SCIENCE

Vol. 91 Friday, June 7, 1940 No. 2371

SCIENCE: A Weekly Journal devoted to the Advancement of Science, edited by J. McKeen Cattell and published every Friday by

THE SCIENCE PRESS
Lancaster, Pa. Garrison, N. Y.
New York City: Grand Central Terminal

Annual Subscription, $6.00 Single Copies, 15 Cts.

SCIENCE is the official organ of the American Association for the Advancement of Science. Information regarding membership in the Association may be secured from the office of the permanent secretary in the Smithsonian Institution Building, Washington, D. C.

PROGRESS IN PETROLEUM[1]

By Dr. GUSTAV EGLOFF

RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY, CHICAGO, ILLINOIS

Crude petroleums range from almost pure gasoline to solid asphalt as produced in the oil fields of the world. They have odors ranging from the rose and musk to a vileness greater than the skunk. Their colors when viewed in transmitted light vary from cherry, amber, yellow, green and reddish-brown to dense black, and under reflected light some crudes are highly fluorescent. Crude oils are composed of paraffinic, olefinic, naphthenic and aromatic hydrocarbons. Many crudes contain sulfur in combination with the hydrocarbons—in amounts from traces to more than six per cent.—while nitrogen and oxygen varies from 0.1 to more than one per cent. Traces of metals such as platinum, gold, silver, uranium, vanadium and titanium have been found in some crude oils. A few Rumanian crude oils are highly radioactive.

Crude oils are literally a wonder source of substances that are the foundation stone of a number of industries with many more to come. Their effect ramifies throughout our social and economic life and they will be a controlling factor in ultimate victory in a world aflame.

A forward-looking group of executives, chemists, physicists, engineers, and a host of other professions have made the oil industry what it is—a $14,000,000,000 organization in the United States. An amazing amount of research is going on in every branch of the industry at an expenditure of over $100,000,000 a year in order to discover and transport crude oil to refining centers for conversion into products useful to man.

The oil industry is doing everything possible to locate

---

[1] Address on the occasion of the presentation of the Medal Award of the American Institute of Chemists at its eighteenth annual meeting, Atlantic City, N. J., May 18, 1940.

and conserve crude oil by calling upon the best scientific and technical knowledge available. Enormous savings have been brought about by the use of geophysics and chemistry, and deeper and directionalized drilling. The Pacific Ocean bed has been drilled from the shore and oil produced. Some lakes in Louisiana and the Gulf of Mexico yield large quantities of crude.

Many of the 360,000 oil wells in operation in the United States were drilled in recent years, but substantial production still comes from wells brought in more than fifty years ago in the original oil state, Pennsylvania. Continued production from these old wells has been brought about by improved methods of oil recovery by so-called repressuring. Water is injected through auxiliary wells surrounding the oil well in order to build a hydrostatic pressure in the oil sand. This water flooding process has increased oil production in the famous Bradford field which was discovered in 1875. Production in this field dropped to its lowest point in 1900, when it was considered almost exhausted. Since then, by the use of water flooding, production has been increased eleven-fold above that of the low.

"Water-flooding, scientifically controlled so that no damage is caused in the oil formation, is one of several secondary recovery methods developed by the oil industry to increase production from oil sands which apparently are depleted. This method recently was legalized in Ohio, and already has been introduced successfully in one of that state's older fields. Gas injection, and air injection, similarly designed to build up pressures in underground oil formations and increase recovery, also have made startling advances in recent years."

As the bit bites its way toward the nether regions, water layers or heaving shales are encountered which are sealed off by chemical means. To control oil well pressures, some above 2,000 pounds, and to prevent the well from blowing out, hurtling the tools, casings, etc., a thousand feet or so in the air, counteracting columns of colloidal muds are used, which allow the well to produce oil quietly under controlled pressure due to the weight of the mud-counter to the oil well pressure.

Some years ago in Texas a huge well came in, ripping a crater into the earth and resulting in a terrific fire. There were no methods known of fighting this type of fire. For years the oil industry had been cursed by drilling crooked holes which was inevitable at that period. At times these holes ran parallel to the ground and in some instances actually made a U-bend with the other end of the pipe coming up about a thousand feet from the derrick floor. One of the engineers suggested purposely drilling a slanting hole so that the bit would enter the oil sand. Water was then pumped into the sand, shutting off the fire.

This directionalized drilling was highly successful. Wells may now be drilled in any direction, by a number of ingenious physical and chemical methods. As many as eight wells have been drilled from a single derrick floor in different directions and levels to study the geology and composition of the earth. The deepest well drilled so far is about three miles. It is certain that wells will be drilled and oil found at depths of five miles or more.

In 1860, one year after the Drake well was brought in at a 69-foot level, an oil shortage was predicted as the prevailing rate of oil consumption would exhaust the supply in a few years. This prediction has been reiterated at about five-year intervals ever since. In 1860 the U. S. A. crude oil production was 500,000 barrels and 1,250,000,000 barrels in 1939. Moreover, crude oil reserves of to-day in the known oil fields are about 20,000,000,000 barrels. During the last year alone, approximately 2,000,000,000 barrels of crude were added to our oil reserves above that actually used. Through the years crude oil reserves have been increasing by finding new oil fields, by deeper drilling in old fields, and by hydrochloric acid treatment, called acidizing, of old and new oil sands.

One of the greatest forces for conservation and well being of our social and economic life is the cracking process developed by chemists and engineers of the oil industry. This process has more than doubled the yield of motor fuel from a barrel of oil with anti-knock quality which gives over 40 per cent. more miles per gallon than Nature's gasoline. Since 1913 when the first commercial cracking plant was used to the present time, a saving of over 13,000,000,000 barrels of crude oil has been brought about. Last year alone, 1,400,000,000 barrels of crude oil were conserved by the use of the cracking units in the United States which cost $450,000,000. In short, the oil industry would have had to refine 2,638,000,000 barrels of crude to produce the volume of gasoline necessary to operate the 31,000,000 cars instead of the 1,238,000,000 barrels actually refined.

There is an ever recurrent cry that crude oil is an irreplaceable asset. However, there is evidence to contradict this view. I believe that petroleum is being formed in the earth at a greater rate than we are consuming it. So far as we know, Nature may still be going ahead with the same biochemical changes, the same heat, pressure, and time processes by which crude oil was made in the beginning at least in part. Investigations have brought to light facts regarding earth processes which from their very nature lead me to the belief that oil is continually being formed, although they have not been sufficiently established to confirm it positively.

The theory of continual petroleum formation is supported by the fact that oceans, lakes and rivers of to-day abound with fish and mollusks closely resembling those found in many petroleum-bearing formations.

Microscopic creatures, such as foraminifera, radiolaria, and diatoms, are present which are identical in body structure with fossils found in the Monterey shale and other oil-producing structures, notably in the Lompoc and Santa Maria fields of California.

Such diatoms, scooped alive from the ocean to-day, yield about two per cent. of oil by ether extraction, altough they contain about sixteen per cent. organic material. The possibility that this oil yield may be greatly increased under the temperature, time and pressure conditions prevailing in the earth, has been considered. It is also likely that some substances such as the silica body structure of the microscopic corpses in the earth exert a catalytic influence which would accelerate oil formation.

Yielding two per cent. of oil, the diatoms in the Monterey shale (which constitutes a bed 800 square miles in extent and half a mile thick in one section of California) would produce two billion barrels of oil. Present-day sedimentation of organic matter is occurring in closed basins of the Continental shelf particularly along the western coast of California. In other oceans and in the deeper waters along the coast, diatoms are depositing with organic content constantly increasing.

From the foregoing we may conclude that Nature is producing oil at a faster rate than gas pressure or pump strokes can bring it to the earth's surface. As a matter of interest, since the foundation of the oil industry, the entire world's production of crude oil would not fill a hole a cubic mile in the earth. This is an insignificant volume compared to what nature must have produced and still is producing during the years of her workmanship.

In view of the increasing volumes of crude oil reserves, the probability of continuous crude oil formation, better utilization of crude oil and its products, and considering the trifling volume of petroleum used to date, one can look with assurance as to the future oil supplies for our every need for thousands of years.

Gasoline distilled at atmospheric pressure from crude oil does not contain the hydrocarbon molecules of the type most useful to man. Some gasolines which nature produced have octane ratings as low as 15, and are worthless as motor fuels in modern cars due to high knocking characteristics. The crude oils and their gasoline content have to be converted into more useful products by thermal or catalytic cracking, polymerization, alkylation, aromatization, hydrogenation and dehydrogenation.

The primary function of cracking is to produce high anti-knock gasoline. As a by-product of this operation, the oil industry has developed motor fuels of 100 and higher octane ratings which make possible greater motor efficiencies whether in airplane or motor car engines.

The automobile industry during its early years gave indications of exceeding the capacity of the oil industry to supply gasoline. This thought spurred technical men to invent means for increasing the yield of gasoline from crude oil. The cracking process not alone provided the means for more than doubling the yield of gasoline, *i.e.,* 21 per cent. to 45 per cent. of the crude oil, but in addition improved the anti-knock properties of the gasoline.

In the past twenty years the number of motor vehicles has increased from about 9,000,000 to more than 31,000,000, while the motor fuel consumption increased annually from 109,000,000 barrels to over 566,000,000 barrels. In addition, the average motor compression ratio increased from 4 to 6.4. This is of tremendous significance from an economic standpoint in that motor efficiencies have increased more than 40 per cent. during this period.

Transportation speeds in the air and on the road have more than doubled which is primarily due to the correspondingly improved anti-knock value of the gasoline and better motor design. Pursuit planes of our Army and Navy powered by 100 octane fuel have speeds of over 400 miles per hour.

About twenty-seven years ago the first commercial cracking units went into operation at the Standard Oil of Indiana Whiting plant, using shell stills having a capacity of about 200 barrels of gas oil per day with a yield of about 30 per cent. To-day, a single topping and cracking unit with polymerization of the cracked gases treats more than 30,000 barrels a day of crude oil with yields of over 70 per cent. of 70 octane gasoline from crude oils derived from East Texas. The cost of such a unit is about $2,000,000 whereas the early shell still cost about $20,000.

Modern cracking installations have been highly flexible since the introduction of multiple heating coils in equiflux furnaces wherein the time, temperature and pressure conditions may be maintained to a nicety. Two-day runs were the maximum in shell-still operation, whereas the modern installation—composed of heaters, reaction chamber, flash chamber, fractionator, coolers and stabilizers—operates continuously for months at a time, producing motor fuel, furnace oil, tractor fuel, fuel oil and gas oil, or gasoline, gas and coke.

The early shell stills (1913) used cracking temperatures around 740° F. and 75 p.s.i.; to-day temperatures ranging from 900 to more than 1,100° F. and more than 1,000 p.s.i. obtain. The yield of gasoline from gas oil was about 30 per cent. with octane rating of 60; to-day units operating on the same type of gas oil produce more than 70 per cent. of motor fuel with 74 octane rating.

The increasing number of high-compression motors has made straight-run gasoline no longer suitable as fuel. Cracking or reforming of the gasoline is necessary to produce hydrocarbons of structures which possess greater anti-knock properties. In order to convert the knocking gasoline into non-knocking types, it is desirable to subject the gasoline to temperatures of the order of 1,025° F. and 750 p.s.i. This is accomplished by pumping straight-run gasoline through a long heating coil distributed in a furnace, until the temperature and pressure are raised to convert the hydrocarbons into high anti-knock gasoline. Under these drastic temperatures and pressures, there is a molecular rearrangement and change in the structures of the hydrocarbons from the straight-chain paraffinic type to branched paraffins, olefins, aromatics and naphthenes. These hydrocarbons burn without detonation in the high-compression motors of to-day.

It was recognized that thermally cracked gasoline was approaching a limit from the anti-knock quality standpoint. The octane number averaged about 70 as produced from gasoline, naphthas, or heavy oils. Hence, catalytic cracking processes have been developed to increase the octane rating and yields above that of thermal. Catalytic cracked gasoline of 80 octane has been produced from gas oil with yields of 85 per cent. on a recycle basis. Catalytic cracking will be an adjunct to thermal cracking for some time to come. An important part of the catalytic cracking process is the quality of the gas produced since the percentage of olefins present is generally more than double that of thermal cracked gas.

The gases produced from the cracking process amount to over 350,000,000,000 cu. ft. a year. These hydrocarbon gases were burned under stills and boilers. But these gases contained olefins such as ethene, propene, butenes and the corresponding paraffins—ethane, propane and butanes. Several processes were developed to convert cracked gases into high octane motor fuel via high temperatures and pressures while the catalytic process using solid phosphoric acid operates at low temperatures and pressures.

There are over 80 U.O.P. catalytic polymerization units in commercial operation, design, or under course of construction at the present time. The capacities of these units, processing cracked gases range from 125,000 cubic feet to 27,000,000, or on a gasoline (81 octane) production basis, from 18 barrels to over 2,500 barrels daily. The combination of selective catalytic polymerization and hydrogenation units produce from 50 barrels to 800 barrels of isooctane gasoline per day. The increased yield of gasoline ranges from two to eight per cent with an octane number rise of one to two on the refinery gasoline output when processing naphtha, kerosene, gas oil, or topped crudes.

The butane-butene fractions from either the cracking or dehydrogenation process may be catalytically polymerized to yield isooctenes, and upon hydrogenation, isooctanes of 95 to 100 octane rating. The conditions for the manufacture of isooctane require temperatures of 250° to 350° F. and approximately 750 p.s.i. with solid phosphoric acid as the catalyst. Debutanization and rerunning of the polymers is carried out and finally catalytic hydrogenation with nickel yields an aviation gasoline of 97 octane rating. The potential yearly production of polymer gasoline is over 300,000,000 barrels derivable from refinery and natural gases.

For years it was believed impossible to react a paraffin with an olefin hydrocarbon, due to the so-called unreactiveness of the paraffins. A new page in organic chemistry has been written based upon an alkylation of isobutane with ethene, propene, and butenes by a number of methods such as aluminum chloride, boron fluoride, sulfuric acid, and at high temperatures and pressures. The latter two processes have gone into commercial use in the past year and are an exceedingly important contribution to high octane aviation gasoline. These two processes produce products having about 95 octane rating and high tetraethyl lead susceptibility. The thermal alkylation process operates best when using charging stocks made up of isobutane and ethene, producing therefrom 2, 2-dimethylbutane or neohexane, whereas the sulfuric acid method functions best on isobutane and butenes, forming isooctanes. When all the alkylation units under design and construction, as well as those in operation, are functioning, about 4,000,000 barrels of high anti-knock aviation gasoline will be produced annually.

Military airplanes in 1928 used gasoline of about 60 octane rating while three years later the standard Army aviation gasoline was 87 octane. Airplane engines were developed to utilize this fuel which gave a 33 per cent. increase in power per unit weight compared to 60 octane gasoline. Engines designed for using 100 octane gasoline produced 30 per cent. greater power output compared to 87 octane, while take-off distances were reduced 20 per cent and climbing speed increased 40 per cent. For transport planes, the advantage of 100 over 87 octane gasoline in a 1,400 mile flight would be the dispensing of "1,200 lbs. of gasoline and carrying instead 7 more passengers, or their equivalent weight in mail or freight."

Leadership in aviation gasoline, with higher speeds and comfort of airplanes, rests in the United States. Aviation gasoline of 100 and higher octane can be produced in the United States in quantities to supply the airplane needs of the world, for civil and military use. A most significant factor in the development of 100-octane gasoline is that the overall efficiency of the airplane gasoline engine is about the same as that of the best Diesel airplane engine performance and in addition surpasses the Diesel in greater take-off and emergency power and flexibility in maneuvering the plane.

Although 100 octane gasolines and higher are now used only in airplanes, it will not be many years before the oil industry's researches will produce them at a price level for use in passenger, truck, and bus vehicles, and they will be sharply competitive with the best high-speed Diesel engine performance.

Dr. Graham Edgar stated:

> The General Motors Corporation carried out an elaborate research project in which an automobile equipped with a valve-in-head engine was operated at a number of compression ratios and a number of gear ratios, using fuels which in each case were just capable of avoiding knock. Approximately 69 octane fuel was required for the standard 5.25 compression ratio, about 95 octane for 8.0 compression ratio, and something better than 100 octane for 10.3 compression ratio.
>
> The results were most striking, showing, for example, that at 40 miles per hour the miles per gallon improved from 12.5 at 5.25 compression ratio to 18 at 8.0 and 21 at 10.3. The average increase in economy, between ten and sixty miles per hour, is about 45 per cent. in going from 5.25 to 8.0 compression ratio under these conditions of constant performance.
>
> It is interesting to note that if we take the average retail price of gasoline as 19 cents per gallon, the driver of the 8.0 compression car could have paid 27.5 cents per gallon at no increase in cents per mile, which would give the refiner a margin of 8.5 cents per gallon above his regular costs of 5 cents per gallon with which to attempt to produce the 95 octane gasoline required by the high compression car. Certainly, such an achievement would appear to be well within the eventual possibilities of the refinery technologist.

The volumes of 100 octane gasoline potentially available yearly in the United States are greater than the volume of all gasolines now being produced. One prolific source which has been tapped recently is natural and refinery gases. From these gases alone 8,345,000,000 gal. of 81 octane, or 3,275,000,000 gal. of 92 octane, unleaded, gasolines are available. About 6,000,000,000 gal. of 100 octane aviation gasoline are available yearly when the 92 octane is blended with isopentane and neohexan and light ends from some crudes plus tetraethyl lead. This volume of aviation gasoline does not take into consideration the vast volumes of aviation stock which are potentially available from catalytic reforming and cracking.

The development of catalytic dehydrogenation of gaseous paraffins to olefins and hydrogen has made possible their utilization for polymerization to gasoline and chemical derivatives. Thermal cracking of paraffin gases is a competing source of olefins; however, catalytic dehydrogenation gives a better yield of the desired products than the thermal method. Catalytic dehydrogenation of ethane, propane, and butanes is highly selective in that side reactions are suppressed. Catalysts for dehydrogenation reactions are oxides of the metals of the fourth, fifth, and sixth group of the periodic system, the most important one being chromium oxide and alumina. This catalyst is highly selective and converts the paraffin to the corresponding olefin in about 85 to 95 per cent. of theoretical.

Butane may also be converted into butadiene by a two-stage catalytic dehydrogenation process. This compound is extremely important for use in synthetic rubber production. Butadiene is available potentially in the U.S. at the rate of more than 160,000,000,000 pounds yearly.

There is a very beautiful reaction called cyclization of paraffin hydrocarbons; *i.e.,* catalytically converting normal hexane, heptane and octane into benzene, toluene and xylenes respectively, with hydrogen as a by-product and almost theoretical yields.

The lower-boiling hydrocarbons in petroleum, particularly those from the Pennsylvania, Mid-Continent, Michigan, East Texas, and Kettleman Hills, California, fields, and gasoline from natural gas, are predominantly straight-chain paraffins. By catalytic cyclization at 932° F. and atmospheric pressure, these hydrocarbons may be converted into the corresponding aromatics which have been obtained heretofore chiefly from coal carbonization.

As of to-day, the aromatic hydrocarbons are not so good for airplane use, although some tests indicate that they will become useful. They are excellent blending hydrocarbons for increasing the octane rating of gasolines.

Benzene, toluene and xylenes are most important for motor fuel use and as basic material for high explosives such as picric acid, T.N.T., and trinitroxylenes. The oil industry can produce any conceivable amount of these hydrocarbons from catalytic cyclization or aromatization of gasoline, the cracking process, and dehydrogenation of ethane. In 1940 about 26,000,000,000 gallons of gasoline will be produced in the United States. If the demand were present, our gasoline output could be increased to over 40,000,000,000 gallons in a short time. Based on this year's gasoline production alone, and using but 20 per cent. of the gasoline, the U.S.A. could manufacture (naturally requiring some time to go into full production) about 33,000,000,000 pounds of picric acid, about 27,000,000,000 pounds of T.N.T., and 25,000,000,000 pounds of trinitroxylene. The 85,000,000,000 pounds of high explosives which are potentially available from gasoline are all present within the shores of the U.S.A. and for many years to come.

In the world war now going on, difficulty will be experienced in obtaining natural rubber for our own needs. It is reported that the United States has but a three months' supply of natural rubber. Some suggestion has been made to plant rubber trees in a South American country such as Brazil. It would require at least ten years to obtain rubber in this way. Benzene and ethylene through alkylation and dehydrogenation yield styrene, a starting hydrocarbon for synthetic rubber manufacture. Butadiene is another hydrocarbon which can be readily produced and converted into synthetic rubber or may be copolymerized with styrene. This latter type of synthetic rubber has about 30 per cent. greater wear quality and strength in tires than natural rubber. The United States has potentially available enormous quantities of these hydrocarbons and other substances which can be converted into synthetic rubbers. In 1939 about 1,100,000,000 pounds of natural rubber were used in this country. Over 200,000,000,000 pounds of synthetic rubber could be produced from ethylene from the cracking process, benzene from cyclization, and butadiene from the dehydrogenation of butane. A unit to produce 10,000 pounds a day of synthetic rubber from butadiene derived from petroleum is being installed.

The U.S.A. can be more than self-sustaining in synthetic rubber from its own vast hydrocarbon resources.

The U.S.A. is more than self-sustaining in motor fuels and aviation gasoline of 100 octane and above. The U.S.A. can produce billions of pounds of explosives for any necessity that may arise and still have more than sufficient gasoline for any form of transportation on land, air, or sea.

OBITUARY

WILFRED THOMAS DAWSON

Wilfred Thomas Dawson, late professor of pharmacology at the Medical Branch of The University of Texas, was born in Windsor, Nova Scotia, on October 3, 1895. He was the son of John Leard Dawson and Florence Lockhart Dawson. He died suddenly on September 19, 1939, at Galveston, Texas.

He was married to Miss Margaret Bishop on September 11, 1926. Their son, Wilfred Thomas, Jr., was born on September 14, 1928. In addition to his widow and son he is survived by two brothers, Kenneth Leard Dawson of Halifax, N. S., and John Chesley Dawson of Quebec.

In 1914 he was graduated from Mount Allison College and the following year received his A.M. in chemistry from that institution. He taught mathematics at the Prince of Wales College during 1915–16. In 1916 he was appointed a Rhodes Scholar at Exeter College, Oxford University. The scholarship was deferred on account of the war.

He enlisted as a private in the heavy artillery of the Canadian Expeditionary Forces and served with distinction through the war. He was discharged in 1919 as a lieutenant.

After the Armistice, he was one of the organizers and professor of chemistry of the Khaki University of the Canadian Expeditionary Forces in England.

In 1919 he took up his Rhodes Scholarship at Oxford and worked there from 1919–1922. He was especially interested in physiology, pharmacology and allied subjects. He received his A.B. in 1923 and in 1927 an A.M. in physiology.

During 1922–1923 he was connected with the physiology department, University of Pennsylvania, and from 1923–1925 was acting professor of physiology and pharmacology at the Women's Medical College of Pennsylvania.

In 1925 he came to the medical branch of the University of Texas as associate professor of physiology and the next year became associate professor of pharmacology. In 1927 he was appointed professor of pharmacology and pharmacologist at the John Sealy Hospital. He filled both positions with distinction.

During the summers he was associated with the division of biological sciences of the University of Chicago, the department of pure research of the Mellon Institute and attended meetings of the Cowles Commission for Research in Economics.

He was a member of the National Malaria Committee, the American Association for the Advancement of Science, the American Physiological Society, the American Society for Pharmacology and Experimental Therapeutics, the Society for Experimental Biology and Medicine, the Society for Tropical Medicine, Oxford Society and the American Association for Rhodes Scholars.

His research interests were varied, including congenital heart disease, carbon monoxide poisoning, chemical structure and physiological activity. He published many papers on the cinchona alkaloids, treatment of malaria, the action of barbiturates as strychnine antidotes and cardiac glucosides. He was very much interested in biological statistics, especially as related to problems of dosage and toxicity.

Professor Dawson was an inspiring teacher. He possessed an unusual command of English and made his points with great clarity. He had a catholicity of taste in reading that is seldom found in a scientific