 to 5	0.4	12	4
		Avg	> 0.5	4.8	22
Packed	Reciprocating	26	16.6	31	42
		5 to 26	4.0	24	10
		0.5 to 5	0.1	9	0
		Avg	> 0.5	5.4	20

<sup>a</sup>Small leaks lose less than 1 pound of hydrocarbon per day.

Table 183. AVERAGE PUMP SEAL LOSSES BY VOLATILITY OF PRODUCT BEING PUMPED (Steigerwald, 1958)

Product, lb Reid	Total number of seals reported	Number of seals inspected	Avg hydrocarbon loss per inspected seal, lb/day
26	765	125	11.1
5 to 26	1,216	204	2.7
0.5 to 5	805	144	0.3

in an oil that is usually paraffinic but can be naphthenic or naphtho-aromatic.

#### RECOVERY OF ASPHALT FROM CRUDE OIL

Over 90 percent of all asphalt used in the United States is recovered from crude oil (Kirk and Othmer, 1947). The method of recovery depends upon the type of crude oil being processed. Practically all types of crudes are first distilled at atmospheric pressure to remove the lower boiling materials such as gasoline, kerosene, diesel oil, and others. Recovery of nondistillable asphalt from selected topped crudes may then be accomplished by vacuum distillation, solvent extraction, or a combination of both.

A typical vacuum distillation unit is depicted in Figure 538. A unit such as this uses a heater, preflash tower, vacuum vessel, and appurtenances for processing topped crudes. Distillation of topped crude under a high vacuum removes oils and wax as distillate products, leaving the asphalt as a residue. The amount of oil distilled from the residue asphalt controls its properties; the more oil and resin or oily constituents removed by dis-

tillation, the harder the residual asphalt. Residual asphalt can be used as paving material or it can be further refined by airblowing.

Asphalt is also produced as a secondary product in solvent extraction processes. As shown in Figure 539, this process separates the asphalt from remaining constituents of topped crudes by differences in chemical types and molecular weights rather than boiling points as in vacuum distillation processes. The solvent, usually a light hydrocarbon such as propane or butane, is used to remove selectively a gas-oil fraction from the asphalt residue.

#### AIRBLOWING OF ASPHALT

Economical removal of the gas-oil fraction from topped crude, leaving an asphaltic product, is occasionally feasible only by airblowing the crude residue at elevated temperatures. Excellent paving-grade asphalts are produced by this method. Another important application of airblowing is in the production of high-quality specialty asphalts for roofing, pipe coating, and similar uses. These asphalts require certain plastic properties imparted by reacting with air.

Airblowing is mainly a dehydrogenation process. Oxygen in the air combines with hydrogen in the oil molecules to form water vapor. The progressive loss of hydrogen results in polymerization or condensation of the asphalt to the desired consistency. Blowing is usually carried out batchwise in horizontal or vertical stills equipped to blanket the charge with steam, but it may also be

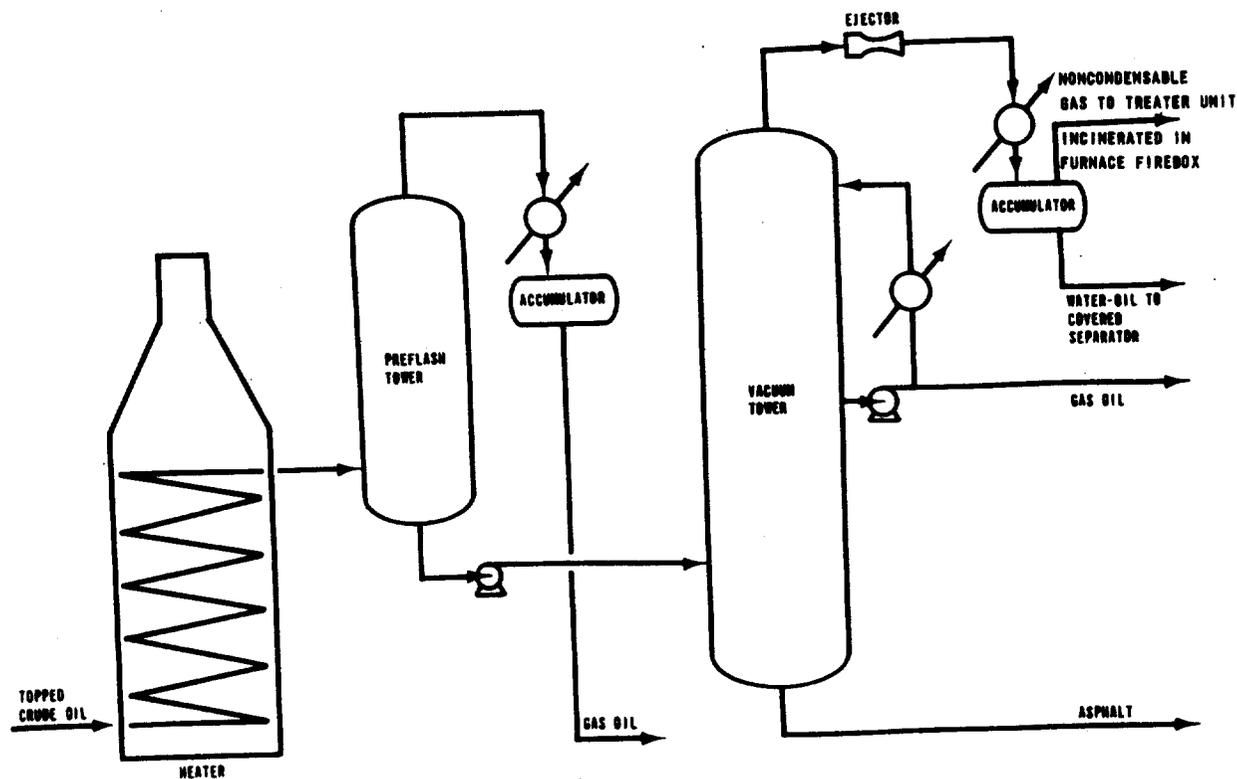


Figure 538. Flow diagram of vacuum distillation unit.

done continuously. Vertical stills are more efficient because of longer air-asphalt contact time. The asphalt is heated by an internal fire-tube heater or by circulating the charge material through a separate tubestill. A temperature of 300° to 400°F is reached before the airblowing cycle begins. Air quantities used range from 5 to 20 cubic feet per minute per ton of charge (Barth, 1958). Little additional heat is then needed since the reaction becomes exothermic. Figure 540 depicts the flow through a typical batch-type unit.

#### THE AIR POLLUTION PROBLEM

Effluents from the asphalt airblowing stills include oxygen, nitrogen and its compounds, water vapor, sulfur compounds, and hydrocarbons as gases, odors, and aerosols. Discharge of these vapors directly to the atmosphere is objectionable from an air pollution control standpoint. The disagreeable odors and airborne oil particles entrained with the gases result in nuisance complaints. Disposal methods are available that can satisfactorily eliminate the pollution potential of the effluents.

#### AIR POLLUTION CONTROL EQUIPMENT

Control of effluent vapors from asphalt airblowing stills has been accomplished by scrubbing and incineration, singly or in combination. Most installations use the combination. Potential air pollutants can be removed from asphalt still gases by scrubbing alone. One effective control installation in Los Angeles County uses sea water for one-pass scrubbing of effluent gases from four asphalt airblowing stills. The fume scrubber is a standard venturi-type unit. The scrubber effluent is discharged into an enclosed oil-water gravity-type separator for recovery of oil, which is reprocessed or used as fuel. Effluent gases from the covered separator that collects the scrubber discharge are not incinerated but flow through a steam-blanketed stack to the atmosphere. The system, shown in Figure 541, removes essentially all potential air pollutants from the effluent stream. A limiting factor in the application of this method of control is the water supply. Since a high water-to-vapor scrubbing ratio (100 gallons/1,000 scf) is necessary, an economical source of water should be readily available to supply the large volume required for one-pass operation.

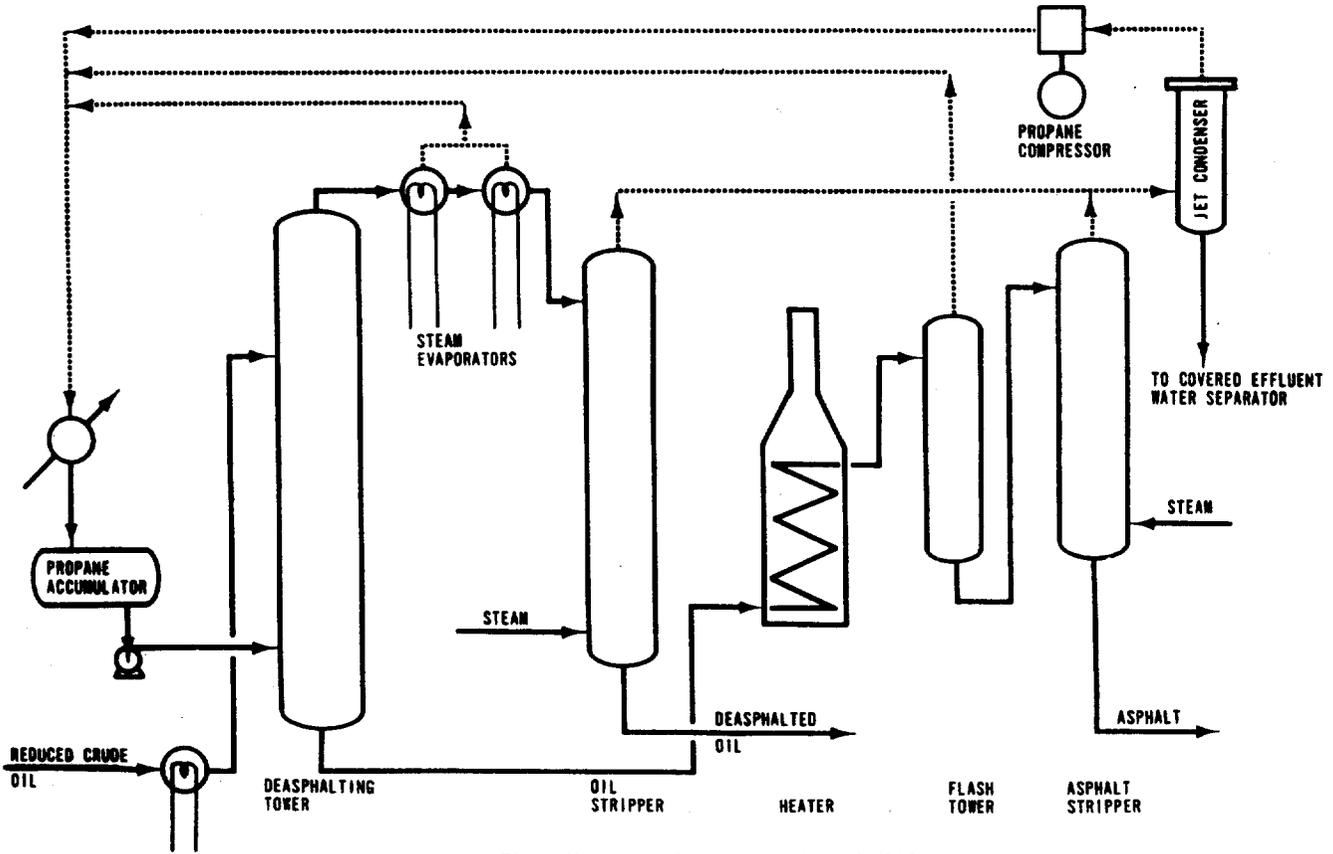


Figure 539. Flow diagram of propane deasphalting unit.

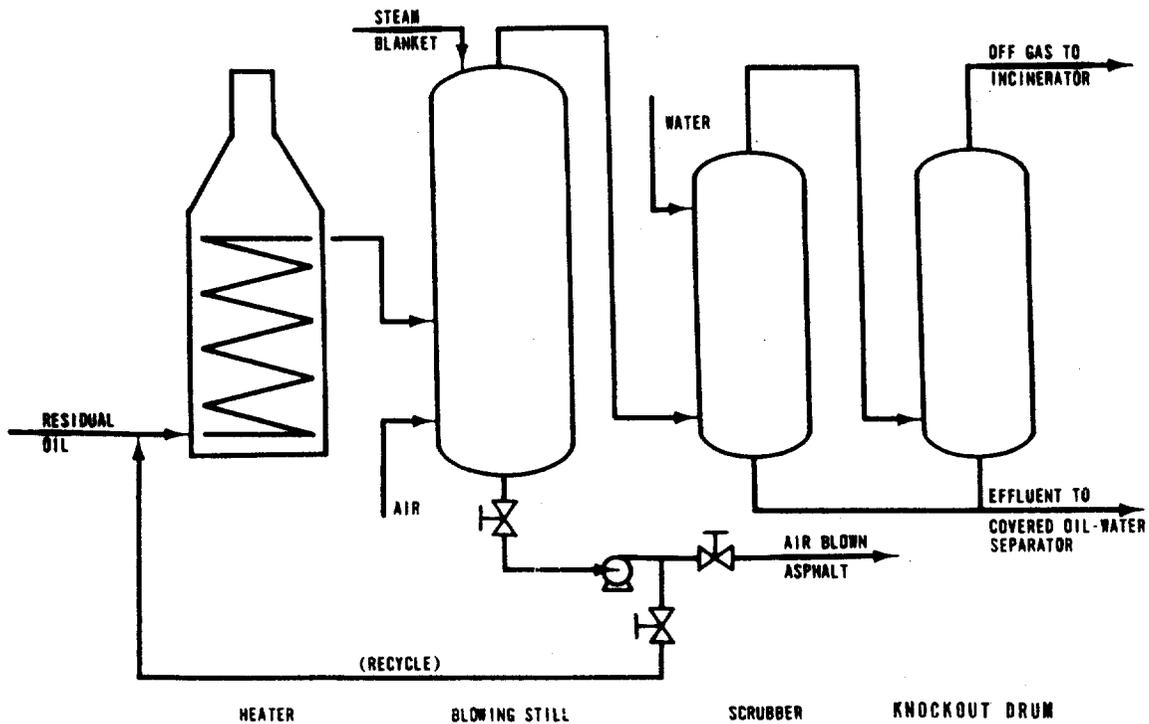


Figure 540. Flow diagram of airblown asphalt manufacture (batch process).

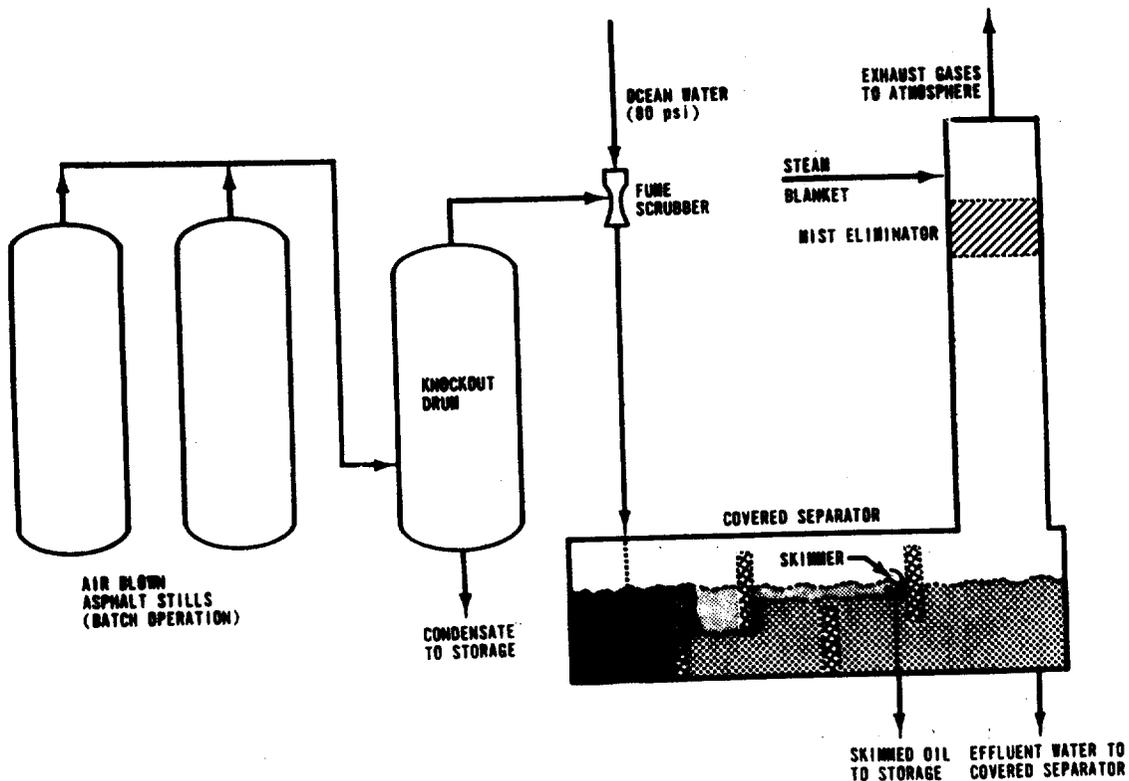


Figure 541. Flow diagram of scrubbing system.

Where removal of most of the potential air pollutants is not feasible by scrubbing alone, the non-condensables must be incinerated. Essential to effective incineration is direct-flame contact with the vapors, a minimum retention time of 0.3 second in the combustion zone, and maintenance of a minimum combustion chamber temperature of 1,200°F. Other desirable features include turbulent mixing of vapors in the combustion chamber, tangential flame entry, and adequate instrumentation. Primary condensation of any steam or water vapor allows use of smaller incinerators and results in fuel savings. Some of the heat released by incineration of the waste gases may be recovered and used for generation of steam. General design features of waste gas afterburners and boilers are discussed elsewhere in this manual.

Catalytic fume burners are not recommended for the disposal of vapors from the airblowing of asphalt because the matter entrained in the vapors would quickly clog the catalyst bed.

## VALVES

### TYPES OF VALVES

Valves are employed in every phase of the petroleum industry where petroleum or petroleum product is transferred by piping from one point to another. There is a great variety of valve designs, but, generally, valves may be classified by their application as flow control or pressure relief.

#### Manual and Automatic Flow Control Valves

Manual and automatic flow control valves are used to regulate the flow of fluids through a system. Included under this classification are the gate, globe, angle, plug, and other common types of valves. These valves are subject to product leakage from the valve stem as a result of the action of vibration, heat, pressure, corrosion, or improper maintenance of valve stem packing (see Figure 542).

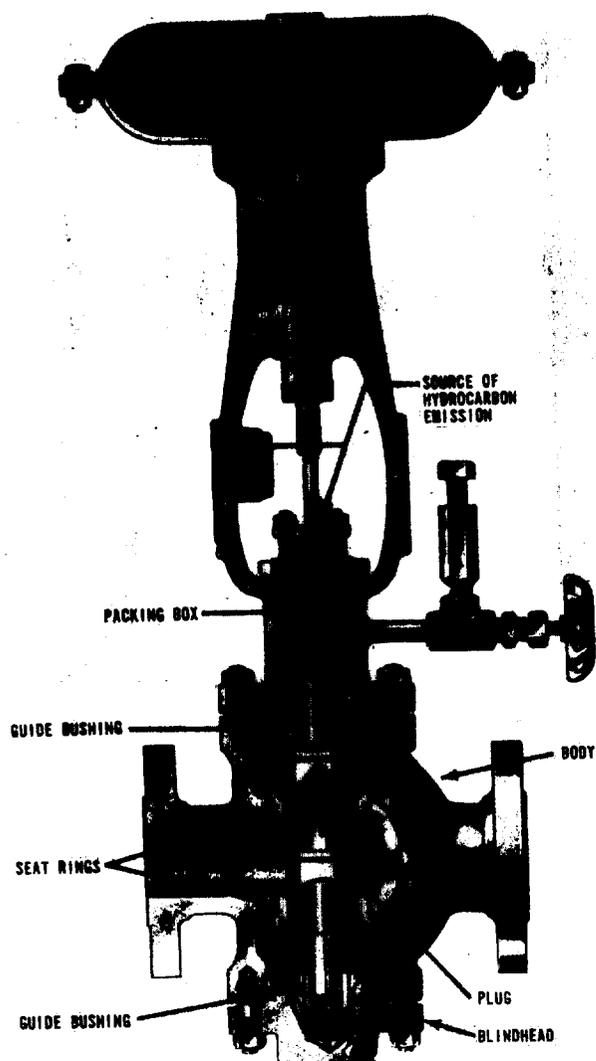


Figure 542. Typical valve showing various parts and potential source of hydrocarbon emission from the valve stem (Mason-Neilan, Division of Worthington Corporation, Norwood, Mass.).

### Pressure Relief and Safety Valves

Pressure relief and safety valves are used to prevent excessive pressures from developing in process vessels and lines. The relief valve designates liquid flow while the safety valve designates vapor or gas flow. These valves may develop leaks because of the corrosive action of the product or because of failure of the valve to reset properly after blowoff. Rupture discs are sometimes used in place of pressure relief valves. Their use is restricted to equipment in batch-type processes. The maintenance and operational difficulties caused by the inaccessibility of many pressure relief valves may allow leakage to become substantial.

### THE AIR POLLUTION PROBLEM

Quantitative data as to actual extent of emissions to the atmosphere from this leakage are somewhat limited, but available data indicate that emissions vary over a wide range. Liquid leakage results in emissions from evaporation of liquid while gas leakage results in immediate emissions. The results of a test program (Kanter et al., 1958) conducted to establish the magnitude of hydrocarbon emissions from valves are presented in Table 184. In this program, valves in a group of 11 Los Angeles County refineries were surveyed. Both liquid and gaseous leaks were measured or estimated in the survey. Leaks were detected by visible means for liquid leaks, and by spraying with soap solution followed by inspection for bubble formation for gaseous leaks. Liquid leakage rates were measured by collecting liquid over a period of time. Flow rates for gaseous leaks were determined by enclosing the valve in polyethylene bags and venting the vapor through a wet test meter.

Apparent from Table 184 is that 70 percent of the measurable leaks in gas service average less than 9.1 pounds of emissions per day. In liquid service, 90 percent of the measurable leaks average less than 8.8 pounds of emissions per day. Consideration of remaining data shows that the frequency distribution of leaks is extremely skewed.

An example of low leakage rate was observed in one refinery where over 3,500 valves handling a wide variety of products under all conditions of temperature and pressure were inspected. The average leak rate was 0.038 pound per day per valve.

Examples of high leakage rates were found in two refineries where all 440 valves inspected in gas service had an average leak rate of 1.6 pounds per day per valve, and in one other refinery where all 1,335 valves inspected in liquid service had an average leak rate of 0.32 pound per day per valve.

These examples illustrate the wide divergence from the average valve leak rate that can exist among refineries in a single area, all subject to the same obligations to restrict their emissions to the greatest possible extent. These results could not be applied, even approximately, to refineries in other areas where standards may be different.

These testing programs were also conducted on pressure relief valves in the same oil refineries. The results of this phase of the program are shown in Table 185. As can be seen from the data, relief valves on operational units have a slightly lower leak incidence but a much higher average

Table 184. LEAKAGE OF HYDROCARBONS FROM VALVES OF REFINERIES IN LOS ANGELES COUNTY (Kanter et al., 1958)

	Valves in gaseous service	Valves in liquid service	All valves
Total number of valves	31,000	101,000	132,000
Number of valves inspected	2,258	7,263	9,521
Small leaks <sup>a</sup>	256	768	1,024
Large leaks	118	79	197
Leaks measured	24	76	100
Total measured leakage, lb/day	218	670	888
Average leak rate--large leaks, lb/day	9.1	8.8	8.9
Total from all large leaks, lb/day	1,072	708	1,780
Estimated total from small leaks, lb/day <sup>b</sup>	26	77	103
Total estimated leakage from all inspected valves, lb/day	1,098	785	1,883
Average leakage per inspected valve, lb/day	0.486	0.108	0.198

<sup>a</sup>Small leaks are defined as leaks too small to be measured--those estimated to be less than 0.2 pound per day.

<sup>b</sup>Leaks too small to be measured were estimated to have an average rate of 0.1 pound per day. This is one-half the smallest measured rate.

leakage rate than valves on pressure storage vessels do. Moreover, dual-type valves (two single relief valves connected in parallel to ensure effective release of abnormal pressures) on pressure storage vessels have a greater leak incidence and a larger average leakage rate than single-type valves on similar service do. For valves on operational vessels, the average for all refineries was 2.9 pounds of hydrocarbons per day per valve. Average losses from specific refineries, however, varied from 0 to 9.1 pounds per day per valve. Under diverse conditions of operation and maintenance, emissions can vary greatly from one refinery to another.

Table 185. LEAKAGE OF HYDROCARBONS FROM PRESSURE RELIEF AND SAFETY VALVES OF REFINERIES IN LOS ANGELES COUNTY (Kanter et al., 1958)

Valve group	Number of valves reported	Number of valves tested	Hydrocarbon emission, lb/day	Emission per tested valve, lb/day <sup>a</sup>	Total emission, lb/day
Operational units	1,113	165	480	2.90	3,230
Pressure storage:					
Single	237	174	56	0.32	80
Dual	115	79	98	1.24	140

<sup>a</sup>Divide hydrocarbon emissions, lb/day, by number of valves tested.

<sup>b</sup>Multiply number of valves reported by emission per tested valve, lb/day.

#### Total Emissions From Valves

Since emissions to the atmosphere from valves are highly dependent upon maintenance, total valve losses cannot be estimated accurately. From the testing program mentioned, emissions from valves averaged 12 percent of the total emissions from all refineries in Los Angeles County. As of 1963, hydrocarbon emissions from valves in Los Angeles County refineries are estimated at about 11 tons per day. As stated previously, however, these emissions varied greatly from one refinery to another, and average percentage figures should not be used in predicting emissions from a given refinery.

#### AIR POLLUTION CONTROL EQUIPMENT

Obviously, the controlling factor in preventing leakage from valves is maintenance. An effective schedule of inspection and preventive maintenance can keep leakage at a minimum. Minor leaks that might not be detected by casual observation can be located and eliminated by thorough periodic inspections. New blind designs are being incorporated in refinery pipeline systems in conjunction with flow valves (see Figure 543). This is done to ensure against normal leakage that can occur through a closed valve.

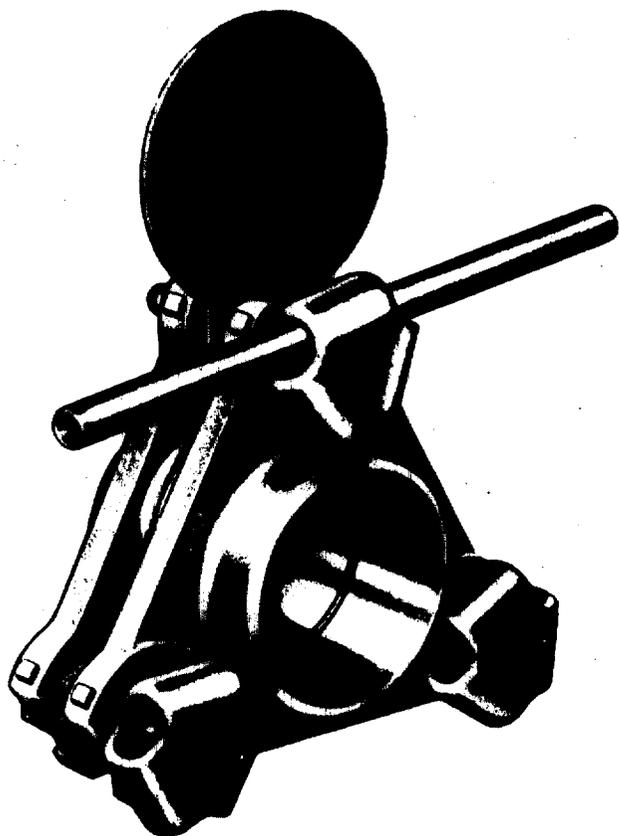


Figure 543. Bar-operated line blind that is ideal for installation ahead of shutoff valve to ensure against valve leaks and vapor emissions from valve stem (Hamer Oil Tool Co. Catalog Sheet., Long Beach, Calif.).

Emissions from pressure relief valves are sometimes controlled by manifolding to a vapor control device, such as described in Chapter 5. Normally, these disposal systems are not designed exclusively to collect vapors from relief valves. The primary function of the system may be to collect off gases produced by a process unit, or vapors released from storage facilities, or those released by depressurizing equipment during shutdowns.

Another method of control to prevent excessive emissions from relief valve leakage is the use of a dual valve with a shutoff interlock. A means of removing and repairing a detected leaking valve without waiting until the equipment can be taken out of service is thus provided. The practice of allowing a valve with a minor leak to continue in service without correction until the operating unit is shut down for general inspection is common in many refineries. This practice should be kept at a minimum.

A rupture disc is sometimes used to protect against relief valve leakage caused by excessive

corrosion. The disc is installed on the pressure side of the relief valve. The space between the rupture disc and relief valve seat should be protected from pinhole leaks that could occur in the rupture disc. Otherwise, an incorrect pressure differential could keep the rupture disc from breaking at its specified pressure. This, in turn, could keep the relief valve from opening, and excessive pressures could occur in the operating equipment.

One method of ensuring against these small leaks in rupture discs is to install a pressure gage and a small manually operated purge valve in the system. The pressure gage would easily detect any pressure increases from even small leaks. In the event of leaks, the vessel would be removed from service, and the faulty rupture disc would then be replaced. A second, but less satisfactory method from an air pollution control standpoint, is to maintain the space at atmospheric pressure by installing a small vent opening. Any minute leaks would then be vented directly to the atmosphere, and a pressure increase could not exist.

## COOLING TOWERS

Cooling towers are major items of heat-transfer equipment in the petroleum and petrochemical industries. They are designed to cool, by air, the water used to cool industrial processes. Cooling of the water by air involves evaporation of a portion of the water into the air so that the remaining water is cooled by furnishing heat for this evaporation process. This cooled water is used, in turn, in heat-exchange equipment to cool other liquids and gases.

There are two styles of cooling towers--classified by means of air movement. In one style, the earliest developed, the prevailing wind is used for the required ventilation. It has become known as the natural draft or atmospheric type of cooling tower (see Figure 544).

The other type of cooling tower employs fans to move the air and is known as a mechanical-draft cooling tower (see Figure 545). Fan location is used in further classifying the tower as a forced- or induced-draft cooling tower. The forced-draft cooling tower has not proved very satisfactory, since it has a tendency to recirculate its hot, humid exhaust vapor in place of fresh air, and its air distribution is poor because of the 90-degree turn the air must make at high velocity (Kern, 1950).

Spray ponds, once used extensively for cooling of water, have been abandoned in favor of cooling towers. Spray ponds are limited in their performance and suffer from high water losses.

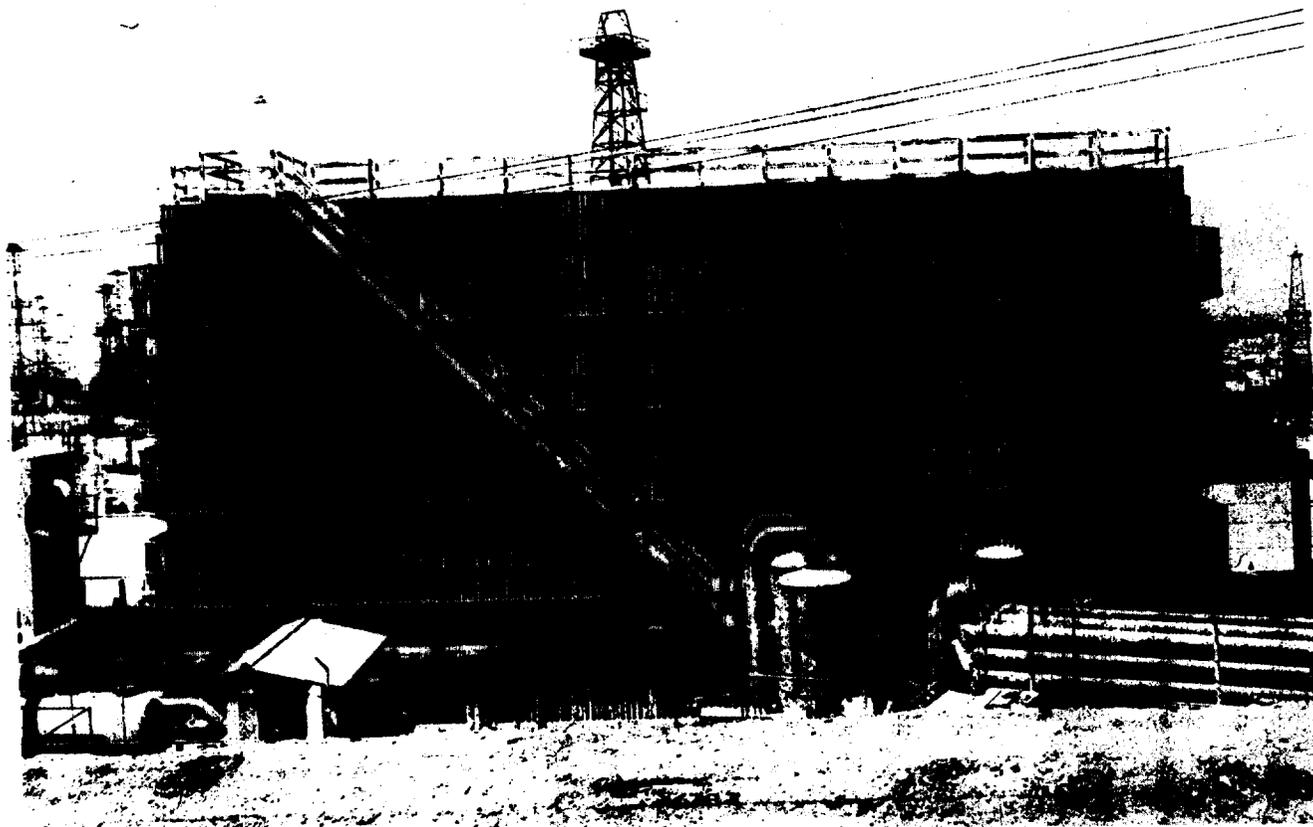


Figure 544. Natural-draft cooling tower (Shell Oil Company, Los Angeles, Calif.).

### CHARACTERISTICS OF COOLING TOWER OPERATION

Petroleum and petrochemical operations require large quantities of water for temperature control purposes. The water is normally circulated by pump between the heat-exchange equipment and the cooling tower. The hydrocarbon stream to be cooled can also be circulated directly through the cooling tower. Approximately 1,000 Btu is required to evaporate 1 pound of water. This is equivalent to cooling 100 pounds of water 10°F. Thus, 1 percent of water is lost through evaporation for every 10 degrees of cooling accomplished. Additionally, a spray loss amounting to no more than 0.2 percent must be included for properly designed atmospheric or mechanical-draft towers. Water cannot be cooled below the wet bulb temperature of the air entering the cooling tower.

The performance of an individual cooling tower is governed by the ratio of weights of air to water and the time of contact between the air and water. Commercially, the variation in the ratio of air to water is first obtained by maintaining the air velocity constant at approximately 350 fpm per square foot of active tower area and by varying

the water concentration (Perry, 1950). A secondary operation calls for varying the air velocity to meet the cooling requirements. The contact time between water and air is a function of the time required for the water to be discharged from distribution nozzles and fall through a series of gridded decks to the tower basin. Thus, the contact time is governed by the tower height. If the contact time is insufficient, the ratio of air to water cannot be increased to obtain the required cooling. A minimum cooling tower height must be maintained. Where a wide approach (difference between the cold water temperature and the wet bulb temperature of the inlet air) of 15° to 20°F to the wet bulb temperature, and a 25° to 35°F cooling range (difference between the temperature of the hot and cold water) are required, a relatively low cooling tower is adequate (15 to 20 feet). Other ranges are shown in Table 186.

The cooling performance of a tower with a set depth of packing varies with water concentration. Maximum contact and performance have been found with a water concentration of 2 to 3 gallons of water per minute per square foot of ground area. The problem in designing a cooling tower is one of determining the proper concentration

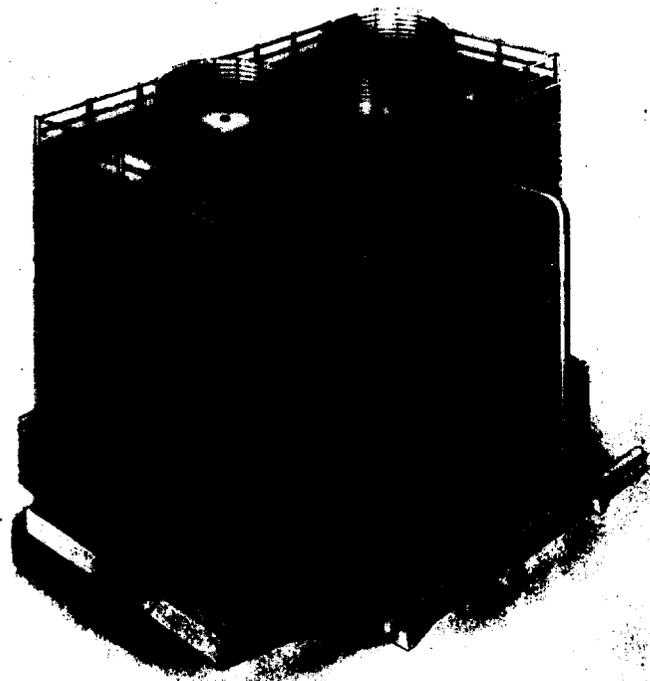


Figure 545. Cutaway view of a mechanical-draft cooling tower (Fluor Products Company, Inc., Santa Rosa, Calif.).

of water to obtain desired cooling. A high cooling tower must be used if the water concentration is less than 1.6 gallons per square foot. Low towers can be employed if the water concentration exceeds 3 gallons per square foot. If the required water concentration is known, the tower area can be found by dividing the water circulation rate (gallons per minute) by the water concentration (gallons per minute per square foot).

The required tower size (Perry, 1950) is thereby dependent upon: (1) cooling range (hot water minus cold water temperature); (2) approach (cold water minus wet bulb temperature); (3) amount of liquid to be cooled; (4) wet bulb temperature; (5) air velocity through cell; and (6) tower height.

Various technical articles are available by which a cooling tower may be designed for a specific duty (Natural Gas Processors Suppliers Association, 1957; Perry, 1950).

#### THE AIR POLLUTION PROBLEM

Cooling towers used in conjunction with equipment processing hydrocarbons and their derivatives are potential sources of air pollution because of possible contamination of the water. The cooling water may be contaminated by leaks from the process side of heat-exchange equipment, di-

Table 186. COOLING TOWER APPROACH VERSUS WATER TRAVEL

Approach, °F	Cooling range, °F	Water travel, ft
15 to 20	25 to 35	15 to 20
8 to 15	25 to 35	25 to 30
4 to 8	25 to 35	35 to 40
4 <sup>a</sup>	-	35 to 40

<sup>a</sup>Designing cooling towers with an approach of less than 4°F is not economical.

rect and intentional contact with process streams, or improper process unit operation. As this water is passed over a cooling tower, volatile hydrocarbons and other materials accumulated in the water readily evaporate into the atmosphere. When odorous materials are contained in the water, a nuisance is easily created.

Inhibitors or additives used in the cooling tower to combat corrosion or algae growth should not cause any significant air pollution emissions, nor should the water-softening facilities common to many cooling towers be a problem.

A survey (Bonamassa and Yee, 1957) of the oil refineries operating in Los Angeles County indicated hydrocarbon concentrations of approximately 20 percent in the cooling water of the cooling towers (see Table 187). Cooling towers in which hydrocarbons were detected were tested quantitatively. Three tons of hydrocarbons per day were found being discharged into the atmosphere from these sources. Individually the emissions varied from 4 to 1,500 pounds per cooling

Table 187. HYDROCARBON EMISSIONS FROM COOLING TOWERS (Bonamassa and Yee, 1957)

Cooling tower	Water circulation, gpm	Hydrocarbon emissions, lb/day (as hexane)
1	14,000	1,570
2	3,120	1,400
3	28,000	700
4	3,000	616
5	1,000	532
6	14,000	318
7	14,000	289
8	12,000	239
9	18,000	186
10	1,000	147
11	15,000	129
12	10,000	56
13	8,000	22
14	1,800	10
15	700	10
16	1,000	8
17	400	4
Total		6,236

tower per day. A study of operating variables failed to indicate any correlation among the emissions, the size of the tower, the water circulation rate, or the particular duty of the tower. Apparently the amount of hydrocarbon present in the water depends upon the state of maintenance of the process equipment, particularly the heat-exchange equipment, condensers, and coolers through which the water is circulated. The quantity and type of emissions should be determined by observing and testing each tower individually.

One survey of the cooling towers in a designated area is felt to be representative of the emissions under existing operating conditions and maintenance practices. The actual emission rate of any specific tower and the degree of odor nuisance vary as leaks develop, are detected, and repaired. Overall leakage probably remains constant in view of the large number of potential sources that can cause new leaks even as the old ones are repaired.

#### AIR POLLUTION CONTROL EQUIPMENT

The control of hydrocarbon discharges or of release of odoriferous compounds at the cooling tower is not practical. Instead, the control must be at the point where the contaminant enters the cooling water. Hence, systems of detection of contamination in water, proper maintenance, speedy repair of leakage from process equipment and piping, and good housekeeping programs in general are necessary to minimize the air pollution occurring at the cooling tower. Water that has been used in contact with process streams, as in direct-contact or barometric-type condensers, should be eliminated from the cooling tower if this air pollution source is to be completely controlled. Greater use of fin-fan coolers can also control the emissions indirectly by reducing or eliminating the volume of cooling water to be aerated in a cooling tower.

### MISCELLANEOUS SOURCES

A number of relatively minor sources of air pollution contribute approximately 10 percent of the total hydrocarbon emissions to the atmosphere from refineries (Kanter et al., 1958). Six of these sources, not discussed elsewhere in this manual, include airblowing, blind changing, equipment turnaround, tank cleaning, use of vacuum jets, and use of compressor engine exhausts.

#### AIRBLOWING

In certain refining operations, air is blown through heavier petroleum fractions (see Figure 546) for the purpose of removing moisture or agitating the

product. The exhaust air is saturated with hydrocarbon vapors or aerosols, and, if discharged directly to the atmosphere, is a source of air pollution. The extent of airblowing operations and the magnitude of emissions from the equipment vary widely among refineries. Results of a survey (Kanter et al., 1958) on the magnitude of hydrocarbon emissions from airblowing of petroleum fractions in Los Angeles County refineries, presented in Table 188, show emissions of less than 1/2 ton per day. These refineries operated a total of seven airblowing units with a combined capacity of 25,000 barrels per day and a total airflow rate of 3,300 cfm. The tabulated results do not include airblowing of asphalt, which has been discussed elsewhere in this chapter. Emissions from airblowing for removal of moisture, or for agitation of products may be minimized by replacing the airblowing equipment with mechanical agitators and incinerating the exhaust vapors.

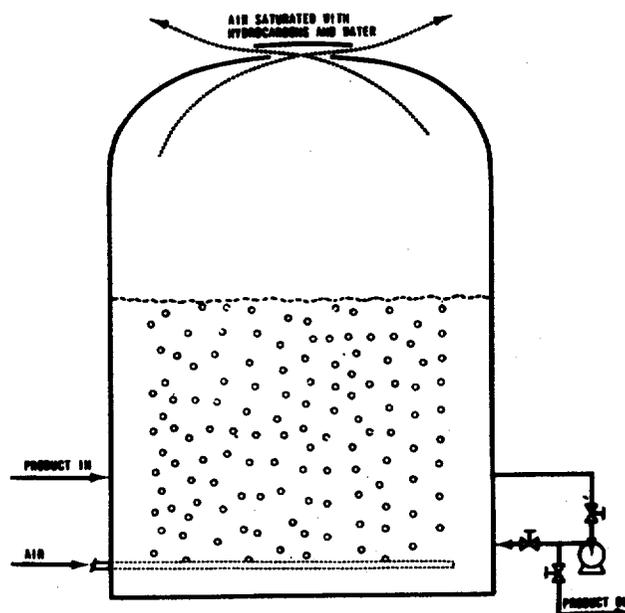


Figure 546. Improvement of product color by means of air agitation, a source of air pollution.

#### BLIND CHANGING

Refinery operations frequently require that a pipeline be used for more than one product. To prevent leakage and contamination of a particular product, other product-connecting and product-feeding lines are customarily "blinded off." "Blinding a line" is the term commonly used for the inserting of a flat, solid plate between two flanges

of a pipe connection. Blinds are normally used instead of valves to isolate pipelines because a more positive shutoff can be secured and because of generally lower costs. In opening, or breaking, the flanged connection to insert the blind, spillage of product in that portion of the pipeline can occur. The magnitude of emissions to the atmosphere from this spillage is a function of the vapor pressure of the product, type of ground surface beneath the blind, distance to the nearest drain, and amount of liquid holdup in the pipeline.

**Table 188. HYDROCARBON EMISSIONS FROM AIRBLOWING OPERATIONS OF REFINERIES IN LOS ANGELES COUNTY (Kanter et al., 1958)**

Number of units	Emissions, lb/day
Refinery A (one unit)	905
Refinery B (five units)	35
Refinery C (one unit)	2
Total	942

Results of a survey (Kanter et al., 1958) conducted to evaluate the emissions from blind changing in Los Angeles County refineries indicated that a wide variation exists in the number of pipeline service and corresponding blind changes and in the amount of spillage for different refineries of comparable size. The average emission from blind changing in Los Angeles County refineries was calculated at 0.1 ton per day.

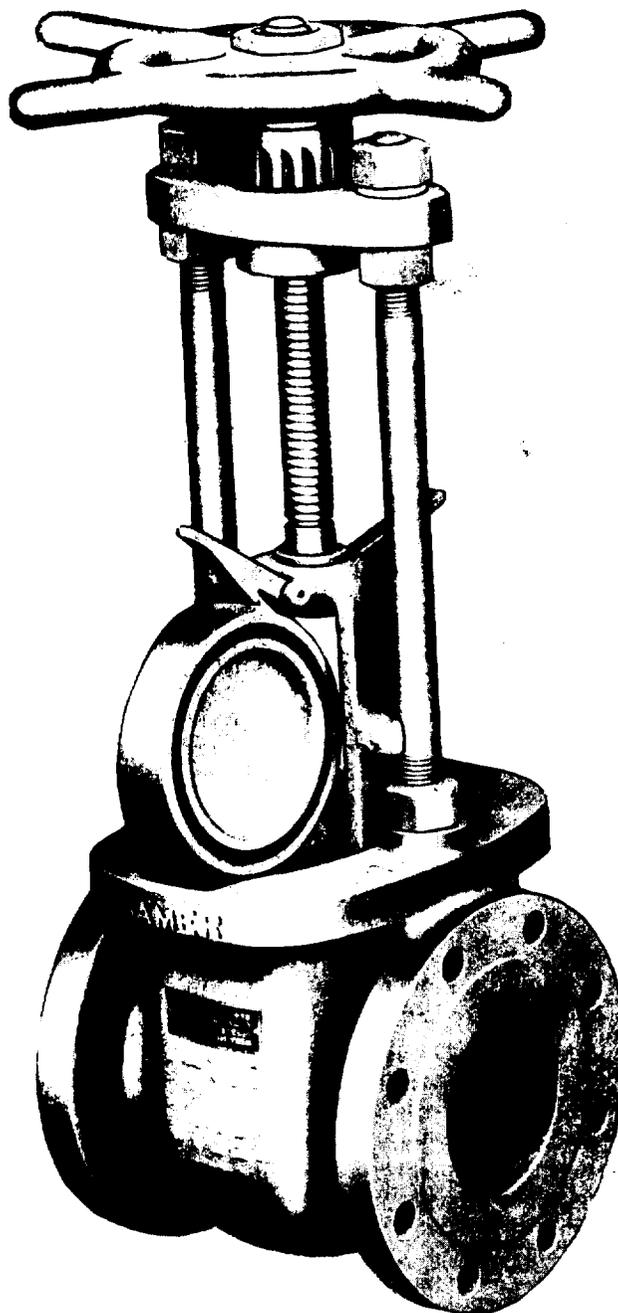
Emissions to the atmosphere from the changing of blinds can be minimized by pumping out the pipeline and then flushing the line with water before breaking the flange. In the case of highly volatile hydrocarbons, a slight vacuum may be maintained in the line. Spillage resulting from blind changing can also be minimized by use of "line" blinds in place of the common "slip" blinds. Line blinds, depicted in Figure 547, do not require a complete break of the flange connection during the changing operation. These blinds use a gear mechanism to release the spectacle plate without actually breaking the line. Combinations of this device in conjunction with gate valves are available to allow changing of the line blind while the line is under pressure from either direction. The line blind is finding many applications in new process equipment where frequent changes in services of pipelines occur. Data compiled during the survey (Kanter et al., 1958) indicate that slip blinds spilled an average of 5 gallons per change compared with line blind valves, which spilled an average of 2 gallons per change.

#### EQUIPMENT TURNAROUNDS

Periodic maintenance and repair of process equipment are essential to refinery operations.

A major phase of the maintenance program is the shutting down and starting up of the various units, usually called a turnaround.

The procedure for shutting down a unit varies from refinery to refinery and between units in a refinery. In general, shutdowns are effected by first shutting off the heat supply to the unit and circulating the feed stock through the unit



**Figure 547. Typical line blind valve (Hamer Oil Tool Company, Long Beach, Calif.).**

as it cools. Gas oil may be blended into the feedstock to prevent its solidification as the temperature drops. The cooled liquid is then pumped out to storage facilities, leaving hydrocarbon vapors in the unit. The pressure of the hydrocarbon vapors in the unit is reduced by evacuating the various items of equipment to a disposal facility such as a fuel gas system, a vapor recovery system, a flare, or in some cases, to the atmosphere. Discharging vapors to the atmosphere is undesirable from the standpoint of air pollution control since as much as several thousand pounds of hydrocarbons or other objectionable vapors or odors can be released during a shutdown. The residual hydrocarbons remaining in the unit after depressuring are purged out with steam, nitrogen, or water. Any purged gases should be discharged to the aforementioned disposal facilities. Condensed steam and water effluent that may be contaminated with hydrocarbons or malodorous compounds during purging should be handled by closed water-treating systems.

Results of a survey (Kanter et al., 1958) to determine the magnitude of hydrocarbon emissions from turnarounds in Los Angeles County refineries showed emissions totaling a maximum of 254 tons per year or 0.7 ton per day. Sixty percent of all shutdowns were found to occur on Sunday and Monday. On this basis, the 2-day emissions totaled 3 tons or 152 tons per year.

#### TANK CLEANING

Storage tanks in a refinery require periodic cleaning and repair. For this purpose, the contents of a tank are removed and residual vapors are purged until the tank is considered safe for entry by maintenance crews. Purging can result in the release of hydrocarbon or odorous material in the form of vapors to the atmosphere. These vapors should be discharged to a vapor recovery system or flare.

Data obtained from the refinery survey (Kanter et al., 1958) were used to estimate the quantity of hydrocarbon emissions to the atmosphere from tank cleaning as follows:

1. When the vapors in the tank were released to a recovery or disposal system before the tank was opened for maintenance, the emissions were considered negligible.
2. When the stored liquid was transferred to another tank, and the emptied vessel was opened for maintenance without purging to a recovery or disposal system, the emission to the atmosphere was considered to be equal to the weight of hydrocarbon vapor occupying the total volume of the tank at the

reported pressure. (For floating-roof tanks, the minimum volume was used.)

3. For vapor storage, when tanks were not purged to a recovery or disposal system, estimates were made as described in item 2.

The calculated emissions, for an average of 174 tanks cleaned per year, were 1.3 tons of hydrocarbons per day.

Steam cleaning of railroad tank cars used for transporting petroleum products can similarly be a source of emissions if the injected steam and entrained hydrocarbons are vented directly to the atmosphere. Although no quantitative data are available to determine the magnitude of these emissions, the main objection to this type of operation is its nuisance-causing potential. Some measure of control of these emissions may be effected by condensing the effluent steam and vapors. The condensate can then be separated into hydrocarbon and water phases for recovery. Noncondensable vapors should be incinerated.

#### USE OF VACUUM JETS

Certain refinery processes are conducted under vacuum conditions. The most practical way to create and maintain the necessary vacuum is to use steam-actuated vacuum jets, singly or in series (see Figure 548). Barometric condensers are often used after each vacuum jet to remove steam and condensable hydrocarbons.

The effluent stream from the last stage of the vacuum jet system should be controlled by condensing as much of the effluent as is practical and incinerating the noncondensables in an afterburner or heater firebox. Condensate should be handled by a closed treating system for recovery of hydrocarbons. The hot well that receives water from the barometric condensers may also have to be enclosed and any off gases incinerated.

#### USE OF COMPRESSOR ENGINE EXHAUSTS

Refining operations require the use of various types of gas compressors. These machines are often driven by internal combustion engines that exhaust air contaminants to the atmosphere. Although these engines are normally fired with natural gas and operate at essentially constant loads, some unburned fuel passes through the engine. Oxides of nitrogen are also found in the exhaust gases as a result of nitrogen fixation in the combustion cylinders.

Results of a survey (Kanter et al., 1958) conducted to determine the contribution made by compressor engine exhausts to overall emis-

sions from refineries are presented in Table 189. The composition of the hydrocarbons shown was generally over 90 percent methane.

In addition to the compounds listed in the table, aldehydes and ammonia may also be present in engine exhausts. Test data on these components were, however, inconclusive.

Table 189. EMISSIONS FROM COMPRESSOR INTERNAL COMBUSTION ENGINES IN LOS ANGELES COUNTY REFINERIES (Kanter et al., 1958)

Number of compressor engines	130
Fuel gas burned, mcf/d	10,500
Exhaust gas, scfm	165,000
Contaminants in exhaust gases, ppm	
Hydrocarbons	1,240
Oxides of nitrogen, as NO <sub>2</sub>	315

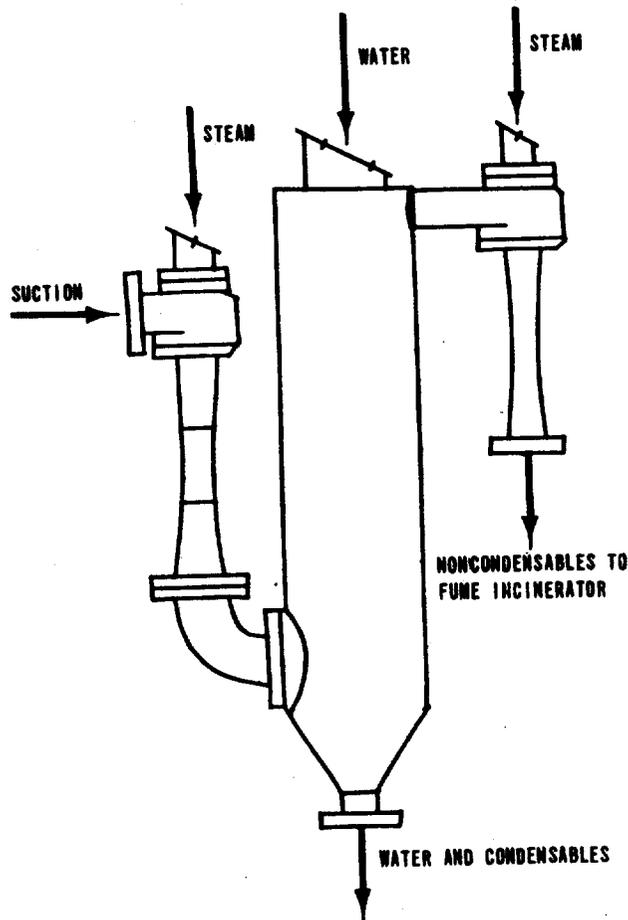


Figure 548. Schematic drawing of a two-stage, steam-actuated vacuum jet.