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CHEMISTRY AND THE PETROLEUM INDUSTRY

MANY of the earlier races of mankind had some knowledge of petroleum and its allied substances. For example, there is a tradition that petroleum was used in the making of mortar for the Tower of Babel, while Herodotus is authority for a similar use of bitumen in the building of the Walls of Babylon, and the Chinese record their own use of natural gas for fuel and light before the Christian era. But the petroleum industry, as we know it, is preëminently a modern industry made possible by developments begun in the nineteenth century, and in progress to this very moment of the twentieth century, in engineering, geology, physics and chemistry.

Chemically, petroleum or rock oil is a liquid consisting predominantly of a mixture of hydrocarbons of several different series. The composition varies greatly from region to region where the oils are found. Some petroleums contain compounds of the paraffin series only, while others may have members of the olefin, acetylene, benzene, naphthene and cyclo-paraffin groups. Four hundred and forty-five of these compounds have been tabulated, but of this number not more than two hundred have been isolated in a reasonably pure state. Some of these compounds have been shown by Mabery to have a molecular weight as high as 1700. It is of interest to note that compounds of the paraffin series are found in the lighter fractions of almost all

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petroleums. These with the exception of methane, ethane and propane are present in and constitute the major portion of commercial gasoline.

In addition to hydrocarbons, petroleum contains sulphur in the free state and combined either with hydrogen alone or with both carbon and hydrogen. Nitrogen is always present but in widely varying amounts from traces up to 1.5 per cent. The oil as it comes from the well may be accompanied by water containing salt. In some cases the water will separate and may be drawn out from under the oil; while in others, the water and oil are emulsified and can be separated only by a special treatment to which reference will be made in a later section of this lecture.

The question of the origin of petroleum and natural gas has received the attention of many distinguished chemists and geologists. The various theories which have been formulated from time to time may be divided into three groups: first, those which attribute to petroleum an inorganic origin; second, those which consider it as derived from the decomposition of land vegetation; third, those which regard it as a product of decay of marine vegetable or animal matter, or of both.

The first to advance a general inorganic theory was Berthelot, who, proceeding upon the hypothesis of Daubree that the interior of the earth contains free alkali metals, ascertained, by experiment, that when carbonic acid or an earthy carbonate comes in contact with the alkali metals at a high temperature, acetylides are formed which will yield hydrocarbons when acted on by water under suitable conditions. He therefore expressed the view, in 1866, that petroleum may have been produced by filtration of water containing carbonic acid gas into the interior of the earth, where it would come in contact with alkali metals at an

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elevated temperature, under great pressure, and produce both liquid and gaseous hydrocarbons. In 1879 Mendeleef published his notable paper on the inorganic origin of petroleum. He ascribes its formation to the action of carbide of iron at high temperatures in the interior of the earth upon water which has penetrated through fissures produced in the earth's crust by the elevation of mountain chains, or by other changes. Both of these theories are considered inadmissible by geologists.

The second school, noticing the relation between petroleum and the oils obtained by distillation from peat, lignite and coal, believed that petroleum originated in one or all of these materials, but this theory had soon to be abandoned by the majority of observers. The objections to the theory that petroleum has been produced from coal are strengthened by the fact that the largest deposits of the former are situated in strata of a period which was not coal-forming, and are usually far distant from coal deposits. It is possible, however, that the particular land plants which are rich in fats may have contributed in some small degree to the production of petroleum.

Finally, there is the more generally accepted theory of Engler which considers petroleum to have an organic origin from marine organisms, both animal and vegetable. The limestones, conglomerates and sandstones serve as porous containers for the oil that is formed. In view of the circumstance that there is an alternation of similarly porous beds free from, and saturated with, petroleum in the California, Tennessee and Texas fields, it is evident that this material cannot have been derived from overlying or underlying beds, but has been generated by the transformation of organic matter in the strata in which it is found. The forms in which petroleum now occurs depend in large

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measure upon the presence or absence of atmospheric oxygen, since, by oxidation and volatilization, the naphtha or petroleum is slowly changed into asphalt or mineral pitch. In these extensive layers of porous earths and shales, there is a vast repository of hydrocarbonaceous matter which may eventually be made to yield an enormous quantity of oil by artificial distillation. Like all other organic matter, this is constantly undergoing spontaneous distillation, except where hermetically sealed deep under rock and water. Such evaporation or distillation has converted the animal and plant remains into oils, the light oils into heavy oils, and these into asphalt and other solid bitumens, the process being accompanied by the evolution of gas. The animal remains in the shales, like those of Texas, the large amount of nitrogen in the oil, and the fact that the fresh oils when exposed soon become the home of the larvæ of insects, support the theory that these types of bitumen are of animal origin. On the other hand, the petroleums of New York, Pennsylvania, Ohio and West Virginia are supposed to be of vegetable origin.

Some experimental evidence has been obtained which lends support to the Engler theory. By fractionation of the distillate from a lime soap of menhaden fish oil, Warren and Sotrer, in 1865, obtained members of the methane, ethylene and benzene groups, such as are found in petroleum. In Japan, petroleum has been prepared experimentally by dry distillation of fish oil with acid clay. Since such clay is found in all the Japanese oil deposits, it is concluded that Japanese petroleum had its origin in marine animals. This is in accord with the Engler theory which presupposes several stages in the formation of petroleum: First, putrefaction takes place, by which albumen and cellulose are eliminated, leaving fatty matters and waxes. The fats are

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then saponified, probably through the action of water, forming free fatty acids; and the waxy esters are either wholly or partially hydrolyzed. Carbon dioxide is next eliminated from the acids and esters and water from the alcohols, leaving hydrocarbons of high molecular weight. Finally, there is a forming of liquid hydrocarbons; the accompanying violent reactions causing "cracking" into lighter and gaseous products.

If Engler's theory of the formation of petroleum is accepted, it follows that none of this product can be present in certain parts of the world. For instance, no petroleum will be found in the immense regions occupied at the surface by rocks of the Archean or Algonkian age, or in those of later periods that are entirely of an igneous or intensely metamorphosed character. Thus, perhaps half of the earth's surface is ruled out at the start. Oil has been removed by natural means from formations of even moderate metamorphism. For example, the strata of the greater part of the Appalachian Mountain system, and other mountain masses, formed previous to Mesozoic time, are folded, faulted and broken and to an oil geologist are obviously unfavorable for oil, the latter having been removed during the mountain-making process.

Conditions essential to the occurrence of petroleum may be stated in the order of their importance: The presence of rocks of sedimentary origin and an absence of intense metamorphism; sandstones, limestones, sands or other strata that are sufficiently porous to hold oil; some source from which the oil may have been formed; such water conditions as not to prohibit the accumulation of oil in pools; suitable cover to prevent the oil from seeping away or being pushed to the surface of the earth by underground waters; and finally, a suitable structure to cause oil to be collected

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locally into pools, with the assistance of such other factors as water, gravitation and rock pressure.

For the occurrence of petroleum, strata of suitable character are essential in order to assure a reservoir, except where there is some substitute for porosity, either in the cavernous nature of the stratum or in the presence of joint-cracks or cleavage planes. Ordinarily the productive stratum consists of sand or sandstone in which the interstices between individual grains furnish the pores. In the case of sandstone, the location of an accumulation is determined not only by structure but by the degree of continuity of the stratum, positions of old shore lines, etc. Not all sandstone throughout an oil region contains oil, even when other conditions are favorable, one essential requirement being that the individual grains shall be sufficiently rounded to make the bed porous and that they shall be comparatively uniform in size, rather than an indiscriminate mixture of grains of all sizes as in the case of many conglomerates. Experimental tests on oil sands and other rocks have been made which showed that productive sands seldom have a porosity of less than 10 per cent., while it may be as high as 30 per cent.

Until a few years ago, geologists and chemists were unable to explain the absence of oil from the regions adjacent to some of the principal mountain systems in the world; and no exact guide had been discovered by which they could delimit the regions where oil may be expected from those where it does not exist. In 1915, however, White published a paper showing that in regions where coal-beds exist, the percentage of fixed carbon decreases in a regular manner from the anthracite regions, or regions of highly bituminous coals, to the softer bituminous coal regions, and that in travelling from soft to harder coal regions this ratio passes

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a line beyond which no commercial oil fields may be expected. This branch of the science is still in its infancy, though it has already been used to considerable advantage. Where these ratios have been studied and used it has been found that oil fields of commercial importance seldom exist beyond the 65 per cent. line and that commercial gas fields seldom exist beyond the 70 per cent. line.

While the evidences of the occurrence of oil which are commonly noted by the geologist, chemist or petroleum engineer are not such as are ordinarily seen and comprehended by the layman, there are, however, in most oil fields, certain surface indications which may have a definite bearing on the existence of oil, either in that particular locality or at a distance. The principal surface evidences may be classified as follows: oil seepages or oil springs; natural gas springs; outcrops of sandstones or limestones impregnated with petroleum or bitumen; bituminous lakes or other bituminous seepages; bituminous dikes; mud volcanoes; burned clays; occurrence of salt; and occurrence of sulphur. Any one of these frequently has some association with oil, but oil may occur at a great distance from the point where the evidence appears on the surface. To illustrate, it is a fact that a formation which reaches the surface of the ground at a particular point, and from which seepages of oil, gas or asphalt are seen to emerge, may descend at such an angle that the locality structurally favorable for the accumulation of oil lies many miles from the exposed outcrop. For this reason, it is generally poor policy to drill on or near seepages unless evidence exists that the main deposit of oil occurs directly below.

As previously noted, salt is frequently associated with petroleum. Water which accompanies petroleum is generally more saline than that normally present in sedimentary

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rocks. On the other hand, extensive masses of salt often exist entirely unassociated with oil. Consequently, recent theories of the origin of oil have in the main ignored any relationship with salt as a factor in the process even though in many Ohio, Texas, Louisiana and Roumanian fields, oil is associated with salt in such a manner that there appears to be a direct relationship. The credit of having discovered the closed saline-dome type of geologic formation containing oil, is due largely to Captain Lucas who, in 1901, drilled at Spindle Top and opened that well-known well. While this structure is typical of most of the Gulf Coast fields, it must not be supposed, that the presence of the geologic structure known as a saline dome is always indicated on the surface by a topographic dome, as many saline-dome pools are situated where the surface is practically flat. Even in the case of the Spindle Top dome, the bulge on the surface is only a few feet in height. Whether or not there is any particular surface topography indicative of a dome in a locality of this class, there is a very marked upward bending of the strata as they approach the edge of the dome.

A marked increase in the value of Geology to oil development is due to the evolution of the "Structural Theory" of oil occurrence proposed in 1910 as an offshoot from the original "Anticline Theory" of Hunt, suggested in 1861. This theory may be stated briefly as follows. By some organic or inorganic agencies, the petroleum and gas have come into, or been generated in, the porous formations in which they are found. The oil, gas and water in the formations—assumed to have been approximately horizontal at the time these substances entered them—were at first widely diffused in the porous formations. In many parts of the world they have remained in their diffused condition up to the present time. Here only small quantities of oil and

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gas, too slight for profitable development, have been found, and the dip of the rocks is very slight. Where beds have been folded, however, as in most of the oil fields of the world, the oil, gas and water have been allowed to separate and arrange themselves according to their relative specific gravities. This separation and concentration may have been assisted by rock pressure, hydraulic pressure, seepage, capillarity, molecular attraction, internal heat or other causes.

The application of chemistry to the petroleum industry is confined for the most part to what is known as the refining process which begins with distillation. The art of distillation is an old one. It was practised by the ancient Egyptians, and the alchemists of the Middle Ages made use of it in their endeavors to find the elixir of life. It is not surprising, therefore, that distillation was employed at an early date in refining petroleum for medical purposes. It is certain that petroleum was distilled in Russia in the eighteenth century and probably earlier, for Johann Lerche, who visited the Caspian district in 1735, found that the crude Caucasian oil required distilling to make it satisfactorily combustible. What is said to be the first attempt to make kerosene from petroleum was carried out in 1823 in a refinery erected by the Dubinian brothers in the village of Mosdok. About the year 1850 Baron Thornau secured the services of the famous German chemist, Liebig, in designing a plant for refining Russian petroleum.

The beginning of the petroleum industry in the United States may be said to date from about 1826, when Dr. S. P. Hildreth visited the oil springs of Ohio and reported that petroleum had great possibilities as an illuminant. A little later Seneca oil and American medicinal oil were put on the market and widely advertised as sure panaceas for most human ills. As early as 1833 Professor Benjamin Silliman,

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of Yale College, had carried out a number of distillations of petroleum in glass retorts; but his most important investigations were made on a sample of oil submitted by the Pennsylvania Rock Oil Company, a corporation formed in 1854 for the purpose of procuring surface oil near Titusville by the method of digging and trenching. Silliman's report, published on April 16, 1855, is a classic document on the chemical technology of petroleum. It brought out not only the economic value of oil but furnished information on the chemistry of petroleum which is of fundamental importance in modern refinery practice. Among other things, Silliman showed that petroleum differs essentially from the fatty oils and can not be regarded as a drying oil. The variation in the boiling point of fractions upon distillation proved that the distillates were mixtures containing many different compounds. Temperature alone was found sufficient to change the constitution of a large number of the compounds and to produce new compounds that were not present in the original sample. After the first distillation, all fractions contained a very small quantity of free acid which could be removed with weak alkali and water. The distilled oil did not attack clean copper, which showed the absence of corrosive properties and therefore indicated that it could be used for lubrication. Distillation at higher temperatures in a copper retort led to the production of a thick mass of pearly crystals of paraffin which could be separated and made into candles.

Even with all the valuable information furnished by Silliman, the Pennsylvania Rock Oil Company was not successful because of the high cost of obtaining the crude oil. However, in 1857 the idea was conceived of drilling through the rock for oil in the same manner as that used in drilling for brine. The result was the drilling, in 1859, of the

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Drake well, which yielded about twenty-five barrels of oil per day. The success of this venture spread like wildfire and in a relatively short time drilling operations became common and there was a large production of oil.

Since the days of Silliman, petroleum research has lagged behind the rapidly growing industry. This is due in large measure to the manner in which the industry has developed. For many years the manufacturing problem was comparatively simple. The principal products of the refinery were kerosene, lubricating oil and paraffin wax. Gasoline was then a by-product for which but little use could be found, and most of it had to be wasted. There was, therefore, no incentive, borne of necessity in the industry, for research of a fundamental nature.

The first serious chemical problem of the industry came, without warning, when the Lima oil of Ohio was discovered. On account of its high sulphur content and its accompanying sulphurous odor this oil could be used for fuel purposes only. Canadian oil was of the same type. The problem of refining these oils was finally solved by Herman Frasch, who found that the sulphur and odors could be removed by heating the oils with copper oxide during the process of distillation. The researches of Frasch increased the value of these oils about seven-fold.

The problem of the refiner is to fill the demands made upon him for the many different grades of petroleum products now required by the industrial and scientific world. Originally, the crude petroleum was broken up into its fractions by dry distillation—that is by heating the oil directly and then condensing the various fractions as they came over. Later, steam distillation was found to be more efficient. By blowing superheated steam into the oil the fractions come over at a lower boiling point, thereby

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preventing any overheating of the contents of the still and thus securing much better distillation.

The fractions obtained from distillation are separated empirically. Thus, by distilling and then redistilling the original fractions, such commercial products are obtained as petroleum ether, naphtha, gasoline, kerosene, gas-oil, stove distillate, fuel oil, lubricating oil, lubricating grease, paraffin, asphaltic residue, tar, etc. Before the time of the automobile, refineries used to attempt to pass off gasoline as kerosene and many disastrous explosions resulted. Now the conditions are reversed and much of the so-called kerosene of yesterday is being sold as the gasoline of to-day.

Each fraction, as it distills, contains impurities that may be detrimental to its use. Thus, gasoline is treated to remove sulphur and nitrogen compounds so as to improve its quality, odor and color; lubricants are treated to remove carbon and sulphur and to improve their appearance. Sulphuric acid is most frequently employed as the purifying agent. In the process, the distillate is agitated with a dilute solution of acid which gradually attacks the resinous and tarry bodies found in the distillate, partly decomposing them and partly absorbing them in a complex mixture which, on standing, separates as a dark brown layer below the unaffected hydrocarbons. Some of the sludge remains in the oil through adherence to the agitator or through incomplete separation. Many hydrocarbons form unstable compounds that are somewhat soluble in the oil. These conditions may result in the formation of stable emulsions during the process of washing. The addition of a small amount of water-soluble soap, and agitation with steam, will often break down such emulsions. Air may then be used to rid the oil of the haze that still persists. The acid treatment is followed by

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washings with dilute alkali for the purpose of neutralizing any acid that may remain.

Other chemicals, in addition to sulphuric acid, that are used in treating certain petroleum distillates to improve their color or odor are sodium plumbate, stannic chloride and calcium hypochlorite. In certain cases decolorization is accomplished by the use of absorbents such as Fuller's earth, Florida earth, bone and blood charcoal, etc.

Attention has been called to the fact that petroleum may contain large amounts of water emulsified in the oil. These emulsions must be broken down and the water removed before the oil is subjected to the distillation process. Various methods are employed to bring about a coalescence of the highly dispersed, colloidal droplets of water. Electrical methods are used with certain emulsions, while with others precipitation of the water is effected by the addition of electrolytes such as acids and iron salts or of water-soluble colloids such as sodium oleate. A commercial treating agent known as "Treatolite" consists of sodium oleate, sodium resinate, sodium silicate, phenol, paraffin and water. Heat alone causes some of the less stable emulsions to break down completely.

Probably the most important problem with which the petroleum technologist is confronted at the present time is the production and conservation of a maximum quantity of the highly volatile fractions that enter into commercial gasoline. The specifications for a satisfactory motor fuel require a certain ratio of light to heavier fractions and the supply of gasoline is determined by the supply of the lighter constituents. As far as the refiner is concerned the only direct means of increasing the more volatile fractions is the process of "cracking." By this is meant the breaking down

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of hydrocarbons of high molecular weight into lighter compounds, by the application of heat and pressure.

Although Silliman discovered, in 1855, that petroleum can be cracked, the first cracking process which was successful in producing gasoline on a large commercial scale was worked out many years later by Dr. W. M. Burton and his associates. This process consists essentially in heating gas or fuel oil under pressure. Beginning in 1906 processes were designed for heating the vaporized oil under pressure. One of the most recent developments is the use of catalytic agents such as anhydrous aluminum chloride and finely divided copper, which give a higher cracking efficiency.

In all cracking processes, both saturated and unsaturated hydrocarbons are produced. Since the unsaturated bodies react with sulphuric acid, the usual method of refining cannot be employed without entailing considerable loss of valuable gasoline constituents. To avoid this waste, cracked gasolines are desulphurized and decolorized by filtration through such media as silica gel, Fuller's earth or dehydrated bauxite containing one per cent. of finely divided copper or copper oxide.

There is considerable prejudice against cracked gasoline in the minds of many refiners and of the public in general; but this prejudice is not justified in view of the results obtained. The percentage of unsaturated hydrocarbons contained in cracked gasoline is usually higher than in gasoline derived from straight distillation; but the presence of such compounds is not objectionable providing the final product is suitably refined. Indeed, many writers consider cracked gasoline to be superior to the natural product as a motor fuel, since the former burns longer and delivers power during the entire stroke of the piston.

All the cracking processes now employed for making gaso-

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line produce a considerable quantity of fixed gas which consists of saturated and unsaturated hydrocarbons. Working under assigned patents, the Standard Oil Company of New Jersey has developed and is operating a process for making higher alcohols from the olefines that are found in these fixed gases. This development has placed on the market a series of higher alcohols all of which have hitherto been exceedingly rare. It is now known that petroleum like coal tar affords a veritable mine of organic compounds—either furnishing the bases for making the compounds or the intermediates by which they can be prepared.

Unfortunately the domestic supply of petroleum is being cut down very rapidly by the enormous increase in the rate of production. In 1859 but two thousand barrels of crude oil were produced; in 1875 about nine million; in 1900 about 64 million; in 1910 about 210 million; in 1920 about 444 million; and in 1923 the enormous total of about 735 million barrels. In addition to this tremendous domestic output, 82 million barrels of crude were imported in 1923. It is of interest to note that the imports in 1923 were 45 million barrels less than in 1922. This marks the first large decrease since imports began in 1909, and emphasizes the changed conditions in Mexico and the falling off in the production of its Southern Field. In 1923 imports of light oil from Mexico constituted approximately 11 per cent. of the total as contrasted with 68 per cent. in 1922.

For the first few months of the year 1923, indicated deliveries were greater than production, but later they did not keep pace with the increasing output and between April and November were less than production. However, the sharp decrease in production during December reversed conditions and deliveries to consumers were almost equal to the production plus imports. Prices of crude oil in 1923, reflecting

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the conditions of oversupply, trended downward. On November 8th, the price declined to the low level reached during the deflation in 1921. However, in January, 1924, after the December decline in production and apparently, in anticipation of the decreasing supply, the market value had increased 25 per cent. of its low mark in November. The year 1924 opened with a distinct change in general conditions. Production, having been sharply checked, was soon less than consumption, so that it was necessary to draw on stocks. The peak of production may have been reached in 1923 and concern with regard to the condition of oversupply may soon give way to anxiety as to a source of petroleum adequate to meet the ever growing demands. But from virtually every producing field in the country and many prospective ones, come reports of preparations for greatly increased drilling activity. Many in the industry do not see any definite indication that a serious situation is imminent. It is pointed out that crude production, despite the falling off in the big fields in 1923, is now running approximately 200 thousand barrels daily above the output of this time last year, while at that time there was an additional 200 thousand barrels going into storage every day. All the large companies are expanding their plants and are building storage for vast amounts of crude. When there was a flood of crude and the price was low these companies bought crude and put it in storage. The fact that stocks are being drawn from storage at the present time, would seem to indicate good business judgment on the part of the refiners inasmuch as the cost of the stored oil was much less than the present market value of similar crude.

Whatever may be the condition, there certainly is need for conservation of this enormously valuable national resource. That gasoline constituents can be extracted from

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natural gas and casinghead gas has long been known, but their recovery has become of commercial importance only within the past few years. In 1904 there were only two small plants producing casinghead gasoline; in 1911 there were 176 plants; in 1920, 650 plants produced 483 million gallons. The Bureau of Mines found that at 13 refineries, from which data were collected, 129 thousand gallons of gasoline were in 1921 being recovered from uncondensed vapors. And yet the magnitude of losses resulting from non-condensation of still vapors has been realized by only a small proportion of the refiners. The Bureau of Mines states further that 141 billion cubic feet of casinghead gas were lost during 1921.

Probably the greatest loss of gasoline at the refineries occurs through evaporation from storage tanks. On finished products, this loss is especially serious since it is at the expense of the most volatile fractions. Tests carried out at various refineries have shown that the average gasoline in standard steel tankage will lose about 6 per cent. per year, equivalent to over \$20,000 for each 55,000 barrel tank. The obvious remedy for this is to provide means for keeping the tanks cool, for preventing diffusion, and for collecting and recovering the vapors. The Standard Oil Company of New Jersey has perfected a mixture, "Sealite", which consists of glucose, starch, glycerine, glue and calcium chloride well beaten with air. This product floats on the oil and so diminishes evaporation; it is insoluble in the oil, is incombustible and non-drying. Floating roofs for oil tanks are also in use which keep the free volume above the oil at a minimum. The tanks should be painted white since the increase in temperature due to absorption of heat was found by experiment to be nearly twice as great if dark instead of light paints are used.

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Efficient fire protection is also necessary. Texas, alone, lost nearly a half million barrels of oil by fire in 1923. Originally the refiner placed his chief reliance on steam as a means of extinguishing fires. Unconfined tank fires yield quite easily to a blanket of carbonic acid foam which is produced, on the spot, by the generation of carbon dioxide in an organic extract. The foam expands and spreads rapidly over the surface of the burning liquid—each bubble being a high non-conductor of heat.

Losses at the refinery and in transportation do not represent all the inefficiency and waste. Tests made by the Bureau of Mines on a large number of motor vehicles, to determine the amount and composition of the exhaust gases produced under various operating conditions, have shown that the average automobile and truck as used in service, waste from 20 to 30 per cent. of gasoline by incomplete combustion. At least 50 per cent. of this loss can be prevented by correct carburetor adjustment. The average Ford touring car, driven under normal conditions, gives not more than 17.5 miles per gallon of gasoline; and compared with other cars, it should give 24 miles per gallon. One cause for this inefficiency is the present carbureting system which can be improved so that 25 miles per gallon may be obtained. If this one improvement were applied to all Ford cars in this country it is estimated that 400 million gallons of gasoline would be saved annually.

According to thermo-dynamics, both the torque and fuel economy of an engine are increased as the compression is raised. Logically, then, the next step is to decrease the clearance volume above the piston, thus increasing the pressure at which the fuel mixture undergoes combustion. But such a procedure gives rise to a violent "knock" in the engine, the intensity of which increases with the pressure.

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It has been found recently that this "knock" can be eliminated by the addition to gasoline of a small fraction of one per cent. of such compounds as tetra-ethyl lead and di-ethyl selenide. The effect of these compounds is probably due either to an increasing of the critical pressure at which detonation takes place or to a decreasing of the rate of combustion, so that no detonation occurs. So-called "anti-knock" or ethyl-gas gasolines are gradually being placed on the market by all the oil companies. This discovery gives an opportunity for revision in the design of gasoline-fired, internal-combustion engines so as to greatly increase their efficiency.

Although the supply of motor fuel that can be obtained by the present method of production is limited, there appears to be an almost inexhaustible amount locked up in crude oil in the strata, in shales and in the vegetable kingdom. About 75 per cent. of the oil in productive sand cannot be obtained by present methods of extraction. The Bureau of Mines, after a survey of the oil districts of California, estimates that over two million barrels of oil could be obtained from sand piles about the producing wells and from the outcroppings in the vicinity of the fields. The mining method seems to be especially applicable to the winning of oil in the numerous cases of upper oil sands not sufficiently productive to be of commercial importance by present drilling methods. Non-productivity of these upper oil sands may not be due to a scarcity of oil. It is possible that the oil is too viscous to flow or that there is insufficient gas pressure to force it out of the sand. In Alsace, there has been much success in the oil-mining venture.

Another depository of fuel oil is the oil-shale that occurs in enormous quantities in nearly all countries. Recently England has found in Northwest Somerset vast deposits

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that are located in a position particularly favorable for cheap mining. From each ton of shale 40 gallons of oil can be distilled. Practical mining engineers are of the opinion that there is a sufficient supply of oil in that area to meet the entire requirements of the United Kingdom for scores of years to come. Even now the shale deposits of Sweden are accessible enough at a cost of production that makes possible competition in the open market with crude oil from wells. The enormous deposits in South Africa yield as high as 100 gallons of oil per ton of shale. There are a number of rich deposits of oil shale in this country. Colorado shale gives a yield up to 65 gallons of oil per ton. Moreover, it may be remarked that oils obtained from shale have better lubricating values than those obtained from free petroleum.

Coal is another source of future oil supplies. If coal is carbonized by a low temperature process there is obtained: coke, gas, sulphate of ammonia for fertilizer, creosote, benzol, gasoline and kerosene, lubricating oils and greases, and a final residual oil which may be utilized as a fuel oil. The available benzol and motor fuel per ton of coal is about 12 gallons as compared with 4 gallons obtained by the usual high temperature process of carbonization. It is said that this material, from both a chemical and physical standpoint, is a true gasoline. If one-half of England's coal, as now consumed, were distilled, one-third of England's entire consumption of motor spirit could be obtained from the process. By this means, Germany derives the major part of her liquid fuel supply.

Vegetation offers a source of large quantities of liquid fuel, the utilization of which awaits only a proper cheapening and simplification of the process of converting cellulose to alcohol. Plants manufacturing alcohol from waste wood

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have been in successful operation in this country for some years. These plants obtain a yield of from 15 to 25 gallons of alcohol per ton of dry wood at a cost approaching the price of gasoline.

It should be pointed out, in conclusion, that the problem of increasing our motor fuel supply from sources other than petroleum is not sufficiently urgent at this time to demand the serious attention of technologists. However, with a gradual decrease in the output of petroleum the chemist and engineer will be forced to turn their attention to the efficient production of substitute fuels.

From this brief survey of the petroleum industry and the rôle that chemistry has played in its development, we must recognize that from the time of the first "commercial discovery" of oil in the United States, the resulting industry has been undergoing continuous development and expansion. The pioneers of this industry have been engaged in a contest of discovery, investigation and invention which has brought forth systematized methods in the production and utilization of petroleum. Looking backward, we may say of these pioneers that their spirit of adventure into the unknown recesses of the earth and their tireless efforts in laboratory and plant have been of immeasurable value to the people of the world. With their record behind us, we, in turn, face a future in which there will be universal demand for greater efficiency and economy in the production and utilization of a wasting asset. And we may look forward to a higher goal of scientific achievement in developing to fuller degree both the petroleum resources or those other natural resources which must be called upon eventually to contribute towards supplying the ever-increasing demand for motor fuels.

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