THE CHEMISTRY AND REFINING OF PETROLEUM

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Petroleum chemistry and improvement of technique in the petroleum refining industry have progressed during the year partly because of economic conditions. In order for refiners to meet the demand for quality products it has been necessary to conduct extensive technical research programs to determine how a better product can be manufactured cheaper than it has been done previously. Equipment and processes that were thought perfect a few years ago are now obsolescent.

The days of operating a petroleum refinery by rule-of-thumb methods are passed, and the industry now recognizes the value of research. The public generally does not have a very clear conception of the true value of such work, but it is more or less critical of the quality of the petroleum products it uses. Improvement in the quality of products demands a comprehensive understanding of the characteristics of the raw material, the finished products, and constant development in methods of manufacture. Utilization of crude petroleum can never be completely accomplished without this continuous development.

An attempt is made in the following paragraphs to give a brief résumé of the outstanding developments in the fields of chemistry and refining of petroleum for the year 1933.

CHEMISTRY OF PETROLEUM

An intelligible survey of the advances in petroleum chemistry is made most easily by considering individually the progress recorded for crude oil and the major products manufactured from it.
CRUDE OIL

Classification.—The Bureau of Mines has been active in the study and classification of crude petroleum. Since 1920 the Bureau has analyzed approximately 2,000 crude oils from all parts of the world. Two additions to the series of papers reporting these analyses concern the crude oils produced in the Oklahoma City 1 and East Texas fields. 2 Further reports on crude oils from several sections of the world are being compiled and will include a classification of crude oil based on the results of the many analyses available.

Through determination of chemical and physical properties of numerous fractions from various crude oils other investigators 3 suggest that petroleum may be divided into the following classes: (1) Methane, (2) naphthene, (3) methane-naphthene, (4) aromatic, (5) methane-naphthene-aromatic, and (6) naphthene-aromatic.

Isolation of pure compounds.—As the number of products manufactured from petroleum increases the need for knowledge concerning the actual components of crude oil is emphasized. During the last few years an impetus has been given to this type of research work through American Petroleum Institute grants. Of particular interest in this regard are projects concerned with hydrocarbons and with nitrogen compounds. The work has been continued for the year under review with the isolation of several aliphatic, naphthenic, and aromatic hydrocarbons from an Oklahoma petroleum. 4 5 6 7 A number of nitrogen bases have been isolated from California petroleum, and methods have been developed whereby such work may be extended to other oils.

Synthesis of pure hydrocarbons and sulphur derivatives.—Some of the major advances in petroleum chemistry have resulted from the synthetic production of pure compounds and studies of their reactions. The synthesis of saturated aliphatics having 2 to 6 methyl groups as side chains 9 10 11 12 and of 50 different naphthenes 13 has been accomplished.

In recent years the aliphatic olefins have been attracting considerable attention because of their possible uses in the manufacture of alcohols and other chemical compounds in conjunction with the fact

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that they are produced in large quantities by the cracking of petroleum. Further, their properties as regards antiknock value and as potential sources of gum have increased their importance. Methods for synthesizing these hydrocarbons and their properties are important.14 15 16 17 18 19

Knowledge concerning the reactions of pure sulphur compounds, especially toward chemicals used for refining gasoline, have been very helpful in improving treating processes. A discussion on the synthesis and reactions of the thiophanes 20 is an example.

A definite relationship between structure and properties exists 21 and may be used to predict the physical constants of an unknown hydrocarbon, to test the validity of an assigned structure, and to detect errors in constants already recorded. These uses have definite value in the study of petroleum.

**NATURAL GAS AND REFINERY GASES**

Within recent years it has become evident that natural gas and refinery gases are great potential sources of useful chemicals. These compounds include not only motor fuels but solvents, intermediates for resins, and lubricating oils. Using as a basis the gaseous paraffin and olefine hydrocarbons available in 1929, it is estimated that the potential yield of benzol produced by pyrolysis would be of the order of 4,750,000 tons per year.22 If these gaseous paraffins were dehydrogenated to olefines and the olefines polymerized to liquid hydrocarbons a potential yield of 17,750,000 tons per year is indicated. The production of natural gas and refinery gases in 1933 can only be estimated, but the trends of the past few years point toward an increase, especially of gases from cracking stills.

Saturated compounds.—The production of liquid products suitable for motor fuel is the chief end of this research and may be approached by two methods: (1) Direct pyrolysis to give liquids and (2) pyrolysis to give gaseous olefines and subsequent polymerization and condensation of the olefines to liquid products. In the first method the chief factors influencing results are temperature, time of contact, pressure, and tube material. Within certain limits temperature and time of contact are reciprocal functions; that is, higher temperature may be compensated by shorter time of contact so that approximately the same yield of similar products is obtained.

The use of mild pyrolysis to form olefines and their subsequent polymerization to motor fuel gives still better yields. This process is preferable in several ways, since (1) temperatures required are lower,

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(2) pressure is an advantage, reducing plant size, (3) high yields are possible, (4) carbon deposits are negligible, (5) tar production is virtually nil, and (6) hydrogen dilution has little influence. The converse of these facts is to a large extent true for straight pyrolysis.

Some of the more theoretical aspects of pyrolysis, including the very important subject of reaction mechanism as well as the influence of time, temperature, and pressure, have been the object of considerable discussion. A theory involving "free radicals" used in conjunction with chain reactions makes possible prediction of results with considerable accuracy. Also no evidence has been found that the C-C chain breaks at a specific point to the exclusion of others. Equilibrium constants and free energies for the dehydrogenation of several paraffins have been determined, using chromium oxide gel as a catalyst. Chain reaction mechanism and velocity constants for the pyrolysis of simple paraffins also have been reported.

The beneficial results of baffled alloy tubes nickel-free and with more than 20 percent chromium has been demonstrated. The Bureau of Mines has studied production of acetylene by the pyrolysis of a methane-carbon dioxide mixture and has reviewed the formation of acetylene by the pyrolysis of methane, ethane, ethylene, gasoline, and petroleum.

An investigation of the production of olefines from propane and butanes showed that the highest yields of olefines and aromatics with negligible yields of carbon and hydrogen were obtained at high temperatures with short contact time. The only commercial material that withstood these temperatures favorably and had no adverse catalytic effect was nichrome. Bureau of Mines studies of the decomposition of methane by a heated carbon filament indicated that the earliest product that can be isolated is ethane. Kassel, of the Bureau, has explained the production of ethane and other products by an equation based on successive dehydrogenation steps following the ethane synthesis.

**Unsaturated Compounds.** —Considerable study has been given the polymerization reactions of the olefines. Floradin polymerizes propylene, producing a high octane-number liquid in the boiling range

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of gasoline. Ethylene under pressure of 50 atmospheres starts to polymerize at 325° to 340° C., and a 63–73 weight percent yield of oil is possible at 300° C., using an autoclave.

The pyrolytic reactions of simple unsaturated hydrocarbons shows that the order of thermal stability is ethylene, propylene, isobutylene, and 2- and 1-pentane. Polymerization at different temperatures causes different products, and reactions are not as simple as usually implied.

**GASOLINE**

Approximately 180,000,000 barrels of gasoline were produced by cracking in 1933, or about half the total gasoline manufactured from petroleum. As the major chemical problems of detonation and gums are largely caused or controlled by cracking, it is natural that these fields should record the most study. A third problem, that of sulphur compounds, continues to receive considerable attention.

**Detonation.**—The detonation problem, which is essentially a problem of hydrocarbon oxidation, progressed through study of the oxidation mechanism of hydrocarbons and the determination of the antiknock qualities of individual hydrocarbons.

The mechanism of gaseous ignition, although not distinctly related to gasoline, helps to formulate oxidation or combustion theory. Ethane, propane, and butane prior to ignition decompose to the corresponding olefines, which appear to oxidize to an aldehyde before ignition. In this connection spectrographic data of gases in an engine just before knock showed formaldehyde to be present with a variety of fuels. The oxidation of hexane, cyclohexane, and cyclohexene in the vapor phase at 1 atmosphere pressure with hydrocarbon-oxygen ratios of 4 to 1 indicated peroxide formation was prominent at temperatures of active oxidation but disappeared completely at higher temperatures. The presence of a double bond appears to cause much more resistance to oxidation than cyclization. When mixtures of a hydrocarbon with air or oxygen at constant volume are heated pressure changes follow the gas laws for a time and then show several inflection points where the pressure rises rapidly, separated by normal pressure increases. The number of points equal the number of carbon atoms in the hydrocarbons.

Detonation characteristics of 69 naphthenic hydrocarbons indicate that (1) antiknock value increases with size of ring, (2) for the same number of carbon atoms ring compounds have a higher value than n-paraffin, (3) increased length of largest unbranched chain causes decrease in value, (4) the most compact space arrangement of side chains gives largest value for isomers, and (5) removal of hydrogen in general causes an increase of antiknock value.

Considerable work has been done in England to determine the blending octane number of pure hydrocarbons. This is an index of

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the change in the octane number of a given reference fuel exerted by individual hydrocarbons. 44

The results indicate that the curve representing concentration of hydrocarbon in a blend and the octane number is not influenced by the reference fuel but is determined by the series to which the hydrocarbon belongs. The knocking tendency of 48 pure compounds, including some alcohols, 45 has been determined. The results of road performance indicate that a closer correlation between actual car tests and laboratory tests is necessary before international standards can be agreed upon. Further, the determination of detonation values of aviation and compression-ignition engine fuels are still in the formulative stage.

Gums.—The increased use of vapor-phase cracking has intensified studies on gums and gum-forming compounds. The literature is crowded with "new" tests for potential and preformed gums, and although a tentative standard method for preformed gums has been listed by the American Society for Testing Materials 46 the determination of potential gum is still the source of much controversy. Numerous methods for potential gum determinations involve ultraviolet rays, 47 stannic chloride, 48 air incubation, 49 and oxidation with oxygen under pressure. 50

From the strictly chemical viewpoint the actual compounds responsible for gums are of more interest. Tests made by adding individual hydrocarbons to straight-run paraffin gasoline 51 indicate that aliphatic and cyclic diolefines, or mono-olefines attached to a benzene ring give the largest amounts of gums. Gum formation seems to be associated with oxidation, and inhibitors appear to prolong the induction period prior to oxidation but do not change the rate of reaction at the end of the induction time.

Tests on several series of gasolines 52 in which peroxides varied over a wide range of concentrations showed that peroxide formation is the first evidence of gasoline deterioration, that peroxidation starts slowly but proceeds rapidly at the end of an induction period, and that gums increase and octane numbers decrease with increase in peroxide. Inhibitors are of value only with low peroxide content. Gasoline made by cracking solar oil at 600° C. 53 formed appreciable amounts of gums in those fractions whose boiling range include the boiling point of conjugated diolefines. Somewhat similar results were found by the Bureau of Mines a few years ago. 54

Sulphur compounds.—The action of several reagents on trimethylene sulphide, ethyl sulphide, and thiophene dissolved in naphtha has been studied.\(^{55}\) Trimethylene sulphide and ethyl sulphide gave stable derivatives in certain instances, and thiophene did not react. Studies of the thermal behavior of \(n\)-butyl sulphides in 0.5 molal solution in benzene\(^{56}\) show that it is stable at 400° C. and undergoes moderate decomposition at 500° C. Up to 515° C. the products are largely hydrogen sulphide and mercaptans, and in the presence of large amounts of these compounds sulphur and thiophene are formed. The thermal decomposition of ethyl mercaptan and sulphide has also been investigated in the gaseous phase.\(^{57}\) These have been found to be first-order reactions producing ethylene and hydrogen sulphide.

LUBRICATING OILS

In recent years some progress has been made toward dividing lubricating oils into two or more groups or classes depending chiefly on such properties as viscosity and specific gravity differentials. Viscous oils are studied and evaluated for the most part through determination of physical properties; very little work has as yet been done in systematically correlating these properties with chemical facts, chiefly owing to lack of the latter.

Separation and classification.—An impetus has been given the separation of lubricant oils into groups by the recent widespread use of solvents. The solvent method generally used is based on the fact that certain parts of the oil are more soluble in many common organic solvents than other parts having properties characteristic of Pennsylvania oils. A more or less artificial grouping has been set up by the use of indices based on the temperature-viscosity relations or on the specific gravity-viscosity relations. Two general groups are formed. One, relative to the other, is characterized by low specific gravity, small viscosity change with temperature, low carbon residue, good resistance to sludging and oxidation, and in some instances reduction in sulphur, steam-emulsion number, and color.

The viscosity-temperature function or the slope of the viscosity-temperature curve has been proposed as an index of an oil.\(^{58}\) Complete analyses of oils from three sources\(^{59}\) according to all the usual means of evaluating lubricants indicated that for oils having the same viscosity at 50° C. the volatility, slope of viscosity-temperature curve, and generally oxidation sludge increased with the specific gravity, but carbon residue decreased. The viscosity-specific gravity constant was the only index figure that remained constant for each member of a group of oil prepared from the same crude oil.

Seemingly, one of the trends is increased production of synthetic lubricants. Oils which are stated to compare favorably with Ameri-
can petroleum oils have been obtained 60 from gases containing 20 to 33 percent of olefins. Condensation experiments with kerosene 61 gave promising results by halogenation and subsequent removal of the halogen and by condensation with acetylene or acetylene and hydrogen. A number of aromatic and aliphatic hydrocarbons have been synthesized 62 and viscosity-temperature curves determined where possible.

**Oxidation.**—The oxidation of mineral oils appears to be the object of considerable attention. It concerns a variety of fields, such as color reversion of lubricating oils, effect on lubricity of oils, and sludge formation. Color reversion 63 of oil in the dark is due to polymerization and condensation and in the light, to oxidation. Inhibitors seem to be more effective in preventing color reversion caused by oxidation than by polymerization. The role oxidation plays in lubricating bearings has been studied 64 under conditions that permitted the bearing to be heated and the oil recirculated and blown with hot air. By this method the seizing temperature of an oil could be determined; the data show that as the oil becomes oxidized its seizing temperature increases.

Apparently there is need for a reliable method of determining the oxidizability of oils if the number of methods proposed annually is a criterion. The Bureau of Mines has developed a test in connection with its study of California lubricants which will be published in 1934. Other tests include one 65 in which the oil is oxidized in the presence of a catalyst and those 66 67 that employ air under different conditions of temperature and applications. The acceleration or deceleration of oxidation caused by different substances 68 shows that organic compounds, although effective below 150° F., are of little use at higher temperatures; whereas of the inorganic materials only tin and lead in several forms showed any inhibitory action.

**Lubricant testing.**—As usual, a number of machines designed to test the lubricant properties of oils or "oiliness" have been developed, but the most interesting and significant development along this line concerns the so-called "extreme-pressure" lubricants. Modern cars and hypoid and worm gears with their high pressures and wiping action exerted by the driving pinion or worms on the driven member of the assembly demand a new type of lubricant. This lubricant must have, among other characteristics, a high load-carrying capacity, stability under operating conditions, and minimum abrasive or wearing action and corrosive effects. Several machines have been developed, but the outstanding ones appear to be the Timken tester 69 and the appa-

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ratus developed by the Bureau of Standards. The latter machine, on the basis of present tests, appears to rate the lubricants with reasonable agreement to service performance. Factors found to be significant are speed of rubbing, lubricant temperature, and rate of loading.

Viscosity.—The most interesting trend in viscometry is the recommendation by many technologists for a common international viscosity unit based on the C.G.S. system. Several interesting viscometers have been developed, notably a pipette type and a falling-ball type capable of an accuracy of 0.5 percent over a range of 0.01 to 500,000 centipoises.

**BYPRODUCTS**

The production of organic compounds from petroleum is the subject of ever increasing research. Aside from the products possible by cracking and polymerization mentioned previously, oxidation, sulphonation, and halogenation offer possibilities of producing alcohols, esters, and other useful solvents and intermediates. During the period under review several interesting developments have been reported.

The production of fatty acids and thence to the synthesis of foods is a possibility. Paraffin hydrocarbons have been oxidized in 20 percent sulphuric acid by electrolysis of the acid in the presence of certain sulphates. Several organic acids have been prepared by catalytic oxidation with air or oxygen.

Mercaptans and disulphides from spent caustic soda may be converted by oxidation into chemicals suitable for plasticizers, detergents, and solvents.

The study of sulphonated acids and sulphonated oils as spray spreaders in insecticides indicates that apparently these substances have good spreading power and are not injurious to the plants.

The chlorination of paraffin wax and the bromination of aliphatic hydrocarbons have been investigated. The latter process is considered a step in the manufacture of alcohols.

**REFINING OF PETROLEUM**

The replacements in refinery equipment during the years 1931 and 1932 were subnormal, particularly during 1932. It has been estimated that, taken as a whole, the replacements for the entire country during 1932 were as low as 25 percent and at the most not greater than 40 percent of the normal rate based on experience in previous years. In comparison it has been reported that at the end of 1933 there were more refineries in operation in the United States than ever before in the history of the petroleum industry.

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References:


The refinery capacity in the United States at the end of 1932 was approximately 4,000,000 barrels per day, and the demand for refined products was slightly over 2,000,000 barrels. A large part of the refinery equipment at the close of the year was obsolescent, and a considerable portion could not operate economically under present prices.

Under existing gasoline prices incident to surplus production installation of equipment to lower manufacturing cost was of prime importance. In conjunction with the factor of reducing manufacturing cost is one of improvement in quality of products. Gasoline especially was subject to this condition because of the race for "octane numbers" during the last 2 years. In fact, during the past year virtually every replacement or modernization of cracking equipment has been due primarily to the necessity for meeting competition in the quality of motor gasoline.

Another reason for refinery construction has been to provide outlets for crude oil that does not have connections with established pipe lines or that, for some reason or other, cannot be disposed of to existing plants. This condition has developed because of flush production in such fields as east Texas and Oklahoma City. Surplus production in these areas gave a new source of supply to refineries which before were using crude oils from other locations, such as fields in Kansas. As a result, new plants are being built at McPherson, Kans., and old plants are being revamped at Hutchinson, Kansas City, Chanute, and elsewhere to take care of crude oil made homeless.

CRACKING

The chief developments in the art of cracking petroleum fractions for 1933 have pointed toward improvement of the octane number of motor gasoline. This was brought about by the increase of compression ratios in the internal-combustion engines of automobiles. During 1932 the average compression ratio of automobile engines was approximately 5.30 to 1; for 1933 the average was raised to approximately 5.54 to 1. A satisfactory motor fuel for these higher compression-ratio motors should have an octane number of about 70.

To meet the demand for increased octane number in motor fuels, particularly those running Pennsylvania-type crude oils, refiners have been installing plants for the re-forming of certain naphtha fractions. The straight-run motor gasolines from Pennsylvania-type crude oils have an octane number of about 48 to 50. The tendency of a motor to knock or ping is greater when climbing than when running on level road; since a large part of the marketing area for Pennsylvania-type crude is in the Appalachian Mountain region these refiners have had to think more about re-forming the straight-run naphtha fractions than those in other refining areas of the United States.

The increase in the demand for lubricating oils from Pennsylvania crude and prospects of further increases have presented a problem of moving the straight-run gasoline which has increased as crude run to stills was stepped up to supply the demand for Pennsylvania neutrals and bright stock. To take care of the straight-run gasoline a central re-forming plant has been proposed.
Although it has not as yet been necessary for the Pacific-coast refiners to re-form the straight-run motor fuels, it has been necessary for them to construct plants to break the viscosity of the heavy fuel oils.

In the Mid-Continent refining area plants for both re-forming the straight-run motor fuels and for breaking the viscosity of the heavy fuels have been built during 1933.

The equipment of a typical modern plant for topping, cracking, and re-forming the naphtha fractions should include: 80 2 furnaces, 1 for light oils and 1 for heavy oils; 2 bubble towers, 1 for the crude oil and 1 for the cracked stock; reaction and flash chambers; heat exchangers; pumps; controls, and other auxiliary equipment.

The customary procedure in a unit of this type is to heat the lighter oils under higher pressures to higher temperatures than those employed for heavy oils because of the greater refractoriness of the lighter oils. Such procedure, however, is not always followed; the conditions depend on many variable factors and may be changed at the will of the operator. Flexibility is the byword for new units of which the above-mentioned is a type.

In designing modern combination units the trend has been toward those of rather large capacity; during 1933 one was constructed 81 with a daily capacity of 19,000 barrels of Mid-Continent crude. This unit operates with four men on a shift and does a complete job of topping the crude, re-forming the naphtha fraction, cracking the heavy fractions of the crude, breaking the viscosity of the heavy fuel oil, and stabilizing the finished gasoline.

**TREating Cracked Gasoline**

The principal developments in the treating of cracked gasoline during 1933 have been made with the aim of retaining a high octane number for the finished gasolines and of keeping them from forming undesirable gum when standing in storage. A new method of clay-treating has been put in operation in refining vapor-phase cracked gasolines. 82 By this method the material under treatment is forced through a bed of fuller’s earth or clay under enough pressure to maintain the liquid phase at 500° to 600° F. The liquid after passing through the clay is flashed in a tower to separate the polymers from the gasoline.

The question of sulphur in gasoline has demanded some attention; methods of treating with sulphuric acid have been developed which give quick contact between the acid and the gasoline, and the acid sludge is separated quickly from the treated product. A method developed by the Bureau of Mines for removing free sulphur from gasoline has been described recently. 83

In treating cracked gasolines advances have been made during the last few months in the use of antioxidants to prevent the formation

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81 Jirasek, J. V., Combination Refining Plant (at Whiting) Unique in Modernity: Refiner and Natural Gasoline Manufacturer, vol. 12, no. 8, August 1933, p. 333.
of undesirable gums during the storage period before the motor fuel is put into use. A large number of compounds have been studied in regard to their antioxidant properties, and a number of compounds are being used commercially as antioxidants. Some are being marketed under trade names, and their exact composition is not known; however, from the data published by different investigators certain substituted phenols are very good antioxidants, chief of which are monobenzyl-para-aminophenol and dibenzyl-para-aminophenol.

In connection with the gum problem in cracked gasolines a number of investigators during the past year have spent considerable time in studying and developing methods for determining the preformed and potential gum in motor fuels. The American Society for Testing Materials studied several methods for determining the gum content of gasolines; during the latter part of the year a vote of the members of committee D-2 of the society was taken and one of the tests made a tentative standard.

**KNOCK CHARACTERISTICS OF MOTOR FUELS**

During the last few years there has been considerable agitation in the petroleum-refining industry concerning the knock characteristics of motor fuels. The Cooperative Fuel Research Committee, composed of representatives of the American Petroleum Institute, National Automobile Chamber of Commerce, Society of Automotive Engineers, and United States Bureau of Standards, developed a method for determining the knock characteristics of motor fuels known as the C.F.R. motor method.

After some work on correlating this method of testing with the actual performance of a motor car on the road the American Society for Testing Materials voted to accept it as a tentative method of test (A.S.T.M. Designation D357-33T). By this method of testing the knock characteristics of motor fuel a standard C.F.R. engine is used and a definite procedure followed.

**LUBRICATED MOTOR FUEL**

The question of top-cylinder lubrication became a live one during the year, and a number of the major refiners in the United States announced the sale of lubricating gasoline.

In addition to the petroleum refineries offering lubricated gasoline, certain companies are marketing a lubricant which is sold to service stations. This is added to the gasoline at the motorist’s request as the gasoline is put in the automobile.

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ALCOHOL AS MOTOR FUEL

To make use of the overproduction of grain in the United States and to help the farmers in distressed areas the use of alcohol blended with gasoline as motor fuel has been advocated by certain groups in the agricultural regions. In fact, the pressure from some sources has been so great that laws have been proposed which would make it compulsory to use a certain amount of alcohol for motor fuel. As yet none of these proposed legislative acts have been passed. The petroleum industry has been opposed to the use of alcohol as a motor fuel; it has been stated that gasoline is a better motor fuel than alcohol and costs less.92

SPECIAL STEELS IN CRACKING EQUIPMENT

The demands for high antiknock gasoline for the modern motor, which in some instances means re-forming of certain light fractions of petroleum, and the hydrogenation process have set up pressure and temperature conditions that put limitations on plain steel in modern refinery practice.93

Plain carbon-steel tubes can be used in the furnace or pipe still for sweet crudes and where severe temperature and pressure conditions are not prevalent, but the alloy steels are gradually crowding the plain steel tube out of the pipe still.

Steel pressure vessels composed of several layers of steel94 have been developed; these seem to have greater strength than a single-walled vessel. The inside layer may be a thin one of an alloy highly resistant to corrosion, while the outer layers may be made of the economical load-carrying steel. Tests on vessels of this type when carried to destruction showed that they developed the full strength of the steels and burst by tearing the plates without shattering, as is typical of thick single-walled vessels tested to failure.

The technique of spraying metal has been improved and now may be used to build up worn pump shafts and piston rods.95 Reaction chambers have been lined with sprayed aluminum to resist sulphur corrosion and so far the work seems to be successful.

MANUFACTURE OF LUBRICATING OIL

One outstanding development in recent years in connection with the refining of petroleum products has been that of solvent-extraction processes. The Edeleanu process, utilizing liquid sulphur dioxide, has been used widely for a number of years in the refining of kerosene to give good-quality burning oils. The Bureau of Mines a few years ago did considerable work on the fractionation of crude oil by solvents.96

In the last few years a number of commercial processes using selective solvents have been developed primarily for the production of high-grade lubricating oils suitable for the most exacting requirements of modern lubrication, such as aero-engine and high-speed automobile-engine lubricating oils.

Nitrobenezene process.—The process is carried out as follows: The charge of oil is mixed with the requisite quantity of nitrobenezene, chilled, and allowed to settle, forming two layers; the lower layer contains the naphthenics in solution in the bulk of the nitrobenezene and the upper layer the solution of the paraffinics. Each layer is separated continuously and passed over steam coils in a vacuum evaporator in which all but 1 to 2 percent of the nitrobenezene is removed, and then through a vacuum stripping tower where the remainder of the nitrobenezene is removed by the application of live steam.

The temperature at which extraction is conducted has an effect on the results obtained and has an important bearing on the plant design. In general, it has been found that the optimum temperature is at least 40°F. below the miscibility temperature of stock and solvent. As the temperature is lowered the difference in solubility between paraffins and naphthenes increases, tending to increase the yield of an oil of given paraffinacity per volume of stock, and the actual solubility of both decreases, tending to decrease the yield per volume of solvent. Separation by selective solvents of the most paraffinic compounds from the viscous fractions of crudes ranging from the nonasphalthic Pennsylvania to the highly asphalthic type promises not only an adequate supply of stock but a control and degree of quality hitherto not practically attainable.

Chlorez (dichloroethyl ether) process.—This method of extraction was used in the manufacture of lubricants during the past year; oils made by this process are now being marketed. The method is carried out in the following manner: It is based on a three-stage countercurrent system of extraction. The flow sheet of the plant in operation shows that the entering stock is heated above its pour point and mixed with thrice-used chlorez before cooling to the desired extraction temperature. The raffinate from the first extraction is treated with once-used chlorez from the last contacting chamber, and raffinate from the second contacting chamber is treated with fresh chlorez. This plant has a capacity of 500 barrels of finished oil a day. Another commercial plant of about 800 barrels a day was put in operation during the last few months of the year.

It is claimed that this process opens up to refiners new possibilities for the production of high-quality lubricating oils.

Edeleanu process.—During the past few months this method has been revised somewhat; a mixture of liquid sulphur dioxide and benzene has been used as a solvent in the manufacture of lubricating oils. Changes in design and construction of Edeleanu plants now make possible the treatment of gasolines or kerosenes with liquid sulphur dioxide and lubricating oils with sulphur dioxide and benzene in the same unit.

Duo-Sol process.—This method of manufacturing lubricating oils differs from the other methods in that 2 solvents are used instead of

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The double-solvent system necessitates the installation of separate recovery units for each solvent. This adds to the initial cost of the extraction plant using this process; based on the oil charged, the unit operating cost is perhaps greater than in plants using a single solvent. It is claimed, however, that this process effects a more complete separation than is possible when a single-solvent system is used, so that higher yields of lubricants of the finest characteristics are obtained.

Furfural process.—This method of manufacturing oils is based on the selective solvent powers of furfural, but the actual plant operation is similar to the other plants using a single solvent. The furfural used in this process must be kept free from mineral acids, caustic alkali, and ammonia and should be protected against severe oxidizing conditions.

The source of raw materials in the manufacture of furfural is agricultural wastes, such as oat hulls, straw, corn cobs, and rice hulls. Furfural compares favorably in price with virtually all of the commercially available refining solvents.

Other solvents than those mentioned have been suggested for use in the manufacture of lubricating oil. Phenol has been used for 3 years in a commercial plant; crotonaldehyde and acrolein have been studied, and methods adapting them to the solvent extraction of lubricating oils have been developed.

A method of refining lubricating oils has been developed in which propane is used as a solvent. In this method of refining, the solvent is used to deasphaltize the lubricating fractions of extremely high molecular weight which are most difficult to distill without decomposition. The operation consists essentially in mixing the residuum with the required quantity of propane at the proper temperature until equilibrium is reached, and the two phases are separated by settling. The propane phase comprises a solution of the lubricating oil and the asphalt phase, a heavy viscous liquid containing sufficient propane to permit transfer by pumping. This process can be operated continuously with relatively simple equipment.

DEWAXING LUBRICATING DISTILLATES

The dewaxing of lubricating distillates from which lubricating oils are made has been rather difficult; it is one of the most expensive steps in the manufacture of lubricating oils, particularly in the production of low pour-point oils.

Considerable study has been given to the use of solvents in studying paraffin wax. The Bureau of Mines worked on this problem several years ago.

4 Poole, John W., and Wadsworth, J. M., Solvent Extraction and Its Application: Refiner and Natural Gasoline Manufacturer, vol. 12, no. 11, November 1933, p. 412.
A process of dewaxing distillates has been developed which involves solution of the oil in liquid propane \(^8\) under pressure followed by adiabatic evaporation of part of the solvent providing self-refrigeration for crystallization of the wax. The remaining propane after separation of wax from the chilled solution is removed by distillation. A plant based on the principles mentioned has been built; it has a charging capacity of 55,000 gallons of wax-bearing oil daily.

The refining industry has used centrifuging methods of separating wax from petroleum wax-bearing fractions for a number of years; during the last few years experimental work has been carried on in developing a centrifuge that could be used with high specific gravity solvents. A machine has now been developed which is somewhat similar to the standard centrifuge,\(^9\) but a special bowl has been designed which discharges the petrodatum from the center of the bowl and the bright stock from the periphery. The solvent used in dewax-petroleum fractions with this machine is trichlorethylene, in which the oil is dissolved. Because of the difference between the specific gravity of the solvent and the oil it is possible to operate the centrifuges at a much lower speed than necessary with naphtha dilution.

The solvent process of dewaxing lubricating fractions of crude petroleum, using as a solvent a mixture of benzene and acetone, has been in commercial use for a number of years.\(^10\) During the last year new dewaxing plants which employ this solvent have been built. This process of dewaxing is carried out as follows: (1) The wax-distillate charge is mixed in the proportion of 3 or 4 to 1 with the solvent composed of approximately 35 percent acetone and 65 percent benzene; (2) the solution is chilled to the desired temperature (approximately the pour point desired of the dewaxed oil) and the wax precipitated; (3) the mixture is then forced through a filter and the wax separated from the solution; (4) the solvent is separated from the filtrate by distillation, leaving a dewaxed oil with a pour point equal to the temperature at which the filtration was conducted; and (5) the solvent is recovered from the wax by distillation, and the recovered solvent is recycled through the apparatus.

Before the development of such methods of dewaxing as mentioned above the refining industry through years of experience had adopted generally three methods of dewaxing for the production of relatively low pour-point oils from wax-bearing crudes. These methods are commonly known as (1) "pressing", (2) "cold-settling", and (3) "centrifuging." These processes have their limitations. They require that a refinery be equipped with two different processes when a complete line of lubricating oils is desired; they also have been improved little in recent years.

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\(^8\) Bahlke, W. N., Giles, R. N., and Adams, C. E., Dewaxing Oils in Propane Solution with Self-Refrigera
tion: Refiner and Natural Gasoline Manufacturer, vol. 12, no. 6, June 1933, p. 229.

\(^9\) Fester, Carl F., Centrifuge Dewaxing with Trichlorethylene: Refiner and Natural Gasoline Manufac
turier, vol. 12, no. 16, June 1933, p. 265.

\(^10\) Govers, Francis X., and Bryant, G. R., Solvent Dewaxing of Oils with Benzol and Acetone: Refiner and Natural Gasoline Manufactures, vol. 12, no. 6, 1933, pp. 222-228.