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HYDROCARBON EMISSIONS FROM REFINERIES



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HYDROCARBON EMISSIONS FROM REFINERIES

July 1973

Committee on Refinery Environmental Control

AMERICAN PETROLEUM INSTITUTE

Washington, D.C.

PUBLICATION NO. 928

HYDROCARBON EMISSIONS FROM REFINERIES

Introduction

At the 1971 Fall Meeting of the API Committee on Refinery Environmental Control, it was decided to set up a special task force to develop and evaluate cost-benefit relationships involved in the control of hydrocarbon emissions. This report presents the results of their study.

The report evaluates the major sources of hydrocarbon emissions from refineries as listed in Table 1. Miscellaneous sources were not evaluated, but have been briefly discussed at the end of the report.

Costs of methods and facilities for reducing hydrocarbon losses were developed. Methods for determination of hydrocarbon losses from various facilities available from literature sources such as API Bulletins 2512 and 2520, inclusive, and the U. S. Government publication "Air Pollution Engineering Manual," No. 99-AP-40, have been summarized and utilized.

To illustrate the evaluation of cost-benefit relationships, a "typical" 100,000 barrel per day refinery that had few or no provisions for control of hydrocarbon losses was assumed and evaluated. The sources of hydrocarbon losses were quantified; the benefits and costs of applicable methods of control estimated, and the resulting cost effectiveness or cost-benefits determined.

The term "hydrocarbon" as used in this report refers to the total vapor phase hydrocarbons, including straight chain, saturated and unsaturated, aromatics, aldehydes, and organic acids. The volatile hydrocarbon components can be measured by means of a gas chromatograph. The use of flame ionization detection devices in connection with a gas chromatograph results in sensitivities as low as 0.20 ppm (vol.) and will respond to almost all organic substances, but not to inorganic compounds. This report does not cover petrochemical emissions, for which the reader is referred to API Bulletin 2523 and also excludes coke particulate fines.

It was assumed that the "typical" refinery observes good housekeeping practices and performs adequate equipment inspection and maintenance. The importance of good housekeeping and maintenance cannot be overemphasized and is essential to safety and minimizing oil and vapor losses.

Task Force

Warren J. Grant, Chairman
Carl Heinrich
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Summary and Conclusions

In the continuing effort to protect the ecology of the environment, it is essential that every effort be made to reduce hydrocarbon emissions from petroleum refineries. In the aggregate, this will involve a very large capital outlay that is, in large part, non-productive. To ensure, therefore, that the greatest reduction is secured at the lowest expenditure, it is essential that suitable priorities be developed. In this report, terms of capital outlay or differential cost required to reduce emissions from individual sources by one ton per year.

There are several factors involved in controlling emissions. It is assumed that the 100,000 barrel refinery involved is typical in every respect, save emission control which, for purposes of this report, is minimal. These factors are:

1. Potential reduction in tons per year of hydrocarbon emission from each individual source.
2. The cost-effectiveness involved in reducing emission from each source by the most suitable cost control method, without consideration of the economic benefits involved.
3. The net cost-effectiveness of the methods involved after making suitable allowance for economic benefits.

Table 1 presents a Summary of Reduction of Major Sources of Hydrocarbon Emissions and Cost-Effectiveness for a "typical" 100,000 bbl/day refinery. This report is concerned chiefly with cost-effectiveness, although other data on itemized losses are also discussed.

On the assumption that the refinery has essentially no equipment to reduce hydrocarbon emissions; e.g., all cone roof storage tanks, the major sources of emission are evaporation from storage tanks and non-condensable gases from vacuum towers. Primary sedimentation devices, such as API separators, are a potentially high source of loss as are gasoline filling operations at the loading rack and catalyst regeneration processes. Post-gravity oil-water separators; e.g., air floatation units, air-blowing of asphalt and mechanical seals are relatively low sources of emissions. However, air-blowing of asphalts can be a source of obnoxious odors. The loss from pressure relief valves is directly related to the system pressure and the number of valves venting directly to atmosphere.

As regards cost effectiveness per se, floating covers for primary sedimentation devices and disposal of incineration of non-condensable from a vacuum tower are the most effective. Floating roof tanks, vapor recovery systems, fixed covers for oil-water separators, and incineration of odors from asphalt blowing are moderately cost effective in terms of dollars per ton per year. Recovery of vapors from a post-gravity oil-water separation device and their disposal by incineration, CO boilers, TCC plume burners, and in most cases mechanical seals, show the lowest benefits in relation to cost.

Reduction of vapor losses from storage tanks by use of floating roof tanks or vapor recovery systems and the installation of a CO boiler result in the greatest economic benefits to the refinery. Where recovered vapors are incinerated in a furnace, there is some economic recovery as heat, but this value is usually relatively low. Vapor disposal to a flare or the installation of a TCC plume burner obviously results in no economic return.

It should be noted that these conclusions are based on the cost data as shown. On all items save Vapor Recovery Systems (Item B), the cost data is based on actual installations. The Vapor Recovery System costs are based on manufacturers' estimates of installed costs which do not include many intangible items, such as ground preparation, power supply, etc. An actual installation in Canada for 10,000,000 gallons per month cost approximately twice the quoted figure. However, the cost data presented for Vapor Recovery Systems do include annual expenditures and depreciation. Annual expenditures, in turn, include proportional, fixed and variable costs, so that if desired, a more complete cost analysis may be made. This technique can be applied to the other sources of loss.

For obvious reasons, it is difficult to summarize these data for any "typical" refinery, regardless of throughput. It seems evident that all highly volatile products should be stored in floating roof tanks and that all non-condensable gases from vacuum distillation should be incinerated in a furnace. Further, the economics and reduction in air pollution involved in installing a CO boiler for incineration of catalyst regeneration gases and the use of covers for an API separator should be carefully evaluated. Vapors from asphalt blowing, while not a major source of emission, are malodorous and obnoxious and should be incinerated. Other items discussed are more marginal, however, and would require a study by the individual refinery. This would include an evaluation of total losses, control methods available, and economic factors involved, and an evaluation of existing, proposed or pending legislation.

Table 1
 Summary and General Data Sheet
 Cost Effectiveness* to Reduce Hydrocarbon Emissions

<u>Item</u>	<u>Description</u>	<u>Loss (uncorrected), Tons per year</u>	<u>Method</u>	<u>Assumptions Involved</u>	<u>Cost Effectiveness \$ per ton per year</u>
<u>A</u>	STORAGE TANKS (Vol. PRODUCTS)	6700 (Gasoline) 5200 (Crude Oil)	Floating Roof Tanks to Replace cone roof	80,000 barrel tank 1.8 MM bbls/year thruput	77 (replace) 121 (Convert 190 (replace) 299 (Convert
<u>B</u>	LOADING RACK Loading and Un- loading losses	700 (vs. splash) 225 (vs. sub-surf)	Vapor Recovery System	Complete vapor recovery (90%), tank Truck and tack car	175 539
<u>C</u>	PRIMARY SEDIMENT- ATION BASIN (API)	1130 1130	Floating Cover Fixed Cover	2 basins-5000 sq. ft. no vapor dis- posal	3 10
<u>D</u>	POST-GRAVITY SED. BASIN (AIR FLOTE)	113	Fixed Cover	2 basins-4000 sq. ft. no vapor (dis- posal)	92
<u>E</u>	PRESSURE RELIEF VALVES	75-350	Minimize valve leakage	Use rupture diaphragm etc.	400
<u>F</u>	VAC. TOWER-GAS DISPOSAL SYSTEM	6570	Incinerate non- condensable gases	Gases to nearest firebox	8
<u>G</u>	GASES-CATALYTIC REGENERATION	1200 (FCC) 400 (TCC)	Incinerate hydro- carbon gases	a) CO boiler (FCC/ TCC) b) TCC plume burner	500-1000 400-600
<u>H</u>	ASPHALT- BLOWING	165	Incinerate vapors (no water scrubbing)	Eliminate mal- odorous vapors	121

Table 1 cont'd.

<u>Item</u>	<u>Description</u>	<u>Loss (uncorrected), Tons per year</u>	<u>Method</u>	<u>Assumptions Involved</u>	<u>Cost Effectiveness \$per ton per year</u>
<u>I</u>	PUMPS-MECHANICAL SEALS	-200	Supply pumps with mechanical seals	a) Average re- finery pumps b) Pumps-poor condition	750 250

Note: No data on cost effectiveness for miscellaneous items

*Typical 100,000 bbls/day refinery; not typical in that for this purpose minimum protection against installed hydrocarbon emissions is assumed.
 Cost effectiveness may be defined as the dollars of cost differential (control vs noncontrol) divided by the tons per year of hydrocarbons received by the control.

MAJOR SOURCES OF HYDROCARBON EMISSIONS

A. Storage Tanks

Potentially, the largest source of hydrocarbon emissions to the atmosphere from a refinery is evaporation loss from tankage. This is particularly true if cone roof tanks are used for the storage of volatile products, such as gasoline and crude oils. Volatile products for this purpose may be defined as those having a true vapor pressure (T.V.P.) of 1.5 pounds or above at ambient temperature, which in terms of the more commonly used Reid vapor pressure (RVP), may be roughly translated as 2.0 pounds or above. A true vapor pressure of 1.5 PSIA was chosen as the minimum vapor pressure (for volatile products) only to be consistent with many state regulations and the August 17, 1971 EPA guidelines. Products having a T.V.P of 11.0 pounds or above at ambient storage temperature are not included because they require pressure storage facilities.

Refineries generally store a variety of products in the 1.5 to 11.0 pound volatility range, all of which must be included for purposes of calculating emissions. As will be seen in Table 2, we have assumed a "typical" 100,000 barrel a day refinery handling two crude oils and producing a regular and a premium gasoline. The assumed production of regular gasoline is 30,000 barrels per day, premium is 15,000 barrels per day, and the assumed storage capacity for unfinished gasolines is 50% of the finished gasoline storage.

The data in this table are based on a "typical" 100,000 barrel per day refinery, in which half of the total crude oil is 2.0 lbs. Reid and half is 6.0 pounds Reid. Also total gasoline production is assumed at 45,000 barrels per day of which two-thirds is regular and one-third premium. Both finished and unfinished gasolines are included. The total tankage capacity for crude oils and gasolines is based on the foregoing assumption for gasolines, however, it is assumed that the conversion of unfinished to finished gasolines is made with 50% of continuous or in-line blending.

Crude Oil Tankage

2.0 lbs. Reid

3-200' x 48' = 268,600 bbls.
 2-125' x 40' = 96,700 bbls.
 3-100' x 40' = 55,960 bbls.
 1,167,080 bbls.

6.0 lbs. Reid

3-200' x 48' = 268,600 bbls.
 2-125' x 40' = 96,700 bbls.
 3-100' x 40' = 55,960 bbls.
 1,167,080 bbls.

Assumed crude oil value (2.0 lb. Reid) = \$2.52/bbl.

Assumed crude oil value (6.0 lb. Reid) = \$3.50/bbl.

Gasoline Tankage

3-125' x 48' = 96,700 bbls.
4-100' x 40' = 55,960 bbls.
8-425' x 40' = 10,100 bbls.
594,740 bbls.

Both regular and premium gasolines are assumed to have 9.0 lb. and 11.0 lb. Reid vapor pressures.

Assumed gasoline values, regular at \$4.62/bbl, premium at \$5.04/bbl.

Sources of Loss

1. Theory

Evaporation from a storage tank is the natural process whereby a liquid is converted to a vapor which subsequently is lost to the atmosphere. Where a vapor space exists, as in a fixed roof tank, this space tends to become saturated with hydrocarbon vapors, depending on the volatility and temperature of the stored liquid. The tank subsequently loses these vapors to the atmosphere primarily from two causes.

- (a) Breathing Loss: This results from thermal action and the daily expansion and contraction of the vapor-space. The vapors are vented to the atmosphere when the setting of the pressure vent is exceeded.
- (b) Filling or Withdrawal Loss: Vapors expelled from a tank as a result of filling, irrespective of the exact mechanism by which the vapors are produced.

There are other losses, such as standing storage, emptying, and boiling. To the extent that these losses are to the atmosphere, they are included in the foregoing.

The floating roof tank also suffers these losses but to a considerably lesser degree. A relatively small vapor space exists between the tank shell and the floating roof proper and vapor may be lost between the seal and the shell, or else may permeate through the sealing fabric. Working losses may occur from wicking action and from wetting action but these losses have been shown to be very low, both by laboratory test and by actual data.

In any tank, fixed roof or floating roof, there are many factors that affect evaporation loss but the most important are:

1. True Vapor Pressure. Probably the most significant of these forces.
2. Temperature Changes in the Tank.
3. Tank Outage.
4. Tank Diameter.
5. Tank Condition.

These are explained in detail in API Bulletin 2513.

2. Calculation of Vapor Losses

The sources of loss and the formulas for calculation of tankage vapor losses are described in some detail in the API Manual on Evaporation Loss¹, and specifically, Bulletins 2513, 2517, and 2518. Bulletin 2513 is general and describes evaporation loss from tankage, causes and control. Bulletins 2518 and 2517 discuss evaporation loss from fixed roof (cone roof) and floating roof tanks respectively.

The following formulas are applicable:

Evaporation Loss--Fixed Roof Tanks

BREATHING LOSS

$$L_y = 0.024 \left(\frac{P}{14.7-P} \right)^{0.68} D^{1.73} H^{0.51} T^{0.50} F_p C K_e$$

where:

L_y = breathing loss, barrels per year

P = vapor pressure of liquid at bulk temperature, psia

D = tank diameter, feet

H = average outage, feet

T = average daily ambient temperature change, degrees fahrenheit

F_p = paint factor

aluminum	1.39
white	1.00

C = adjustment factor for small diameter tanks

K_e = factor to adjust gasoline breathing loss equation to breathing loss of crude oil = 0.58

FILLING LOSS

$$F = 0.0003 P V K_t K_e$$

where:

F = filling loss, barrels per year

P = vapor pressure of liquid at bulk temperature, psia

V = volume of liquid pumped into tank, barrels per year

K_t = turnover factor

K_e = factor to adjust gasoline filling loss equation to filling loss of crude oil = 0.75.

Evaporation Losses--Floating Roof Tanks

In a refinery, there are two major types of floating roof tanks. The common open floater (single or double deck) and the more recent covered floater, described under Methods of Control. Losses given in the equation below apply to both types.

STANDING--STORAGE LOSS

$$L_y = K_f D^{1.5} \left(\frac{P}{14.7-P} \right)^{0.7} V_w^{0.7} K_s K_c K_p$$

where:

L_y = standing-storage loss in barrels per year

K_f = tank type factor

0.045 for welded tanks

0.13 for riveted tanks with pontoon roof and single seal

D = tank diameter in feet, for tanks less than 150 foot diameter

P = vapor pressure liquid at bulk temperature in psia

V_w = average wind velocity in miles per hour

K_s = seal factor

1.00 for tight-fitting seals

1.33 for loose-fitting seals

K_c = factor for tank content

1.00 for gasoline

0.75 for crude oil

NOTE: For tanks larger than 150 foot diameter, multiply loss for 150 foot diameter tank by ratio of

$\frac{\text{TANK DIAMETER}}{150}$

150

K_p = paint factor
 1.00 for aluminum
 0.90 for white

WITHDRAWAL LOSS

$$W = 0.000448 \frac{V}{D}$$

where:

W = withdrawal loss, barrels per year

V = volume of liquid withdrawn from tank, barrels per year

D = tank diameter, feet

The losses from fixed roof tanks and floating roof tanks are given by these equations. Bulletins 2518 and 2517 also include relatively simple nomographs which may be used in lieu of these equations.

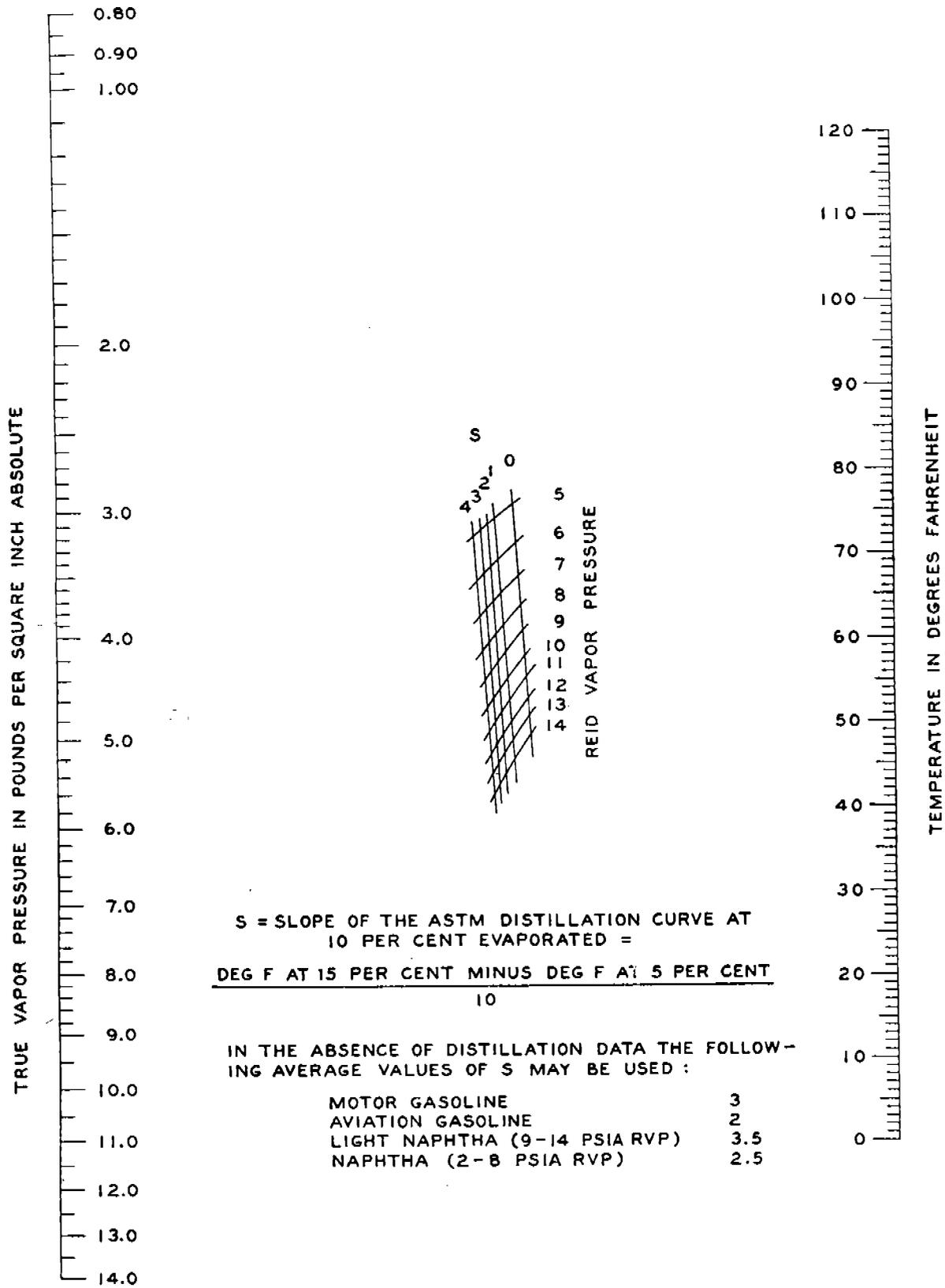
The methods for determining true vapor pressure at any given temperature from Reid vapor pressure, both for crude oils and gasolines are given in Figs. 1 and 2. Figure 3 is a nomograph designed to show the working loss of gasoline and crude oil from fixed roof tanks.

Methods of Control

In a refinery, the usual method for reducing storage tank losses is to install a floating roof in place of, or by converting, a fixed roof tank. While floating roofs would normally be part of a new refinery, they can also be installed on welded fixed roof tanks. In the past, floating roofs have also been installed on riveted fixed roof tanks but because of the age of the riveted tanks, this is generally not a recommended practice.

In lieu of floating roof tankage, vapor recovery systems involving interconnection with the vapor spaces of cone roof tanks have also been used. The individual tank is usually repressured with natural gas and is operated at a slight vacuum and pressure differential. This system has been somewhat limited by safety and corrosion considerations, which present a maintenance problem. Safety is an important factor, particularly in areas of frequent electrical storms.

An optional choice in new tankage is whether to use an open floater or covered floater. An internal floating cover differs from a covered floater in use of materials. The internal floating cover is described in API Bulletin No. 2519. It has found limited application in marketing terminals but almost none in the refineries. The covered floater has found applications in refineries.



Source: Nomograph drawn from data of the National Bureau of Standards.

Fig. 1 - Vapor Pressures of Gasolines and Finished Petroleum Products - 5 psi to 14 psi RVP.

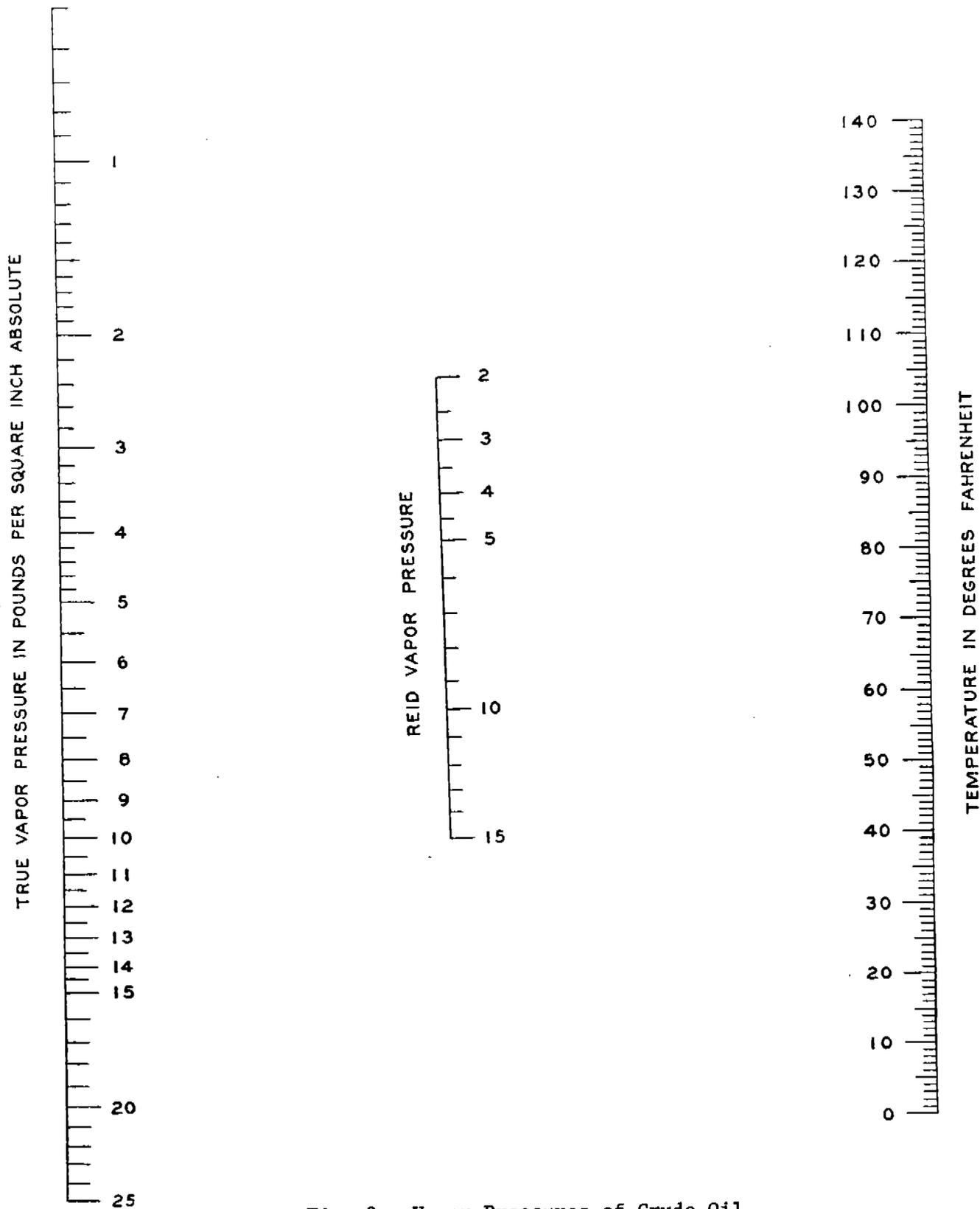
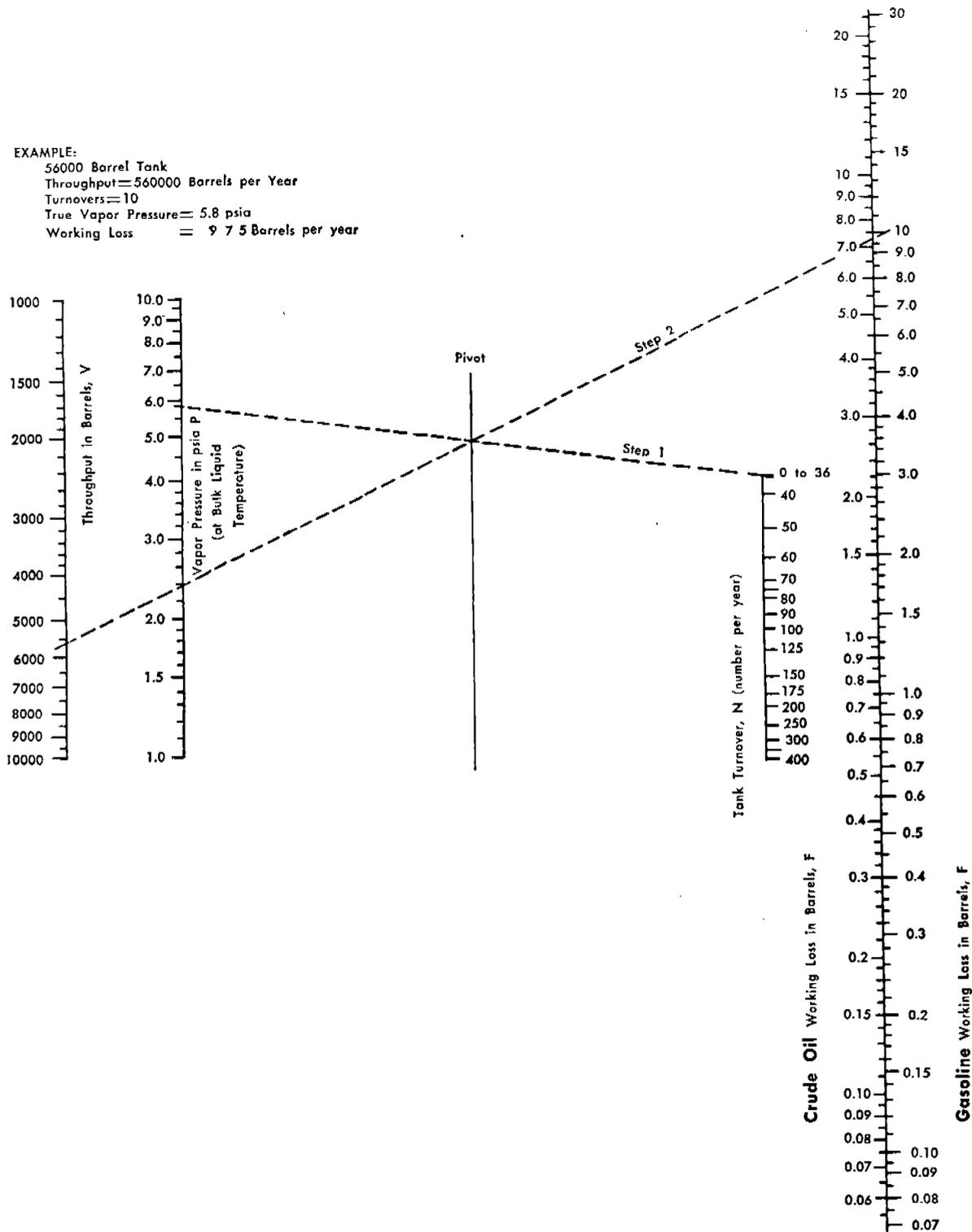


Fig. 2 - Vapor Pressures of Crude Oil.

EXAMPLE:
 56000 Barrel Tank
 Throughput=560000 Barrels per Year
 Turnovers=10
 True Vapor Pressure= 5.8 psia
 Working Loss = 9 7 5 Barrels per year



Note:

The throughput is divided by a number (1, 10, 100, 1,000) to bring it into the range of the scale. The working loss, read from the scale, must then be multiplied by the same number.

Fig. 3 - Working Loss of Gasoline and Crude Oil from Fixed-Roof Tanks.

A comparison of the open and covered floaters involves not only evaporation losses and relative cost, discussed further herein, but operation, maintenance, and safety which are beyond the scope of this discussion.

The covered floater may be described as a simple pan-type floater with an overall cover to exclude rain and snow and to exclude water from entering the product in any manner. As the name implies, the entire roof is covered, usually with a self-supporting roof in the smaller sizes, although one or more column supports may be used in larger sizes. The outside top cover does not usually rest directly on the shell but a slight distance above so that the space over the floating roof is adequately ventilated. Usually, it is equipped with a non-metallic seal, although a metallic seal may be used. These seals are essentially similar to those used on open floating roofs. The calculation of losses for floating roof tanks were obtained from open floaters. A covered floater, especially in the smaller sizes, would probably have lower losses. Because actual data are not available on covered floaters and because differences in any event would be slight, losses for open and covered floaters are assumed to be the same.

Using the data shown in the foregoing tables, the difference in annual loss for fixed vs. floating roof tankage at the "typical" 100,000 barrel refinery is found to be:

Crude Oil (2.0 lbs. Reid)	=	\$11,260 annually
Crude Oil (6.0 lbs. Reid)	=	\$76,120 annually
Gasoline (Regular)	=	\$159,600 annually
Gasoline (Premium)	=	\$ 87,060 annually

Both gasolines are 9.0 lb. Reid (summer) and 11.0 lb. Reid (winter).

Thus, annual savings of nearly \$350,000 would accrue if floating roof tanks were built in lieu of fixed roof tanks or alternatively, if fixed roof tanks are converted to floating roofs.

Cost

The data on cost of construction of fixed and floating roof tanks, and on cost of conversion (Tables 2,3,4, and 5) were supplied by Gulf Oil (Canada). U. S. prices, which are probably somewhat higher, would have to be determined for the particular locality.

Considering floating roof tanks only, it is evident that the erected cost of covered floaters is less than that of open floaters for sizes below 55,000 barrels, equal at 55,000-80,000 barrels (approximately 110' x 40'), and higher than open floaters for sizes above 80,000 barrels.

The comparative costs of either type in sizes from 2,000 barrels to 600,000 barrels and that of a similar size cone roof tank can be determined from these tables. Thus, for an 80,000 barrel tank, the cost of a floater is approximately \$35,000 higher than that of a cone roof tank.

If a cone roof tank is converted to a floater, the cost of conversion can be estimated from Table 5. Thus, for an 80,000 barrel tank, the cost of conversion is approximately \$55,000. This cost is obtained from 1971 data, and to bring the costs up to date, the applicable Nelson cost indices should be used.

Cost-Effectiveness

Cost-effectiveness (C.E.) of floating roof storage tanks varies with many factors such as product vapor pressure, size of tank, and tank throughput. Data are presented both for crude oil and gasoline, assuming a tank size of 80,000 barrels (approximately 110' x 40'). The Reid vapor pressure of the crude oil has been assumed at 6.0 pounds that of gasoline at 9.0 pounds summer and 11.0 pounds winter. Storage temperature are similar to those given in Tables 6,7, and 8.

Crude Oil

Throughput = 1,250,000 barrels per year.

New Floater vs. New Cone Roof

$$\text{C.E.} = (\$212,113 - 177,113) \div 184 = \underline{\$190} \text{ per ton per year.}$$

where 184 = tons crude oil saved per year.

For conversion of fixed roof to covered floater

$$\text{C.E.} = \$55,000 \div 184 = \underline{\$299} \text{ per ton per year.}$$

Gasoline

Throughput = 1,833,000 barrels per year.

New Floater vs. New cone Roof

$$\text{C.E.} = (\$212,113 - \$177,113) \div 455 = \underline{\$77} \text{ per ton per year}$$

where 455 = tons gasoline saved per year.

For conversion of fixed roof to covered floater

$$\text{C.E.} = \$55,000 \div 455 = \underline{\$121} \text{ per ton per year.}$$

TABLE 2

CONE ROOF TANKAGE COSTS

CONE ROOF TANKAGE COSTS: PROV TAX INCL'D. FED TAX EXEMPT JUNE 1970

SIZE BBLs	BARE TANK	S/BBL	FTTG TANK	RADIOG COST	PAD COST	DIKE COST	TOTAL TK COST
500	7,911	15.82	1,899	475	198	1,419	11,902
1,000	9,889	9.89	2,215	475	301	1,799	14,679
2,000	25,000	12.50	2,700	630	381	2,332	31,043
5,000	35,000	7.00	2,900	750	586	3,396	42,632
10,000	38,000	3.80	3,300	1,150	1,045	4,591	48,086
20,000	52,000	2.60	4,200	1,900	1,519	6,283	65,902
40,000	84,000	2.10	6,000	3,300	2,801	8,676	104,777
55,000	105,000	1.91	7,300	4,000	3,800	10,078	130,178
80,000	145,000	1.81	9,600	5,200	5,253	12,060	177,113
100,000	170,000	1.70	11,500	6,000	6,511	13,424	207,435
120,000	200,000	1.67	13,200	6,800	6,511	14,656	241,167

CONE ROOF TANKAGE COSTS: PROV TAX INCL'D. FED TAX EXEMPT JUNE 1970

SIZE BBLs	BARE TANK	S/BBL	FTTG TANK	RADIOG COST	PAD COST	DIKE COST	TOTAL TK COST
150,000	245,000	1.67	16,000	7,800	7,911	16,326	293,037
180,000	285,000	1.58	18,700	8,800	9,616	17,835	339,951
200,000	315,000	1.58	20,600	9,500	10,747	18,773	374,620
250,000	385,000	1.54	24,000	11,000	13,196	20,929	454,125
300,000	455,000	1.52	26,500	12,500	16,611	22,878	533,489
350,000	525,000	1.50	29,000	14,000	18,086	24,670	610,756
400,000	600,000	1.50	31,000	15,500	18,848	26,339	691,687
450,000	670,000	1.49	32,500	17,000	19,625	27,906	767,031
500,000	740,000	1.48	36,000	18,500	21,226	29,388	845,114
600,000	867,000	1.46	41,000	21,000	24,746	32,145	994,391

Costs are for Ontario, Quebec & Maritimes. Add 7% for Mid-Continent, 20% for West Coast.

Dike costs are for four sides.

TABLE 3

OPEN TOP FLOATING ROOF TANKAGE COSTSOPEN TOP FLOATING ROOF TANKAGE COSTS: PROV TAX INCL'D. FED TAX EXEMPT

JUNE 1970

SIZE BBLs	BARE TANK	S/BBL	FTTG TANK	RADIOG COST	PAD COST	DIKE COST	TOTAL TK COST
500	--	--	--	--	--	--	--
1,000	--	--	--	--	--	--	--
2,000	50,000	25.00	2,700	630	381	2,332	56,043
5,000	60,000	12.00	2,900	750	586	3,396	67,632
10,000	65,000	6.50	3,300	1,150	1,045	4,591	73,086
20,000	80,000	4.00	4,200	1,900	1,519	6,283	93,902
40,000	110,000	2.75	6,000	3,300	2,801	8,676	130,777
55,000	135,000	2.45	7,300	4,000	3,800	10,078	160,178
80,000	180,000	2.25	9,600	5,200	5,253	12,060	212,113
100,000	205,000	2.05	11,500	6,000	6,511	13,424	242,435
120,000	240,000	2.00	13,200	6,800	6,511	14,656	281,167

OPEN TOP FLOATING ROOF TANKAGE COSTS: PROV TAX INCL'D. FED TAX EXEMPT

JUNE 1970

SIZE BBLs	BARE TANK	S/BBL	FTTG TANK	RADIOG COST	PAD COST	DIKE COST	TOTAL TK COST
150,000	285,000	1.90	16,000	7,800	7,911	16,326	333,037
180,000	335,000	1.86	18,700	8,800	9,616	17,835	389,951
200,000	365,000	1.83	20,600	9,500	10,747	18,773	424,620
250,000	440,000	1.76	24,000	11,000	13,196	20,929	509,125
300,000	520,000	1.73	26,500	12,500	16,611	22,878	598,489
350,000	600,000	1.71	29,000	14,000	18,086	24,670	685,756
400,000	675,000	1.69	31,000	15,500	18,848	26,339	766,687
450,000	750,000	1.67	32,500	17,000	19,625	27,906	847,031
500,000	825,000	1.65	36,000	18,500	21,226	29,388	930,114
600,000	966,000	1.61	41,000	21,500	23,746	32,145	1,084,391

Costs are for Ontario, Quebec & Maritimes. Add 7% for Mid-Continent, 20% for West Coast.

Dike costs are for four sides.

TABLE 4

COVERED FLOATING ROOF TANKAGE COSTSCOVERED FLOATING ROOF TANKAGE COSTS: PROV TAX INCL'D. FED TAX EXEMPT

JUNE 1970

SIZE BBLs	BARE TANK	S/BBL	FTTG TANK	RADIOG COST	PAD COST	DIKE COST	TOTAL TK COST
500	--	--	--	--	--	--	--
1,000	--	--	--	--	--	--	--
2,000	35,000	17.50	2,700	630	381	2,332	41,043
5,000	45,000	9.00	2,900	750	586	3,396	52,632
10,000	55,000	5.50	3,300	1,150	1,045	4,591	65,086
20,000	70,000	3.50	4,200	1,900	1,519	6,283	83,902
40,000	105,000	2.63	6,000	3,300	2,801	8,676	125,777
55,000	135,000	2.45	7,300	4,000	3,800	10,078	160,178
80,000	180,000	2.25	9,600	5,200	5,253	12,060	212,111
100,000	210,000	2.10	11,500	6,000	6,511	13,424	247,435
120,000	250,000	2.08	13,200	6,800	6,511	14,656	291,167

COVERED FLOATING ROOF TANKAGE COSTS: PROV TAX INCL'D. FED TAX EXEMPT

JUNE 1970

SIZE BBLs	BARE TANK	S/BBL	FTTG TANK	RADIOG COST	PAD COST	DIKE COST	TOTAL TK COST
150,000	300,000	2.00	16,000	7,800	7,911	16,326	348,037
180,000	355,000	1.97	18,700	8,800	9,616	17,835	409,951
200,000	390,000	1.95	20,600	9,500	10,747	18,773	449,620
250,000	480,000	1.92	24,000	11,000	13,196	20,929	549,125
300,000	575,000	1.92	26,500	12,500	16,611	22,878	653,489
350,000	660,000	1.89	29,000	14,000	18,086	24,670	745,756
400,000	750,000	1.88	31,000	15,500	18,848	26,339	841,687
450,000	830,000	1.84	32,500	17,000	19,625	27,906	927,031
500,000	910,000	1.82	36,000	18,500	21,226	29,388	1,015,114
600,000	1,080,000	1.80	41,000	21,500	23,746	32,145	1,198,391

Costs are for Ontario, Quebec & Maritimes. Add 7% for Mid-Continent, 20% for West Coast.

Dike costs are for four sides.

If we average the difference in cost of new tanks and conversions from cone roof to floater, the cost effectiveness would approximate 245 per ton per year for crude oil and \$99 per ton per year for gasoline. In conversions, the cost of cleanout should also be considered.

Table 5

Cost of conversion of Cone Roof Tanks
to Covered Floating Roofs

<u>Year</u>	<u>Size</u>	<u>Total Installed Cost</u>
1963	46' x 78'	\$19,500.
1963	46' x 78'	19,500.
1971	40' x 140'	73,000.
1970	40' x 150'	66,000.
1970	40' x 150'	66,000.
1971	40' x 80'	39,500.
1971	40' x 80'	39,500.
1972	35' x 70'	31,200.

These conversions were all to covered floaters, i.e., steel floating roofs with plastic seals around the vertical members and the shell.

Table 6

Evaporation Losses-Typical 100,000 bbl/day Refinery
Crude Oil Tankage and Data

	<u>2.0 lbs. Reid</u>		<u>6.0 lbs. Reid</u>
a) 3-200' x 48' =	805,800 bbls	3-200' x 48' =	805,800 bbls
b) 2-125 x 48 =	193,400 bbls	2-125 x 48 =	193,400 bbls
c) 3-100 x 40 =	<u>167,880 bbls</u>	3-100 x 40 =	<u>167,880 bbls</u>
	1,167,080 bbls		1,167,080 bbls
Throughput	= 50,000 bbls/day	Throughput	= 50,000 bbls/day
Aver. Stor. Temp.	= 52°F	Aver. Stor. Temp.	= 52°F
True Vapor Press.	= 0.5 lbs.	True Vapor Press.	3.0 lbs.

Gasoline Tankage and Data

	<u>Regular Gasoline</u>		<u>Premium Gasoline</u>
a) 2-125' x 48' =	193,400 bbls	1-125' x 48' =	96,700 bbls
b) 4-100 x 40 =	223,840 bbls	2-100 x 40 =	111,920 bbls
c) 6-42.5 x 40 =	<u>60,600 bbls</u>	3-42.5 x 40 =	<u>30,300 bbls</u>
	477,840 bbls		238,920 bbls

Throughput

30,000 bbls/day (finished)	15,000 bbls/day (finished)
<u>15,000 bbls/day*</u> (unfinished)	<u>7,500 bbls/day*</u> (unfinished)
45,000 bbls/day	22,500 bbls/day

*Use factor of 1.5. In-line blending approaches 1.0, Tank mixing approaches 2.0.

True Vapor Pressure (TVP)

6 months at 9 lbs. Reid @ 72°F = 6.0 lbs. TVP

6 months at 11 lbs. Reid @ 41°F = 4.0 lbs. TVP

Average TVP = 5.0 lbs., annual average

Table 7

Crude Oil LossesFixed Roof2.0 lbs. ReidBreathing

$$\begin{array}{r}
 \text{a) } 3 \times 759 = 2,277 \text{ bbls} \\
 \text{b) } 2 \times 337 = 674 \text{ bbls} \\
 \text{c) } 3 \times 209 = 627 \text{ bbls} \\
 \hline
 3,578 \text{ bbls}
 \end{array}$$

$$\begin{array}{r}
 \text{a) } 3 \times 2,929 = 8,787 \text{ bbls} \\
 \text{b) } 2 \times 1,299 = 2,598 \text{ bbls} \\
 \text{c) } 3 \times 805 = 2,415 \text{ bbls} \\
 \hline
 13,800 \text{ bbls}
 \end{array}$$

$$2,578 \times 0.75 = 2684 \text{ bbls}$$

$$13,800 \times 0.75 = 10350 \text{ bbls}$$

Throughput or Filling

$$F = 0.0003 \text{ PVK}_t \text{ K}_c$$

$$\begin{array}{r}
 = 0.003 \times 0.5 \times 50000 \times 365 \times 1.0 \times 0.75 \\
 = 0.00015 \times (13,688,000) \\
 = .2054 \text{ bbls (Throughput)} \\
 \underline{.2684 \text{ bbls (Breathing)}} \\
 4738 \text{ bbls/year} \qquad \underline{\underline{\text{TOTAL LOSS}}}
 \end{array}$$

$$\begin{array}{r}
 = 0.0003 \times 3.0 \times 18,250,000 \times 1.0 \times 0.75 \\
 = 0.0009 \times (13,688,000) \\
 = 12319 \text{ bbls (Throughput)} \\
 \underline{10350 \text{ bbls (Breathing)}} \\
 22669 \text{ bbls/year}
 \end{array}$$

Floating Roof (Welded)Breathing

$$\begin{array}{r}
 \text{a) } 3 \times 56.7 = 170.7 \text{ bbls} \\
 \text{b) } 2 \times 28.1 = 56.2 \text{ bbls} \\
 \text{c) } 3 \times 20.1 = 60.3 \text{ bbls} \\
 \hline
 287.0 \text{ bbls}
 \end{array}$$

$$\begin{array}{r}
 \text{a) } 3 \times 228.5 = 685.5 \text{ bbls} \\
 \text{b) } 2 \times 112.9 = 225.8 \text{ bbls} \\
 \text{c) } 3 \times 80.8 = 242.4 \text{ bbls} \\
 \hline
 1154.0 \text{ bbls}
 \end{array}$$

$$287.0 \times 0.75 = 215 \text{ bbls}$$

$$1154 \times 0.75 = 866 \text{ bbls}$$

Throughput or Withdrawal

$$W = 0.000448 \frac{V}{D}$$

$$\begin{array}{r}
 = 0.000448 \times \frac{50,000 \times 365}{150^*} \\
 = 0.000448 \times 121,667 \\
 = 55 \text{ bbls (Throughput)} \\
 \underline{215 \text{ bbls (Breathing)}} \\
 270 \text{ bbls} \qquad \underline{\underline{\text{TOTAL LOSS}}}
 \end{array}$$

$$\begin{array}{r}
 = 0.000448 \times \frac{50,000 \times 365}{150} \\
 = 0.000448 \times 121,667 \\
 = 55 \text{ bbls (Throughput)} \\
 \underline{866 \text{ bbls (Breathing)}} \\
 921 \text{ bbls}
 \end{array}$$

* Assume average diameter is 150 ft. Any error would be slight.

Table 8

Gasoline Losses

<u>Regular</u>	<u>Fixed Roof</u>	<u>Premium</u>
<u>Breathing</u>	<u>Capacity</u>	
a) 2-125' x 48' = 193,400 bbls		a) 1-125' x 48' = 96,700 bbls
b) 4-100' x 40' = 223,840 bbls		b) 20100' x 40' = 111,920 bbls
c) 6-42.5' x 40' = 60,600 bbls		c) 3-42.5' x 40' = <u>30,300 bbls</u>
	477,840 bbls	238,920 bbls

Breathing

a) 2 x 2090 = 4,180 bbls	a) 1 x 2,090 = 2,090 bbls
b) 4 x 1294 = 5,176 bbls	b) 2 x 1,294 = 2,588 bbls
c) 6 x 294 = <u>1,764 bbls</u>	c) 3 x 294 = <u>882 bbls</u>
11,120 bbls	5,560 bbls

Throughput

$$F = 0.0003 PVK_t$$

= 0.0003 x 5.0 x 45000 x 365 x 1.0	= 0.0003 x 5.0 x 22,500 x 365 x 1.0
= 0.0015 x 16,425,000	= 0.0015 x 8,212,500
= 24638 bbls (Throughput)	= 12319 bbls (Throughput)
<u>11.120 bbls (Breathing)</u>	<u>5560 bbls (Heating)</u>
35,758 bbls/year	17,897 bbls/year
<u>TOTAL LOSS</u>	

Floating Roof (Welded)Breathing

a) 2 x 184.1 = 368.2 bbls	a) 1 x 184.1 = 184.1 bbls
b) 4 x 131.8 = 527.2 bbls	b) 2 x 131.8 = 263.6 bbls
c) 6 x 36.5 = <u>219.0 bbls</u>	c) 3 x 36.5 = <u>109.5 bbls</u>
1,114.0 bbls	557.0 bbls

Throughput

= 0.000448 x $\frac{45000 \times 365}{75^*}$	= 0.000448 x $\frac{22,500 \times 365}{75^*}$
= 98 bbls (Throughput)	= 49 bbls
<u>1114 bbls (Breathing)</u>	<u>557 bbls</u>
1212 bbls/year	606 bbls/year
<u>TOTAL LOSS</u>	

*Assume average diameter is 75 ft. Any error would be slight.

B. Transportation Facilities

Loading and Unloading Losses

Introduction

In transporting and handling of gasolines and crude oils, evaporation and entrainment losses occur in both the loading and unloading operations. As these losses occur to the atmosphere only when the carrier is being filled, the loading and unloading losses are combined in the following discussion except where noted for marine operations. The transport carriers involved are tank trucks and tank cars for smaller deliveries and barges and tankers for larger movements. Pipeline deliveries are the most efficient insofar as losses are concerned and losses may be considered negligible for purposes of this study.

Losses involved in crude oil shipments are considered only for marine carriers, i.e., barges and tankers. It is sufficiently accurate to assume that the percent by volume of crude oil lost is similar to that of a gasoline having the same true vapor pressure.

The discussion compares loading losses both for splash and subsurface loading, and the efficiency and the cost of a typical vapor recovery system in affecting savings in loading losses.

Tank Trucks and Tank Cars

The greatest determinant in the total loss experienced in loading tank cars and tank trucks is the method of loading, i.e., whether splash loading, submerged fill, or bottom loading.

In splash loading, the liquid is discharged by short spout into the upper part of the compartment. The resultant free fall not only increases evaporation but may result in a fine mist of liquid droplets.

In submerged surface loading, the bottom of the loading pipe is within a few inches of the bottom. At first, until the tip of the loading arm is covered, higher losses ensue. When the bottom of the loading arm is covered, there is a marked decrease in turbulence, and losses by evaporation are correspondingly reduced. Bottom loading is a complete type of subsurface loading and is, therefore, even more effective from a loss reduction point of view.

Losses in loading may be further reduced by vapor recovery in which essentially all* of the vapor evolved in the loading operation is recovered.

*Where vapor recovery is required by law, it must be at least 90% efficient.

In the initial part of this discussion, however, only splash loading and subsurface loading, which have been generally accepted methods for many years, are considered.

Losses experienced in splash and sub-surface loading are proportional to the true vapor pressure of the product and the degree of saturation of the vapor spaces after unloading and before loading. A careful study of the magnitude of these losses is presented in graph form as Fig. 4, taken from API Bulletin 2514. In this Figure, the saturation has been given the average value of 30%. This value is the average of many tests but may not apply in the given instance. The data shown in Figure 4 do not include losses by entrainment during splash loading which may exceed evaporation losses by twofold.

Methods of Control

Sub-surface or Bottom Loading

To obtain the savings for sub-surface loading in Tables 10 and 11, sub-surface loading arms supplied by various manufacturers should be installed. This will not only reduce hydrocarbon emissions but will decrease refinery losses and secure various other advantages which are beyond the scope of this report.

There are technical as well as practical considerations which rule out a 100% sub-surface loading installation, although bottom loading approaches this ideal. If bottom loading is not utilized, the length of the drop pipe determines the efficiency achieved. Although company equipment can usually be standardized to approach 100% sub-surface loading, this is usually not true of outside haulers' trucks, thus reducing the total savings obtained.

Tables 10 and 11 compare the losses per million gallons loaded for splash and sub-surface loading respectively, assuming 9.0 pound and 11.0 pound Reid gasolines, each at three different temperatures.

Considering the 9.0 pound Reid gasoline at an average temperature of 60°F, the difference in the value of the loss--sub-surface vs. splash--is 1,730 gallons or \$190.00 for regular gasoline, \$205.00 for premium gasoline. 11.0 pound Reid gasoline at 40°F would have slightly lower losses in gallonage and in value.

Splash Loading vs. Sub-surface Loading

Throughput is 1,000,000 gallons in all cases, Tables 10 and 11.

Table 10-Splash Loading

R.V.P. (Pounds)	<u>9.0 pounds</u>			<u>11.0 pounds</u>		
	40°F	60	80	20°F	40	60
Temp. (Gasoline)	40°F	60	80	20°F	40	60
T.V.P.	3.1 lbs.	4.6	6.6	2.5	3.8	5.6
Vol. % loss (Exh. 1)	0.105	0.173	0.301	0.083	0.135	0.233
Total Vol. % Loss	0.158	0.260	0.452	0.125	0.203	0.350
<u>NOTE:</u> All loss values for splash loading have been increased by 50% over the values determined from Fig. 4 to allow for entrainment losses.						
Total Loss, gallons	1580	2600	4520	1250	2030	3500
<u>Value</u>						
Regular (\$4.62/bbl)	\$175	\$285	\$495	\$140	\$225	\$385
Premium (\$5.04/bbl)	\$190	\$310	\$540	\$150	\$245	\$420

Table 11-Sub-surface Loading

R.V.P. (Pounds)	<u>9.0 pounds</u>			<u>11.0 pounds</u>		
	40°F	60	80	20°F	40	60
Temp. (Gasoline)	40°F	60	80	20°F	40	60
T.V.P.	3.1 lbs	4.6	6.6	2.5	3.8	5.6
Vol. % loss (Exh. 1)	0.058	0.087	0.126	0.046	0.071	0.106
Total Loss, gallons	580	870	1260	460	710	1060
<u>Value</u>						
Regular (\$4.62/bbl)	\$65	\$95	\$140	\$50	\$80	\$115
Premium (\$5.04/bbl)	\$70	\$105	\$150	\$55	\$85	\$125

On the average, the reduction in loading loss sub-surface over splash will approximate 60 to 75% increasing at the higher true vapor pressure (T.V.P.). Bottom loading, for which no data is available, is even more efficient than sub-surface loading and will result in even greater savings.

Vapor Recovery

A more complete method of control involves vapor recovery. The most common method employed involves absorption of hydrocarbons from a hydrocarbon-air mixture. A recovery factor of 90% (or greater) is assumed as this is the minimum permissible recovery for the system to obtain the approval of the Los Angeles County Air Pollution Control District where most of these installations have been made. The efficiency actually obtained ranges from 90-95%.

Although several manufacturers claim to make vapor recovery equipment, most of the equipment sold to date has been that supplied by one manufacturer, and a brief description of this system is given below:

Recovered vapor is first saturated with gasoline from an existing tank and cooled, and subsequently, it is stored in a variable volume vapor storage vessel which is part of the system. On a set level basis, a compressor withdraws vapor from the vessel, compressing it to 200 psig, and delivers it to the absorber after passing through a heat exchanger. Gasoline from an existing tank is also pumped to the top of the absorber, thus recovering the gasoline in the vapor in the bottom of the absorber. All of the recovered gasoline is pumped to the existing storage tank, and the remaining vapor is vented to the atmosphere.

This system requires a vapor recovery loading arm. Such a loading arm is available from several suppliers at a cost of about \$2,500 - \$3,000 for a 4" arm. These arms are of the splash type, which tends to increase the load on and the size of the vapor recovery system. The arm, by means of a pipe section extension, can presumably be converted, at least in part, to a sub-surface type.

Vapor recovery is available with bottom loading by means of a vapor header manifolded to all truck compartments. Vapor is exhausted through a common connection to a supported hose, which in turn is connected to the vapor handling unit through rigid pipe.

Vapor Disposal in a Firebox

This method is feasible if tank truck loading is relatively close to fired heaters. The vapors displaced during loading are conducted to a knockout pot and thence to a vaporholder. The vapors are then periodically compressed and discharged to the firebox. To prevent explosive mixtures, the vaporholder is gas blanketed.

It is not known whether any such system exists. There are potential difficulties in operating the vaporholder and hazards that exist because of the presence of air would seem to rule out this system on a safety basis.

Cost and Cost-Effectiveness

Cost and Cost-Effectiveness are calculated for a vapor recovery system as listed in Tables 13 and 14. All capital costs for equipment and operation are based on the typical vapor recovery system which has been used in most of the installations in California. Invested capital includes the vapor recovery unit, piping, electrical, installation, and loading arms. Annual expenditures or operating costs include proportional costs such as electrical costs; fixed costs such as maintenance and painting; and variable costs such as taxes and insurance. Basis for calculation of savings is also indicated.

The annual savings shown in Tables 13 and 14 are based on regular gasoline at \$4.62/bbl or \$0.11 per gallon. In both tables, if premium gasoline were used, gross dollar savings would be approximately 9% higher and this will change net dollar savings, payouts, and cost-effectiveness.

As might be anticipated, the initial cost of a vapor recovery system, including annual operating costs, is comparatively high per million gallons of throughput for low refinery throughput but decreases rapidly as the throughput increases. Thus, at a throughput of 1,000,000 gallons per month there is no payout; but at 90 million gallons per month, the payout for vapor recovery over splash loading and over sub-surface loading is 0.9 years and 3.1 years respectively.

The capital cost to effect savings in hydrocarbon emissions of 1 ton per year for the same five throughputs as shown in Table 13 is shown in Table 14. This is a direct measure of the cost effectiveness.

In an inspection of Tables 13 and 14, it is apparent that whether or not vapor recovery equipment is presently required by law it is economically desirable at the high throughputs, starting at 10 million gallons per month and certainly at any higher rate.

Data for Calculation of Savings

The annual savings and the resultant payouts are based on the following assumptions:

1. True vapor pressure (TVP) of gasoline is assumed to be 4.0 pounds average, i.e., 9.0 lbs. Reid at 52°F or 11.0 lbs. Reid at 40°F.
2. Volume percent loss of gasoline based on a TVP of 4.0 lbs. is estimated as follows:
 - a. Vol. % loss by splash loading = 0.20%

Note: Loss by Figure 4 = 0.145% add 50% for entrainment

 - b. Vol. % loss by sub-surface loading = 0.075%
3. Recovery of vapor by vapor recovery is assumed at 92.5% of the splash loading rate (e.g., loss = 0.015%)
4. Savings by vapor recovery
 - a. Splash loading: $0.200 - 0.015 = 0.185\%$
 - b. Sub-surface loading: $0.075 - 0.015 = 0.060\%$

5. Throughput rates are assumed at 1 million, 5, 10, 20, and 90 million gallons per month
6. Value of regular gasoline at refinery = \$4.62/barrel or \$0.11 per gallon. Gasoline assumed at 58.5° API, or 6.2 pounds per gallon.

Barges and Tankers

Hydrocarbon emission occurs as evaporation loss from marine vessels when they are being loaded and also during unloading. The unloading losses which might be incurred in unloading of crude oil shipments at a refinery may not appear as a hydrocarbon emission at the refinery but rather when the compartment is being refilled or when it is being cleaned or ballasted. This ballasting, incidentally, may occur at the refinery. This loss has been estimated as approximately the same as the analogous shore tank withdrawal loss or 0.007 percent per psia T.V.P.

As regards loading losses, this is similar in principle to that incurred in loading tank trucks, although two actual or potential differences should be noted. The average percent saturation for a barge or tanker compartment prior to loading is usually zero or close to it, particularly when the compartment has previously been cleaned or ballasted. In a tank truck, the average percent saturation prior to loading approximates 30%. Also, submerged fill is usually achieved by means of fill pipes which should be integral parts of the carriers and should be arranged so as to minimize splashing.

The loss from loading tankers and barges is generally lower than that from loading tank trucks or tank cars in accordance with the following theory:

The initial oil-fill encounters a compartment containing no vapors, and in the initial fill, the rate of saturation of the air space above the liquid is rapid. When the bottom of the oil inlet pipe is covered, turbulence decreases markedly and filling proceeds smoothly. The layer highest in hydrocarbon vapors is directly above the surface and dispersion throughout the balance of the compartment proceeds slowly. The gas leaving the top initially is relatively low in hydrocarbon vapors at the start but becomes richer rapidly as the oil surface approaches the top of the compartment, at which point the expelled gas may contain 30-50% of hydrocarbon vapors. The total loss of hydrocarbons is the average of the hydrocarbon concentration during the entire period of fill.

FIGURE 4

LOADING LOSSES FROM MARINE VESSELS, TANK CARS AND TANK TRUCKS

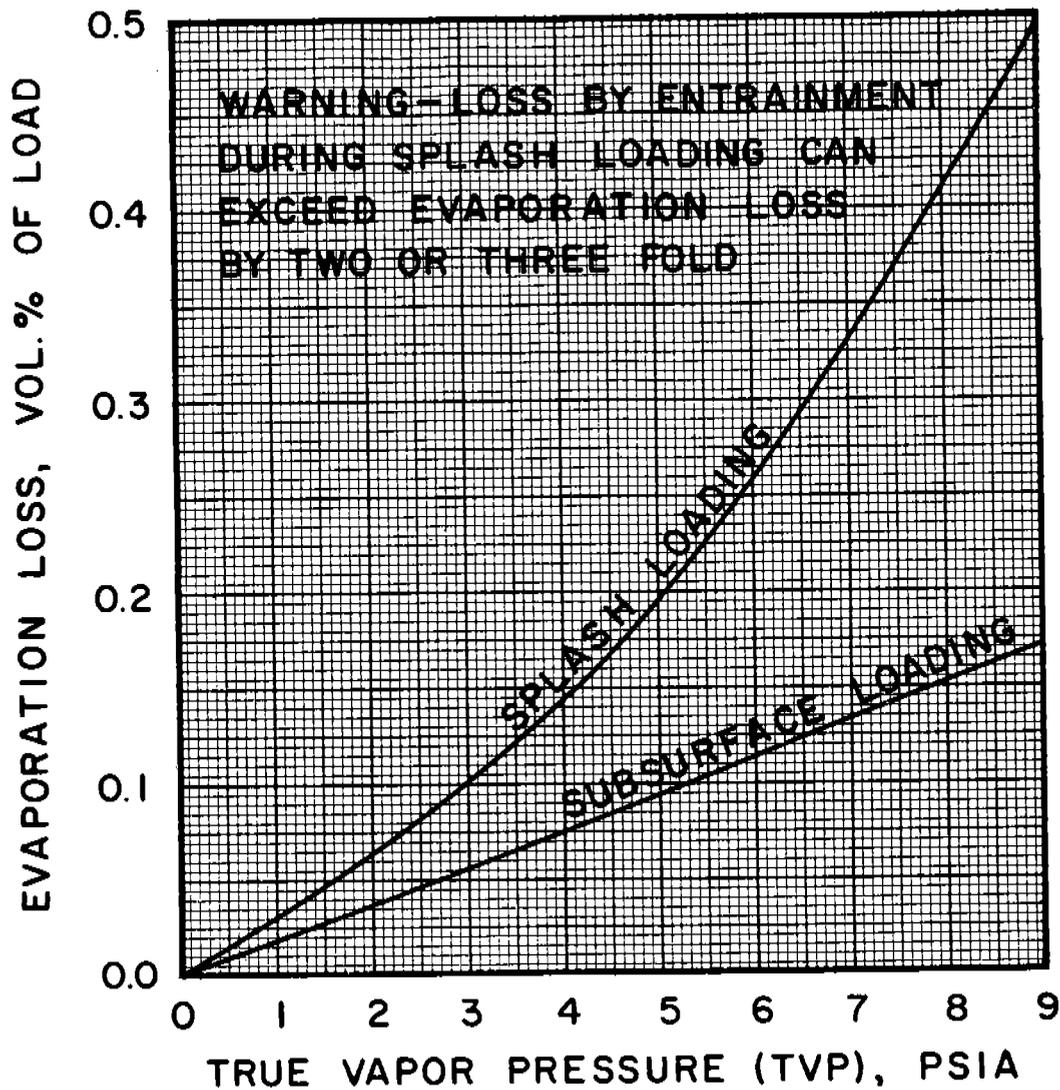
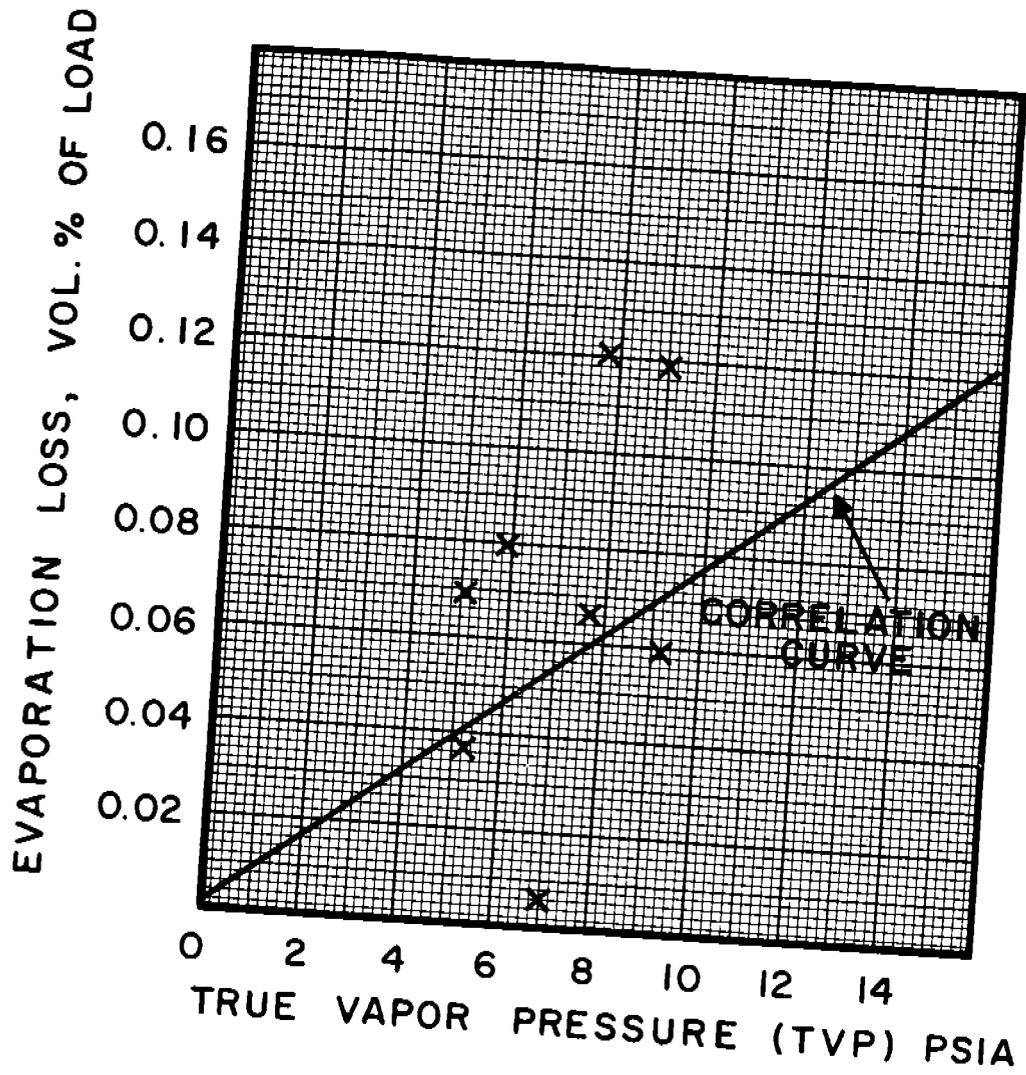


FIGURE 5

LOSS FROM LOADING TANKERS AND BARGES



The total emission of hydrocarbon vapors during filling of a tanker initially gas-free, is given by the following table⁵:

Table 12

Estimates of Total Hydrocarbon Gas Evolution
(high vapor-pressure non-boiling cargoes)

Capacity of Tanker	dwt	40,000	100,000	200,000	300,000
Tank depth	ft	50	70	80	95
Final oil depth	ft	49	68.6	78.4	93.1
Mass of oil per sq. ft of surface in full tanks (SG = 0.85)	ton	1.17	1.62	1.87	2.22
Gas vented per sq. ft of oil surface	cu. ft	1.25	1.25	1.25	1.25
Hence, hydrocarbon gas vented per ton of oil	cu. ft/ton	1.07	0.772	0.667	0.563
Total volume hydrocarbon gas vented	cu. ft	42,800	77,200	133,400	168,900
Mass of hydrocarbon gas vented (Mol. Wt. = 44, Temp. = 100 F)	ton	2.05	3.70	6.38	8.10

It should be noted that the total loss is of the order of a few tons and that it is less relative to the size of the cargo carried in big ships because of the greater depth of oil in the larger tankers. If the vapor space in tanker compartments were saturated or partly saturated prior to loading, the total hydrocarbon gas liberated could be several times as great.

In Figure 5, the loading loss (for the correlation equation) is given by the equation:

$$\text{Loading loss \% by volume} = 0.008 \times \text{T.V.P.}$$

This equation represents a loss appreciably higher than that given by the above table, and does not differentiate between size of tankers. However, if some saturation (on the average) is assumed prior to loading, the discrepancies in loss of hydrocarbon vapors or hydrocarbon emissions to the atmosphere are not great.

Theoretically, at least, vapor recovery systems can be adapted to barges and tankers loading. Practically, for tankers at least rates are usually very high, which would require large vapor

equipment sizes and concurrently high installation costs. The same difficulty, to a lesser degree, applies when loading barges. There are known marine vapor recovery installations in the U. S. or throughout the world at the present time. Furthermore, Coast Guard approval would be required for any vapor recovery system for barges or tankers.

Table 13

Economic Study Results

Refinery Thruput Gal./Month	Invested Capital	Annual Expenditure	Depreciation \$/year	Annual Savings (Costs)
1x10 ⁶	\$88,200 (15 M Cu. Ft. Vapor Holder)	\$4,150	\$5,850	22,200-SL 7,200-SSL
5x10 ⁶	\$92,200 (25 M Cu. Ft. Vapor Holder)	4,350	\$6,150	111,000-SL 36,000-SSL
10x10 ⁶	\$120,200 (30 M Cu. Ft. Vapor Holder)	5,052	\$8,020	222,000-SL 72,000-SSL
20x10 ⁶	\$133,200 (30 M Cu. Ft. Vapor Holder)	5,360	\$8,850	44,000-SL 144,000-SSL
90x10 ⁶	\$200,000 (40 M Cu. Ft. Vapor Holder)	6,700	\$13,340	1,995,000-SL 648,000-SSL

Table 14

Cost-Effectiveness to Reduce Hydrocarbon Emissions

Refinery Thruput Gal./year	Investment Cost	Cost \$/T per year	Savings Vapor Recovery vs. Splash (tons/year)	Savings-Vapor Recovery vs SSL (tons/year)	Cost \$/T Per year
12,000,000	\$ 88,200	\$1,278	69.0	22.3	\$3,995
60,000,000	\$ 92,200	265	344.0	111.6	826
120,000,000	\$120,200	175	688.0	223.2	539
240,000,000	\$133,200	97	1376.0	446.0	298
1,080,000,000	\$200,000	32	6192.0	2008.0	100

*SL-Splash loading

SSL-Sub-surface loading

*Annual Expenditures for Operation can be classified into three categories:

1. Proportional Costs: Includes expenditures which vary with length of time system is in operation such as electric power.
2. Fixed Costs: Expenditures which tend to remain more or less constant on a yearly basis such as maintenance, operations, and overhead.
3. Variable Costs: Expenditures which either come up unexpectedly, such as major breakdowns which may require the presence of factory or distributor service personnel or costs which are incurred on a yearly basis but differ from year to year. These include taxes which are paid based on the assessed equipment value and the outstanding insurance rates which are also based on assessed value.

C. Primary Gravity Sedimentation Devices

The sedimentation device used is normally an API separator but other basins or devices may also be used for sedimentation purposes. These include ponds or lagoons and, more recently, stilling tanks, all of which receive influent water directly from the refinery, prior to any settling treatment.

In the process of sedimentation, oil contained in the waste water rises to the top of the basins and if the area is uncovered, evaporation occurs and hydrocarbon vapors are emitted.

Source of Loss

There are many factors which contribute to the extent of the loss, and the major factors are as follows:

a. True vapor pressure of the slop oil

1. Reid vapor pressure
2. Oil temperature (same as waste water)

NOTE: To determine true vapor pressure, consider slop oil as crude oil.

b. Sedimentation Area

For a given quantity of oil, the larger the area, the greater the loss in the same period of time.

c. Total time of exposure

d. Film thickness

e. Average wind velocity

Much of the data on sources of loss used herein is taken from an article by Litchfield¹⁰, in which factors d and e are not discussed. It has been assumed in this article that film thickness are finite and range from 1/4" to 1". Obviously, the same quantity and quality of oil in a much larger area, as in a pond or lagoon, would for the same period of exposure undergo considerably more evaporation, possibly several times as great. Wind velocity is also a factor, particularly when combined with total time of exposure. For example, it is conceivable that an oil of the same volatility as indicated later (constant 10% ASTM point of 300°F) exposed for 24-48 hours in a wind velocity of 15 miles per hour or greater in a thin film (less than 0.10") on a pond might lose 50% or its total volume rather than the 10% shown later.

Normal slop oils vary greatly in gravity, depending on the crude oil being processed and the sum of the various sources from which it is collected. While slop oil gravity provides a rough indication of volatility, a more precise method of determination is by ASTM distillation, indicating percent distilled at 300°F. In the article noted, the slop oil is assumed to have a constant ASTM 10% point of 300°F.

In this article, a correlation for volume % loss has been developed as follows:

$$\text{Vol. \% loss} = -6.6339 + 0.0319 X - 0.0286 Y + 0.2145Z$$

Where X = ambient temperature, °F
 Y = 10% point, TBP (converted from ASTM)
 Z = influent temperature, °F

The three variables shown account for 88.2% of the total losses. In Fig. 6, a series of curves is presented showing volume % loss versus ambient temperature for differing inlet water temperatures. Thus, the volume % loss for an ambient temperature of 50°F, 10% point of 300°F, separator influent water temperature of 120°F is 12%.

The effect of influent temperature is shown in Fig. 7. It is apparent that API separator influent temperature and the 10% distillation point have a considerable effect on evaporation losses experienced. In Fig. 7, for the constant conditions shown and for inlet water temperatures ranging from 90° to 160°F, the volume % loss varies from 5% to 20%.

The following example, for illustrative purposes, compares the losses in a 100,000 barrel/day refinery for three different types of sedimentation basins:

Vol. % loss (see above example) = 12.0%
 Rate of waste water flow = 5000 gpm
 Influent oil content = 0.15% (1500 ppm) = 10,800 gals/day

API Separator

If the API separator is assumed to have two 20' x 100' sections plus 25' x 40' forebay = 5000 sq. ft.

Vol. % loss of uncovered = 12% x 10,800 = 1296 gal/day
 This will approximate an annual loss of 0.25 gal/sq. ft/day
 Assume gravity at 36.8° = 7.0#/gal

1296 x 7.0 = 9072 #/day lost, or, for the assumed conditions, about 9.1 lbs. per 1000 bbls/day of refinery throughput. More frequent with-drawls than used in the Litchfield¹⁰ article should reduce this loss somewhat.

A separate investigation, by another company, was less precise but did involve higher ambient temperatures. This study showed an annual loss of about 0.5 gal/sq. ft./day.

Open Pond or Lagoon

For the same assumptions as above, the greater area would result in a greater loss, possibly two or three times as great as that indicated above.

The loss of oil can be expressed by the formula:

$$\text{Oil loss/day (gallons)} = (\text{Oil (ppm) entering} - \text{Oil (ppm) leaving}) \times \text{total daily waste water flow} - \text{oil collected/day.}$$

The oil loss in gallons per day is due to evaporation.

Stilling Tank

The stilling tank is usually a covered tank with an area approximately the same as an API separator in which wind velocity can be disregarded. Vapors caused by evaporation are collected in a gas-blanketed atmosphere (for safety) and are disposed of by burning in a firebox or flare. In this case, hydrocarbon emissions to the atmosphere are insignificant.

Methods of Control

There are two basic methods of control. The first involves design modifications to and suitable maintenance in the waste water collection system upstream of the separator so as to reduce the total amount of oil. This may also reduce the volatility of the oil. The second method involves covering the separator, utilizing either a floating roof or a fixed roof.

These methods are as follows:

1. Reduce quantity and volatility of oil
 - a. Quantity-Minimize the volume of oil by periodic inspection and maintenance.
 - b. Volatility-If the temperature of the waste water is reduced, evaporation is decreased. Thus, a 20°F reduction in water temperature will reduce evaporation by over 35%. This method may not have practical significance.
2. Covering the separator
 - a. Floating roof-Provide floating cover on primary separation device. On an API separator this would

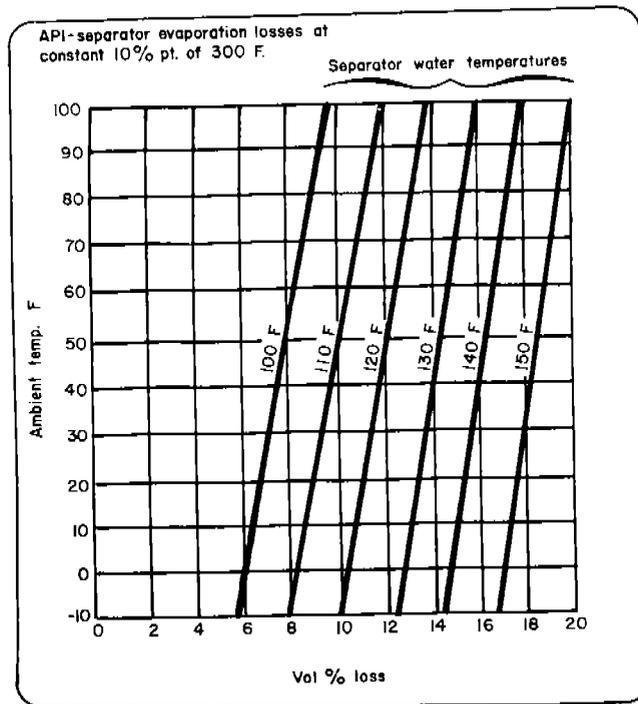


Figure 6. Correlation of evaporation vs. water temperature.

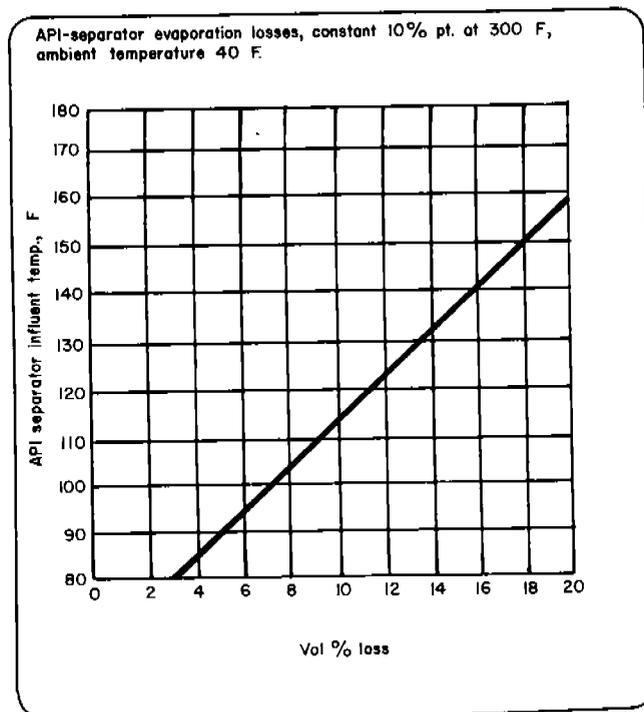


Figure 7. Correlation of evaporation vs. influent temperature.

include forebay and API separator itself. A pond could also be covered but at much greater expense.

NOTE: Floating covers must be installed so as not to interfere with the efficiency of the oil-collecting device.

- b. Fixed roof-A fixed roof is more easily installed but the resulting vapor space might constitute a hazard unless this space is gas-blanketed with hydrocarbon or nitrogen. The space under the fixed roof may be maintained at a slight pressure (or vacuum) with resultant vapors flared. Gulf Oil Canada used a fixed cover made of truncated cone aluminum segments (or galvanized steel) which is self-supporting. This deck is mounted in concrete with neoprene gasketing.

Costs

- a. Floating roof-Amoco reports an installation cost including labor and materials of 50 to 60 cents/sq. ft. for 2" thick foamglas slabs.
- b. Fixed roof-Gulf Oil (Canada) reports a cost (for the above decking) of \$1.75/sq/ft/ installed. This cost does not include collection and disposal of the vapors in a flare or firebox. Mobil Oil, using a different cover, reports \$2.75/sq.ft/ installed and in this study, we have used \$2.25/sq. ft. as an average value.

Cost-Effectiveness

Cost-effectiveness is estimated for floating covers and fixed covers only. Floating covers minimize evaporation and hence do not require vapor disposal. Under most conditions, fixed covers will require vapor disposal.

It has been estimated, based on available data, that for the average 100,000 bbl/day refinery, oil collection in the primary sedimentation device might approximate 10,800 gal/day (see Sources of Loss), and, in general, would range from 100 bbls to 500 bbls per day.

Cost-effectiveness for:

- a. Floating covers: The loss reduction in floating covers would depend on the tightness of the floating seal. In addition to the 85% reduction in loss figure reported by Litchfield¹⁰, another company has reported approximately the same figure.

A two-bay separator (each bay 20' x 100') with forebay would approximate 5000 sq. ft. which, at \$0.60 per sq. ft. would cost \$3000 installed. If 12% of the collected oil is normally evaporated, and if 85% of this loss is prevented by a floating cover, the savings are:

$$10,800 \times 0.12 \times 0.85 = 1100 \text{ gals/day or } 26 \text{ bbls/day}$$

$$26 \text{ barrels at } 36.8^\circ\text{API (7.0\#/gal.)} = 7700 \text{ lbs. or}$$

$$3.85 \text{ tons/day}$$

$$3.85 \times 365 = 1405 \text{ tons/yr } \$3000 \div 1405 = \$2.15/\text{ton/yr}$$

- b. Fixed Roof Covers: The fixed roof may not require a vapor disposal system, in which case it would be difficult to evaluate potential savings. These would depend on design and method of operation. A vapor disposal system would eliminate hydrocarbon emissions and the cost effectiveness would be:

$$10,800 \text{ gals/day} \times 0.12 = 1296 \text{ gals/day or } 3/\text{tons/day}$$

$$31 \times 365 = 1130 \text{ tons/yr}$$

$$\text{The cost of supplying a cover is } 5000 \text{ sq.ft.} \times \$2.25 =$$

$$\$11,250$$

$$\$11,250 \div 1130 = \$10.00/\text{ton/yr (approximately)}$$

NOTE: This figure is exclusive of the cost of the vapor collection and disposal system.

D. Post-Gravity Sedimentation Devices (Intermediate Separation)

The basic mechanism of oil evaporation from post-gravity sedimentation devices is similar to that of primary gravity separation devices. Several important differences in degree exist, however, all of which will tend to reduce evaporation losses. As a result, losses from these devices would tend to present a problem only where stringent air pollution regulations are in effect, such as in The Los Angeles Air Pollution Control District.

Sources of Loss

The major factor contributing to evaporation losses from these devices is the true vapor pressure of the oil and the carrying capacity of dissolved or entrained air when used. Losses are considerably less than in a primary device for the following reasons.

1. The removal of oil in a primary gravity separation device varies from 80-95% of the total oil and depends on many factors. Therefore, only 10-15% of the oil remains for further or potential evaporation.
2. A variable portion of volatile light ends has been removed

as further described below.

- a. In any covered primary basin, the loss by evaporation, especially of the volatile material, is assumed at 15%.
- b. Under certain conditions e.g., involving the use of a stilling tank, all volatile vapors are recovered and burned in a firebox or flare. Hence, residue light hydrocarbons available for vaporization are slight.

The combination of Items 1 and 2a above--the least damaging from the point of view of additional losses sustained--results in a potential evaporation loss of only about 10% of that sustained in Item C, Primary Gravity Sedimentation Devices i.e., 0.9 pounds per 1,000 barrels per day or 910 pounds per day for a 100,000 barrel refinery. These estimates, while inferential, are believed reasonable accurate. There are no statistical data available on volatility losses in post-gravity sedimentation devices.

Accordingly, hydrocarbon emissions are considered negligible for most post-gravity sedimentation devices and especially for secondary ponds and lagoons in which there are no aeration devices. As regards air flotation units, a slight problem may exist. In these devices, oil and air bubbles collect on the surface in a frothy scum. Some volatilization will occur from the oil and released air bubbles will contain a slight amount of hydrocarbon vapors. Under some conditions, hydrocarbon vapors may be detected in the immediate vicinity of an air flotation unit on the downwind side. There are two types of these units:

- a. Standard Air Flotation devices in which the release of dissolved air causes oil and sediment particles to rise to the surface. Oil removal efficiency is 50-70% which may be increased to 60-90% with chemical additives.
- b. Air mixing device in which atmospheric air intimately mixed with the incoming waste water. Oil removal efficiency has not been established but may approximate 50-80% and normally requires chemical additives.

Methods of Control

Only fixed covers are used in either the standard dissolved air floatation device or the air mixing device. If floating covers were used, they would interfere with the collection and removal of oil and scum.

When a fixed cover is used, it may or may not be connected to a vapor disposal system. If it is not used, hydrocarbon emissions would be difficult

to evaluate but would approach 10% of the loss figures shown for uncovered primary sedimentation devices as a maximum. If a vapor disposal system is used, hydrocarbon emissions are essentially zero.

Cost

The cost of a fixed roof cover would approximate the cost of the same cover in a primary sedimentation device but would be somewhat higher per unit area because a smaller area is involved. It is assumed that the cost would be \$2.60/sq.ft. installed.

Cost-Effectiveness

In the primary sedimentation device, 1130 tons/year were saved, and 10% of this figure is 113 tons/year.

A 4,000 sq. ft. air flotation unit (2 bays and forebay) at \$2.60 sq.ft. would cost \$10,000 installed; and the cost-effectiveness is, therefore, $\$10,000 \div 113 = \$92/\text{ton}/\text{year}$. This figure is exclusive of the cost of the vapor collection and disposal system.

E. Pressure Relief Systems

The generic term pressure relief valve includes the relief valve for liquid flow and the safety valve for gas flow, both designed as a safeguard against overpressure. These valves discharge during periods of overpressure and, in addition, usually have a slight continual leakage rate. Both sources, of course, result in hydrocarbon emissions to the atmosphere.

Vapors are generally discharged to the atmosphere provided that this does not contravene federal, state, and local regulations and that the vapors are below their autoignition temperature. New proposed restrictions on hydrocarbon emissions, however, are quite severe and may further limit such discharge to the atmosphere.

Hydrocarbon vapors are discharged to the atmosphere from relief vents under varied conditions but the most common discharge is that of flammable vapors heavier than air but of relatively low molecular weight. This type of discharge is subject to the safe practices provision that the minimum discharge velocity is 500 feet per second.

Source of Loss

The number of pressure relief valves in a 100,000 barrel refinery will vary considerable but might approximate 1,000-2,000 valves. These valves may discharge into the atmosphere or into a closed pressure relief system that terminates in a flare. For practical purposes, hydrocarbon emissions from a flare may be considered negligible. From present indications, the percentage of valves discharging into the flare system varies greatly

from a low of 10% to a high of 90%.

The amount of daily or annual emission of hydrocarbons to the atmosphere or to a pressure relief system depends on two factors:

- a. Overpressuring of relief valve, depending on the pressure and on the duration of venting.
- b. Average daily or annual leakage rate of each valve in service.

As regards overpressuring, this obviously cannot be predicted in advance and there is no known way in which hydrocarbon emissions from this source can be quantified.

Emissions from valve leakage are the result of poor valve seatings which may be caused by slight, initial defects in manufacture, by corrosion products or other dirt, or by improper seating after a valve releases. Two sources^{7,8} indicate leakage rates to range from 0.0 to 9.1 pounds per day per valve, with an average leakage of 2.4 to 2.9 pounds per day per valve. This leakage has also been estimated at the higher figure of 11.0 pounds per day per 1000 bbls of refinery capacity, or 11,000 pounds per day for a 100,000 barrel refinery.

Current systems used for discharge of vapor or liquid or both are:

- a. Vapor discharge to atmosphere
- b. Closed pressure relief system (See Methods of Control)
- c. Vapor depressuring system. This system is used to reduce pressure by voluntary, rapid removal of vapors from pressure vessels. It is essentially a method of operation and is not further discussed.

Methods of Control

Three basic methods of control are available:

- a. Discharge vapors to a closed pressure relief system that terminates in a flare.
- b. Establish a system of periodic inspection and maintenance.
- c. Provide each relief valve with a rupture disc to minimize or eliminate leakage.

These basic methods are discussed in greater detail below.

- a. A closed pressure relief system will handle vapors from volatile liquids and flammable vapors. This system will minimize hydrocarbon emission to the atmosphere and will release combustion products at a safe location. Continuously burning pilots are recommended to ensure combustion of vapors. Methods for the determination of individual pressure relief loads from fire and other causes and also to determine the maximum relief loads for headers are given in API RP 520, Part I and RP 521.

A typical pressure relief system is shown in Figure 8 and includes:

- a. Flare headers from process units
- b. Knockout drums for accumulation of condensed or settled-out liquids
- c. Seals or purge gas, or both, for flashback protection
- d. Flare stacks
- e. Igniter
- f. Dispersant steam for smokeless flaring

Two of these items, knockout drums and flares, are discussed briefly in the following.

It is essential that the knockout drum be properly sized and be provided with steam coils to prevent freezing and to vaporize condensables. Also, each knockout drum should be equipped with an automatic liquid-level-controlled pump.

The flare may be an elevated stack, a ground flare, or a burning pit with a heat shield. Selection of the proper type of flare is dependent upon such factors as location, proximity to populated areas, local regulations and meteorological conditions.

- b. An inspection procedure is greatly simplified if the pressure relief valve is downstream from a gate valve (sealed open) which permits the inspection to be made. If this valve seats poorly, usually due to corrosion but for whatever reason, the seat should be cleaned or ground when necessary. The availability of suitable manpower for this service may present a problem.

- c. This method utilizes a rupture disc device termed a valve isolator. This unit, capable of being operated at 90% of the relief pressure, is placed between the relief valve and the companion inlet flange. This device has several advantages, the most important of which is to eliminate leakage which would otherwise require periodic inspection and maintenance. Obviously, if the disc should rupture, it must be replaced.

Cost Data

Cost data is available for a rupture disc, also called a valve isolator. This valve, complete in stainless steel (maximum relief 1000 lbs.), costs \$67.50 for a 2" valve and \$97.65 for a 4" valve. Other materials of construction are somewhat less expensive.

As regards flares, the only available cost data is for an elevated flare. The installed cost of such a flare, exclusive of piping, is \$50,000 to \$100,000 for a capacity of 50,000 cu.ft. per hour. For a newer type of completely smokeless flare, which requires a considerable amount of steam, the installed cost is \$440,000.

Cost-Effectiveness

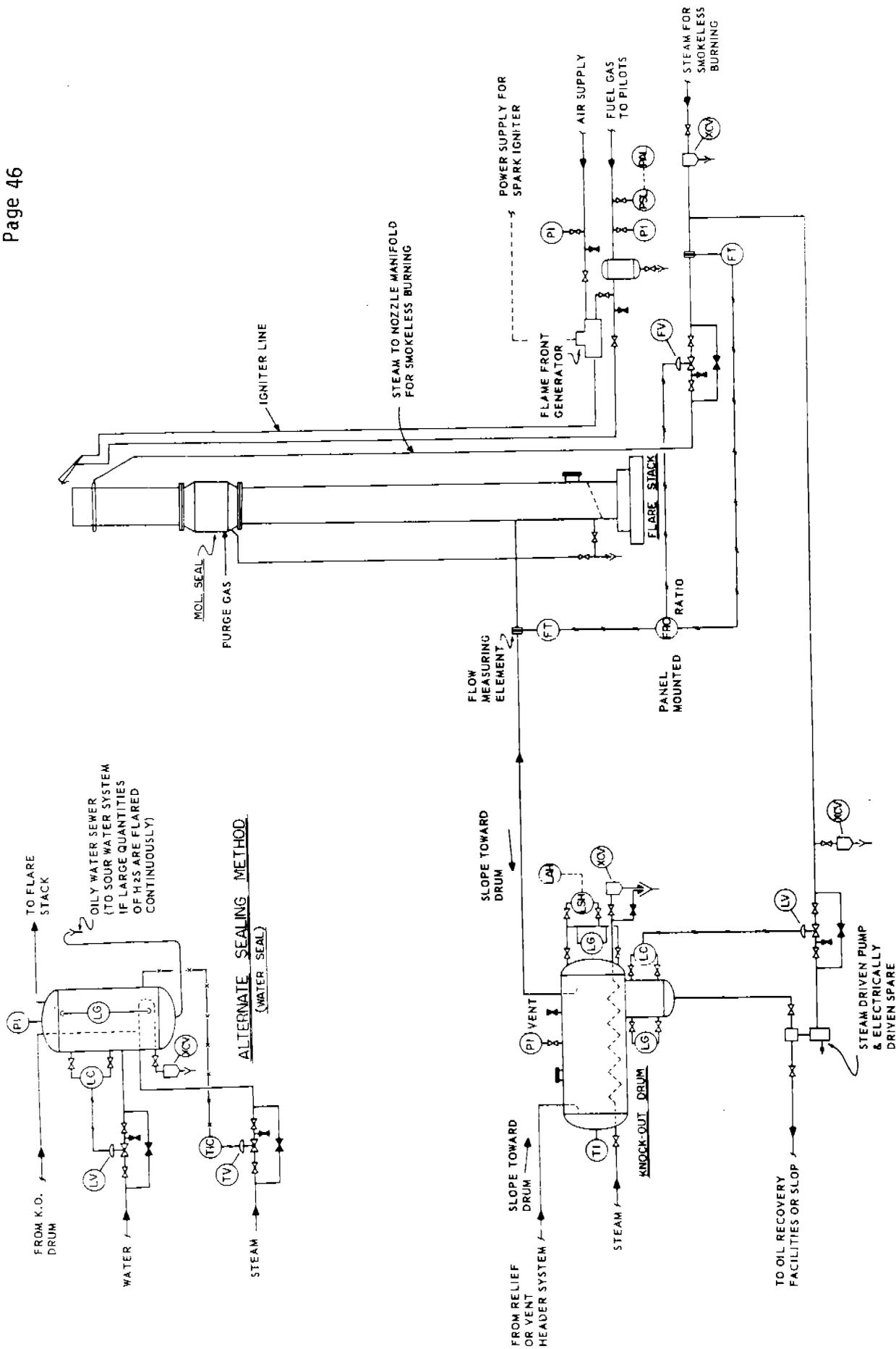
If a relief valve isolator saves the leakage rate at an average of 2.65 pounds/day/valve, it will save about 1000 pounds per year. The 4" valve costs nearly \$100.00 and the total installed cost will approximate \$200.00. On this basis, the cost-effectiveness will approximate \$400/ton/year.

The cost-effectiveness of a flare system is not readily calculated.

F. Vacuum Devices and Hydrocarbon Emissions

In refinery processing and particularly in crude distillation, it is frequently desirable to conduct the process under vacuum conditions to avoid excessive temperature, excessive steam consumption or both. Two common methods of producing this vacuum are by barometric condensers in conjunction with steam-actuated vacuum jets (singly or in series) and by surface condensers which also require auxiliary vacuum jets. Vacuum compressors are seldom used except for clean gas removal and moderate vacuum.

When barometric condensers and steam-actuated vacuum jets are used concurrently, the barometric condenser serves to remove condensed steam and condensable hydrocarbons (see Fig. 9). Occasionally, to obtain a higher vacuum, a booster jet is used between the vacuum tower and the condenser. This serves to further minimize non-condensable vapors.



Note: This represents an operable system arrangement and its components. Arrangement of the system will vary with the performance required. Correspondingly, the selection of types and quantities of components, as well as their applications, must match the needs of the particular plant and its specifications.

FIGURE 8 - TYPICAL FLARE INSTALLATION

In the barometric condenser, the vapor and the water cooling media are intimately mixed, and cooling occurs by conduction. As heat transfer by mixing is highly efficient, this is the cheapest means of transferring heat. The barometric condenser has a high water consumption. This is true because the amount of water vapor that will saturate the non-condensable gases and hence require removal by the jets is determined by the highest water temperature plus an allowance of about 5°F for inadequate mixing.

Occasionally, for lower capacities or when lower vacuum is required, vacuum jets are used without barometric legs. As there is no condensation, this will usually result in higher quantities of non-condensables i.e., hydrocarbon emissions.

In more recent refinery applications, the vacuum is obtained using a surface condenser which represents a more costly investment and maintenance expense. Essentially, however, the cooling water is oil-free and can be used in a recirculating cooling water system. The major advantage is to practically eliminate the amount of emulsified water which must be treated in the waste water system. It also serves to reduce a hazard. In addition, non-condensable vapors are now at ground level, thereby facilitating ultimate disposal.

Sources of Loss

The source of loss to the atmosphere for either barometric or surface condenser are the non-condensable gases. The term non-condensable is related to the final water temperature obtained, lower temperatures being associated with lower volumes of non-condensables. In vacuum distillation, non-condensables will include lighter gases, propane, butanes, and pentanes.

The quantity of such vapors is dependent on many factors including composition of crude (or composition of charge to vacuum tower) and the pressure maintained in the atmospheric tower. In general, however, the normal concentration of vapors will be in the range of 15 to 50 pounds per hour per 1000 barrels of charge to the vacuum furnace and design rates are usually closer to the higher figure. Non-condensable vapors as high as 130 pounds per 1000 barrels of charge have been recorded.

Methods of Control

Although cooling water temperatures can be lowered to reduce non-condensables, this is frequently not practical for an existing installation. In any event, it would only serve to reduce the magnitude of the problem.

There are two methods by which non-condensables may be minimized or handled to eliminate hydrocarbon emissions:

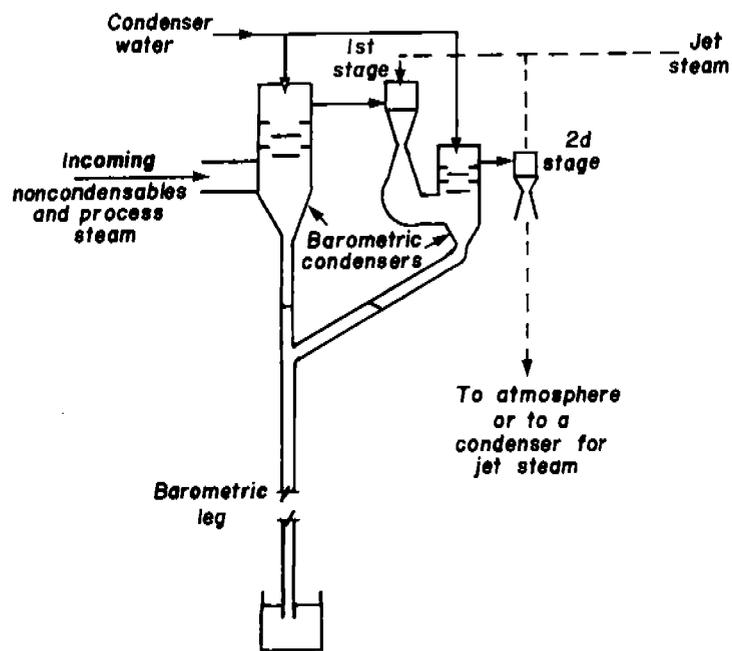


Figure 9. Two stages of ejectors with a barometric condenser.

- a. Installation of an absorption system between vacuum tower and first stage vacuum jet.
- b. Incinerate non-condensables or else discharge to the vapor recovery system*.

On an economic basis, an absorption system would only be used where the quantity of non-condensables and the cost of the installation provided a justification. Where these systems have been used, the absorber tower is relatively small in size and the rich oil is reused as charge stock and not regenerated.

When non-condensables are incinerated, a compressor is required as well as the necessary piping directed either to an afterburner or to the nearest available firebox. Barring leaks, the composition of the vapors is largely hydrocarbons and steam which should not present a safety problem, although a special burner will be required. This incineration eliminates hydrocarbon emissions.

Cost

The cost of the two control methods discussed will vary widely depending in large part on the quantity of the vapors, in pounds per thousand barrels charged, and indirectly on the maximum summer water temperature anticipated.

In some instances, usually involving a smaller vapor production which may contain richer vapors because of higher water temperatures, an absorber may be economically justifiable.

If absorption is not justified, the vapors are usually either incinerated or sent to a vapor recovery system. In one instance, the cost of installing a compressor, piping to the nearest firebox and suitable burner approximated \$50,000 installed. This cost does not include the cost of a condensate receiver for a surface condenser or the cost of supplying a cover to the barometric hot well. This installation was designed for 2200 lbs. hour of non-condensables and the charge to the vacuum furnace was 39,000 bbls/stream day.

Cost-Effectiveness

For the above installation, the installed cost was \$50,000. If it is assumed that the actual production of vapors is about two-thirds of the design rate i.e., 1500 pounds per hour, the annual savings in tons per year are:

*Hot well holding barometric condensate waters may emit vapors. If so, vapors may require collection and incineration.

$0.75 \times 24 \times 365 = 6570$ tons/year
 $\$50,000 \div 6570 = \7.60 per ton per year. This is a very low cost figure (i.e., highly cost-effective) but does not include the cost of a barometric hot well hood or a surface condenser condensate receiver.

G. Regeneration of Catalyst in Catalytic Cracking

The use of catalysts, either alone or else impregnated into solid carriers, accelerates the reactions involved in splitting of large molecules to form gasolines. Catalytic cracking reactions find wide and ever-increasing applications in the refinery.

The catalysts involved absorb impurities such as metals, carbon, and oxide hydrocarbons and must be regenerated to maintain their catalyst activity. In fixed bed systems, they are regenerated periodically in the reactor while moving bed catalysts are regenerated continuously in a separate vessel. In regeneration, carbon is burned to carbon monoxide. Hydrocarbons are also burned, although this burning is not complete. This regeneration restores catalyst activity.

Catalytic reformers, hydrocrackers, and desulfurizers are also contributory to hydrocarbon emissions to some degree but there is considerably less carbon formed and regeneration may occur only once or twice a year. If necessary, the resultant gases can be conducted through a heater firebox to reduce hydrocarbon emissions. These units are not further considered.

In the control of particulate emission, centrifugal collectors, alone or in combination with electrostatic precipitators, have found extensive application. This equipment has little or no effect on carbon monoxide or on hydrocarbons.

Source of Loss

The loss to the atmosphere during catalyst regeneration is largely carbon monoxide. Typical losses in percent by weight, which apply to both FCC and TCC units are as follows:

Carbon Monoxide.....	96.0%
Sulfur Dioxide.....	2.0%
Hydrocarbons.....	1.0%
All others (including aldehydes).....	1.0%

In typical FCC units, with a capacity of 30,000-40,000 barrels per day, aggregate losses of the contaminants shown will average 25,000-30,000 lbs/hr. Losses of hydrocarbons from TCC units are only about one-third of this figure.

Another source lists hydrocarbon emissions from catalyst regeneration in cracking units as follows:

FCC units	220 lbs/1000 bbls of fresh feed
TCC units	87 lbs/1000 bbls of fresh feed

These two sets of data show a reasonable correlation although the latter data are somewhat lower.

Methods of Control

There are two methods of control, both methods resulting in essentially complete elimination of the hydrocarbon content by conversion to carbon dioxide, carbon monoxide, and water.

- a. Carbon Monoxide Waste Heat Boilers
- b. TCC Smoke Plume Burners

The major purpose of the carbon monoxide waste heat boiler is to convert carbon monoxide into carbon dioxide, thereby utilizing the heat of combustion of carbon monoxide and the sensible heat of the gases. In so doing, however, the hydrocarbons are also essentially eliminated.

This heat is utilized by conversion to steam in a more or less standard boiler design, thus providing a direct savings in fuel costs. Waste heat boilers are presently used for both FCC and TCC units. It may be summarized, then, that carbon monoxide heaters are required:

1. When there is a need for excess steam and when fuel value is high
2. To eliminate hydrocarbon and carbon monoxide emissions i.e., to abate pollution

Cost Effectiveness

Cost of carbon monoxide boilers range upward of half a million dollars and also involve a maintenance and operating cost as well as the cost of auxiliary fuel. The capital cost of a carbon monoxide boiler per pound of steam generated is nearly twice that of a steam boiler. There is a cash return in the value of the steam generated. The resultant payout varies with the size of the catalytic cracking unit i.e., the coke burning rate and with various other factors by far the most important of which is fuel value. Where fuel value at the particular refinery is relatively high the boiler may be justified or nearly so by the savings in fuel costs.

Obviously, where fuel is relatively cheap, justification must be related to pollution abatement. Cost-effectiveness, related only to

hydrocarbon emissions would range from \$500 to \$1,000 per ton per year, although this figure would be reduced if proper credit were taken in the specific refinery for the steam generated.

The TCC plume burner is less expensive to construct but generates no revenue and, hence, must be considered solely on the basis of minimizing air pollution. The TCC plume burners installed in 1969-1970, designed for a fresh feed charge rate of 30,000 bbls/day, cost in the range of \$150,000 to \$250,000. On this basis, their cost-effectiveness, based on reduction in hydrocarbon emissions, would range from \$400 to \$600 per ton per year.

H. Air-Blowing

Air-blowing of petroleum products is today confined largely to the manufacture of asphalt, although air is occasionally blown through heavier petroleum products for the purpose of removing moisture. Air or steam-blowing is still used occasionally to strip spent chemicals. The use of air for general purposes of agitation, formerly quite common in treating operations, is today practically non-existent.

In the production of high quality asphalts for applications such as roofing, the crude still asphaltic residue must be further refined to the desired consistency. This is accomplished by air-blowing at elevated temperatures, usually 350-500°F, which serves to remove any residual gas oil and also serves to polymerize the asphalt. Paving grade asphalts are usually produced by steam refining directly to specification with vacuum distillation, if necessary.

The polymerization reaction in air-blowing proceeds because of dehydrogenation of the asphalt, resulting from hydrogen removal by the oxygen in the air (to form moisture). The air-blowing may be performed in batch stills or continuously, using 10 to 40 cubic feet of air per ton of charge.

Source of Loss

Regardless of the purpose for which air-blowing is used, asphalt-blowing, moisture removal, or other, the resultant exhaust air contains hydrocarbons and aerosols. In asphalt-blowing particularly, and in the stripping of spent chemicals, noxious odors are produced and disposal should be practiced.

The amount of hydrocarbons generated depends on the amount of air used per ton of charge, volatility of the charge, and the temperature at which the air-blowing is conducted. Available data for asphalt-blowing indicate losses from 2% to 4% by weight of the asphalt being blown which may be expressed as 40 to 80 lbs. per ton of charge.*

*May also be expressed as 0.02 to 0.03 weight percent loss per degree increase in softening point.

The losses involved in air-blowing for moisture removal are much lower and in 1958 were estimated at less than 1/2 ton per day in Los Angeles County.⁸ Losses of hydrocarbons resulting from stripping of spent chemicals are very low and may be considered negligible.

The recovery of hydrocarbons from asphalt-blowing operations is important, not only because of the quantity, but also because of their malodorous characteristics. The poor quality of the gaseous hydrocarbons makes them suitable only for use as fuel.

Methods of Control

There are two methods normally used for removal of hydrocarbon vapors in exhaust gases.

1. Scrubbing vapors with water.
2. Incinerate vapors in an afterburner or heater firebox.

These methods may be used separately but are frequently used in combination.

Scrubbing of the vapors will serve to condense steam, aerosols, and essentially all of the hydrocarbon vapors. Usually, there is a small amount of non-condensable gas of pungent odor. This method requires a readily available adequate water supply as there is a high ratio of water to vapor. This quantity is reported⁸ as 100 gallons of water to 1,000 standard cubic feet. This method has the disadvantage that it will result in additional contaminated waste water.

The fume scrubber used may be a standard venturi type unit, and a typical installation is shown in Fig. 10. Another system features a small absorber tower in which water flows down and vapor upwards. Water is introduced as a spray, and trayed towers are equipped with bubble caps. The condensate is discharged to the waste water treatment system. Two potential problems are emulsion formation and an odor problem in the condensate (the latter may necessitate a closed system and vapor disposal).

When an adequate water supply is not available or where handling condensate may result in hydrocarbon emission, incineration of the vapors by direct flame contact may be used. The firebox should provide for turbulent mixing of vapors in the combustion zone (i.e., a special burner is required) a minimum retention time of 0.3 seconds, and a minimum combustion chamber temperature of 1250-1550°F.

These two systems, scrubbing and incineration, may be combined. Where incineration is used alone, a precondenser or even a knockout drum is desirable prior to incineration as the resultant condensate (to waste water) will permit a smaller firebox and a lower fuel consumption.

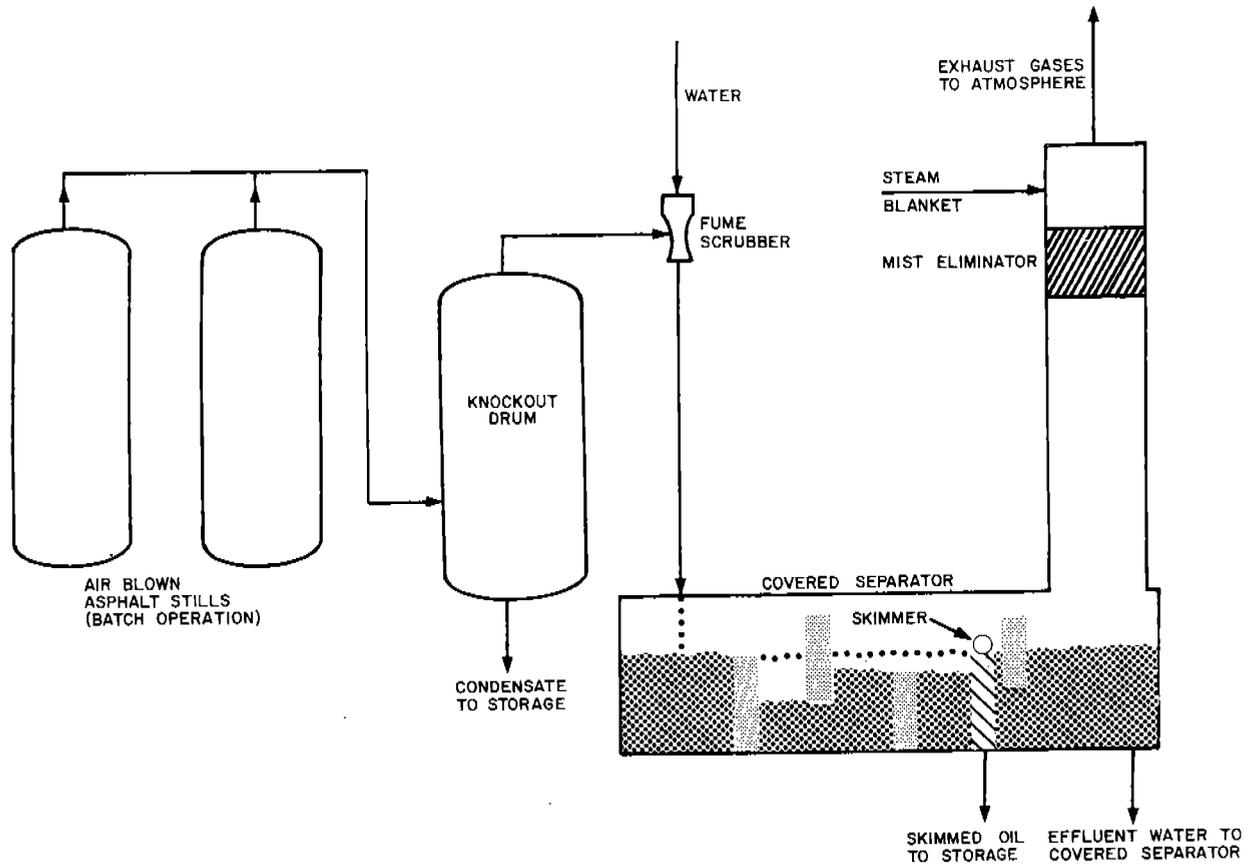


Figure 10. Flow diagram of scrubbing system.

Cost and Cost-Effectiveness

For the most part, refineries utilizing asphalt-blowing depend finally on incineration, sometimes in combination with a water wash. Most systems presently in operation were installed a long time ago at relatively low cost and very little recent cost data is

A disposal system similar to that for a barometric or surface condenser i.e., vapor compressor, piping to an existing firebox, and a burner, may suffice. The cost of such a system, exclusive of knockout drum or water scrubbing, might approximate \$20,000 installed, to handle 165 tons per year of hydrocarbon emissions. This is based on a system designed for a daily production of 200 barrels but producing 100 barrels of asphalt in 12 hours.

100 barrels per day = 15 tons per day
 15 tons x 60 lbs/ton of charge X 365 = 165 tons per year. The cost-effectiveness is $\$20,000 \div 165 = \121 per ton per year.

It is assumed that asphalt production is 100 bbls per day for 365 days per year. For most refineries, asphalt production is a year-round activity.

I. Pump Losses and Mechanical Seals

The most common refinery pumps are centrifugal pumps and positive displacement pumps. On these pumps leakage losses occur where the driving shaft passes through the pump casting. Leakage losses include volatile as well as nonvolatile products but our present concern is with volatile products only.

In refinery application, the pump leakage area is usually protected with a packed seal. In a typical packed seal, the driving shaft is equipped with a stuffing box which is filled with coils and spirals to form closed or nearly closed rings. This packing can be tightened around the shaft.

Lubrication is effected either by a lantern ring or else by a controlled amount of leakage to the atmosphere. The lantern ring is usually used on pumps handling volatile products. The ring provides an opening for the forced feeding of oil or grease into the packing, thus giving a constant supply of lubricant.

Sources of Loss

Losses occur from packed seals, as previously described, and also from the improved mechanical seals which are described under "Methods of Control;" Steigerwald¹¹ tabulated losses from both types of seals as follows (Table 15):

TABLE 15
EFFECTIVENESS OF MECHANICAL
AND PACKED SEALS ON
VARIOUS TYPES OF HYDROCARBONS

SEAL TYPE	PUMP TYPE	TYPE HYDROCARBON BEING PUMPED lb REID	AVG. HYDROCARBON LOSS PER INSPECTED SEAL lb/day	LEAK INCIDENCE	
				SMALL LEAKS, ^a % 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
		> 0.5	3.2	19	13
Avg.					
Packed	Centrifugal	> 26	10.3	20	37
		5 to 26	5.9	32	34
		0.5 to 5	0.4	12	4
		> 0.5	4.8	22	23
Avg.					
Packed	Reciprocating	> 26	16.6	31	42
		5 to 26	4.0	24	10
		0.5 to 5	0.1	9	0
		> 0.5	5.4	20	13
Avg.					

^aSmall Leaks lose less than 1 pound of hydrocarbon per day.

The average losses indicated above are relatively low and losses under actual conditions for specific pumps may be considerably higher. Thus, pumps with loose, worn or unlubricated packing may leak at the rate of a steady drip or even a small stream. Steigerwald himself noted that the above data are averages and that when running continuously, the average loss per seal was 18.8 and 7.9 pounds per day for packed and mechanical seals respectively.¹¹ On spare or standby service, however, there is little to choose between the seals.

The above tabulation also indicates the relation of leak losses to volatility. Thus, for all seals, mechanical and packed, the average loss for over 26 pounds Reid product is 12.0 pounds per day, for 5 to 26 pound Reid the loss is 3.5 pounds per day, and for 0.5 to 5.0 pounds Reid the loss is only 0.3 pounds per day.

Methods of Control

For reasons indicated below, mechanical seals reduce leakage and therefore reduce emissions to the atmosphere. They can be specified for new pumps or can be installed in existing pumps by replacing the packed seal. The mechanical seal is recommended to reduce hydrocarbon emissions for more or less continuous pumping of products having a Reid vapor pressure of 5 pounds or greater.

The term mechanical seal denotes a prefabricated assembly that operates as a thrust bearing and forms a running seal between flat surfaces. The seal consists of two rings, one stationary, the other attached to the shaft and rotating with it. The wearing faces are at right angles to the shaft and are lubricated by a thin film of the material being pumped. The seal depends upon continuous contact between rotating and fixed collars to limit leakage.

Face materials used vary to some extent with pressure and with temperature and also the properties of the fluid being pumped. Carbon-graphite has been used extensively for this purpose. Testing of seal materials is extremely important to determine the compatibility of a material with its environment.

Mechanical seals are particularly advantageous when fluids are under substantial pressure. They also secure other advantages such as reduced friction on the shaft compared with conventional packed seals. Mechanical seals are precision components and must be carefully installed and handled.

Another method is also applicable to pumps with ordinary packing or pumps that have been equipped with mechanical seals. On this application a liquid less volatile than the product being pumped is introduced between a dual set of mechanical seals (or between two sets of packing). This liquid is at a higher pressure than the product and, hence, passes by the

packing into the product with which it must be compatible. The original product cannot leak past the packing or seal. Some of the pressure-sealing liquid, however, will pass through the outer packing or seal and should be collected at this point. The value and effectiveness of this method in reducing hydrocarbon emissions is dependent on the use of a low-volatility liquid which will not contaminate the product.

Finally, for some applications, seals vent directly to a vapor recovery system.

Cost

It has been reported that the cost of a mechanical seal installed, including a cooler, labor and materials, would approximate \$1000 to \$1500. About one-half of the installations require coolers to keep seal faces within tolerable operating temperatures.

There is no data for costs on pressure-sealing liquid appliances.

Cost-Effectiveness

The mechanical seal, installed on pumps in more or less continual operation, reduces losses by 10.9 pounds per day or approximately 2 tons per year per seal. The cost-effectiveness is, therefore, $\$1500 \div 2 = \750 per ton per year. This figure would be lower if a cooler were not required.

Where higher losses are experienced, either for reasons of severe pressure or temperature or even for inadequate maintenance, mechanical seals may secure savings three times that shown above which would increase the cost-effectiveness to \$250 per ton per year.

It is apparent that an individual study of the pumps in any refinery is desirable. Mechanical seals should be prescribed only for pumps that are known to be bad offenders with high leakage rates.

Miscellaneous Sources of Loss

In addition to the major sources of potential loss discussed in this report, there are various other miscellaneous sources, relatively minor, that contribute to hydrocarbon emissions. Probably the most important of these sources are as follows:

1. Equipment leakage
2. Unit burners or furnaces
3. Equipment turnaround
4. Tank cleaning
5. Cooling towers
6. Gas-fired engines

Other refinery operations, such as blowdown systems, blind changes, sewers and process drains, and sampling, represent potential sources of loss. These losses cannot be quantified but can usually be kept to relatively minor values by suitable, normal precautions.

1. Equipment Leakage

This includes pipeline valves, pump seals and compressor seals and is probably the largest source of loss of the items listed above. In the pamphlet on "Atmospheric Emissions from Petroleum Refineries"¹³ this source of loss is listed at 33 pounds per day per 1000 bbl of refinery throughput, exclusive of pump seals, which have been previously discussed. This figure, 3300 lbs per day for the average 100,000 bbl/day refinery, is probably high and can be reduced considerably by adequate inspection and maintenance.

2. Unit Burners or Furnaces

Modern boiler equipment, whether in refinery heaters or steam boilers, is usually quite efficient in operation; and total emission of contaminants, per ton of fuel burned, is low compared with earlier periods. Nevertheless, the presence of relatively small amounts of unburned hydrocarbons, including also aldehydes and organic acids, has been verified. Their presence is due less to fuel characteristics than to burner design and, of even greater importance, to maloperation of the burners.

A considerable series of tests in the field, some of which were conducted by the Armour Research Foundation in the Chicago area, indicated that these emissions were insignificant and were all in amounts less than 100 ppm, including samples from the first few seconds of operation. Under more normal burning conditions, the concentration of hydrocarbons, aldehydes, and organic acids in the gaseous emissions products do not usually exceed 20 ppm when burning No. 6 Fuel Oil. Usually these emissions cannot be measured by quantitative techniques now available.

In the Armour research project it was the considered opinion that maloperation, including malfunction and misadjustment, occurred "in only a fraction of a percent of all combustion units in use and is almost immediately detected and rectified."

Because hydrocarbon emissions from this source are so low--in most cases below the range of available quantitative techniques--the only method of control is good maintenance of burners.

3. Equipment Turnaround

Equipment turnarounds occur more or less periodically in all refineries. On such occasions, hydrocarbon vapors are left in vessels, towers, furnaces, etc., subsequent to liquid removal and prior to final opening of the unit. While it would be desirable to purge these vapors to a vapor recovery system or to a flare, observing due safety precautions (e.g., use of steam eductor), this would depend to some extent on the frequency of occurrence and the volume of the vapors involved. The possibility of purging should certainly be considered.

4. Tank Cleaning

From the point of view of hydrocarbon emissions to the atmosphere, tank cleaning does represent a problem for fixed roof tanks. If all products having a Reid vapor pressure of 2.0 pounds or above were stored in floating roof tanks, the problem would be reduced considerably in magnitude.

For fixed-roof tanks containing products having a Reid vapor pressure of 2.0 pounds or above, the vapor space contains hydrocarbons, the percentage of which (based on total vapors) is related to the absolute vapor pressure and the degree of saturation which may vary from 10% to 100%.

For practical purposes, the potential loss from a fixed-roof tank is equal in cubic feet to the total volume of the tank, times the ratio of absolute vapor pressure to 14.7 pounds, times the percent saturation. This volume can then be converted to pounds of hydrocarbon if the density of vapors is known or can be assumed (30 cubic feet of pure gasoline vapor is approximately equal to 1 gallon or 6.5 pounds).

On new construction for the storage of products having Reid vapor pressures as specified, essentially all tankage should be of the floating roof type. Concurrently, many existing fixed-roof tanks are

being converted to floating roof types.

5. Cooling Towers

Cooling towers find wide application in existing refineries to cool water so that the water may be used and reused for heat transfer purposes, e.g., cooling and condensing of petroleum products. Newer refineries, especially where favorable atmospheric conditions exist, tend more to air-cooling but water cooling is still required under certain conditions.

Hydrocarbon emissions occur only as a result of the contamination of the cooling water. Some degree of contamination is unavoidable, owing to leaks from the process side of the system. The contamination of the water is measured by the hydrocarbon contents which, under proper conditions of operation, should not exceed about 50-100 ppm.

The total hydrocarbon emissions from a cooling tower are a function of the water circulation rate (gpm), the hydrocarbon concentration, and the volatility of the hydrocarbons present. An L. A. County study in 1957 by Bonamassa and Lee indicated, on the basis of a circulation rate of 1000 gpm, hydrocarbon emissions which varied from 3-2000 lbs/day as hexane (and 2 higher readings). What might be termed "average" data, which has been used by some refineries, is in the range of 8 to 10 pounds per 1000 gpm.

If the cooling water is contaminated, no practical method of control of hydrocarbon emissions is practical. Rather, efforts should be directed to inspection and detection of leaks, and maintenance when required. Direct contact of cooling water with process streams should be avoided although under certain conditions, provided that water so contaminated has been properly treated to remove hydrocarbons, some latitude in this regard may be practical.

6. Gas-Fired Engines

Gas-fired engines are used for various purposes in some refineries, especially where this fuel is readily available. The fuel is usually natural gas although refinery gas may also be used. These engines usually

operate at substantially constant loads, but some fuel remains unburned and is discharged through the exhaust.

Results of one survey, where natural gas was used, indicate that the exhaust may contain 1250 ppm of hydrocarbons, over 90% of which was methane. Engines operating on refinery fuel gas would exhaust fewer hydrocarbons but the hydrocarbons would be of a higher molecular weight.

This problem is common to all industries using gas-fired engines. On all new installations, the pollutant effect of these hydrocarbon emissions should be evaluated in deciding on the type of power to be used.

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