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RECOVERY OF GASOLINE FROM UNCONDENSED STILL VAPORS

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INTRODUCTION

In collecting and disseminating information on improved practices used in the production of petroleum and in the manufacture of gasoline, the Bureau of Mines has aided in creating an interest in efficient methods in all phases of the oil and gas industry. In the refining industry there is a growing tendency for increased efficiency, and information relating to improved practices should be of value not only to the larger and more efficient plants, but particularly to small refineries unable to carry out a large experimental program.

The refineries of the United States required 433,915,029 barrels of crude oil during the year 1920\*, including 61,136,210 barrels of Mexican crude. This yielded 4,882,546,599 gallons of gasoline, an average daily production of 13,340,291 gallons. Besides the gasoline obtained from crude oil by fractional distillation and from heavy oils by cracking, this amount includes 3,152,924 barrels of natural-gas gasoline blended with gasoline from the other two sources.

This report shows the possibilities of increasing the gasoline yield from the crude by recovering the appreciable amounts that are lost by remaining uncondensed. Unless preventive measures are adopted, these losses will increase in the future, because crudes are being handled in the field with more and more care to avoid evaporation, so that they will contain much lighter and more volatile fractions than at present. The magnitude of the loss from non-condensation of these vapors, has been realized only by few refiners, judging from the number of plants that have recovery systems. The 13 refineries studied are obtaining 128,651 gallons of gasoline daily from uncondensed still vapors. These plants are situated in the various refining centers, other than the Pacific Coast, and are running crude representative of all the producing fields east of the Rocky Mountains. In addition, several are running Mexican crude. Information from California refineries indicates that on account of the smaller gasoline content of the California crudes, there are no recovery plants of importance in that State.

J. O. Lewis, A. W. Ambrose, H. H. Hill, E. W. Dean, C. R. Bopp, and N. A. C. Smith of the Bureau of Mines assisted in the work.

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\* Refinery Statistics for 1920 - Bureau of Mines, Mason, H. F., Petroleum Economist.

Messrs. H. R. Harwood, N. E. Loomis, T. G. Delbridge, H. H. Rathvon, J. Hansen, A. S. Hopkins, J. W. Newton, William Slater, and John Noble, cooperated by permitted inspection of their plants. Messrs. W. E. Espey, A. J. Rodger, W. F. Stroud, R. L. Spencer and H. G. Smith furnished data on operating methods and experimental results in several refineries which recover gasoline from uncondensed still vapors. Also, valuable information was obtained from Messrs. W. H. Leavitt, W. D. Rial, R. O. Neal and I. P. Parkhurst.

## THE DISTILLATION OF PETROLEUM

### Physical and Chemical Characteristics of Petroleum Hydrocarbons

Crude petroleum consists of various hydrocarbons, each having its own physical characteristics (such as boiling point and specific gravity), with compounds of sulphur, oxygen and nitrogen present as impurities. The hydrocarbons of the paraffin series, having the general formula  $C_nH_{2n+2}$ , predominate in the paraffin and mixed base crudes from the Eastern, Mid-Centiment and Rocky Mountain fields. The naphthene base crudes of the Gulf Coast and California fields consist largely of hydrocarbons of the naphthene series, having the general formula  $C_nH_{2n}$ . Certain crudes contain unsaturated hydrocarbons of the olefin series in small amounts, and some also contain aromatic hydrocarbons of the benzene series.

The hydrocarbons comprising the gasoline and gas considered in this paper are mostly of the paraffin series, although gases from cracking stills contain relatively high percentages of unsaturated hydrocarbons and appreciable amounts of those belonging to the benzene series. The first few members of the paraffin series (methane, ethane, propane, etc.,) are gases at ordinary temperatures. Normal pentane, having a boiling point of 97° F., normal hexane, boiling point 154° F. (68° C.), normal heptane, boiling point, 208° F., (98° C), and normal octane, boiling point 259° F. (126° C.) are the main constituents of the gasoline recovered from still vapors, although these vapors contain some of the lower members of the series dissolved as gases and certain higher members that are carried over in the still vapors, either mechanically or on account of their partial pressures. With each succeeding member of the paraffin series, the boiling point becomes higher. Hexadecane, for example, has a boiling point of 549° F., as compared with pentane which has a boiling point of 97° F.

### Laboratory Distillation of Crude Petroleum

Fractional distillation of crude oil separates it into cuts or fractions containing mixtures of hydrocarbons having similar physical properties. In distilling crude oil complete separation of individual hydrocarbons is exceedingly difficult, even in the laboratory, unless countless refractionations are made. Redistillation of a sample of distillate which was driven over between any two given temperatures will show the presence of hydrocarbons boiling at lower temperatures as well as higher temperatures than the limits of the previous distillation. This is due to the fact that in a mixture of hydrocarbons, the boiling point of each is influenced by the presence of the others.

In the distillation of crude oil, hydrocarbons of the lowest boiling points are the first to be vaporized. Therefore, the first fraction has a much higher percentage of low-boiling hydrocarbons than the original liquid and is the most difficult to condense, as the temperature of liquefaction is quite low. As distillation proceeds, the temperature required to vaporize the remaining hydrocarbons becomes higher, and the resulting vapor is consequently more easily condensed.

Condensation of the vapors formed by heating crude oil is effected in the refinery by leading vapors through coils of pipe submerged in water. On cooling, most of the vapor becomes liquefied, but a certain amount of vapor, due to insufficient time for proper cooling or the fact that its condensing point is lower than the temperature of the water, will remain uncondensed. Also, certain other fractions will not be condensed, for the reason that their liquefaction points are affected by the presence of other hydrocarbons. A small part of this uncondensed vapor is dissolved in the liquid that has condensed.

## METHODS OF DISTILLATION EMPLOYED IN PETROLEUM REFINERIES

### Fire Distillation

The first step in refining crude oil into its various products is accomplished by fractional distillation, or more commonly termed "fire distillation", in stills that are heated directly with fire. The "fire stills" are horizontal, riveted or welded steel shells mounted in brickwork, the upper part above the brickwork is often covered with insulating material. A vapor line connected to the top of the still carries the hot vapors to the condenser, from which the condensed liquid flows through "run-down" lines to the receiving house or "tail house", where the "stream" of condensate passes into the "lock-box", to the proper receiving tanks by means of pipe manifolds.

### "Batch" and Continuous Process of Distillation

In the "batch" process formerly employed the entire distillation is conducted in one still, the different fractions, such as crude benzene, kerosene distillates, gas oil, etc., being successively obtained as the temperature of the charge is raised. The "batch" method is used exclusively where crude oil is run down to coke and in reducing paraffin base crudes to cylinder stocks, also to some extent for obtaining wax distillates from the residue from continuous crude stills. Stills employed for the latter purpose are commonly known as "tar stills".

In the continuous process, crude oil is pumped into the first still of a battery, passes successively through each of the stills and the residuum discharged from the last still of the battery. Each successive still is maintained at a higher temperature than the preceding one. Fractions coming from each still in the battery do not change from lighter to heavier products, as in the batch process, but have fairly uniform gravities and boiling points. For example, a battery of continuous stills operating on average Mid-Continent crude gives cuts of light naphtha, heavy naphtha, kerosene distillate and gas oil in the order named. The continuous process also includes the method of distilling oil in pipe stills. In this method, the oil is pumped continuously through heated pipes, from which the vapors are taken off and the different fractions condensed.

### Steam Coils

Both the "batch" and "continuous" stills of the shell type are generally equipped with steam coils, so perforated that the steam is directed against the bottom of the still. These perforations tend to distribute the steam evenly throughout the body of oil. The introduction of steam minimizes cracking, since it agitates the oil and prevents local overheating. The addition of steam also helps distillation by carrying some fractions over mechanically and by reducing the temperature at which they distil.

## Pressure Distillation

When heavy oils are distilled at temperatures higher than their normal boiling points, decomposition takes place and the distillate is made up of hydrocarbons with much higher Baumé gravity and lower boiling points than the original oil.

If heavy oil is distilled under pressure it is possible to reach the decomposition point before the temperature of the charge attains the boiling point of the oil at the pressure in question.

The decomposition of oil by heat is commonly known as "cracking", and the stills in which this operation is conducted are known as "cracking stills" or pressure stills.

Distillation under pressure is commonly used for producing gasoline and light distillates from heavy oils such as gas oil. On account of the decomposition that takes place, the products obtained contain a high percentage of unsaturated hydrocarbons.

## Steam Distillation

After fractional distillation in fire stills, the light distillates are treated in agitators with acid and caustic, and then made into marketable gasoline by redistilling in steam stills. A steam still has the same general construction as a fire still, but a larger number of perforated steam coils. Distillation in this type of still is largely by steam, although a fire is sometimes kept beneath the still to regulate distillation. The steam causes hydrocarbons to distill, as pointed out above, at temperatures much below their normal boiling points. Much closer cuts are obtained in this way than in fractional distillation. Distillation by steam may be conducted either as a "batch" or continuous process.

## Condensation of Distillates

Condensation of the vapors coming from the still into liquid is accomplished by (a) aerial condensation, or (b) condensation in coils submerged in water.

### Aerial Condensation

Considerable condensation can be effected by passing the vapor from the stills through pipes or shells having large surfaces exposed to the air. This method is employed in the aerial condensers used in connection with pressure stills. The heavier fractions are condensed and drain back into the still, where they are again subjected to cracking. In fractionating towers or dephlegmators, aerial condensation is also employed for separating the distillates into fractions having comparatively narrow boiling ranges.

### Condensation in Submerged Coils.

The common method of condensation is by means of coils, either in series or in parallel, submerged in a condenser box through which water is circulated, the cold water entering at the bottom and the warm water discharging at the top. The coils are smaller in diameter at the bottom of the box than at the top, as less capacity is required after the vapors condense to liquid. The amount of water circulated is based on the heat transfer necessary to condense the vapors.

## NATURE AND AMOUNT OF UNCONDENSED VAPORS

### Uncondensed Vapors from Different Distillation Processes

Uncondensed vapors from the condenser are generally classified under two heads, "sweet gas" and "sour gas". The term "sweet gas" refers to those vapors remaining uncondensed during the distillation of the lighter ends of the crude. In the batch process these vapors are formed with the light and heavy naphthas, and in the continuous process from the first few stills of the battery, which remove the naphthas. The term "sour gas" refers to those vapors formed by cracking, either in tar stills or in pressure stills. This term is very descriptive, since cracked gases are largely unsaturated and have the marked odor peculiar to cracked products. Sulphur compounds are usually present in cracked gases and are partly responsible for the unpleasant odor.

The distillation process that is used not only governs the nature of the gas, but also the amount that is formed from a definite quantity of crude. A skimming plant that removes only gasoline, kerosene and gas oil will not produce the same amount of vapor as a plant that is equipped with pressure stills or one that is producing comparatively large quantities of cracked gases in distilling down to coke.

### Uncondensed Vapors in Skimming Plants

In skimming plants practically all the vapors that remain uncondensed are formed during the distillation of the first fifteen per cent of the crude. After this fraction has been removed the vapors consist largely of hydrocarbons that can be readily condensed at temperatures maintained in the ordinary condenser. In addition to the uncondensed vapor from the crude stills, large quantities of vapor remain uncondensed when the naphtha fractions are rerun in the steam stills.

With these two sources of gas it is rather inexpensive to install gas lines for removing the vapors as rapidly as formed. The problem of collecting the vapors is correspondingly simple, since the lines from both sources can be joined and taken to a central point where a small vacuum is held. The gas can then be treated either by compression or absorption. There is generally no need for "scrubbing" this gas to remove sulphur, since the sulphur content of the gas from the naphtha fractions of the crude is very low and not objectionable. In some plants an even simpler installation is made, consisting of a 6-inch header into which the gas passes under its own pressure. This header is cooled by sprays, and recovers a considerable quantity of gasoline. The entering gas is nearly all gasoline vapor without any appreciable amount of permanent gas. Tests of this type of gas have shown it to contain as much as 30 gallons of gasoline per 1000 cu. ft. of vapor. In other words, as high as 90 per cent of the vapor can be condensed and held as gasoline. In the plants visited by the writer an average of about 7 gallons per 1000 cu. ft. was obtained.

### Uncondensed Vapors in Refineries with Pressure Stills

The conditions existing in refineries operating pressure stills are different from those at skimming plants. Uncondensed vapors are obtained not

Only from crude and steam stills, but also from pressure stills. Large amounts of very rich uncondensed vapor are also obtained from the rerunning of pressure-still distillate. These vapors yield as high as 24 gallons of gasoline per 1000 cu. ft. Experiments have shown that in running a barrel of Cushing crude about 52 cu. ft. of vapor remains uncondensed. Under the same conditions of condensation a barrel of gas oil distilled under pressure gave 163 cu. ft. of gas with an average gasoline content of 2.8 gallons per 1000 cu. ft. In distillation under pressure large quantities of fixed gases are formed. When the gas from cracking stills is added to the gas from the crude oil and steam stills, the gasoline content of the mixture will be lower than that of the gas from the latter two sources. The volume of gas, however, will be so increased that the total amount of gasoline recovered will be considerably greater.

Since the sources of gas are more widely separated in a refinery of this character, the problem of installing a recovery system is much more complicated than in a skimming plant. In the latter, the gathering line takes gas only from the crude stills that are running light distillates and from the steam stills, whereas in the complete refinery the gases are obtained from crude, steam, pressure and rerun stills. This requires a much more extensive system of gathering lines, and careful provision for covering distances not met with in skimming plants. If the gases are all collected by one central exhaustor, as is usually done, there is danger of too high a vacuum being held on some of the stills, while on account of the frictional resistance in long lines and the small amounts of gas produced, those stills at a greater distance may be under no vacuum at all.

The removal of sulphur is generally necessary in a refinery which uses pressure stills, because the hydrocarbon sulphur compounds are thrown down at the existing temperature and pressures. This would result in considerable trouble from depositions of sulphur, and large expenditures must therefore be made in providing scrubbers for the removal of sulphur.

#### Effect of Atmospheric Temperatures on Condensation

Atmospheric temperature is an important factor in the production of gasoline from uncondensed refinery vapors. It is found that during winter months, due to more complete condensation of the vapors, the production of the "gas" plant will fall off to some extent. An unusual example of this is a certain skimming plant which produces about 6000 gallons of compression gasoline daily through the summer months, but drops to as low as 500 gallons per day in the winter. Ordinarily, the difference is far less, but there is always a tendency for production to drop in cooler weather. Another factor which tends to produce this result is where the evaporation from storage tanks is picked up and recondensed. This evaporation, of course, is much greater during the summer months.

#### Other Factors Governing Amount of Uncondensed Vapor.

Three other factors which determine the gasoline content of the uncondensed vapors, are the nature of the still charge, the temperature of the stream, and the vacuum carried on the run-down lines.

The distillates from crude oil which has only a small amount of low-boiling fractions will condense very easily. The loss in uncondensed vapor from this type of crude is very low when compared with the losses from a crude with a very high gasoline content. Likewise, the amount of vapor remaining uncondensed during distillation in the steam still depends upon the charge. For example, a light naphtha forms more gas than a heavier distillate.

The vacuum carried on the run-down lines influences the yield of vapor, since any increase in vacuum causes a corresponding decrease in boiling points of the distillate. The vacuum carried should be as low as possible and only serve to remove the vapors formed, rather than to lower the boiling point of the charge being distilled.

The temperature of the stream is an important factor, since with an increase in the temperature of the distillate there is a corresponding increase in the gasoline content of the gas. The temperature of the stream depends in turn upon the temperature of the cooling water in the condenser and upon the rate of distillation. These two factors determine the condenser surface per gallon per hour. For light fractions the condenser surface is generally about two square feet per gallon per hour. If this figure is lowered the gasoline content of the vapors will become higher, and if raised the gasoline content will be lower, provided, of course, that the temperature of the cooling water is constant.

### GASOLINE RECOVERABLE FROM VAPORS

#### Experimental Results on Fractional Distillation:

In an effort to determine as nearly as possible the effect of the temperature of the stream on the uncondensed gasoline, a series of runs was made in the Bureau of Mines experimental refinery at Bartlesville, Oklahoma. Cushing crude of a gravity of 38.5 B. was used, with a condenser surface of two square feet per gallon per hour. The vapors were drawn off under a vacuum of two inches (of water) and collected in a small test absorber, filled with "mineral seal" oil as an absorbent.

After each test run, the absorbed gasoline was distilled by the usual laboratory method. Figure 1 shows results obtained. It will be noted that the yield of gasoline from the uncondensed vapors of the crude still increases with the temperature of the stream. The gasoline content of the uncondensed vapors, per barrel of crude charged to the still, varies from 0.05 gallon at a stream temperature of 75° F., to 1.01 gallons at 120° F.

The gasoline produced from the crude still at each stream temperature shown, was redistilled in the steam still at the same stream temperature. For example, gasoline produced from the crude still at a stream temperature of 75° F., was redistilled at a stream temperature of 75° F., gasoline produced at a stream temperature of 90° F., was redistilled at 90° F., and so on. The amount of gasoline obtained from the uncondensed vapors from the steam still, decreases as temperatures of stream increase. When the stream from the crude still has a temperature of, say 75° F., the vapors are so cooled that little gasoline remains uncondensed. The the condensate is redistilled in the steam still with the stream temperature at 75° F., the vapors are much richer in high gravity hydrocarbons than the vapors from the crude, and this results in a larger amount of vapor remaining uncondensed.

With the stream running at 90° F. from both crude and steam stills, the increased amount of uncondensed vapors from the crude distillation results in a lower recovery of gasoline from the uncondensed vapors of the steam still. In other words, the distillate charged to the steam still has been robbed of the lighter fractions, so the amount of vapors uncondensed in this distillation is smaller than in the previous run. As the temperature of the stream from both stills increases, the quantity of uncondensed gasoline from the steam still decreases, until at 120° F., practically all of the light fractions that will re-

main uncondensed have been taken off at the crude still condenser.

The total gasoline obtained from the uncondensed vapors from both the crude still and from the steam still is shown in curve 3, Figure 1. This indicates the amount of gasoline that can be recovered under like conditions in refineries operating on Mid-Continent crude.

The following information on amounts of uncondensed vapor obtained from different crudes was supplied by Mr. Franklin Stroud, Jr., of the Atlantic Refining Co., Philadelphia. Somerset and Mid-Continent crudes give approximately 4 cu. ft. of vapor per barrel of crude charged, at a stream temperature of 70° F., and Mexican crude, 3 cu. ft. The vapor from the two former contains 12 gallons of gasoline per 1000 cu. ft., and from the latter, 10 gallons. The number of cubic feet of uncondensed vapor varies three per cent for every two degrees between 50° and 90° F., which gives the following formula for this range:

$$\text{Gallons per barrel} = \frac{A}{1000} \times (F \pm \frac{T}{2} \times .03)$$

Here A represents the number of gallons of gasoline per 1000 cu. ft. (12 for Mid-Continent crude and 10 for Mexican crude); F the number of cu. ft. at 70° F. for each crude, (4 cu. ft. for Mid-Continent and 3 for Mexican crude); and T the degrees difference in the temperature of the stream from 70° F. This gives a straight-line curve which checks the part of curve 1, Figure 1, below 90° F. Above 90° F. this formula would not apply, since the amount of uncondensed gasoline increases more rapidly with each succeeding rise in temperature.

#### Experimental Results of Pressure Still Distillation

On cracked gases, which include gases formed in running crude to coke, gases from pressure stills and gases from the running of pressure-still distillates, Mr. Stroud gives the following: Mexican light crude, 200 cu. ft. of gas per barrel charged, containing four gallons of gasoline per 1000 cu. ft.; Mid-Continent crude, 80 cu. ft. per barrel with a gasoline content of seven gallons per 1000 cu. ft.; average slop, 120 cu. ft. per barrel; with five gallons of gasoline recoverable per 1000 cu. ft.; gas oil, in pressure stills, 140 cu. ft. per barrel with a gasoline content of three gallons per 1000 cu. ft., with a variation of 2-1/2 per cent in the quantity of gas for every hour over or under 38 hours per 1000 barrels. In tests conducted by Mr. A. J. Rodgers of the Tide Water Oil Co., where the pressure on the still amounted to 95 pounds, 95 cu. ft. of gas was obtained from each barrel charged. The specific gravity of this gas was about 0.85.

Experiments in pressure-still distillation by Mr. W. E. Espey of Cosden and Co., Tulsa, Okla., showed that 163 cu. ft. of gas was produced per barrel of gas oil charged to the still. This gas had an average gasoline content of about two gallons per 1000 cu. ft.

#### Survey of Plants Having Recovery Systems

Table 1 shows representative refineries on the Eastern Coast, Gulf Coast, in Oklahoma, Wyoming and Kansas that have installed plants for treating uncondensed still vapors. Column 10 shows that in these plants the recovery of gasoline ranges from 0.05 to 0.84 gallon per barrel of crude charged. Where the recovery value is low, several refineries do not have efficient recovery plants, and others have not been fully equipped for taking care of all the gases formed. In some it is due to the low gasoline content of the crude and to the absence of pressure stills. Others are equipped with pressure stills, but do



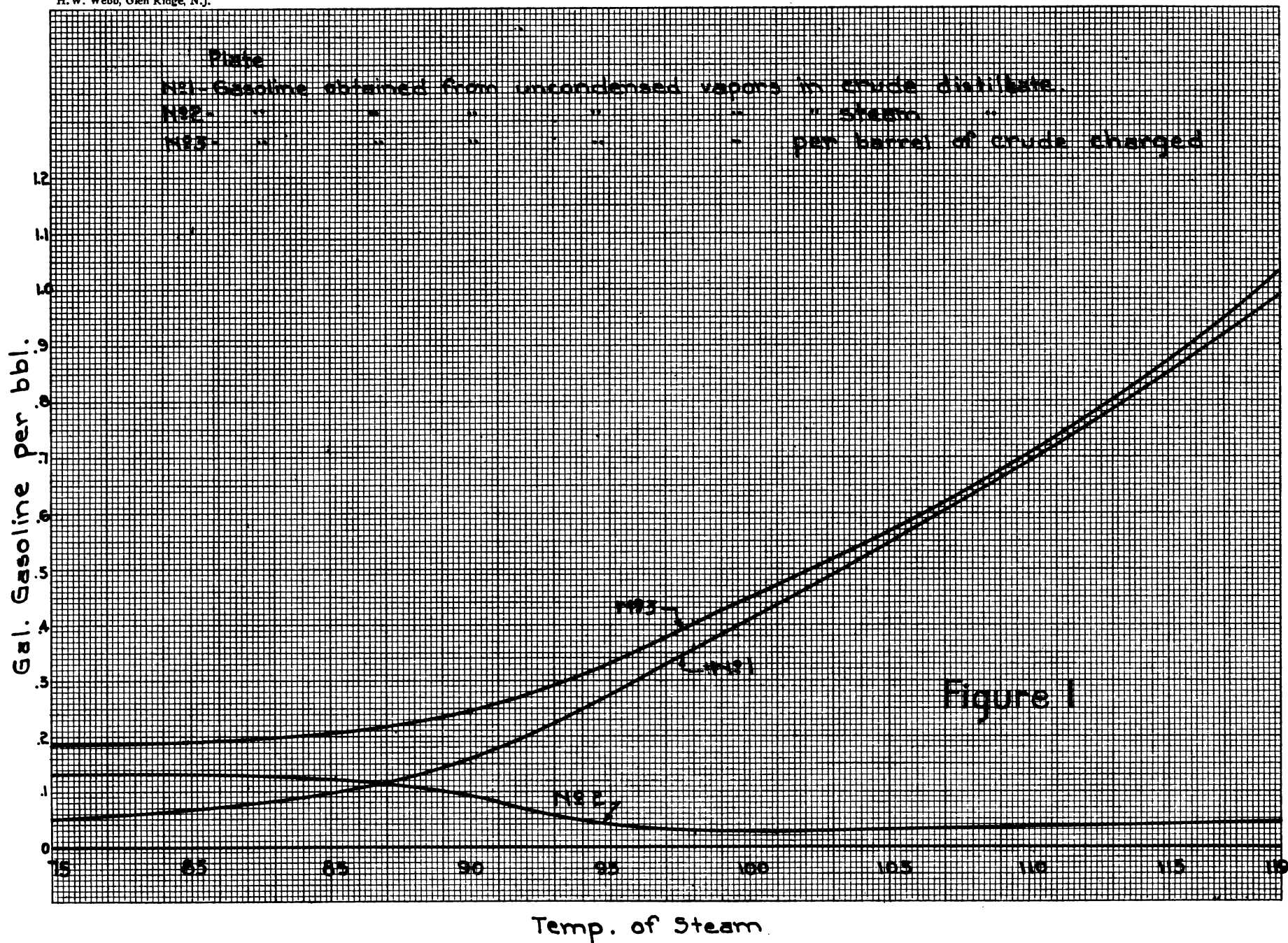




TABLE - 1. - - SHOWING GENERAL DATA ON PLANTS THAT RECOVER GASOLINE FROM UNCONDENSED STILL VAPORS.

1	2	3	4	5	6	7	8	9	10	11		
Index	Nature of Refinery	Nature of Crude	Type of Scrubber for Removal of Sulphur	Sulphur Content	Exhauster Type	Vacuum carried - ins. of water	Type of Recovery Plant	Crude Charged Bbls. per Day	Cu.Ft. of Gas per day	Gas. per Day, gal.	Gasoline Recovered Per Bbl. of Crude Charged Gals.	P.c.t. of Crude Charge
1	Complete	Mid-Cont.	Lye	High	Rotary	4	Compression	20,000	3,500,000	14,500	.72	1.71
2	do	Mid-Cont. Mexican Penn.	do	Very High	do	1	Compression & Absorption on Residue	13,246	1,382,977	11,203	.84	2.00
3	do	do	None	do	do	6-8	Abs. in gas oil	25,000	5,000,000	12,000	.48	1.14
4	do	do	Iron Oxide	do	do	2	Compression & Absorption on Residue	40,000	2,560,000	14,100	.35	.83
5	do	Mid-Cont. Illinois Ohio	Lye	High	do	3	Abs. in 50° Naphtha	40,000	5,600,000	16,000	.40	.95
6	Skimming & Lubricating	Mid-Cont.	None	Low	Intake on Compressor	1	Compression	10,000	700,000	4,200	.42	1.00
7	do	do	do	do	do	1	do	4,240	350,000	2,780	.65	1.55
8	Complete but no asphalt or coke	Wyoming	do	do	Rotary	1 1/2	Abs. in 50° Naphtha	30,000	875,000	7,359	.26	.62
9	Complete	Mid-Cont.	do	do	do	1	Abs. in gas oil, then to pressure still	12,000	*	8,000	.67	1.59
10	do	Electra Ranger Healdton	do	Low - No sour gas Treated	Intake on Comp.	2	Compression abs. on Residue	38,000	*	5,000	.13	.31
11	do	Gulf Coast North Texas La. - Mex.	do	Varies with Crude	do	2	do	55,000	*	10,000	.18	.43
12	do	Oklahoma North Texas	do	Rather High	Rotary	2	do	33,000	6,331,000	21,000	.63	1.50
13	do	Mex. - La. North Texas Gulf Coast	Water Scrubbers.	High	do	3	Horizontal Absorber	35,000	4,000,000	2,000	.05	.12
TOTAL												
*No data on gas volume								355,486		128,651	Avg. -.444	Avg. 1.05



not utilize the cracked gases because they lack equipment for removing the large sulphur content usually found in such gases.

The figures on crude charge, volume of gas and gasoline recovered are average figures, and of course, vary greatly from time to time. The greatest error probably exists in the figures for gas volumes since a number of these have been calculated from compressor displacement.

The total crude oil charged to the refineries listed in this table amounts to 355,486 barrels a day. By treating the uncondensed still vapors in these refineries, a total daily gasoline yield of 128,651 gallons is obtained. This shows an average recovery in these plants of 1.05 per cent or 0.444 gallon of gasoline for every barrel of crude oil charged. If the gases were not treated, this amount would be lost or burned as fuel.

#### Removal from Run-down Lines.

#### COLLECTION OF UNCONDENSED VAPORS

In distilling crude petroleum the first vapors or gases driven off are naturally the lightest hydrocarbons and have the highest vapor pressure of any hydrocarbons present in the crude. In order to condense these vapors, it is necessary to have condenser coils with large surface area held at low temperatures.

Under these conditions all the vapors would condense except the very lightest, which would be more correctly called permanent gas than gasoline vapor. The small amount of gas left uncondensed would under these conditions be almost entirely dissolved in the condensate. Ordinarily, however, the temperatures of the condenser boxes are high enough so that a large part of the first few per cent distilled remains uncondensed. By removing these vapors as rapidly as they are formed, and by submitting them to subsequent compression and cooling, or by dissolving them in a low gravity oil, a large part of such vapor can be recovered as gasoline.

After passing through the condensers, the vapors can be removed from the run-down lines at any point. Sometimes they are taken from the bottom of the coil by a riser passing upward through the water in the condenser box. This arrangement is less desirable than taking the gas off outside the condenser box, as the latter method cuts down repair costs. More frequently, they are removed at the "tail-house". A goose-neck or trap is usually placed between the gas gathering line and the "look-box". This prevents air from being drawn into the line from leaks in the "look-box". A small vapor line is also frequently seen leading from the look-box to the gathering line, but in most cases, it discharges into the air (fig. 3), since the amount of gas led off from this point is very small and would be largely diluted with air leaking into the look-box.

The risers from the bottom of the worm, or from the goose-neck, vary in diameter, depending on the volume of gas to be handled, generally from  $1\frac{1}{4}$  to 3 inches. In a large plant with several tail houses, the small risers enter a larger line which, in turn, discharges into a still larger main line leading through the trap to the gas plant.

A vacuum held on these lines is so regulated that the vapors are removed as rapidly as formed. In the different plants visited, this vacuum varies from  $\frac{3}{4}$  inch to 6 inches of water. As regards best general operation, 1 inch would probably be sufficient, since higher vacuums cause a considerable amount of the condensate to be re-evaporated and may also produce a vacuum on the still, which

is to be avoided. Great difficulty is experienced with higher vacuum from leakage of air into the lines. In some refineries, vacuum valves are used and in case the vacuum becomes too high on any unit, these valves open and permit air to enter. On other plants, instead of this valve, a small "clapper" valve is situated on the top of each reamer. This serves the opposite purpose, for should the pressure of the still exceed the vapor capacity of the vacuum line, the valve permits the excess vapor to escape.

A simple and efficient device to avoid excess pressure from the still is a 2-inch pipe which extends from a tee at the top of the gas riser to about 2 inches below the water surface in the condenser. If the pressure in the gas line becomes more than two inches of water, gas will escape through this pipe and relieve the pressure. The pipe should be long enough so that any excess vacuum will not draw water into the gas line.

A combination of these valves is desirable, so that the still will never be under any pressure or vacuum resulting from the gas system.

### Traps on Gathering Lines

In building a recovery system for uncondensed still vapors, it is well to install traps between the exhaustor or intake of the compressor and the source of the gas. These traps serve several purposes; they remove condensate caused by air cooling or any heavy products carried over mechanically which would destroy lubrication in the exhaustor or compressor; they act as a pressure equalizer, so that no sharp changes of pressure will take place on the run-down lines; and they serve to remove sulphur.

### Form of Traps

In the different refineries visited the traps were practically of the same type, consisting of a steel tank varying in size from about 4 ft. in diameter by 5 ft. high, to 15 ft. in diameter by 18 ft. high. In these traps the gas receives a preliminary washing with water, which removes sulphur, condensate, and heavy hydrocarbons, carried over mechanically.

Various methods of washing are used, from a simple gas inlet below the water level, to a small perforated water pipe placed inside the gas inlet pipe, which sprays the gas before it passes through the water seal.

In some plants traps are placed at every "tail" house, and in others only one large trap at the exhaustor house. In one refinery visited where a trap is installed at each unit, a steel tank 15 by 18 feet is used. A 12-inch gas intake line enters the top and drops to within three feet of the bottom where the gas bubbles upward through water, after being washed by a spray. The washed gas rises and leaves the trap by a line from the top, where it goes directly to an exhaustor. A diagram of this trap is shown in Figure 3.

### Valves on Traps

The trap previously described has a relief valve which vents gas into the air whenever pressure builds up on the lines, and thus prevents trouble at the still. A butterfly valve is regulated from time to time to hold the same vacuum on the run-down lines. Regulating devices of this sort are necessary, since the volume of gas given off from the condenser coils varies through wide ranges, and in case the vacuum carried on the trap is not sufficient to handle the vapors as rapidly as they are formed, back pressure is built up on the still. This condition should be avoided. The amount of gas formed varies with changing conditions

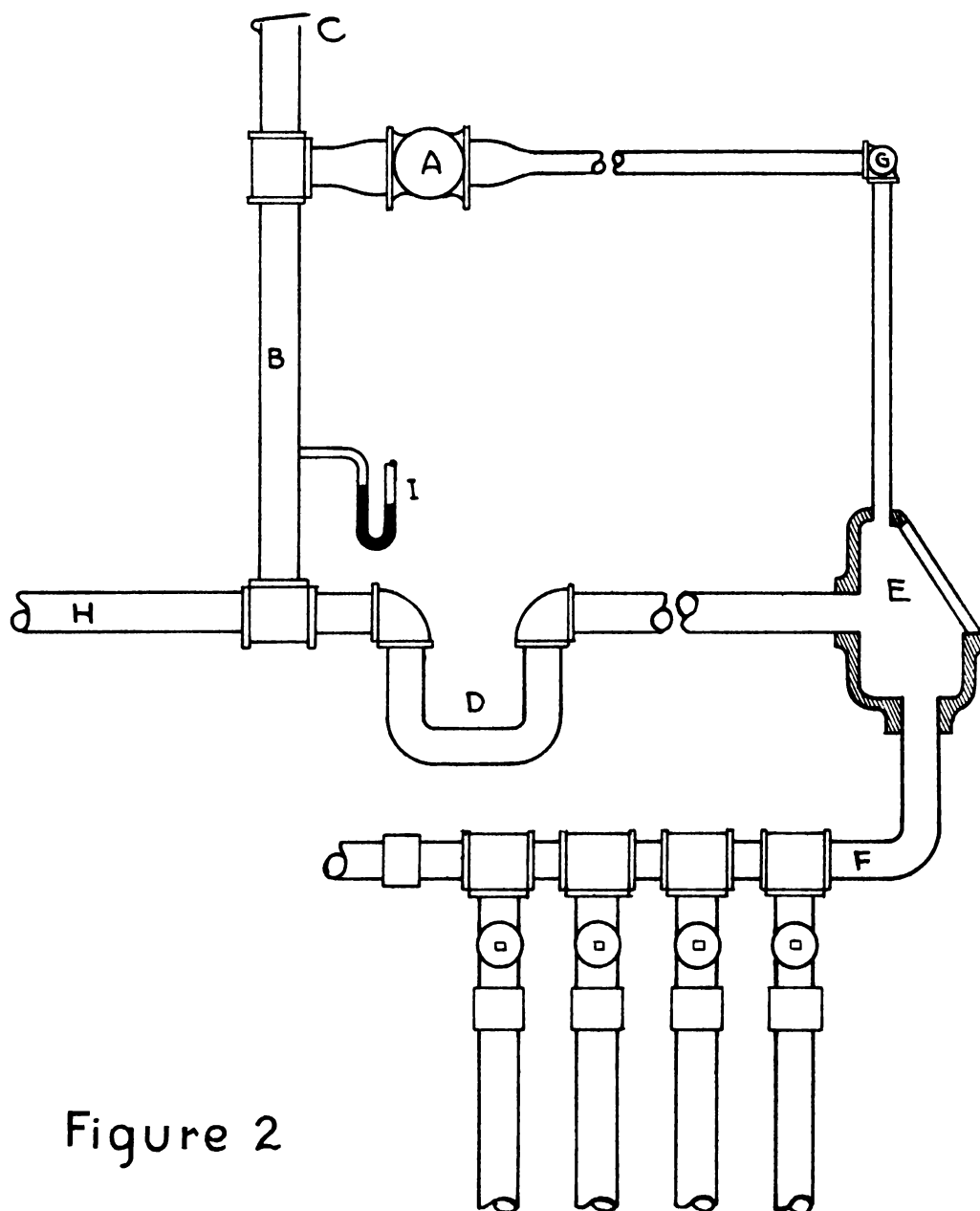
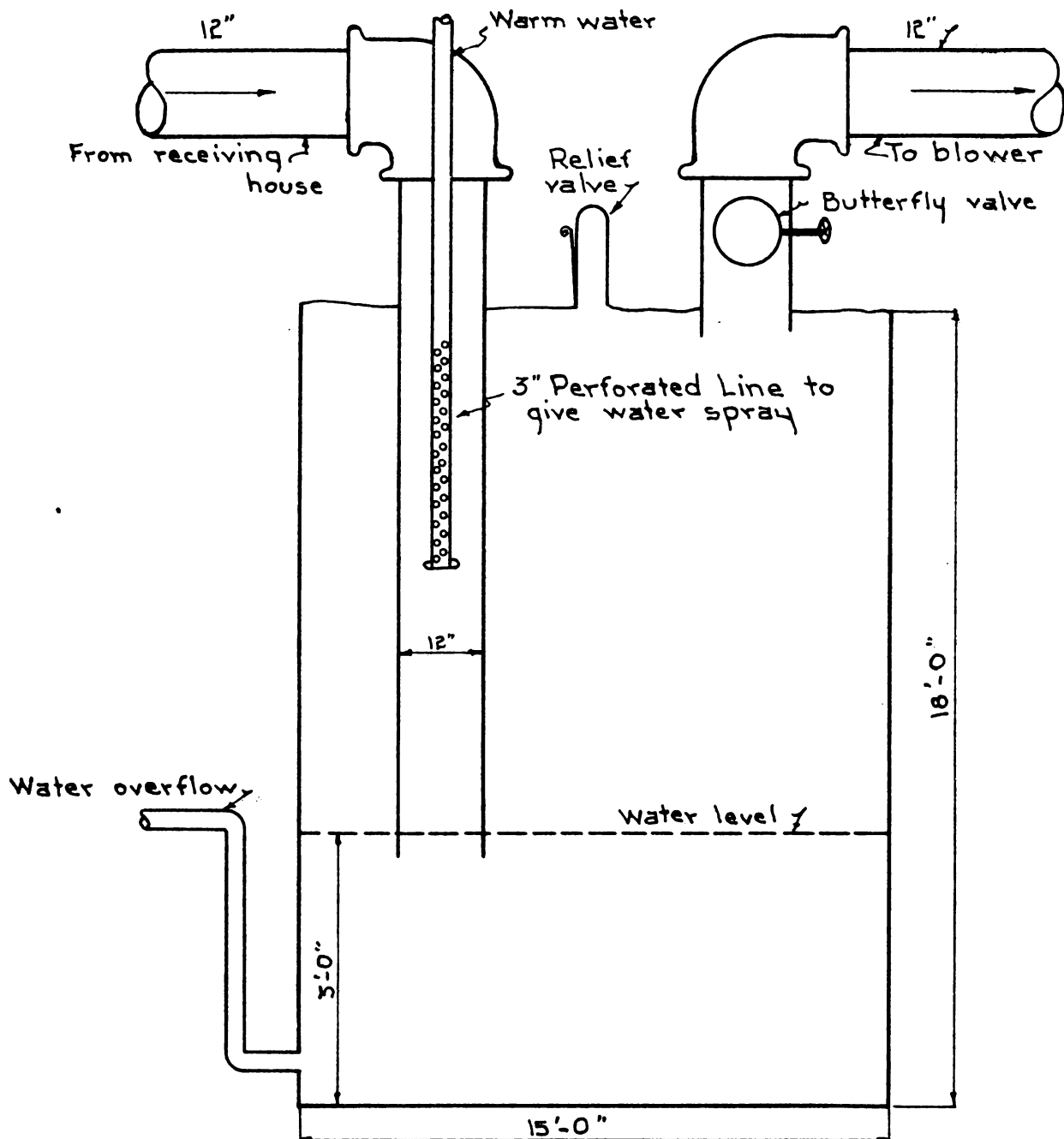


Figure 2

- A -- Main gathering line or header.
- B -- Riser carrying gas to header.
- C -- Clapper valve to prevent pressure.
- D -- Gas trap.
- E -- Look box.
- F -- Manifolds.
- G -- Small header carrying gas from look box, either to vent or gathering line.
- H -- Run down line from condenser.
- I -- U tubes registering vacuum in water held on the run down line.







**Figure 3**

Type of trap used which washes gas and provides relief valve for excess pressure and butterfly valve to prevent excess vacuum.



such as temperature of water, difference in crude, etc. If the vacuum carried on the lines is so high that the gas formed is not sufficient to compensate, a vacuum would be exerted directly on the still. This condition should also be avoided. There should be just enough vacuum on the lines to take care of the vapors, no more, no less. This will always give the same conditions of pressure as if the uncondensed vapors were passing directly into the air.

In some plants, the condensate formed in these traps is wasted into the sewer, but in other plants it is recovered from the surface of the water.

#### Use of Exhausters for Gathering Vapors

The recovery systems installed in complete refineries are necessarily much larger and much more complicated than in skimming plants, since the wide separation of sources of gas makes it difficult to carry the same vacuum on all run-down lines. Skimming plants with a crude charging capacity fully as large or larger than complete refineries have a smaller number of stills, and this results in shorter and less complicated gathering lines. In a plant of this character an exhauster is not necessary, as the vacuum needed for gathering the vapors can be developed by the intake of the compressor.

In complete refineries, however, where various types of stills are all being used, the area of the plant is much larger, the gases formed differ widely in composition and volume, the pressures vary over wide limits and the gathering lines are more complex and much longer. Hence in this type of refinery, installations must be made which will gather all of these different gases without allowing pressure to build up on any still that is making a large amount of gas, or without producing a vacuum on a still that is making very little gas.

#### Advantages Gained by Use of Exhausters

Positive-pressure, rotary blowers or exhausters are used for gathering uncondensed vapors, since they fill the requirements better than any other type of compressor or blower. They can handle large volumes of gas, <sup>hold</sup> a vacuum on the run-down lines of one to four inches of water, and discharge at a pressure high enough to force the gas through the sulphur scrubbers. A reciprocating machine is not so practical for this work, since a machine capable of handling large quantities of gas at the low pressures would be so large that the installation and operation would be prohibitive. In such a machine the surface friction of the gas due to the high velocities through the valves and ports, for large volumes at low pressure becomes very high, as compared with that in the rotary exhauster with its large inlet and discharge openings and attending low velocity. The mechanical friction in the rotary machine is very low, since it is confined to slow speed journals and gears which run in oil. In the piston machine the mechanical friction is much higher, because there is considerable friction in the piston and rod packing, journals, valve gear, and sliding parts.

The fan or turbo machine which might be used has the disadvantage of loss of mechanical friction, by journals running at high speeds, and leakage loss due to the fan not fitting the shell. Corrosion of the thin steel blades also gives continuous trouble. These disadvantages are all eliminated in the rotary blower which results not only in better and cheaper operation but also eliminates shutdowns for repairs. Due to these advantages, the rotary exhauster requires very little attention.

## Lubrication of Exhausters

In one refinery visited, two exhausters are used, which have a daily capacity of 2,500,000 cu. ft. of gas. These exhausters have been used for several years and after a series of operating tests employing different methods of lubrication, it was found that best results were obtained by feeding a half gallon of 50-54 naphtha into the exhauster in a half hour, followed by feeding lubricating oil for about  $5\frac{1}{2}$  hours. This operation is then repeated, with the result that in 24 hours runs two gallons of the naphtha and two quarts of lubricating oil are used.

With this method of lubrication no trouble is ever experienced. In eight years' time there has been only one forced shut-down, which was due to accumulation of sulphur. It is now the practice to take the blowers apart once a year and clean out any sulphur that may have been deposited.

## PRESENCE OF SULPHUR IN UNCONDENSED STILL VAPORS

### The Presence of Sulphur in Petroleum

While plants do not provide for removal of sulphur from uncondensed still vapors, this is a very important factor in refineries where vapors from cracking stills are treated.

This problem also depends upon the nature of the crude, since the sulphur content varies widely in different crudes. Mexican crude in some cases runs as high as 5 per cent sulphur, California crudes 0.34 to 3.55 per cent, Gulf Coast crudes, about 1.75 per cent, Oklahoma and North Texas crudes about 0.4 per cent, (except that from Healdton which has 0.76 per cent), Pennsylvania crude about 0.06 per cent, Lima, Ohio, crude 0.65 per cent, and Canadian crude, as high as 1.00 per cent.

The sulphur is present in the crude, partly as free sulphur and partly combined with hydrocarbons which, according to Mabery\* have the general empirical formula of  $C_nH_{2n}S$ . The compound  $C_{10}H_{20}S$  is representative of this class. These compounds are "unstable when heated in contact with air, but distilled without decomposition in vacuum. This structure is uncertain but probably cyclic with sulphur the connecting link".

### Decomposition of Sulphur Compounds

The temperatures and pressures commonly employed in stills do not break down the sulphur compounds in the crude to the point where much free sulphur is deposited in the vapor lines to the gas house. Generally, the sulphur compounds are largely dissolved in the distillate and are removed by chemical treatment, and any sulphur compounds that remain in the vapors are not ordinarily considered of enough importance to warrant the installation of scrubbers. However, in refineries using pressure stills or running crudes rather high in sulphur, the temperatures and pressures are such that these organic sulphur compounds are more completely broken down. This results probably in the formation of hydrogen sulphide, which, in turn, is readily oxidized to sulphur and water, and also breaks down at high temperatures to form hydrogen and free sulphur. That the

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\* Mabery, Charles F. "Elements that compose petroleum". Oil & Gas Journal, Vol. Sept. 10, 1920, p. 68.

decomposition of sulphur compounds takes place is evidenced by deposits of free sulphur on look-bones and the presence of sulphur dust in the gas system, which if not removed, fills up the lines, blowars and valves of the gas plant. In one instance a 2-inch cast-iron tee had been as completely filled with sulphur as if it had been melted and poured into the tee.

As stated before, the amount of sulphur depends upon the crude being refined, and in several refineries where varying amounts of Mexican crude are used the sulphur content of the uncondensed vapors varies between 600 and 3,000 grains per 100 cu. ft. of gas.

### Use of Lye Scrubbers

Several methods have been used for the removal of sulphur from uncondensed still vapors. Probably the most extensively used process is that of scrubbing the gas with a lye solution after the gas is discharged from the exhauster.

In this method the gas is passed countercurrent through a series of scrubbers filled with wooden baffles. It is first scrubbed with water, which removes the free sulphur and dissolves some of the hydrogen sulphide. The gas then passes into a lye scrubber where a solution of lye (caustic soda) made up to 15° B. (1.115 sp. gr.) removes the hydrogen sulphide, and other sulphur compounds. The gas then passes through a last water scrubber which removes any alkali that might have been carried over from the lye scrubbers.

A plant on the Atlantic Seaboard which uses this system has six tower scrubbers 20 feet high and 4 feet in diameter connected in series as shown in Figure 4. These scrubbers are filled with wooden baffling made of 1-inch by 6-inch boards and supported by angle iron riveted inside the tower. The gas inlet is 2 feet from the bottom and the outlet 4 inches from the top. The gas entering the first scrubber, passes up countercurrent to warm salt water. The water is about five degrees warmer than the gas, being pumped directly from condensers. The higher temperature of the water serves to keep any of the gasoline in the vapor from being condensed. The salinity of this water has no advantage, but only sea water is available in unlimited quantities. In fact, the salts in the water are very corrosive and are detrimental to the steel in the towers.

The gas passes through four of these water scrubbers and then into a lye scrubber. In the sixth and last scrubber the gas receives a final washing with warm sea water to remove any lye carried over mechanically. The water and lye are circulated by duplex pumps, the lye being recirculated until the absorbing efficiency is lowered to the point where fresh lye is required. The source of the crude again becomes a factor since, according to the men operating the plants, lye does not absorb sulphur from the vapors of Mexican crude as readily as it does from Mid-Continent crude.

### Chemicals Required

In this plant twelve 600-pound drums of sodium hydroxide (lye) made up with water to 15° B. treats 1,500,000 cu. ft. of vapor a day and will last from three to four weeks, the crude refined being 20 per cent Mexican of 24° B., 60 per cent Mid-Continent of 33.4° B., and 20 per cent Pennsylvania crude of 41.5° B. A fresh solution of lye lowers the sulphur content from about 3,000 grains per 100 cu. ft. of gas to about 60 grains per 100 cu. ft. but this efficiency drops rather rapidly. Blowing the lye with air revivifies the charge and the life of the solution can thus be made much longer. In order to determine the efficiency of lye treatment a test was made at this plant on gas with very high sulphur content, using fresh lye of 13° B.

The cost of this treatment is not excessive, the price of sodium hydroxide being in the neighborhood of \$6 per 100 pounds. The spent lye is wasted into the sewers.

#### Removal of Sulphur by the Iron Oxide Method

A second method of removing sulphur from the gas is by the use of iron oxide. This method is not employed as extensively as the lye method, but due to certain advantages is coming into more general use. It consists of scrubbing the gas with iron oxide suspended in water. The iron oxide removes the sulphur from the gas and is changed to an iron sulphide. The oxide is held in suspension in the water by agitation with air. The air also serves in revivifying the suspension by furnishing oxygen for the conversion of iron sulphides to iron oxides.

#### Methods of Recovering Gasoline from Uncondensed Still Vapors

The uncondensed still vapors may be treated for the recovery of the gasoline present in several ways; by compression and cooling, which condenses the gasoline as a liquid; by absorption, where the vapors are brought into intimate contact with an absorbing oil and the heavier hydrocarbons are selectively absorbed from the lighter ones present (permanent gases); or by a combination of the two methods, which consists of an absorption system on the residual gas from a compression plant\*.

#### Physical Laws Governing Recovery of Gasoline By Compression and Absorption Processes

Uncondensed still vapors contain a large percentage of gasoline vapor, and the boiling point of this gasoline may be much higher than atmospheric temperature. The molecular movement in a liquid depends on its temperature and with any molecular movement, a definite amount of evaporation takes place. If the evaporation of gasoline were taking place in a closed vessel, it would continue until the pressure exerted by the gas above the liquid was just sufficient to balance the vapor tension of the liquid, that is, the tendency of the liquid to vaporize. Under these conditions, a state of equilibrium is said to exist. If this vapor and liquid were cooled a few degrees, (the pressure remaining constant), or, if the vapor were held at the same temperature and more pressure applied, some of the vapor would condense to restore the equilibrium. With these principles in mind, it will be seen that by compressing a gas which contains a large percentage of gasoline vapor and then removing the heat which was formed by compression (by means of some cooling agent - in this case water) an equilibrium must be reached, which can only be done by condensation of the gasoline. This process is so regulated by experiment that the pressures

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\* These processes as applied to natural-gas gasoline practice has been covered in the following Bureau of Mines publications:

Dykema, W. P., Recovery of Gasoline from Natural Gas Gasoline by Compression and Refrigeration. Bull. 151. 119 pp.

Dykema, W. P., Recent Developments in the Absorption Process for Recovering Gasoline from Natural Gas. Bull. 176. 84 pp.

Dykema, W. P. and Neal, R. O. Absorption as Applied to Recovery of Gasoline Left in Residual Gas from Compression Plants. Tech. Paper 232. 40 pp.

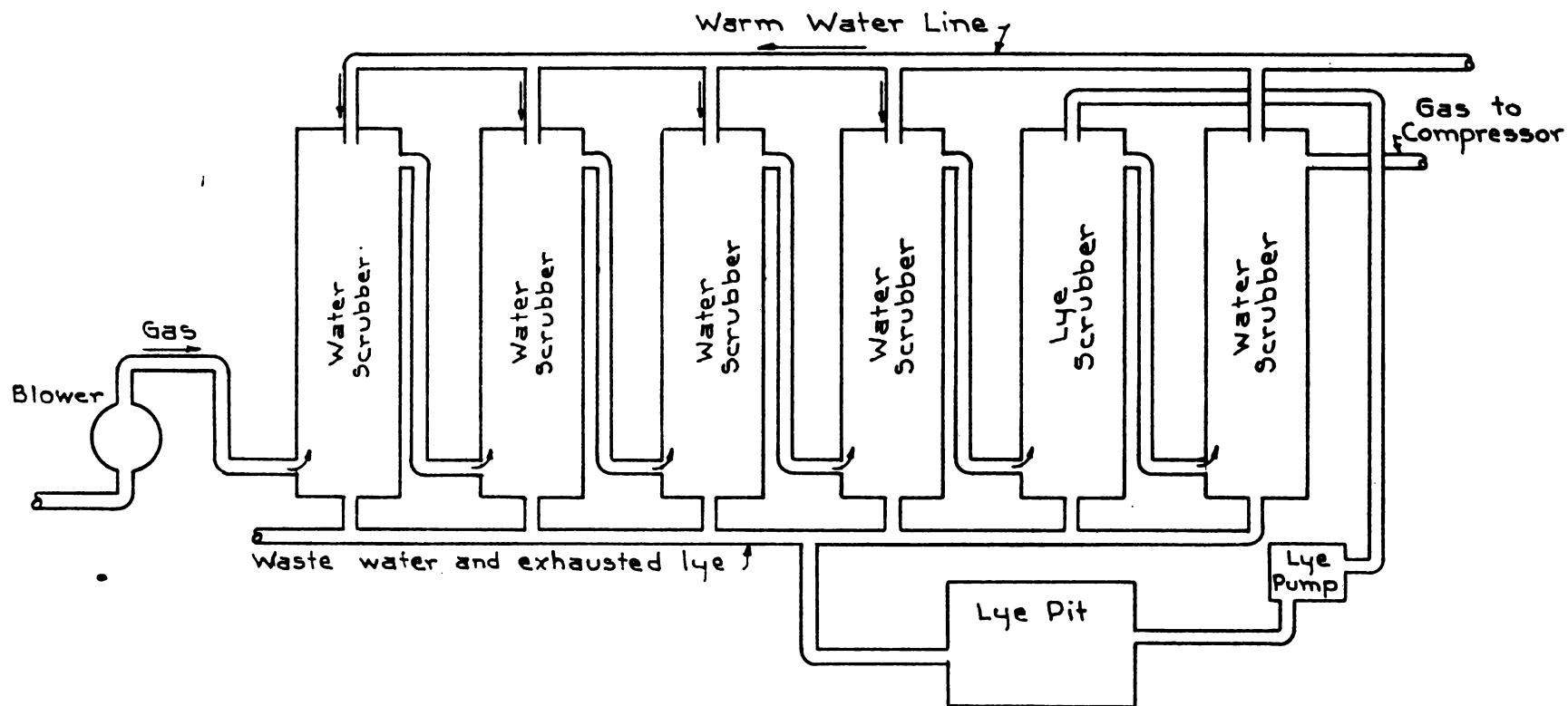


Figure 4

Flow Sheet of Sulphur Removal  
Plant using Lye.





and temperatures are such that the gasoline is condensed without the precipitation of some of the very volatile hydrocarbons of such low boiling point and high vapor pressures that they can not be held as gasoline when the pressure is relieved. It is well to mention, however, that no close separation can be made, and that in this system of recovering gasoline some of the vapors remain uncondensed, and also that some of the lighter hydrocarbons are obtained, either by condensation or as gases dissolved in the gasoline produced.

The absorption process depends on the solubilities of light hydrocarbon vapors in heavier oils. The solubilities depend very largely on the vapor pressures of the light fractions and of the absorbing oil; for example, a very much smaller percentage of methane than pentane will dissolve in a given oil. Hence, by bringing the gases from the run-down lines into intimate contact with an oil, the heavier hydrocarbons in the gas are selectively absorbed and the permanent gases pass through without being dissolved to any great extent.

In a combination of the compression and absorption methods, the discharge gas from the compression plant is washed with 500 B. naphtha. This naphtha is then blended with the raw compression gasoline.

#### The Compression Process - - Adaptability of Process to Uncondensed Still Vapors

The compression process for recovering gasoline from refinery gases is more widely used than the absorption process. The compression process was first developed for recovering gasoline from casing-head gas, and since uncondensed refinery vapors are very similar to casing-head gas this process naturally was utilized.

The compression process is very adaptable for the recovery of gasoline from uncondensed still vapors, since the gasoline content is very high, and excessively high pressures are not necessary to recover the greater part of the gasoline present. In visiting the many refineries which use this method the highest pressure observed by the writer did not exceed 200 pounds per square inch, and most of the plants operated at pressures below 100 pounds. This is to be expected when it is considered that the gases treated are almost entirely gasoline vapors, only a small amount of permanent gas being present. Only a few plants compressed in two stages, the greater number used single-stage compression entirely, and depended upon a naphtha absorption system for absorption of gasoline in the residual gas. This naphtha was then used in blending with the compression product.

In the smaller recovery plants the intake on the compressor is sufficient to carry the required vacuum on the run-down lines, thus eliminating the installation of an exhaustor. This system of removing the vapors, while lower in initial cost than a system that makes use of an exhaustor, frequently gives considerable trouble and for that reason must be kept under continuous supervision. In case the intake of the compressor is used for removing the gases from the run-down lines, the vapors treated will be limited to the sweet gases (those with very low sulphur content). When the sulphur content of the gas is high, its removal by scrubbing is absolutely necessary. Since this must be done before the gas reaches the compressors, an exhaustor will be necessary to carry the vacuum and discharge at a pressure high enough to force the gas through the sulphur scrubbers. Several refineries are treating sweet gas only and carrying the sour gas in separate lines to the boilers where it is burned without the gasoline being removed. The installation of an exhaustor and a system of sulphur purification, would greatly increase the output of this type of recovery plant.

## Two-Stage Compression

In a plant where the compression of the gas is accomplished in two stages, compressors should be operated in such a way as to give each the same load. The power expended in the low-stage compression should equal the power expended in the high-stage compression. This will result in an equal discharge temperature of the gas from both compressors provided, of course, that the intake temperature of the gas is the same in both cases. This is accomplished under the best operating conditions, an example of which is shown in one plant where the discharge temperature of the low stage is 225° F. and the high stage 230° F. In order to keep this relationship, relief-valves are placed on the discharge line from each compressor, and are set approximately 15 pounds higher than the pressure carried. These valves protect the machine from excess pressures due to any clogging of the line or closing of valves further along in the system. A diagram of a two-stage compression is shown in Figure 5. In the single-stage plant this balance of work is eliminated since the pressure desired is reached in the one machine. The compressors used in these installations are of the various well-known makes and are generally steam driven, since steam is always available around a refinery. In one plant visited the compressors were driven by motors of 150 hp.

## Condenser Surface of Coils

From the foregoing paragraph it becomes evident that in order to have efficient operation, the gas from each compressor must be reduced in temperature to approximately the same as its intake temperature. Under this condition the amount of cooling for each stage would be identical, since the power expended would be the same.

In order to obtain this cooling, the temperature of the water and the surface area of the condenser must be the same for each stage. The former is generally constant; therefore the area of condenser surface must be based on the volumes of gas which are to be cooled. This area in practice is generally about 0.8 square foot of surface per 1000 cu. ft. of gas treated daily. Since in refineries the volume of gas is varying and generally is not metered, the surface would be rather difficult to determine. Thus surface area might better be shown in relationship to the horsepower used in compression, rather than to the cubic feet of gas treated. This figure should be about four square feet per horsepower.

## Types of Coils

Condensation is effected by passing the hot compressed vapors through cooling coils, which are of two general classes: the submerged type, where coils are covered with circulating water in a condenser box, resulting in a direct transfer of heat from the gas to the water, and the aerial type over which water falls as a spray. By spraying the water over the coils better cooling is obtained than by using submerged coils. The water in the spray has a much greater surface for evaporation than the water in the condenser box, and this results in lower temperatures. Unless a large supply of cold water is obtainable, the spray system is, generally speaking, the more desirable, although the loss of water from evaporation is much higher. It might be mentioned that in some parts of the country where the humidity of the atmosphere is always high, the cooling effect from evaporation will be small, and no better than would be obtained from coils submerged in water at the same temperature.

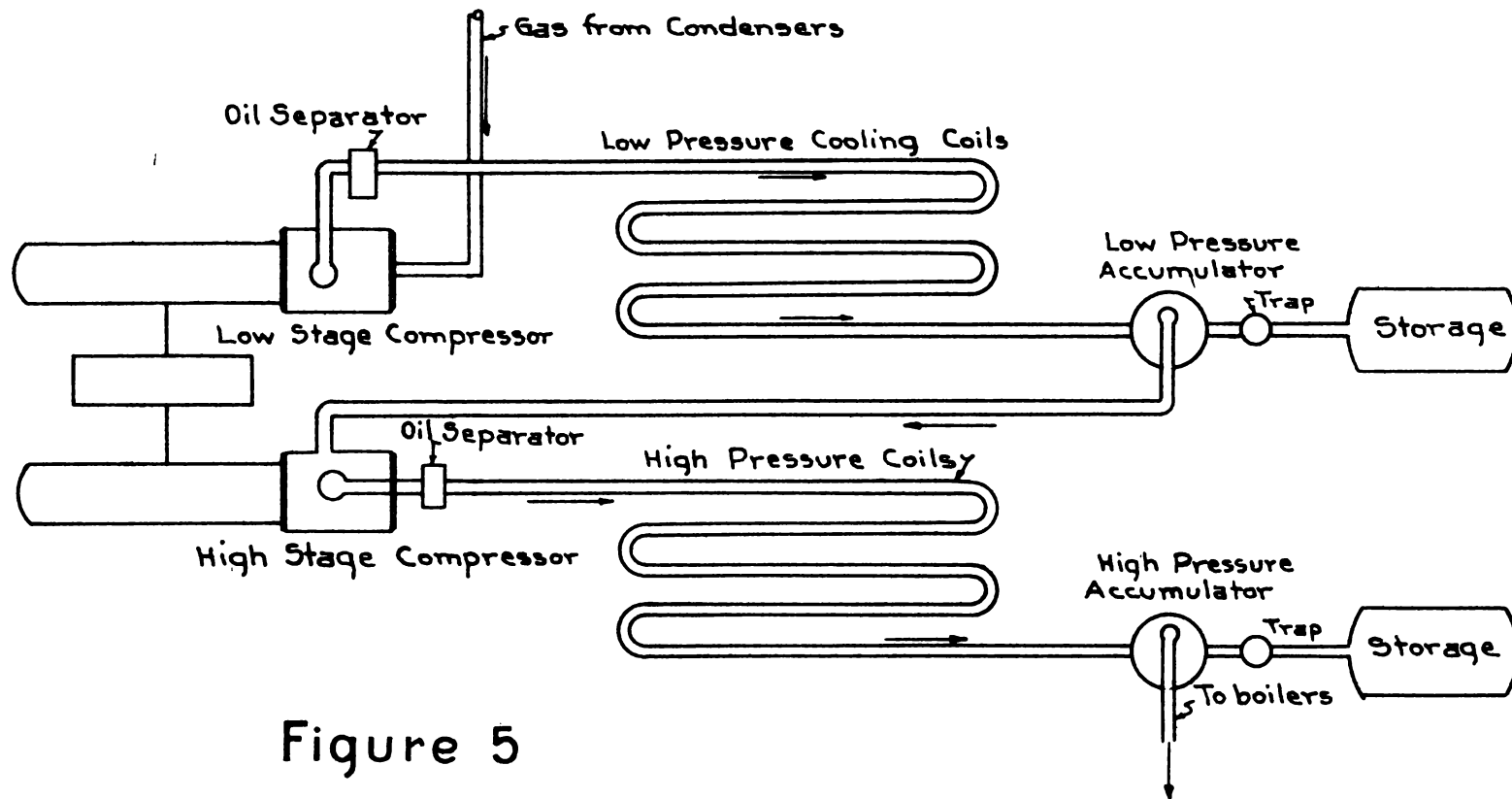


Figure 5

Diagram of Two Stage  
Compression Plant



## Construction of Coils

In building coils for cooling the compressed gases, two general types of construction are used, as in coils for condensing vapors from the stills. The gas may pass through one long coil or it may be divided by means of a header and be cooled in several lengths of short coils. The cooling should be the same in each case provided the area was the same, but some difficulty has been found in the latter type in maintaining an equal flow of gas through the different lengths of coils. This results in some of the gas receiving insufficient cooling.

## Flow of Gas Through Coils

The gas enters the coils at the top and discharges at the bottom. By this arrangement the condensate formed travels in the same path as the gas. This is a much better arrangement than having the gas flow countercurrent to the condensate, since with that method, undoubtedly much of the condensate would be carried away mechanically by the gas.

## Accumulator Tanks

The gasoline formed by compression with subsequent cooling is collected in a so-called accumulator, which consists of a high pressure tank, generally about 4 feet in diameter and 9 feet high. The tank is equipped with gauge glasses which show the amount of condensate collected. This tank is under the same pressure as the coils. The condensate is blown out of the accumulator into the "make tank" where it is blended with naphtha. This blending may be a continuous process in which the naphtha is pumped in slowly, at such a rate that the desired blend is made, or the required amount of naphtha may be pumped in and held there until enough of the condensate has been mixed with it to reach the desired blend. Difficulty is experienced with the latter method in obtaining an intimate mixture of the gasoline and naphtha.

## Blending of Condensate

In many plants the blending with naphtha is done in the accumulator. By pumping in naphtha to a certain height on the gauge glass, the condensing gasoline mixes with the naphtha until the total volume reaches a height on the gauge glass which has been found to give the right proportions to obtain the desired blend. A second and better method of blending in the accumulator is in pumping the naphtha through the top of the accumulator and allowing it to fall in a spray or over baffling material, where it acts as an absorbent for uncondensed vapors above the condensate. With a predetermined rate of speed the naphtha pumped will, after its absorbent action, blend with the compression gasoline and give the mixture desired.

Still another method of blending consists of pumping naphtha into the cooling coils, where it comes into intimate contact with the hot compressed vapors. A better blend is obtained by this method, since very intimate contact is assured while the gas and naphtha pass through the cooling coils. Absorption of uncondensed gasoline is also effected, due to the naphtha being in contact with the gas throughout the length of the coil. This method has been found very satisfactory in several installations. One plant, which had blended in the accumulator by means of a continuous spray falling through the residual gas and subsequently blending this condensate with the compression product, recently changed from this system to that of "hot blending" (introduction of naphtha into the coils). The change proved very satisfactory, the production for the month of September 1920, showing an increase of 61 barrels over the highest September production for eight years.

The blended gasoline produced in the compression plants is taken from the gas plant to the gasoline storage where it is mixed with straight-run gasoline. The naphtha used in blending generally has an end point around  $437^{\circ}$  F., and when blended gives a product with a somewhat lower end point.

Distillations of the raw naphtha and the blended stock are shown in Table 2. The naphtha in this case had a gravity of  $55.9^{\circ}$  B., and was blended to  $60.9^{\circ}$  B., with two-stage compression of  $71.5^{\circ}$  B. and  $84.5^{\circ}$  B., respectively, also with the gasoline obtained from the gas by absorption. In the plant from which these figures are taken the blending stock has a gravity above  $52^{\circ}$  B. In many plants, however, naphtha of a gravity of  $50$ - $52^{\circ}$  B. (where Mid-Continent crude is refined) is used and is blended to around  $58^{\circ}$  B.

### The Absorption Process

The absorption process for recovering gasoline from uncondensed still vapors consists of bringing the vapors into intimate contact with an absorption oil. Gasoline contained in the vapors as well as some permanent gases are dissolved. A flow sheet of a naphtha absorption system is shown in Figure 6. Absorption may be accomplished in a naphtha of about  $50^{\circ}$  B., when the gravity is raised to  $56^{\circ}$  or  $57^{\circ}$  B. and the product pumped directly to the gasoline storage. The absorption may take place in a gas oil of about  $35^{\circ}$  B., the gasoline being subsequently removed by steam distillation. The gas oil is then returned to the absorption plant to be again used as an absorbent.

In an absorption plant operating on refinery vapors, the gases are generally collected by an exhaustor which gives enough pressure on the discharge to force the gas through the absorption tower. These towers vary greatly in size, dependent, of course, on the volume of gas to be treated and the amount of pressure on the gas. As will be shown later, the use of low-pressure absorption is more practical in a refinery than high-pressure absorption - necessitating the use of large towers.

### Absorption in Naphtha

In one plant where naphtha having a gravity of  $50^{\circ}$  B. is used as the absorbent, five towers are employed for treating about a million feet of gas daily. These towers are 10 by 30 feet with steel baffles and cone plates. The baffles have 22 circles of 5/8-inch holes drilled 2 inches apart.

The gas enters the first absorber at the bottom and discharges at the top, from there it passes to the bottom of the second absorber, and so on through the series. The naphtha is circulated counter-current in each absorber. Pumps keep the naphtha circulating continuously in each absorber until the gravity of the naphtha in the last absorber has been raised to the desired point. When this has been accomplished, the blend from this tower is drawn off to storage and the naphtha from each tower is moved to the succeeding tower, where the same process is repeated. Another method of absorption which is more generally used is that of a series of towers with the gas passing counter-current to the naphtha, both flowing through the system in series. This method has the advantage over the previously described method in that the naphtha is handled but once and upon its discharge the gravity has been raised to the desired point. There are difficulties to be met with, however, which are not experienced in the first plant, in that the gas being treated has a gasoline content which varies widely and with this condition the rate of flow of the naphtha must be watched very carefully in order to obtain a uniform product.

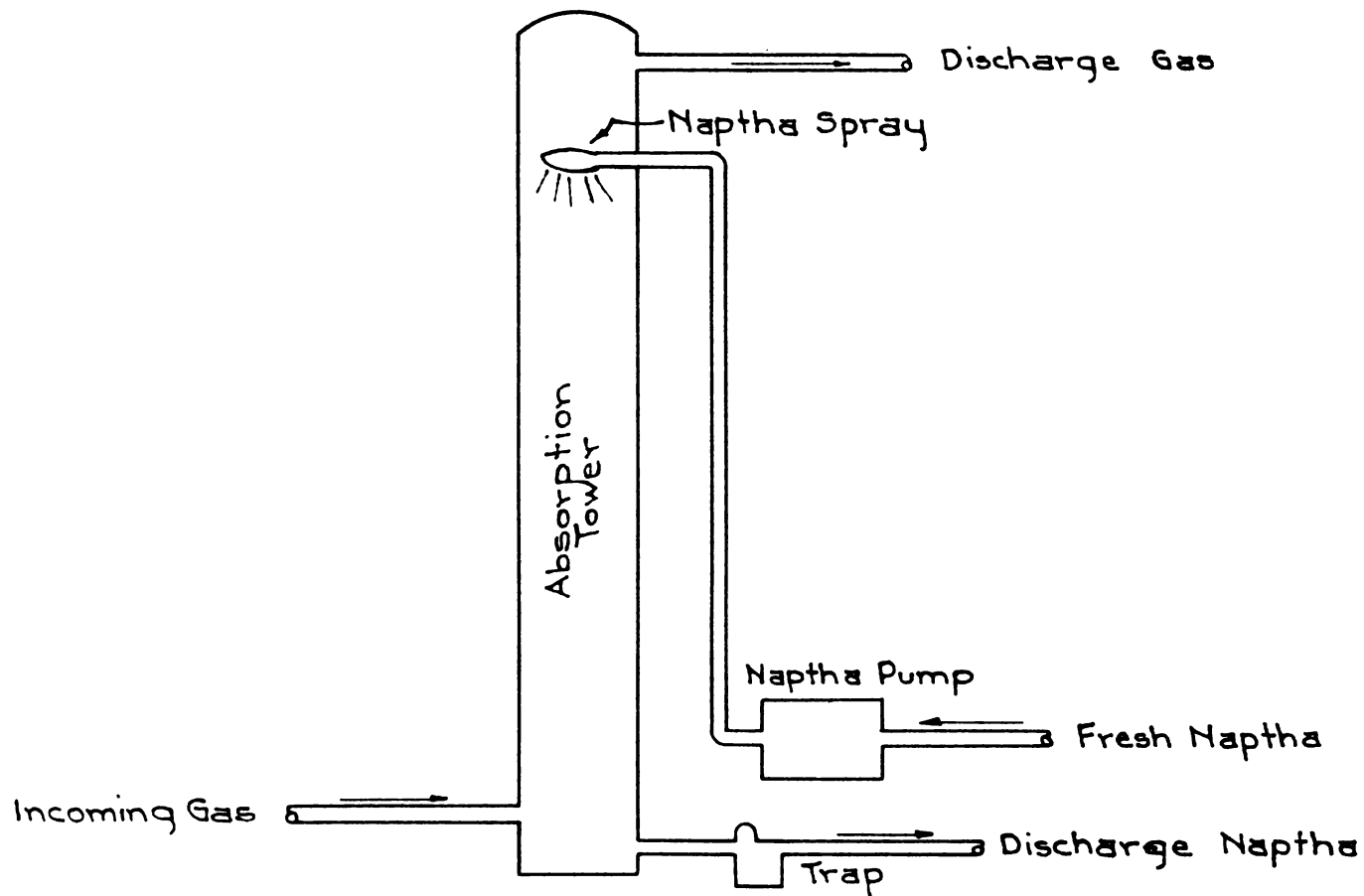


Figure 6

Flow Sheet of Naptha  
Absorption System





TABLE 2 - Showing Distillation Range of Naphtha, Low and High  
Stage Compression Gasoline and Final Blend

	Gravity	Initial	% Off at 212	% Off at 221	% Off at 275	% Off at 302	% Off at 356	% Off at 400	End Point	Recovery
Naphtha	55.9	152	9%	15%	52%	68%	89%	96%	406	98%
Low Stage Gasoline	71.5	86	77%	81%					239	93%
High Stage Gasoline	84.5	78.8	68%	72%	74%	76%			320	80%
Blend	60.9	97	22%	26.5%	61%	71.3%	86%		395	97%

## Absorption in Gas Oil

The absorption plant which uses a gas oil as an absorbent is more similar to the absorption plant of the natural gas gasoline industry than the naphtha absorption plant. In this type of plant the gas oil is continuously circulated through the absorbers, where it dissolves the gasoline vapors. This is accomplished in the same manner as described in the naphtha absorption system, by oil flowing counter-current to the gas in vertical absorbers, which are filled with baffling material. The baffling material spreads the oil over a large surface which results in intimate contact between the gas and oil. The oil is then pumped to a steam still where live steam strips it of the absorbed gasoline. The gasoline is condensed in cooling coils and taken to storage. The hot oil is then passed through a series of heat exchangers counter-current to the cold oil coming to the steam still, is then further cooled by spray towers and enters the absorbers in starting another cycle.

In one case, the gas oil containing the absorbed gasoline was taken directly to the pressure stills, where the gasoline was recovered with the cracked distillate.

When gas oil is used as an absorbent, much additional expense is encountered in removal of the gasoline, whereas in the case of naphtha, when the gravity is raised to the desired point, nothing remains but to pump the product to the gasoline storage. In the natural gas gasoline industry, the price paid for naphtha frequently equals or exceeds the price obtained for the finished product. Absorption plants treating natural gas generally use gas oil as an absorbing medium instead of naphtha, since the gas oil is a more efficient absorbent and since absorption gasoline commands a higher price than naphtha blends. Consequently naphtha absorption is not met with except in compression plants where it is required for blending, and is there frequently used as an absorbent on residual gases. However, in refineries where gasoline can be recovered from the gases, naphtha absorption probably offers the greater advantage since the questions of price and transportation are not met with, and because of the fact that these gases are made up of a much larger per cent of higher hydrocarbons than is the case in natural gas, where only a small percentage of the total volume is gasoline vapor. Due to the large percentage of gasoline in uncondensed still vapors, absorption in naphtha is much more efficient than is the absorption of gasoline from natural gas. In the naphtha absorption process as used in a refinery, the naphtha cut from the crude stills is passed through the absorption system where it is increased in volume and gravity. This product is then pumped to the straight-run gasoline storage, the only expense involved being that of pumping.

In the example previously cited, where gas oil passed through the absorption system to the pressure stills, the same advantage is obtained in that no additional expense is involved in the use of gas oil. It is very possible, however, that a considerable percentage of the absorbed gasoline would be lost either by being broken down into permanent gas or by being carried away with the cracked gases.

## The Effect of Temperature on Absorption

In the absorption process the temperature in the tower is very important since the absorbing power of naphtha or gas oil (especially the former) is very much decreased with rise in temperature. The decrease in absorbing efficiency is not so pronounced below about 85° F. but above that figure the efficiency falls rapidly. It is also true that although the lowering of the temperature in the absorption towers increases the efficiency, this increased recovery represents largely hydrocarbons which can not be considered gasoline, and which can never be saved as such. This results, of course, in excessive weathering losses when the naphtha reaches normal temperature, or when the gas oil is distilled by steam. Therefore, the increase due to lower temperatures is not only lost by this evaporation, but a large amount of gasoline is mechanically carried away by this permanent gas.

The temperatures of the absorbent and the gas should be well below 85° F., and there should not be a great difference in temperature between the two. When gasoline vapor is absorbed by naphtha or gas oil there is a certain amount of heat given off, which will be great enough to raise the absorber temperature above 85° F. if the temperature of the gas and gas oil is not well below that figure.

Temperatures below 85° F. can generally be obtained by passing the gas through water traps (described elsewhere), but in many instances it would be advantageous and would materially increase production to cool the gas and oil in a lower tower. The installation of a recovery system on the uncondensed still vapors is very necessary in refineries where the condensers are inefficient. Therefore the gas that is obtained at this source will always have a rather high temperature. This is especially true where the gas risers pass directly upward through the water in the condenser box. The absorbing oil will never be cooler than the atmosphere and frequently when taken directly from the manifolds will be much higher.

## Volume of Gas and Size of Absorbers

Since in the refinery the gas is delivered to the absorption plant at a very low pressure, it is necessary to build large absorption towers to handle the amount of gas produced. The pressure and temperature determine the actual volume of gas which must be treated, and this in turn determines the diameter of the tower in order to have the proper velocity of gas flow. In case the velocity of the gas through the tower is too great, oil is carried over with gas, Dykema\* states that velocities through absorption towers should not exceed 75 feet per minute.

The height of absorbers largely determines the length of time and intimacy of contact between the gas and absorbent. This in turn governs the saturation of gasoline obtainable in the absorbing oil.

## Types of Baffling Used in Absorbers

The absorption plants visited make use of several different types of baffles; in one case wooden grids, in another perforated baffle plates, and in another chemical tile are used. In the natural gas gasoline industry these

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\* Bulletin 176. U. S. Bureau of Mines. Recent Developments in the Absorption Process for Removing Gasoline from Natural Gas - Dykema, W.P.

various types of baffling have been employed as well as shavings, crocks, tin cans, etc. The main object, of course, is to obtain a maximum surface with as high a voidage as possible. There are, however disadvantages with some of the best baffling material especially when applied to refinery gases. These gases usually contain higher percentages of sulphur than ordinary natural gas, which makes use of wooden and earthenware baffling imperative.

### Economics of Recovery of Uncondensed Vapors

As shown previously, there are a certain number of factors which are responsible for the noncondensation of gasoline vapors, and the question rises as to whether it would be more economical to change plants already built, in order to reduce this loss, or to install a plant to recover these vapors as gasoline. It must be understood that the recovery plant is in reality a secondary condensing system which acts as an auxiliary to the primary condensers. This means that if the stream temperatures from the condensers can be maintained at a low temperature, the recovery plant would be of no advantage.

A low stream temperature, is however, dependent upon cold water and large condenser area. With the loss of gasoline due to the high temperature of the stream it becomes an economic problem as to whether the cost would be greater for enlarging the condensers, obtaining colder and larger supplies of water, or building a secondary condensing system in the form of a compression or absorption plant.

The nature of the crude is another point which must be taken into consideration, for if the crude contains only a very small amount of the lighter hydrocarbons, the condensers even though they may be too small and have insufficient cooling for the large amount of light vapors in a high gravity crude, are capable of handling the vapors from crudes of low gravity.

Plants which have pressure stills in operation, offer still another consideration, for in cracking, gases are formed which are permanent in character and can never be recovered by gasoline. In cracking processes where the pressure is not released until the vapors have passed through the condensers, all of the gasoline vapor worth recovering will be condensed. In the cracking processes that condense the distillates at atmospheric pressure the condensations of very light vapors are entirely dependent upon condenser areas and temperatures of cooling water. Another feature that should be considered in connection with the installation of a recovery system is that by extending lines to storage tanks for crude oil and gasoline, large quantities of vapor can be recovered which would otherwise be lost by evaporation. It has been shown by Wiggins\* that a comparatively high percentage of gasoline and crude oil in storage is lost due to evaporation, and that the portions lost by evaporation represent the most volatile fractions of crude oil.

In the plants already in operation, it is obviously much cheaper to install a compression or absorption plant, than it would be to enlarge condensers, especially when cold water is scarce. Probably there is no other expenditure in a refinery which will give a quicker return on the investment than this parti-

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\* Wiggins, J. H. Evaporation of Crude Oil in the Mid-Continent Field.  
U. S. Bureau of Mines Bulletin No. 200.

cular installation. For example, one refinery paid for the cost of the recovery plant in two months' operation. This could not be done in every refinery, but if all the factors discussed are taken into consideration before the plant is installed, there is little doubt but that appreciable quantities of gasoline could be saved.

#### Testing Vapors in Plant Previous to the Installation of a Recovery System.

While there is probably no refinery which does not suffer losses of gasoline by reason of some of the still vapors remaining uncondensed, yet it would be poor policy to erect a recovery plant without previous knowledge as to the amount of gas which would be treated and the possible recovery of gasoline by the installation of a recovery system. In general a much more thorough investigation will be required than is necessary in testing a natural gas gasoline property, since the quality of the gas changes continually and the volumes vary widely. Consequently, all factors must be taken into consideration. Measurements should be made of volumes of gas produced from all stills, under varying operating conditions. Compression tests or absorption tests should be made on the vapors so that by the end of the investigation definite knowledge will be available regarding the volume of gas to be treated and the quantity of gasoline that might be produced under different conditions. With this information the installation can be planned to meet the requirements. Since the recovery of gasoline from uncondensed refinery vapors is an outgrowth of the processes used in the extraction of gasoline from natural gas, the methods of testing natural gas can be applied in the testing of uncondensed still vapors for gasoline content.

#### Compression Test

This test is carried out by means of a small compressor which compresses a metered volume of gas to generally about 250 pounds. The gas is cooled in passing through a condenser tube submerged in cold water, the gasoline precipitated and collected in an accumulator where it is drawn off, weathered and then measured. This is a very convenient and rapid method and sufficiently accurate for the purpose.

#### Absorption Test

This test is made by passing a metered volume of gas through an apparatus filled with absorbing oil. The oil used has a rather high initial boiling point, such as "mineral seal" oil (B. P. 470° F.) By bringing the gas in intimate contact with the oil, the gasoline from the gas is practically all absorbed. The oil is removed from the apparatus and distilled. The gasoline is recovered and measured, from which data the gasoline content of the gas can be determined.

#### Charcoal Test

In this method a metered volume of gas is passed through a small tube holding about 250 c.c. of activated charcoal. The charcoal acts as an absorbent and removes the gasoline from the gas. After the absorption, the charcoal is removed and placed in a flask containing glycerin, from which by the addition of heat all of the gasoline is distilled, collected and measured.

## Measurement of Volumes

It is rather difficult to obtain an exact measurement of the volumes of gas remaining uncondensed, since the volume, of course, will vary with different conditions. However, a meter can be connected to the run-down line from the condenser in such a manner that all of the gas is trapped and passes through the meter. The meter should be left on the gas flow long enough to measure the average amount of uncondensed vapor under various prevailing conditions. The volumes should be determined on all of the run-down lines from the stills producing gas, and upon this information some definite idea of the volume of gas available for treating in a recovery plant can be obtained.

## Cost of Plants -- Cost of Construction

It is difficult to estimate the cost of installing gasoline recovery plants. The cost will vary with different plants, depending on local conditions such as the distances between different stills which are sources of gas, the nature of gas, especially in regard to sulphur content, and the plant efficiency. However, a cost of approximately \$15 per gallon of gasoline (daily capacity) should, in the opinion of the writer, be amply sufficient. This is much lower than the cost of the average gasoline plant operating on natural gas or casing-head gas, but it must be remembered that much of the cost in the natural gas gasoline industry can be dispensed with in refineries, since gathering lines and gasoline lines will be much shorter, tankage and loading racks are already provided for, and the plant will have a supply of gas as long as the refinery is in operation. In the natural-gas gasoline industry only a few years supply of gas can be expected from one source. Based on one per cent recovery of gasoline from the total crude charge, the cost of construction when applied to the daily refinery capacity, would be approximately \$4 per barrel of crude charged.

One plant which the writer visited was so situated that the gathering lines were of great length, and after completion of the plant it was found that a large amount of cracked gas could not be used unless a sulphur removal plant was installed. This confined the operations to sweet gas only, necessarily cutting down the output of gasoline, and since the investment in lines which were not used remained the same, the cost of installation amounted to about \$50 a gallon (daily capacity) of gasoline.

## Cost of Operation

The operating cost of the gas plant is relatively low. Generally not more than two men are required on a tour and in a large number of cases only one man is in charge of the compressors or exhausters. In the average plant a cost of about 1-1/2 cents per gallon is charged to operation. This includes pay for operators and cost of steam. One refinery shows a cost of four cents a gallon, but this is largely due to the high price charged to steam consumption. When compared with natural gas gasoline plants as to cost of operation, the labor would be about the same in each case. It must be remembered, however, that in the natural-gas gasoline plant the cost of the gas frequently is a large item, whereas in the refinery the gas has no particular value, since the gasoline must be removed before it can even be used successfully as fuel under boilers or stills.

## Summary

The following paragraphs briefly summarize the information contained in this report.

1. In the distillation in refineries appreciable amounts of the vapors are not condensed by the ordinary condensing equipment. The amount of vapor remaining uncondensed depends upon the following factors:

(a) The amount of uncondensed vapors is proportional to amounts of gasoline produced. Other conditions being equal, more uncondensed vapor will be lost from a refinery which has increased the gasoline yield from crude by installing cracking stills, than in a skimming plant which obtains only the gasoline present in the natural state.

(b) A crude oil which gives a very volatile gasoline will lose more from uncondensed vapors than will a crude which contains gasoline of low volatility.

(c) Summer losses due to uncondensed vapors are higher than winter losses.

(d) The higher the temperature of the stream, the greater will be the amount of uncondensed vapor. The stream temperature is directly dependent upon the temperature of cooling water and coil surface.

Experiments show that with stream temperatures exceeding 85° F. the volumes of uncondensed vapors become increasingly large. Experimental data and plant data are given which show effects of varying conditions of temperature.

2. A survey of refineries of the United States which recover the gasoline from uncondensed vapors shows: A total crude charge for these refineries of 355,486 barrels per day - a recovery of gasoline from uncondensed vapors of 128,651 gallons per day, which gives an average recovery of 0.444 gallon of gasoline per barrel of crude - or a recovery of 1.05 per cent of crude as gasoline which would otherwise be lost.

3. In operating a recovery plant on uncondensed vapors methods used for collecting vapors are shown. A small vacuum is held on run-down lines where the vapors are trapped off by means of goose-necks. This gas passes through traps which remove any condensate carried in the lines. The vacuum is held by either the intake of a compressor or in larger installations by means of an exhaustor.

4. When gas of high sulphur content is encountered, a unit for the removal of sulphur must be installed. This is accomplished by scrubbing the gas with a solution of caustic soda or suspended solutions of oxides of iron or lime.

5. In recovering gasoline from still vapors several different processes can be used:

(a) The compression process is the more common, and consists of compressing the gas to a high pressure and cooling. This condenses the gasoline vapors and does not materially affect any permanent gas which may be present.

(b) The absorption process consists of absorbing gasoline from the gas by passing it through a lower gravity distillate. When naphtha is used as the absorbent the naphtha is raised in gravity to the point where it may be marketed as gasoline. When a heavy gas oil distillate is used, the gasoline is separated from the gas oil by distillation.

(c) Combination of the two methods is made use of when the gas after compression is passed through absorption towers.

6. General figures are given on the cost of construction of recovery plants based on the capacity of the refinery.

-- Reports of Investigations, Bureau of Mines, Department of the Interior. --





