WARTIME CHEMICALS FROM NATURAL GAS[1]

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FOR many years natural gas has been used mainly for heating and generation of steam and electrical power. In the last few years, however, the tempo of research and development has increased enormously. A much higher field of utilization for natural gas than as fuel is seen in the conversion of the hydrocarbons into superior aviation gasolines, lubricants, synthetic rubber, explosives, acetylene, anesthetics, plant life promoters, plastics, solvents and many other chemical derivatives. A vast supply of these derivatives is available in natural gas produced in this country.

The processes and methods for such conversion in some instances are already in commercial use in the petroleum refining and other industries. Other methods have been worked out in the research laboratories and the processes and yields that can be achieved are known; but it remains necessary for further research to establish the means to reduce costs to the level of commercial practicability. Another wide avenue for future development in the natural gasoline and refining industries is thus foreseen.

Natural gas is consumed at the rate of over 2.6 trillion cubic feet per year. The United States has proven reserves of 85 trillion cubic feet and another 85 trillion as potential reserves. The yearly consumption of natural gas is equivalent in fuel value to 100,000,000 tons of coal or over 500,000,000 barrels of fuel oil.

In the Axis countries, methane gas is a widely used substitute motor fuel. As a matter of fact, there are over 107,000 compressed gas (methane, ethane, propane, butanes) propelled motor vehicles operating in continental Europe, which conserved about 2,300,000 barrels of gasoline for military use. The compressed gas is sold at filling stations in exactly the same way as gasoline in the United States. The gases are compressed under pressures up to 5,000 p.s.i. into steel cylinders attached to the running board of the car or under the floor of trucks and buses. Italy has a number of natural gas wells and is operating many buses and trucks plus a number of locomotives on methane gas. This looks like a desperate measure, since it requires on the average about 135 pounds of steel for each of these high-pressure steel alloy cylinders in order to withstand the high pressures. The products of fermentation of sewage are also used as a source of methane gas in Germany. Methane from coal gas is used for running motor vehicles of one sort or another in many of the European cities. Many coal hydrogenation units produce gasoline in addition to methane, ethane, propane and butanes by the Bergius and Fischer-Tropsch processes. The latter process will be referred to later in more detail because it is a potential source of many products. Buses, trucks, tractors and power shovels, totaling over 25,000 in the United States, use compressed propane and butane. One truck company has liquefied butane functioning in a dual role as a refrigerant for fruits and meats and as motor fuel for the truck after the cooling has taken place.

Hydrocarbons present in natural gas are methane, ethane, propane, butanes, pentanes, hexanes and heptanes, etc. The first four of those are gases, while from pentane on they are liquids useful as gasoline.

The individual hydrocarbons have a variety of uses in a number of industries. Propane has been suggested for use as a fuel for breaking in aviation engines on the "test block" since it has a high octane value and is readily available. Such a procedure would conserve the 100 octane liquid fuels needed for fighter, bombing and cargo airplanes in the war effort. Other uses for propane which have gained wide commercial application are as refrigerants and solvents in the refining of lubricating oils. Paraffin wax, asphaltic substances, naphthenic hydrocarbons and other materials are eliminated from lubricants when propane is used as the solvent. Over 50 per cent. of the world's lubricating oils are improved in quality by the use of propane.

Two hydrocarbons present in natural gas of great utility are isobutane and isopentane. Isobutane is the key hydrocarbon in the production of aviation gasoline by alkylation with olefins. In general, there is not enough isobutane available, hence it has been necessary to isomerize the normal butane present in natural gas to the iso compound. A number of commercial installations are in operation and under construction to isomerize normal butane to isobutane. Normal and iso pentane are also present in natural gas, and it is highly desirable to fractionate out the iso compound due to its 91 octane rating in contrast to the normal, which has an octane number of 64. Isopentane is blended with aviation gasoline in percentages ranging from 10 to 20, depending upon the other components in the final blend.

Olefinic hydrocarbons, not contained in natural gas as such, are important for many reactions not alone

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[1] Address before the American Institute of Chemists, Chemists' Club, New York, N. Y., October 23, 1942.

for aviation gasoline but for synthetic rubber and a host of other products. There are several routings to produce olefins from natural gas: one is high temperature, and the other by catalysis. The olefinic hydrocarbons which are now in great demand are ethylene, propylene, butylenes, pentylenes and butadiene. Natural gas, particularly the propane-butane fraction, when subjected to high temperature cracking, produces ethylene, propylene, butylenes and butadiene. Normal butane is readily converted into butadiene in one or two stages by catalytic means at high temperature with yields reported of over 60 per cent.

A branched chain paraffin, isooctane, is of great importance in the aviation fuel program. There are two methods whereby this hydrocarbon is derived—one is by polymerization, in which isobutylene is polymerized to a dimer in the presence of phosphoric acid as a catalyst. Isooctene is the product, and upon the addition of hydrogen, isooctane results. Isooctane has an octane rating of 95–100. Another method of producing aviation gasoline is to polymerize the propylene, butylenes and pentylenes present in cracked gases to a polymer gasoline under selective conditions which upon hydrogenation yields an aviation gasoline blending product of 90 octane rating.

The polymerization process has been largely replaced by the alkylation process in which isobutane is alkylated by butylenes in the presence of sulfuric or hydrofluoric acid catalysts. The resulting alkylate ranges in octane value from 91 to 96. The simplest of the olefins is ethylene, which is used to alkylate isobutane at temperatures in the order of 950° F. and pressures up to 5,000 pounds. This reaction produces neohexane having an octane rating of 94, an important hydrocarbon for aviation gasoline. In addition to alkylating ethylene and butylenes, propylene and pentylenes are also being alkylated with isobutane to form additional quantities of high quality aviation gasoline. It is proposed in some type of operation to utilize the mixtures of propylene, butylenes and pentylenes in the alkylation reaction with isobutane using hydrofluoric acid as alkylating catalyst to produce alkylate of 91 octane rating highly suitable for aviation gasoline blending stock.

An important aviation blending fuel of an entirely different type is cumene, which is produced from the alkylation of propylene and benzene in the presence of solid phosphoric acid. A number of commercial units are now in operation.

Normal hexane and heptane are two hydrocarbons which from a motor fuel standpoint are practically worthless unless their molecular structure is changed. Normal heptane has a zero octane rating and hexane about 25. These straight-chain paraffin hydrocarbons, hexane and heptane, can be changed in configuration and also in their properties to improve their antiknock properties. Hexane and heptane can also be converted into benzene and toluene—two important hydrocarbons for high explosives. Benzene is of vital importance in the production of styrene, which is produced by the alkylation of benzene with ethylene forming ethyl benzene. Dehydrogenation of this compound yields styrene. When styrene (25 per cent.) and butadiene (75 per cent.) are mixed in the presence of a catalyst such as peroxide, polymerization takes place to form the synthetic rubber Buna-S.

The synthetic rubber program in the United States calls for 886,000 tons as planned in September, 1942, distributed as follows:

Types	Tons
Buna-S	705,000
Butyl	132,000
Neoprene	49,000

However, the recommendations of the Baruch Committee called for an increase of 220,000 tons to be apportioned as:

Types	Tons
Buna-S	140,000
Neoprene	20,000
Thiokol	60,000

Out of the total 886,000 tons of synthetic rubber planned for the United States, 705,000 tons of it will come from butadiene and styrene. The normal butane that will be used for butadiene will represent about 80,000 tons a year derived largely from natural gas. One plant has a rated capacity of 66,000 tons and the other 15,000 tons a year.

More than 100,000 barrels a day of normal butane are available from natural gas. If this were used just for butadiene making, it would satisfy the entire butadiene requirements in our present synthetic rubber program. Hence, it can be seen that the natural gas industry has more than enough of the hydrocarbons which can be converted into raw materials to supply the entire synthetic rubber program. Another important source of butadiene is through the dehydrogenation of butylene derived from catalytic cracking. This source will yield at the rate of 283,000 tons annually.

Another type of synthetic rubber is called Thiokol, made by chlorination of ethylene, which is then refluxed with sodium polysulfide. The synthetic rubber program calls for 60,000 tons of Thiokol yearly. Hydrogen sulfide is present in varying percentages in natural gas and is readily converted into flowers of sulfur. This sulfur may react with caustic soda to produce sodium polysulfide. After reacting ethylene with chlorine, the dichlorethane is formed which reacts with the polysulfide yielding Thiokol. The plans call for the use of Thiokol in retreading of tires.

Besides butadiene, styrene and ethylene, a hydrocarbon of great importance is acetylene used in the production of the synthetic rubber, neoprene; it is also the base material for nylon, a replacement product for silk. Calcium carbide is produced from coal and lime in electric furnaces requiring much electrical power. When water is added to this compound, acetylene is formed.

Natural gas or products therefrom under high temperature conditions yield acetylene readily. Two commercial acetylene units are being installed at the present time, one of which will produce at the rate of 75 tons per day or 27,000 tons a year. Other units are also under way. The charging stock may be either propane, butane, natural gasoline or fractions from petroleum. It is believed that acetylene can be produced at a lower cost from processing natural gas than by the electrochemical method of producing calcium carbide. The natural gas industry has enormous volumes of propane and other hydrocarbons available to supply the whole needs of the United Nations for acetylene and its derivatives.

Germany uses acetylene made from calcium carbide, converting it into butadiene by a four-stage chemical process. Neoprene rubber is made from acetylene treated with hydrochloric acid. This type of rubber will be produced at the rate of 49,000 tons a year in the United States.

The Russians start primarily with ethyl alcohol from grain to produce butadiene. Butadiene from ethyl alcohol derived from grain will be one of the sources in the United States synthetic rubber program. The tonnage of butadiene from grain alcohol will be at the rate of 242,000 a year, representing about one third of the Buna-S type production.

There are several other types of rubber which are in commercial production, one of which is the type based on isobutylene from dehydrogenation of isobutane from natural gas or from cracking of oil. Isobutylene is copolymerized with about 2 per cent. of butadiene or isoprene, resulting in a product called Butyl rubber. In the government program this type of rubber will be produced at the rate of 132,000 tons a year. Butyl rubber, as of to-day, is not as good a synthetic rubber for tire use as the Buna-S. Tires made of Butyl rubber have a mileage life of about 12,000 miles with a maximum road speed of thirty-five miles an hour. This will naturally be improved upon.

There is an important use for synthetic rubber which is fabricated so that billions of minute air cells are present; it is used as a liner in gasoline tanks in fighting, bombing and pursuit planes. When a bullet goes through the tank, the rubber causes it to be self-sealing.

Another type of synthetic rubber is the acrylonitrile butadiene which can be produced also from natural gas and is known as Buna-N or Perbunan.

One of the necessary materials in the compounding of either natural or synthetic rubber is carbon black, which is made from natural gas. Carbon black is an important component in tires or other rubber goods whether it is blended with natural or synthetic rubber, as the properties of rubber, particularly from the standpoint of the tensile strength and wearing qualities under service conditions, are greatly improved. During the year 1940 about 369 billion cubic feet of natural gas were converted, largely by the channel process (air oxidation), into carbon black with an average of 1.54 pounds per cubic foot of gas or about 285,000 tons, of which about 85 per cent. was used in tires. Furnace black appears to be superior for use in synthetic rubber.

The world's natural rubber production for 1941 was about 1,675,000 long tons, of which the United States imported over 800,000 long tons. The United Nations have lost over 95 per cent. of the world's natural rubber sources and Russia has lost two of its synthetic rubber plants in the Ukraine.

With the tremendous increased demand for airplanes, tanks, motor trucks, ships, trains, gun mountings, etc., rubber is required in ever-increasing quantities by both the fighting forces and the necessary civilian users for the successful conclusion of World War II. A medium-sized tank requires 500 pounds of rubber, small pontoon bridges, 1,000 pounds; for flying fortresses the gasoline tank alone requires 500 pounds of bullet-sealing rubber, while a large bomber uses 1,250 pounds, gas masks 0.75 pounds, and battleships between 75,000 and 150,000 pounds. Tires for large excavation trucks used by the Army have a diameter of 9.5 feet and weigh over 3,500 pounds. There are many hundred more products requiring rubber that are vital in the war effort, such as blimps, barrage balloons, rubber boats, rafts and life vests and suits for flyers, hospital rubber needs, etc. Millions of soldiers on the fighting fronts require rubber in one form or another.

The synthetic rubber picture in the United States, with its 886,000 tons a year at plant costs of about $800,000,000 is already well under way. The Baruch Committee has recommended that this tonnage be increased to 1,106,000 tons a year. In addition to being the arsenal for many other war products, synthetic rubber will also have to come from the United States to supply our allies' needs. It may well be assumed that even 1,106,000 tons of synthetic rubber will be too low for the United Nations' requirements.

The question arises now: Is the synthetic rubber product equal to the natural? In general, one can say that synthetic rubber is at least equivalent to the natural; the chemist's goal is not necessarily to synthesize a duplicate of natural rubber, but it is certain that whatever properties rubber has that are needed will not only be duplicated, but radically improved and new ones added. Synthetic rubber is superior to natural rubber in gasoline, oil and chemical resistance. The synthetic product is more stable to light and air, and has greater wearing properties. Some trucks using synthetic rubber tires have gone over 35,000 miles. Sidewall tire strength is greater, meaning greater safety and better road gripability. The latter property has been tested out thoroughly on wet and muddy roads. Tests on hills with different trucks have shown that the synthetic rubber-tired vehicle goes up a hill with very little side-slipping, whereas the tires of natural rubber slipped all over the road. On curves when operating the car at high speeds, the synthetic tire is safer than the natural.

(*To be concluded*)

INFLUENCE OF THE ENVIRONMENT ON THE EXPRESSION OF HEREDITARY FACTORS IN RELATION TO PLANT BREEDING[1]

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ENVIRONMENTAL influence on the expression of hereditary factors has many aspects. To the geneticist this is the cause of non-hereditary variation. To the experimental taxonomist it helps to explain the status of geographic races. To the breeder it may represent the opportunity to provide adaptability. To the horticulturist interested in cultural problems, differential varietal response to the environment is being increasingly recognized as an important factor in making cultural recommendations. Each aspect has as its fundamental basis the response of the hereditary factors or genes, either singly or more commonly in groups, to the many conditions external to the organism, under which it develops. These outside influences are usually rather complex and difficult to control experimentally. Those most frequently studied are temperature, light intensity and duration, soil and air moisture, wind movement and a variety of nutritional factors.

One of the first careful studies of the effect of the environment on the expression of the gene was made by T. H. Morgan and reported by him in 1915. A strain of Drosophila was found in which the abdomen was defective. This was shown to be sex-linked and to be due to a single mendelian factor. The remarkable thing about it was that only the flies that hatched while the colony was young had the defect, while flies emerging later were normal in every respect. By suitable tests it was shown that flies developing from larvae whose food had been moist had the defective abdomen, while flies whose larval stage was spent on drier food were normal.

A second component of the environment that has received considerable attention from the geneticists working with fruit-flies is temperature. Zeleny in 1923 showed that an increase of 1° C. during the larval stage decreases the number of facets of bar eye by 10 per cent., of ultra-bar by 8 per cent. and of normal flies by 2.5 per cent. He pointed out that the same effect can be obtained either by increasing the temperature or by adding another bar gene.

Passing on to another insect, the Hymenopterous parasite of the oriental fruit moth (*Trichogramma minutum*) consists of several morphologically similar races that carry different factors for body color which are entirely dependent upon an appropriate temperature for their expression. According to Peterson, when the average daily temperature exceeds 62° F. the females of one race have a distinct lemon-yellow body color, but when the temperature drops below this average these same individuals become a metallic brown. Flanders finds that four races of this parasite can be identified on a basis of color when raised at the same temperature, but when raised at different appropriate temperatures they are indistinguishable. Temperature with this insect not only affects body color but also influences the length of the life cycle, an important character in determining adaptability to climate.

The effect of temperature on the expression of hereditary factors is by no means limited to insects. In Canna, Honing finds that the anthocyanin pigment producing "old purple" is recessive to another factor for yellow. Plants that are homozygous recessive for old purple and heterozygous for yellow (ssWw) are completely yellow during the heat of summer, but later flowers of the same plant developing during cool weather in the fall have a bluish cast. *Primula sinensis* has a form in which the flower is red

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[1] Condensed address of the retiring chairman of the Southern Section of the American Society for Horticultural Science, presented at the Memphis meeting on February 5, 1942. Citations to literature have been published with the complete paper in Volume 41, Proceedings, Amer. Soc. Hort. Sci., 1942.