I. C. 6388

DECEMBER, 1930

DEPARTMENT OF COMMERCE

UNITED STATES BUREAU OF MINES
SCOTT TURNER, DIRECTOR

INFORMATION CIRCULAR

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POSSIBLE UTILIZATION OF NATURAL GAS FOR THE PRODUCTION OF CHEMICAL PRODUCTS[1]

By Harold M. Smith[2]

The production of oil during the early development of new oil fields is usually accompanied by large quantities of natural gas. Since in most fields gas under pressure is the main source of the energy causing the oil to move through the sands into the wells and thence to the surface, this coincident production of natural gas will continue as long as present day producing methods are used. Generally the use of this gas is restricted, and markets are not readily available. Consequently, a large portion of the gas produced at such times is often wasted by being blown into the air.

The magnitude of gas waste is well brought out in the following statement by Miller[3]:

> "Only a few outstanding examples need be cited to show the enormous production of gas that accompanies the discovery of new sources. In April, 1927, the Ventura field produced approximately 210,000,000 cubic feet of gas a day; and during the summer of 1927 Alamitos Heights reached a peak gas production of 102,000,000 cubic feet a day; on December 1, 1928, as a result of the summer's deeper drilling in the Long Beach field, surplus gas production amounted to 125,000,000 cubic feet a day. It is estimated that in January, 1929, the Santa Fe Springs field will have a daily gas production of 387,000,000 cubic feet from the recently discovered Buckbee oil zone. Of this amount 274,000,000 cubic feet a day will be the surplus above the amount required for field and plant fuel, taken out by utility corporations, and that used in repressuring the Meyer sand which lies above the Buckbee zone".

Another instance of a large volume of gas being wasted is found in the Turner Valley field of Canada.[4] Here 250,000,000 cubic feet of gas is being burned daily in flambeaus, as there is no present outlet for the gas except at prohibitive cost. It is estimated that $30,000,000 to $40,000,000 would be required to build

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1 - The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from U. S. Bureau of Mines Information Circular 6388."

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3 - Miller, H. C., Function of Natural Gas in the Production of Oil: A report of the Bureau of Mines in cooperation with the American Petroleum Institute, 1929, 321 pp.

4 - Hazlett, A. J. Rocky Mountain Producers Visit Turner Valley Field as Guest of Canadians: Nat. Petrol. News, vol. 21, Oct. 2, 1929, pp. 73-76.

a pipe line to Winnepeg, the nearest industrial center, which is more than 800 miles distant from the field. Even with such a line in operation, only a part of the present open flow from this field would be used commercially.

These illustrations are typical of the gas loss in oil fields all over the world, and within the last few years a large amount of thought and engineering effort has been directed toward finding means of utilizing this gas profitably.

One possible method of utilization is in the manufacture of chemical products, and much work has been done on the various types of reactions that might be of commercial value. The reactions offering means of approach to the problem may be divided roughly into three general classes: (1) Controlled oxidation, either with steam, or by oxygen, or by gases containing oxygen; (2) pyrolysis, the breaking up of the hydrocarbon molecules with heat and the uniting of these parts to form new substances, or, in the extreme, the decomposition to carbon and hydrogen; (3) chlorination, the replacement by chlorine of more or less hydrogen in the hydrocarbon molecules.

The Bureau of Mines has been actively studying certain of these reactions for some time, the purpose being to develop simple and economical means for utilizing gas which otherwise would be wasted. The Pittsburgh station has been studying the oxidation processes particularly, and the Bartlesville station has been investigating the possibilities of pyrolysis, exclusive of cracking direct to the elements carbon and hydrogen.

Some of the products which are obtainable by the various reactions are indicated in the accompanying chart, the data for which have been in a large part obtained from the literature. At present very few of these products can be obtained on a commercial basis by synthesis from natural gas, and in fact some of the products have been found only in relatively small amounts in laboratory experiments. In the present-day development of chemistry, however, that which is curious today becomes commonplace tomorrow, so that in studying the possibilities of these various reactions the chemist makes no apology for considering the apparently insignificant products that are of minor commercial importance at present.

A brief description of the principle reactions by which natural gas may be transformed into other chemical products follows. The more important application of these products is also indicated at the same time.

Oxidation

"Recently there has been much interest in the hydrogenation of oils. An important method of obtaining the necessary hydrogen is by the interaction of natural gas and steam at temperatures of about 500 C. or lower in the presence of catalysts such as iron oxide. The products are chiefly hydrogen and carbon dioxide. The latter is removed by suitable scrubbing, and fairly pure hydrogen is thus obtained. Its major uses are as a reducing agent in the process industries; the hydrogenation of mineral and vegetable oils and coal; and the synthetic production of ammonia, which is widely used as a refrigerant,

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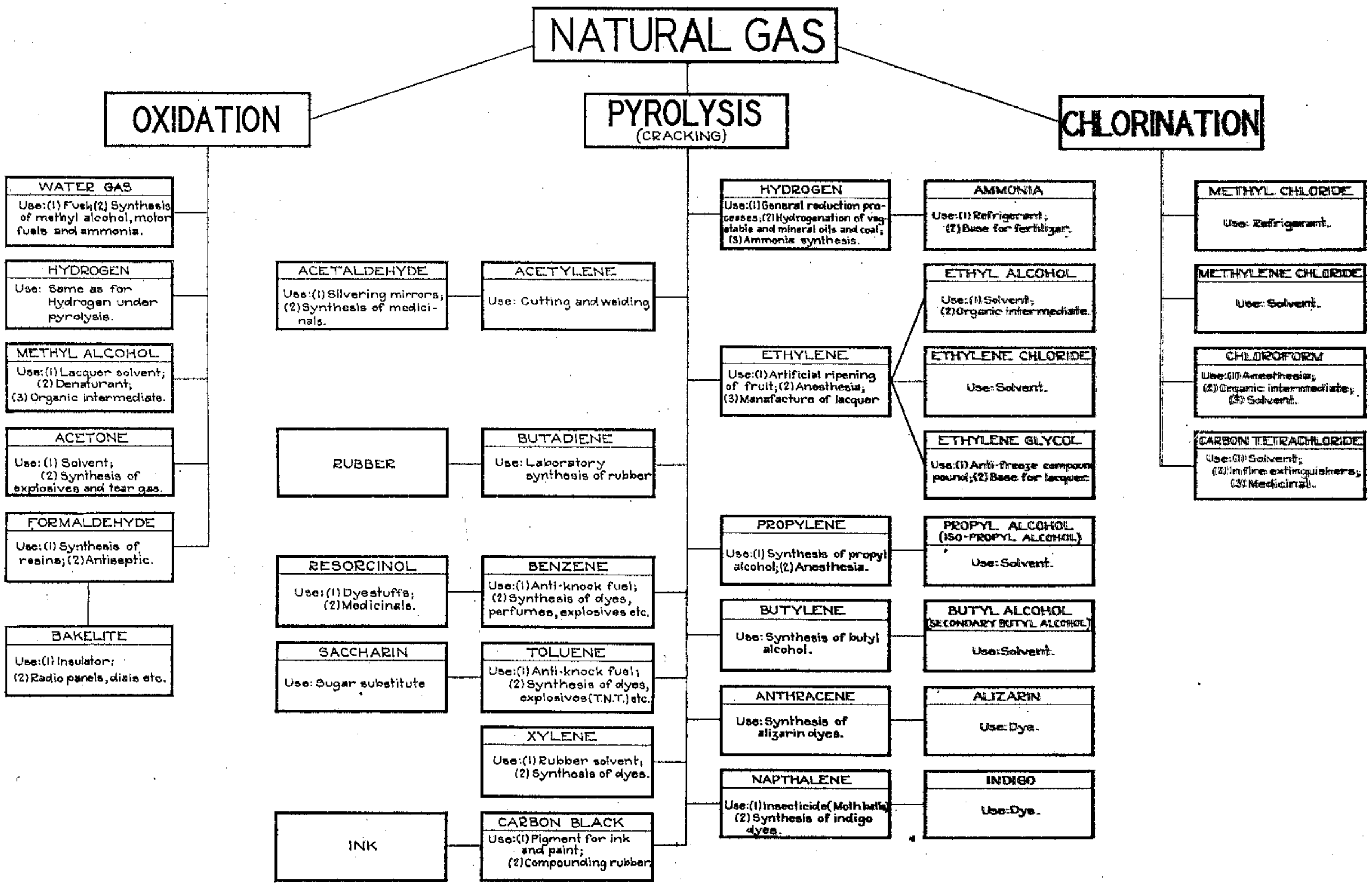

and in the manufacture of fertilizer."

Methane also reacts with steam at 900°C. (1652°F.) in the presence of suitable catalysts to give a mixture containing one volume of carbon monoxide and three volumes of hydrogen:

$$CH_4 + H_2O = CO + 3H_2$$

This mixture of carbon monoxide and hydrogen (water-gas) is the basis for several catalytic syntheses. (1) At high pressures (50-200 atmospheres) and at temperatures of 200 to 400°C. (392-752°F.) in the presence of suitable catalysts water gas yields methanol (methyl or wood alcohol). Methanol is used widely as a solvent, a denaturant, and an organic intermediate in the formation of other compounds. (2) At atmospheric pressure in the presence of iron or cobalt catalysts many compounds may be formed, among them liquid hydrocarbons and oxygenated compounds which could be blended with gasoline. Acetone, a valuable solvent and intermediate for nitrocellulose lacquers and explosives may be obtained by a similar process.

Methane, with the proper catalysts and under suitable conditions of temperature and pressure may be oxidized directly by oxygen, or oxygen-containing gases such as air or NO_2 to formaldehyde:

$$CH_4 + O_2 = CH_2O + H_2O$$

Formaldehyde has in recent years become of much importance in the synthesis of resins such as bakelite. Formaldehyde is also a valuable antiseptic.

Pyrolysis

When methane is subjected to temperatures of 1,800 to 2,200°F. it breaks up or "cracks". At slightly lower temperatures the parts reunite, but form new products as they combine. The higher hydrocarbon gases also break up and reunite to give various products different from the parent substances. At sufficiently high temperatures the gas will decompose to carbon and hydrogen.

In either type of cracking, hydrogen is always set free and by suitable means can be isolated and used commercially, as previously mentioned under the discussion of production of hydrogen by oxidation. Its major uses are as a reducing agent in the process industries; the hydrogenation of mineral and vegetable oils and coal; and the synthetic production of ammonia, which is widely used as a refrigerant and in the manufacture of fertilizer.

Other gases formed in the pyrolysis of natural gas are acetylene, butadiene, ethylene, propylene and butylene. Acetylene is used in welding and cutting metal; and may be used to prepare acetaldehyde, which is further used in silvering mirrors or in the preparation of medicinals such as chloral, a soporific. Butadiene under proper treatment condenses to form an artificial rubber having the same general composition as natural rubber. Ethylene has recently come into use in ripening fruits. It is also finding use as an anesthetic. However, its major use at present is in the synthesis of ethylene glycol, an excellent anti-freeze for water-cooled motors. Ethylene is also the basis for a series of important lacquer solvents. If desired, ethyl alcohol, widely used as a solvent, and also in the preparation of other compounds such as ether, may be prepared from ethylene. Again by the proper reaction with chlorine, ethylene chloride is formed. This is a valuable solvent, especially for fats and essential oils, and is also used as an anesthetic. Propylene finds use as an anesthetic, and also in the synthesis of isopropyl alcohol, which is being substituted for ethyl alcohol with good results in certain instances. Butylene is also used in the preparation of certain butyl alcohols which are being used as solvents in the chemical industries.

The principal liquids formed in the pyrolysis of hydrocarbon gases are benzene, toluene, and xylene. Benzene is a valuable product and forms the basis of many of our chemical processes. Thus we obtain aniline and the entire series of aniline dyes, and many explosives, perfumes, and medicinals. In addition benzene is an excellent solvent and antiknock motor fuel. Toluene is the basis of the familiar T.N.T. (trinitritoluol), of dyes, and of saccharin, a sugar substitute 400 times as sweet as sugar. Xylene is similarly used in the synthesis of dyes and other products, and also to a large extent as a solvent.

The solids resulting from pyrolysis are chiefly napthalene and anthracene. Naphthalene is well known as an insecticide in the form of moth balls. It is also the basis for the important indigo dyes. Anthracene is used in the synthesis of alizarin dyestuffs. Finally, under certain conditions of cracking we obtain carbon black, widely used in making ink, compounding rubber, and as a pigment for paint.

Chlorination

Chlorination is generally applied to methane, although the other gases may be chlorinated. From methane four products may be made: Methyl chloride, much used as a refrigerant; methylene chloride, a solvent; chloroform, a general anesthetic, solvent, and intermediate in the formation of other compounds, carbon tetrachloride, a solvent, used in fire extinguishers and medicinally in combatting the hook worm.

In conclusion it should be pointed out that even if the technical difficulties attendant upon the commercial production of the various products mentioned are solved, the economic side of the problem should receive serious consideration. Since, however, the raw material under consideration is virtually a waste product, any return, however small, would be profitable and an aid to conservation of our natural resources. Moreover, it has happened many times in the development of the chemical industries that the large production of a chemical product at an attractive price has stimulated its use. For example, benzene, which at present is too high in price for widespread use as an antiknock medium in motor fuel, would undoubtedly be attractive to many refineries if available at a more moderate cost. Finally, most of these processes, while they may appear simple on paper, probably will not be ready for general use for several years, as there are many technical difficulties to be solved before commercial application is feasible. When the processes are ready for commercial use many of the present economic hindrances may have disappeared. But regardless of economic considerations the study of these reactions involving the use of natural gas is of importance both at present and for the future, for as mentioned previously, that which is a chemical curiosity today becomes the commonplace and important chemical tomorrow.