# Oil[1]

## II.—REFINING: THE WORK OF CHEMIST AND ENGINEER.

By A. B. Cox.

In its natural state petroleum as it comes from the interior of the earth has little usefulness. At best it can only be used for fuel, heavy cheap fuel, to burn in industrial plants in competition with coal and natural gas. The research and inventive genius of the " refining man " of the oil industry, chemist and engineer, were brought into full play to discover methods whereby this valuable resource—crude petroleum—could be turned into products of use to the world (in innumerable ways) and, as a result, the refining industry, or that part of the petroleum industry dealing with the treatment of crude petroleum from the time it is brought from the earth until it is ready for the consumer, has developed to a point where the value of its plants and processes amounts to more than £8,000,000 in investments in the United States alone.

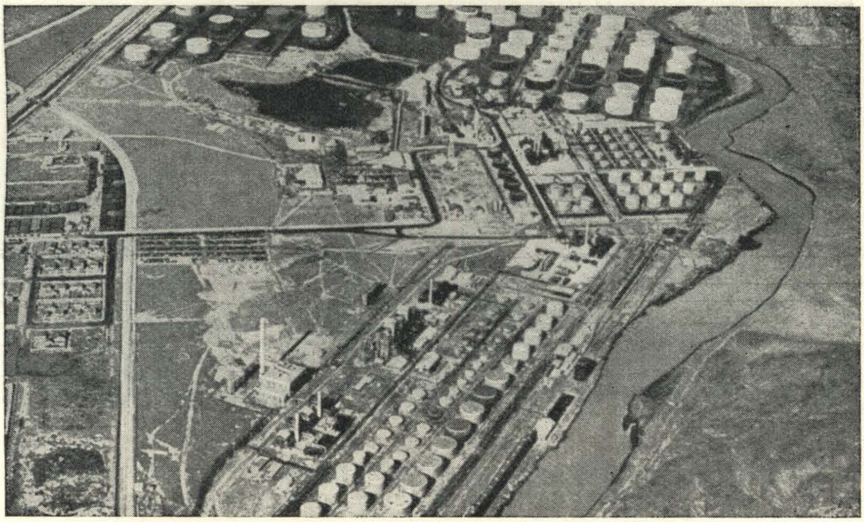

Fig. 1.

Texas Company's Los Angeles (California, U.S.A.) Refinery. Located two miles from Long Beach, California. Area : 262 acres. Daily crude capacity : 30,000 barrels. Daily cracking capacity : 5,500 barrels.

There, this branch of the industry employs more than 100,000 men, in some 600 refining plants with a capacity sufficient, if necessary, to refine more than 4,000,000 barrels (one barrel equalling 35 imperial gallons) of raw crude oil per day.

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[1] Part I appeared in the March issue, Vol. III, No. 1. It dealt with the geology of the subject.

Developed over a period of seventy-six years, the refining industry has grown to be one of the largest consumers—as distinguished from a fabricator, such as the automobile industry—of steel, cement, paints, chemicals, and one of the largest employers in many other industries, such as building and protective industries. In fact, it is difficult to name a material that is not used, to some extent, or a trade that is not employed in a modern refinery.

To accomplish the separation of the crude petroleum into the many products required for use by modern industry and for public consumption a complete refinery unit must necessarily comprise a great amount of equipment. Tank farms must be able to receive and store large quantities of crude petroleum, in proportion to their daily capacity, the method by which they receive the crude supplies, and the variety of crudes they are required to treat.

FIG. 2.
Texas Company's Tank Farm at Los Alamitos (California, U.S.A.). Fifty-four 118,000 barrel tanks containing 6,372,000 barrels of oil.

These large tank farms contain hundreds of tanks ranging in capacity from 55,000 barrels (1,955,000 imperial gallons) to 125,000 barrels (4,375,000 imperial gallons), and range in diameter from 114 feet to 125 feet and in height from 30 feet to 45 feet.

These tanks are cylindrical in shape, built of steel plates riveted together, and with steel roofs made gas-tight in order to minimise evaporation of the lighter fractions that would otherwise be " breathed " off into the atmosphere and lost.

Provision of storage for products during the process and for the finished products also requires many hundreds of tanks of all sizes. Crude storage is usually segregated in one large area called a " tank farm ", where all the tanks are set out symmetrically in rows, and pipelines are laid down from these tanks to the manifolds outside the pump house.

Many miles of pipeline are required in a modern refinery to move the crude from storage to stills, and the various products during the refining process, as well as to transfer the finished product to storage.

Over the comparatively few years of development the research and genius of the oil engineers and chemists has not only increased the number and quality of useful products that can be taken from a barrel of crude, but these scientists have worked equally hard and successfully to develop flexible refining methods that would allow oil companies to produce in greater volume the products for which there is the largest demand, and to keep down the manufacture of products which are in little demand. Today, for example, it is possible to secure yields of motor fuel, gasoline or petrol, as high as 75% of the crude, while twenty-five years ago the recovery was only 20%.

The old-time refiner had little (if any) knowledge of chemistry, and but a few known varieties of crude; his refining processes were comparatively simple, and involved mainly the application of heat and simple fractionation, which meant merely taking advantage of the physical characteristics of the crude to obtain the few and simple products that were at that period demanded by industry and the public.

The advent of the internal combustion engine, and later the larger and more complex industrial machinery, made demands upon the refiner for greater specialisation in products and for better "performance". The early refiner was concerned, principally, with the production of kerosene, of one or two light machinery oils, and of heavy cylinder oil for use in steam engines. The need for gasoline in ever increasing quantities and of improved quality, to keep step with improvements in internal combustion engines, brought into the industry the chemical engineer, and any improvements in refining process since that time have mainly come about through the application of the chemistry of petroleum.

The chemical engineer, through his research, developed the knowledge that certain results can be obtained in the breaking up of petroleum hydrocarbons, the processes involving high temperatures and consequently high pressures in order to separate certain molecules, to interchange them or change their position characteristics.

When it was found, by this research, what could be accomplished by distillation under pressure, the problem of constructing a "pressure still" 6 feet in diameter and 60 feet long to withstand a pressure of 800 pounds to the square inch (with suitable factor of safety) was one which engaged the best engineering brains in the country.

The first pressure stills were hand forged. Then it was found that the original valve was not suitable to stand this pressure and temperature, and special types of steel valve had to be constructed. The electric welding industry received its greatest impetus through the development of the equipment of oil refineries. It was found that previous methods of welding did not maintain a sufficiently high standard of efficiency to be depended upon when very high pressures and temperatures were taken into consideration, and an entirely new school of welding was developed within the oil industry.

The development of materials with which to construct this new equipment required the services of trained metallurgists, not only in the development of metals and alloys to withstand pressures and chemical action, but systematically to test the strength of all materials and of welded joints in order to maintain the necessary safety factor.

The need for a safety factor can readily be conceived when we visualise a split in the side of the 60 feet tower, operating under pressure of 600 pounds to the square inch, with the oil at a temperature of 1200° F. to 1500° F. (hundreds of degrees above its flashing temperature) released to the atmosphere and sprayed over the surrounding plant causlng almost instant incineration of everything in its path.

It is therefore just as necessary that the design of the equipment be such as to prevent failure as it is to carry out the process along the lines dictated by laboratory research.

Probably one of the most important problems in a modern refinery is the conservation of beat; because every B.T.U. of heat that can be recovered from products that have already gone through the distillation process and that can again be used in the heating of the cold charging stock amounts to a saving in fuel, in time, and in the reduction in the size not only of the furnaces, but in a corresponding reduction in the size of equipment components such as boilers, stills, condensers and pumping equipment.

When we think of the amount of heat required to raise the temperature of 7,000 gallons of crude oil from 60° F. to 525° F., and that this is supplied in one hour's time in order to maintain the outlet temperature of the single pipe still at 525° F., we get some realisation of the enormous amount of fuel that would be required in a refinery if there were no interchange of heat. Further, it must be realised that all of this added heat must be taken away from the finished products before pumping them to storage.

By passing the hot distillates through the heat exchangers in one direction and the cold charging stock through the same exchanger in the opposite direction (separated by a thin wall of metal), a large proportion of the heat from the hot distillates is absorbed by the charging stock, this process serving the dual purpose of bringing the charging stock to the tube still at a higher temperature, and of making it possible to reduce condenser capacity, thus saving water and equipment that would otherwise be required to cool the hot distillates before they could be taken into storage.

The design of these exchangers, and the metal of which they are constructed, to accomplish the maximum transfer of heat, have been the subject of a great deal of study and invention.

The treatment of crude petroleum (which may be defined as a mixture of hydrocarbons, consisting of many compounds of hydrogen and carbon, together with varying percentages of oxygen, hydrogen and sulphur) presents from a chemical standpoint the problem of breaking up, rearranging and recombining the constituents of these many compounds, so as to produce products of different volatilities ranging from gas (having the smallest, lightest or most loosely packed molecules) to, possibly, materials such as asphalt (having the largest, heaviest or most closely packed molecules).

In theory this sorting process is simple. It has been likened to the screening of coal; but crude petroleum is liquid, and even the largest of its molecules is infinitesimally smaller than the finest particle of coal dust.

The separation of molecules of different sizes in liquids of varying boiling points is brought about by applying heat and by segregating the condensate at various temperature stages; and this, in a general way, is what is termed "distillation process".

To understand the underlying principles of refining, a knowledge of organic chemistry is necessary, particularly that part applying to hydrocarbons, with their immense variety of different compounds, each having definite properties, definite molecular structure and definite proportion of carbon and hydrogen in this composition.

Without involving us in a discussion on organic chemistry, a description of some of the terms used may be of interest.

When we speak of " saturated hydrocarbons " we mean the paraffin series or chain compounds where each carbon atom is incapable of combining with or attaching itself to more hydrogen atoms. Likewise, reference to " unsaturated hydrocarbons " involves what might be termed " incomplete compounds " that are capable of absorbing more hydrogen, thus being converted to saturated hydrocarbons.

" Aromatic hydrocarbons " differ from the abovementioned hydrocarbons in that in their structure carbon atoms are in rings and are connected to but one hydrogen atom. Further, in many such compounds one or more of the hydrogen atoms may be replaced by other compounds or elements such as oxygen, sulphur and nitrogen, forming more complex molecules.

The variation of boiling point and of specific gravity in these different hydrocarbons makes it possible to separate them by process of distillation, whereby the smaller or lighter molecules are turned into vapour, and these vapours removed and condensed. By separating the condensate at various stages of temperature, products such as gasoline, kerosene, gas oils and lubricating oils are obtained. As the temperatures are increased the distillates become less volatile ; e.g. temperatures below 100° F. yield very light gases, temperatures of 100° F. to 400° F. yield gasoline or petrol, and temperatures above these give kerosene, gas oil and lubricating distillates.

Refinery distillation processes can be grouped under several basic heads classified in accordance with conditions and operating methods characteristic of each type. These are :

(1) Distillation by fire (meaning the application of dry heat).
(2) Distillation by steam (by which the heating is accomplished by the introduction of steam into the liquid).
(3) Distillation under vacuum (low temperature).
(4) Distillation under pressure (or what is generally termed " cracking process ").

In the early days of the industry distillation was carried out in " batch stills ", the earlier stills being of " cheese box " type. These were charged with a batch of crude oil, heat applied by fires, and distillates (condensed vapour) segregated by diverting the stream from the condenser to the various tanks as the temperature of the liquid in the still increased. The lighter fractions are the first to come over, being gasoline, then come the kerosene, gas oil, fuel oil, and finally the lubricating oil.

Before the invention of the internal combustion engine, and the consequent need for gasoline, the refining process was carried out mainly for the production of kerosene. All the lighter fractions taken off ahead of the kerosene were largely waste product.

Thirty-seven years ago the relation of gasoline produced to crude treated was 5·4%, while today over 40% of present production of crude is made into gasoline, by far the most important single product of the petroleum industry.

The old type " cheese box " still was quickly replaced by the " horizontal batch " still, and later by a " battery " of horizontal stills working continuously. These stills were about 10 feet in diameter by 40 feet long, erected horizontally on brick supports, with the fire box underneath.

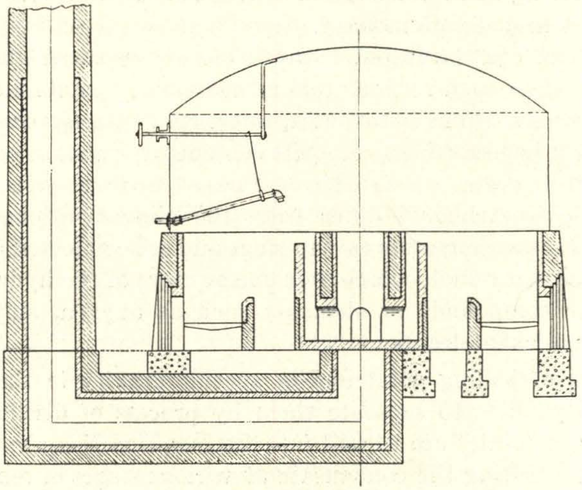

FIG. 3.

" Cheese Box " Still with conventional setting.

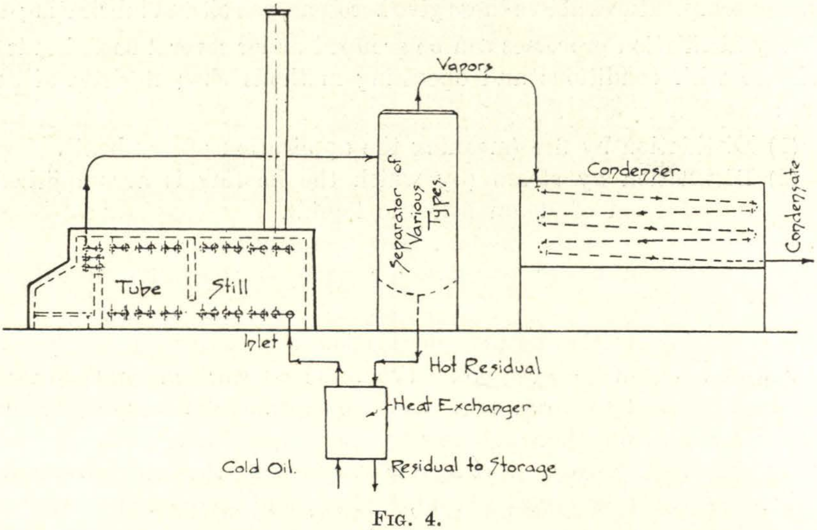

FIG. 4.

Diagram of Tube or Pipe Still.

From the top of the still a vapour line consisting of pipe about 12 feet in diameter is connected to a series of coils made of cast iron pipe contained in a steel box. This box is filled with cold water, and during the operation of the still a continuous stream of water flows through the box. This type of condensing equipment was often supplemented by " aerial condensers " consisting of a vertical series of coils dependent upon the air for cooling.

From the condenser, lines run to the receiving house, and the stream from the condenser passes through what is termed a " look box ", where the colour of the stream can be observed and where samples can be taken to determine specific gravity. These look boxes are so constructed that the stream can be turned into the various tanks (called " run down tanks ") according to the type of distillates required.

A battery of stills consists of a number of the same type of still erected close together, the No. 1 still of the battery being erected at the highest elevation and the other stills stepping down, each approximately six inches lower in elevation.

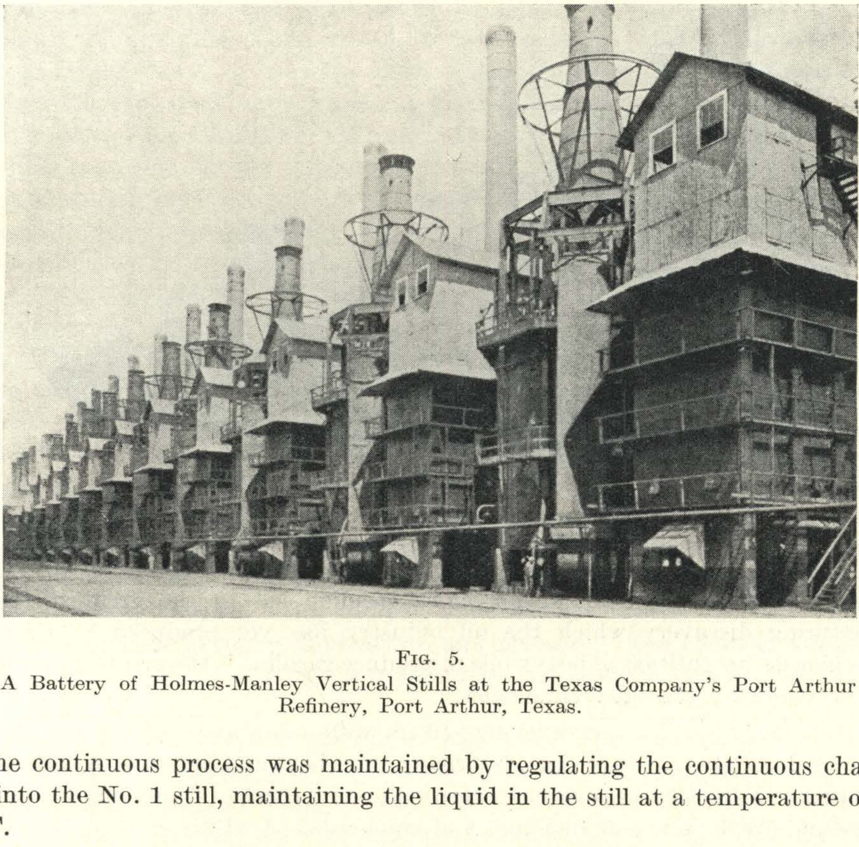

Fig. 5.
A Battery of Holmes-Manley Vertical Stills at the Texas Company's Port Arthur Refinery, Port Arthur, Texas.

The continuous process was maintained by regulating the continuous charge of crude into the No. 1 still, maintaining the liquid in the still at a temperature of, say, 400° F.

The product that was not distilled off at this temperature overflowed into the No. 2 still, which was maintained at a temperature of, say, 500° F. The liquid that was not boiled off at 500° F. overflowed into the No. 3 still ; and the process continued on down until all the distillates were removed, leaving in the last still the residuum, which might be cylinder stock, asphalt or coke, depending upon the type of crude being run, and the products required.

In many installations a stone tower was used, this being a tower 3 feet to 6 feet in diameter and 20 feet to 30 feet high, filled with broken stone of roughly six inches in size. The vapour line from the still was connected near the bottom of this tower, and from the top of the tower the vapour line was continued to the condensers.

A short distance down from the top of the tower was installed a cone-shaped reflector called an " umbrella ", and crude oil was pumped into the tower near the top, percolating down through the stone. Hot vapours rising through the stone were brought into contact with the cold crude, and some of the heavier distillates were precipitated. The lighter vapours, carrying some of the lighter fractions from the crude, passed on through and out the top of the tower to the condensers, where they were condensed into liquid. The stone towers were " hooked up " to No. 1 still of the battery.

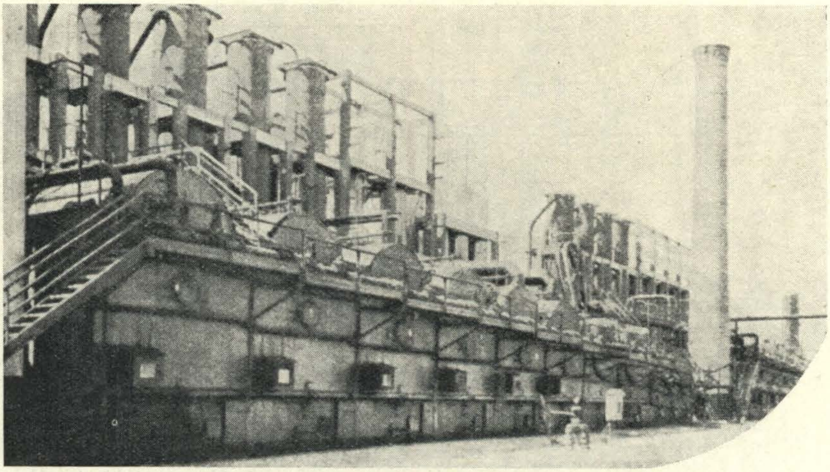

FIG. 6.
No. 4 Battery Crude Stills used for running South Texas Crude Oil.

The ever-increasing demand for more gasoline led to the greatest technical manufacturing discovery which the oil industry has yet produced. " Cracking " or molecular decomposition of heavy oils to produce gasoline is the greatest accomplishment yet made by the oil technologist.

In 1909-1912 the Burton cracking still, a wide adaptation of the old shell still used for all distillation at that time, but using more heat and pressure, was developed. By this means a fraction heavier than kerosene was " cracked " to yield 30% or more of a gasoline-like liquid, evil smelling, and coloured, but which increased by a small percentage the total gasoline recovered from the then increasingly scarce crude.

Other cracking processes were developed, and the shell still, slow in its yields, and producing a product far from satisfactory, was replaced by the pipe or tube still, which developed a speedier and more efficient means of vaporising large quantities of crude.

The pipe or tube still, consisting of many banks or coils of continuous pipe (through which a continuous stream of oil is forced), set in a chamber heated by highly efficient oil or gas-fired furnaces, made it possible to subject only a small amount of oil to the heat zone at a time ; this avoided the necessity of having huge bodies of oil under high temperature and elevated pressures for hours, with the consequent danger from failure of any of the metal parts of the containers.

Maintaining a steady flow throughout the pipe prevents overheating and carbon deposits in the tubes. This, together with high pressure, keeps the " crude " and the products for cracking as far as possible in a liquid state. The liquid leaving the tube still in some cracking processes passes through a reaction chamber ; in others it goes direct to a dephlegmator or " bubble tower ", where the pressure drop (from that maintained in the tube still of 200 to 900 pounds per square inch, down to 50 pounds or less) immediately converts the liquid to a vapour.

Dephlegmators or bubble towers vary slightly in design, but in general are 50 feet to 70 feet high and 6 feet to 10 feet in diameter. The vapour enters the column at a point about one-third of the way up from the bottom. The bubble tower is fitted with horizontal trays 12 to 30 inches apart. Each tray is fitted with " bubble caps ", and a liquid level of about three inches is maintained by the height of the discontinuous vertical discharge pipe leading down from tray to tray. The vapours pass up through the bubble caps, the heavier vapours condensing and the lighter vapours passing on through to the next succeeding tray above.

Condensates drawn off from the trays vary in distillation range, making it possible to select the desired fractions.

By the time the vapour has reached the top of the bubble tower it has cooled considerably, and the lighter vapours that have not condensed in the bubble tower pass on through condenser coils maintained at low temperatures to effect the condensing of these vapours. In some systems, to maintain proper degree of fractionation, cold gasoline is pumped into the tower near the top, giving a reflux action through interchange of heat between cold gasoline and the hot vapour.

A certain amount of vapour, because of its extremely low boiling point, does not condense, and this passes through a gas separator and from there it is brought into contact with an absorbing oil. Oftentimes " charging stock " is used as the absorbing material for " stripping " the gas. The condensate formed in the bubble tower is, in some processes, recycled, being pumped while still hot directly to a tube still, where it is again subjected to high temperatures and pressure. The effect of the recycling is to increase very considerably (in relation to the charging stock) the yield from cracking plants.

Where a distillate, such as gas oil, is employed in the cracking process, the yield by volume ranges from 60% to 70% of the raw material charged. Some cracking processes employ a vapour phase system, which differs from the liquid phase in that the vapours of the oil only are subjected to the cracking process. The vapour phase system has certain advantages in that the plant can be designed to operate at low pressures, and the product, as a rule, has a very high " anti-knock " property, placing it at a premium for use as a blending stock for raising the anti-knock properties of lower grade gasolines.

Unlike most manufacturing plants, where the materials can be followed closely through each process, in a modern refinery the observer is told that crude is being charged, that the bubble tower is working, but he sees nothing but the silent equipment absorbing enormous quantities of heat and steam, and apparently producing nothing.

As a visiting scientist once remarked : " I know that thousands of barrels of oil are going through this equipment, but I can't see it."

In modern practice it may be said, generally, that the gasoline produced in a refinery consists partly of the straight run product from stills carried at atmospheric pressure and partly of cracked gasoline, each from a variety of crudes having different characteristics and properties from the standpoint of anti-knock quality, colour stability and distillation range.

Depending upon the characteristics of crude and the distillates obtained, it is necessary further to treat some of the gasoline by " steam stilling ", where the product is again heated by the introduction of steam into the liquid, again vaporising the product, portion of the vapour being carried over mechanically by the steam, and all of it recondensed.

The result of the steam stilling is to remove certain of the objectionable unsaturated hydrocarbons, increasing colour stability and making the product more satisfactory for use in internal combustion engines.

Likewise, the presence of various sulphur compounds makes it necessary to treat someof the gasoline with acid or with "doctor solution" and with flowers of sulphur. Some of the sulphur compounds can be removed from petroleum by washing in sulphuric acid. Nitrogen compounds generally exhibit alkaline properties, and can be removed by washing with sulphuric acid. This treatment is carried out in agitators, which may be of the batch or continuous types, wherein the gasoline is brought into contact with sulphuric acid, after which the sludge is settled out and the oil washed and neutralised with an alkaline solution.

The doctor solution consists of a mixture of caustic soda and litharge. Flowers of sulphur are used to complete certain of the incomplete compounds in the product.

The gasolines obtained from various processes of stilling and treating are then blended to obtain the high quality product that is necessary to give maximum efficiency in the modern internal combustion engine. In the blending of these products consideration must be given to the lowest boiling point fractions, maintaining some sufficiently low to make starting easy ; and yet they must not be so volatile as to be quickly lost by evaporation. Distillation range must be kept at an " even curve " to give maximum acceleration and smooth power. Anti-knock quality must also be given considerable consideration in order that optimum efficiency in the modern high compression engines may be obtained.

The refiner with a variety of products to select from, and with sufficient flexibility in his manufacturing process is, therefore, in a position to blend and deliver for public consumption a high quality product that will give this maximum efficiency.

(Part III will appear in the next issue.)