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INFORMATION CIRCULAR

UTILIZATION OF NATURAL GAS FOR CHEMICAL PRODUCTS



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BY

HAROLD M. SMITH AND W. C. HOLLIMAN

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UTILIZATION OF NATURAL GAS FOR CHEMICAL PRODUCTS^{1/}

By Harold M. Smith^{2/} and W. C. Holliman^{3/}

Among the more important raw materials now utilized for the commercial production of synthetic organic chemicals is natural gas. Natural gas has been used as a fuel and source of energy almost from its discovery, but its potentialities as a chemical raw material were not realized until recently.

Research in the use of natural gas for chemical synthesis received great impetus from the discovery by Brooks and Humphrey^{4/} in 1918 of alcohols in the diluted "acid oil" obtained by sulfuric acid treatment of cracked petroleum distillates. Experimental data soon showed that hydrocarbons from natural gas could be converted to these same products. Laboratory methods for chlorination of natural-gas hydrocarbons, particularly of methane for the production of methyl chloride, methylene chloride, carbon tetrachloride, and chloroform were known before that time but were not developed commercially. Methods for obtaining alcohol by oxidation of hydrocarbons derived from natural gas also were known before 1918 but had not received commercial consideration. Since 1918, and particularly during the past 15 years, the work of chemists and chemical manufacturers throughout the world has resulted in an accumulation of data regarding the reactivity of natural-gas hydrocarbons, and related hydrocarbons found in refinery gases or made synthetically. These data have been used to develop methods for converting hydrocarbons into chemical products and thus form the basis for a large and growing industry.

Wartime demands for chemicals during 1939-1945 gave impetus to this development, especially to the application of engineering technology to methods already known in the laboratory but which had not been developed commercially. The production of plastics as substitutes for rubber and silk; of ammonia, glycerine, toluene, and nitroparaffins for use in explosives; of synthetic rubber; and of aviation gasoline are examples of this technologic growth. The demand for these products required new sources of raw materials, and as a result many processes were developed and plants constructed to utilize natural gas and other petroleum hydrocarbons. With the cessation of hostilities, the conversion of these plants and processes to peacetime activities has been rapid. Additional postwar construction of plants for chemical utilization of petroleum gases indicates that the growth of this phase of the petroleum industry will continue.

- ^{1/} The Bureau of Mines will welcome reprinting of this paper provided the following footnote acknowledgment is used: "Reprinted from Bureau of Mines Information Circular 7347."
- ^{2/} Principal petroleum chemist, Petroleum Experiment Station, Bureau of Mines, Bartlesville, Okla.
- ^{3/} Research chemist (petroleum), Petroleum Experiment Station, Bureau of Mines, Bartlesville, Okla.
- ^{4/} Brooks, B. T., and Humphrey, I., The Action of Concentrated Sulfuric Acid on Olefins with Particular Reference to the Refining of Petroleum Distillates: Jour. Amer. Chem. Soc., vol. 40, 1918, pp. 822-856.

The quantity of natural gas that is, or that under present demands can be, utilized in the production of chemicals is not great in comparison with the amount used as fuel. Some data showing present consumption of natural gas for several purposes are presented and discussed with chart 2. Generally, an organic chemical product can be made from any one of several starting materials as well as by several routes from a single substance. This is illustrated by and discussed with chart 5. This versatility of hydrocarbon conversion processes is important, as ordinarily it may be assumed that a substance will not be made synthetically from naturally occurring raw materials if it can be obtained in sufficient quantities as a byproduct from an active commercial process. The cheapness and availability of natural gas, however, has caused unusual consideration to be given to its chemical utilization. Many chemicals not previously procurable commercially have been made from natural-gas hydrocarbons, and in many instances they have filled needs that had not been met by other known substances.

The production, from natural gas, of aviation gasoline and of high anti-knock blending agents for enrichment of motor fuels is not strictly a "utilization for chemical products." Many of these gasoline components, however, are relatively pure chemicals, and the processes employed in their manufacture are applicable to the manufacture of products intended for chemical rather than energy uses. Investigations of production of motor fuels from natural gas and refinery byproduct gases, which were begun actively about 1928, resulted in the discovery of many processes. These investigations also disclosed additional methods and technology for production of pure chemicals and chemical raw materials from natural-gas hydrocarbons. A report giving the results of some of the early investigations of this problem by the Bureau of Mines were published in October 1931.^{5/} In that report, previous and concurrent work by other investigators is cited.

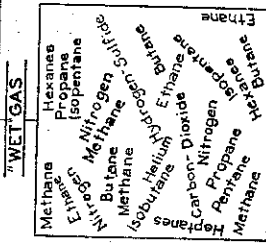
An information circular concerning the utilization of natural gas for chemical products was published by the Bureau in 1930.^{6/} and a revision was issued in 1940.^{7/} The present paper is a revision of the 1940 publication. Its purpose is to show in graphic form the general reactions used and the chemical products that may be obtained when natural gas is used as a raw material. The number of products presently obtainable from natural gas is very large, and the field is continuing to develop, so that it is possible that some products that are now important (or soon may be so) have been omitted, but every effort has been made to make this publication as inclusive as available information permits. The products listed may be

^{5/} Smith, H. M., Grandone, Peter, and Rall, H. T., The Production of Motor Fuels from Natural Gas: Bureau of Mines Rept. of Investigations 3143, 1931, 12 pp.

^{6/} Smith, Harold M., Possible Use of Natural Gas for the Production of Chemical Products: Bureau of Mines Inf. Circ. 6388, 1930, 5 pp.

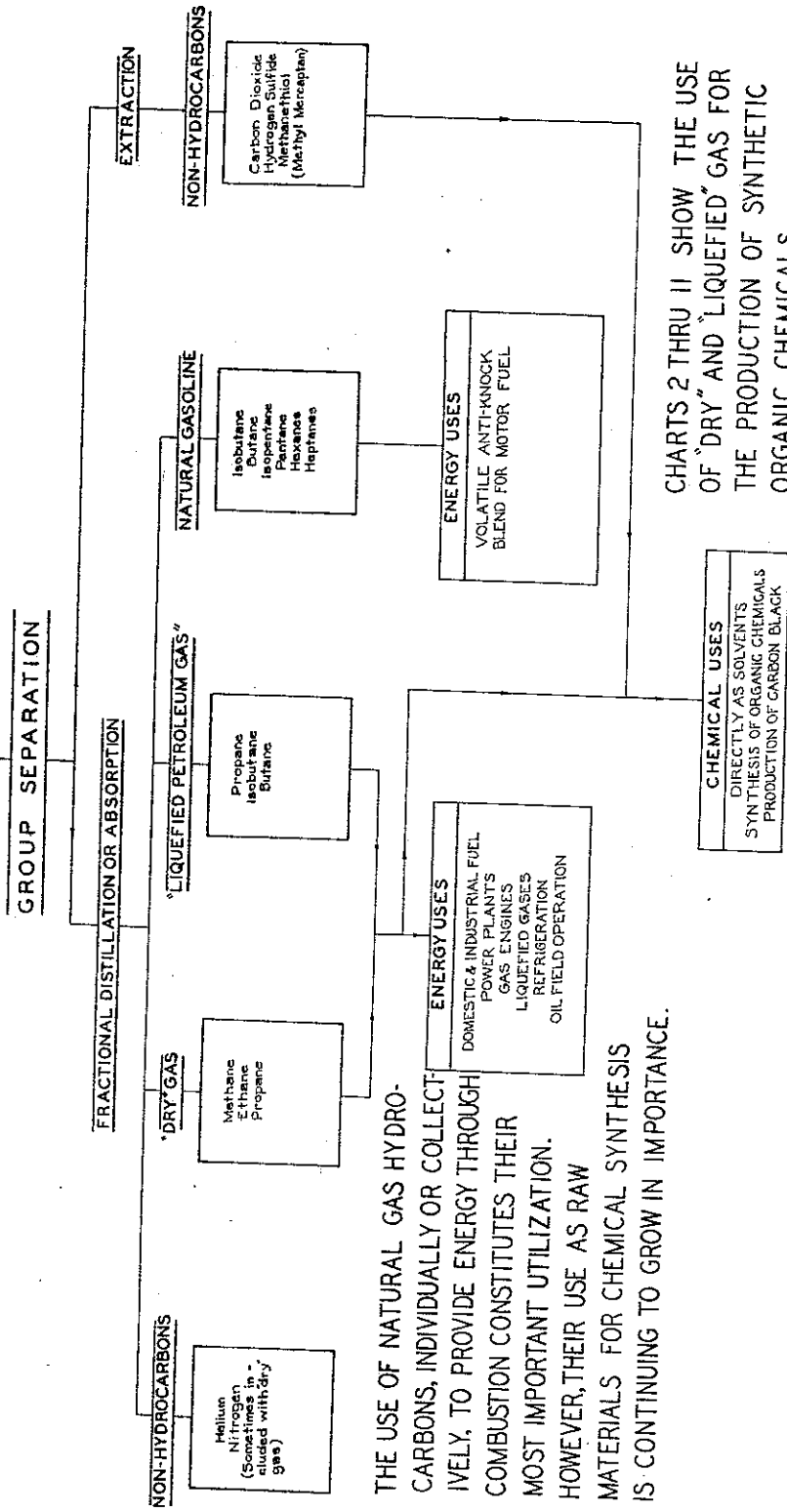
^{7/} Smith, Harold M., Utilization of Natural Gas for Chemical Products: Bureau of Mines Inf. Circ. 7108, 1940, 18 pp.

CHART 1
NATURAL GAS



NATURAL GAS IS A MIXTURE OF HYDROCARBON AND NON-HYDROCARBON GASES. THE SEVERAL HYDROCARBON COMPONENTS MAY BE SEPARATED INTO GROUPS BY ABSORPTION OR DISTILLATION. IN THE FIRST SEPARATION THREE GROUPS OF PRODUCTS MAY BE MADE.

THERE IS SOME OVERLAPPING BETWEEN THESE GROUPS AS SHOWN BELOW. INDIVIDUAL COMPONENTS CAN BE ISOLATED WHEN DESIRED BY FRACTIONAL DISTILLATION PROCEDURES. SOME NON-HYDROCARBON GASES ARE SEPARATED BY EXTRACTION WITH SOLVENTS.



THE USE OF NATURAL GAS HYDROCARBONS, INDIVIDUALLY OR COLLECTIVELY, TO PROVIDE ENERGY THROUGH COMBUSTION CONSTITUTES THEIR MOST IMPORTANT UTILIZATION. HOWEVER, THEIR USE AS RAW MATERIALS FOR CHEMICAL SYNTHESIS IS CONTINUING TO GROW IN IMPORTANCE.

CHARTS 2 THRU 11 SHOW THE USE OF "DRY" AND "LIQUEFIED" GAS FOR THE PRODUCTION OF SYNTHETIC ORGANIC CHEMICALS.

produced from natural gas from wells or natural gasoline plants, but ordinarily natural gas would not be used where refinery-process gases or other raw materials are available that will yield the desired product in fewer steps and more cheaply. Some statistics relating to the economics and growth of the industry are shown in the first charts, and the principal processes and their products are shown in the others.

It would be desirable to include brief descriptions of some of the processes, but choices of methods and operating conditions are so varied that no simple explanation seems possible. Actually, few of the reactions are as simple as the charts may indicate. The subject of catalysts alone is so complex that it cannot be presented adequately in a report such as this. The nontechnical reader is interested mainly in the general picture which is adequately shown by the charts. A selected bibliography is included for the technical reader who may wish to obtain such chemical and engineering information as is generally available and for the nontechnical reader who may wish to inquire further into the subject. Historical and bibliographical reviews of work done in the field have appeared in the literature from time to time, some of which are listed among the references.

Chart 1.

Natural gas is a mixture of gaseous hydrocarbons consisting predominantly of those containing not more than four carbon atoms. It occurs in natural reservoirs separately as gas or may be found with or in solution in nongaseous hydrocarbons. The composition of natural gas may differ from field to field and also with production methods. Methane is the hydrocarbon usually present in greatest volume, with ethane, propane, and heavier hydrocarbons successively next in order. The composition of a "wet" gas typical of much of that produced lies within the following limits in volume percent: Methane, 80-90 percent; ethane, 5-10 percent; propane, 3-5 percent; isobutane and butane, 1-2 percent; pentanes and heavier hydrocarbons, 1-2 percent. Nonhydrocarbon components, including nitrogen, hydrogen sulfide, traces of organic sulfur compounds, carbon dioxide, and helium, may occur with the natural gas. Certain of these may be extracted from natural gas either as impurities or for individual utilization. (Chart 12.)

Chart 1 shows the general composition and major uses of natural gas. The gaseous mixture or "wet" gas produced at the wellhead, as shown in the top square of the chart, usually is separated in the field in absorption or natural-gasoline plants. Nonhydrocarbons are removed under certain conditions, and the hydrocarbons are separated into "dry gas," "liquefied petroleum gas" (sometimes referred to as LPG), and natural gasoline or condensate. ("Dry" gas occurs as such in some fields. When gas is produced with crude oil, a rough field separation gives a wet gas.) Such separations are not ordinarily complete, and there is some overlapping between the groups. Further group separation or separation into individual components is accomplished when desired by fractional distillation, or in special cases by extractive distillation, azeotropic distillation, superfractionation, or other extractive methods.

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Data regarding uses of the several constituents are shown in chart Charts 7 to 11, which show chemical products, are concerned primarily with "dry" and "liquefied petroleum gases" hydrocarbons - methane, ethane, propane, isobutane, and n-butane.

Chart 2

Some data regarding the consumption and use of natural and liquefied petroleum gas are shown graphically in charts 2a and 2b. Unfortunately, figures for the quantity of natural gas used in the manufacture of synthetic organic chemicals are not available separately but are included under "other industrial" uses. Data on the use of liquefied petroleum gases in the manufacture of synthetic rubber components were available for the first time in 1944. Data concerning the use of liquefied petroleum gas in the production of aviation gasoline and other motor-fuel components are not included. Chart 2c shows annual synthetic production from all sources of certain non-coal-tar chemicals since 1936. Chart 2d shows the increase in total production and sales of non-coal-tar synthetic organic chemicals from 1925 to 1944 and production and sales of chemicals raw materials derived from petroleum from 1942 to 1944.

Statistics showing the portion of this production using natural gas as the raw material are not available.

Chart 3

Chart 3 shows the general composition of crude petroleum and of refinery-processed petroleum and also lists some nonpetroleum materials suitable for hydrocarbon synthesis. Petroleum is an extremely complex mixture of hydrocarbons and other substances that is found in nature in the solid, liquid, and gaseous states. Natural gas is a form of petroleum that consists of hydrocarbons and other substances (chart 1) that exists in the gaseous state under ordinary conditions of temperature and pressure at the earth's surface. The natural-gas hydrocarbons frequently occur in solution with crude oil. Hydrocarbons identical with those in natural gas, together with unsaturated gaseous hydrocarbons, are formed as byproducts in refinery operations during the manufacture of petroleum products, by decomposition and conversion of natural gas, natural gasoline or crude-oil hydrocarbons. Such hydrocarbons also may be made synthetically from nonpetroleum materials. These gaseous products, regardless of source, are important raw materials or intermediates for chemical products. The fact that the gaseous products of petroleum may be obtained by processing the heavier fractions and, similarly, that heavier hydrocarbons may be made from the gases is significant. Methods whereby such interconversion of petroleum hydrocarbons can be accomplished are presented in the next chart.

Chart 4

Raw materials other than petroleum hydrocarbons were used for the first commercial syntheses of organic chemicals. The processes, however,

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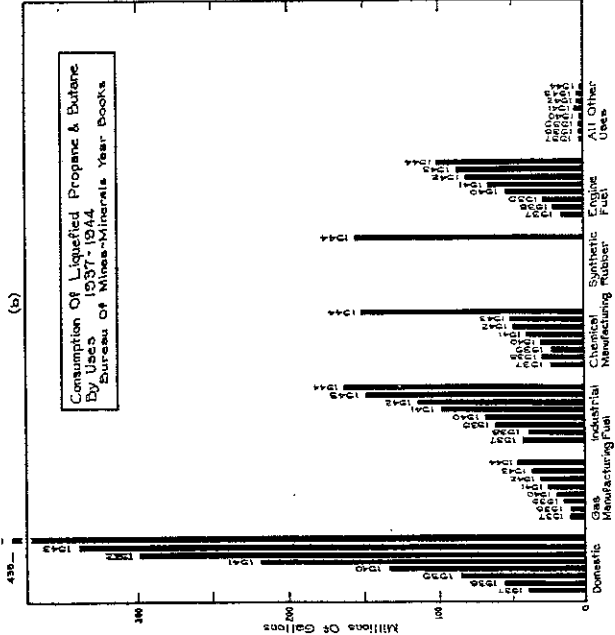
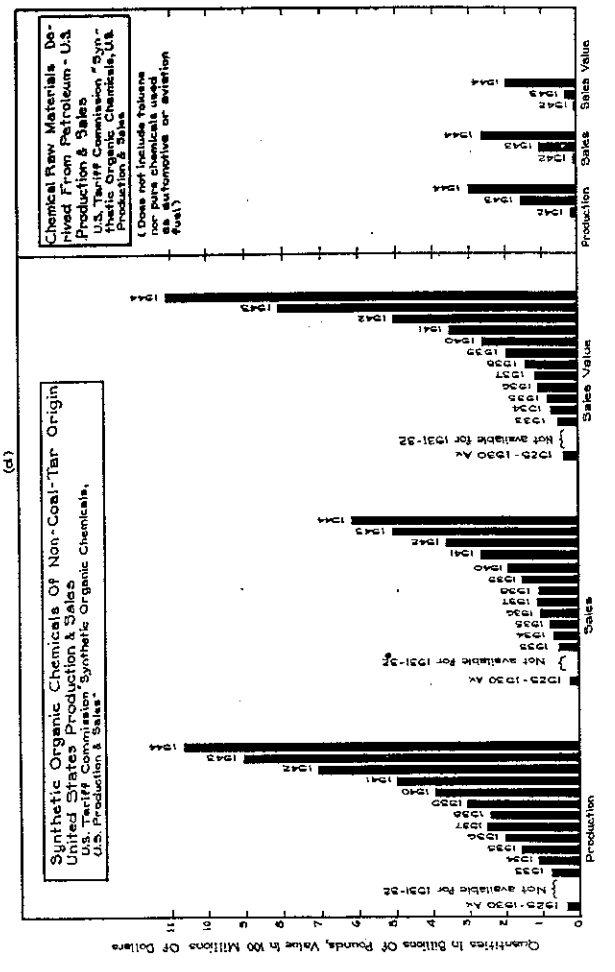
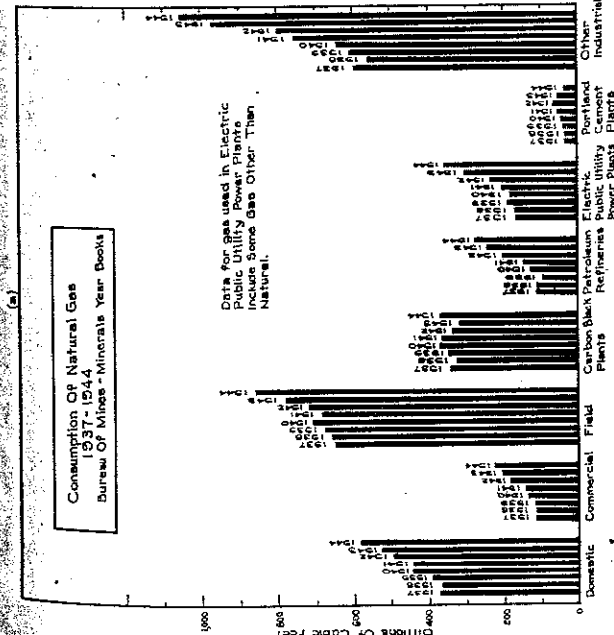
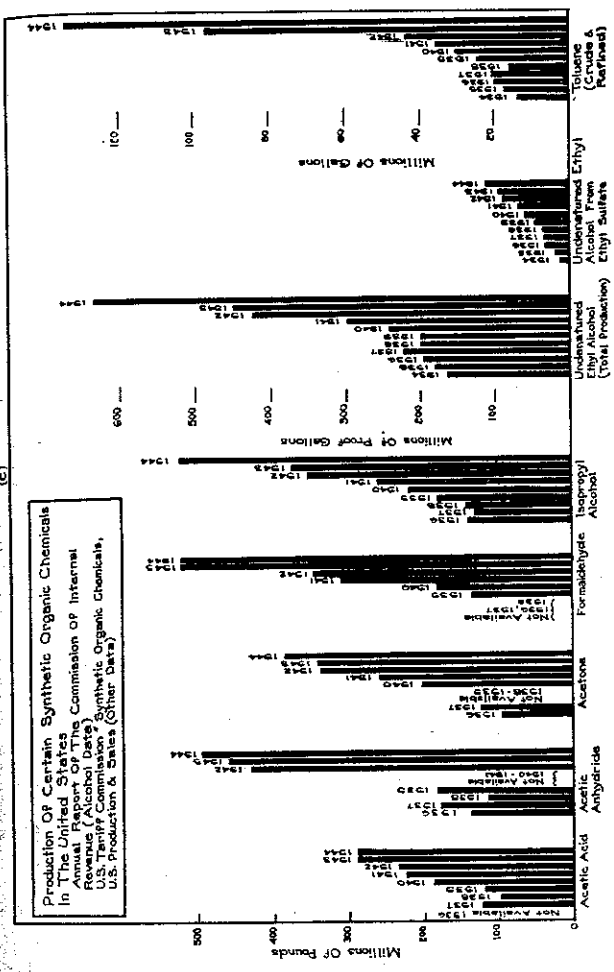
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CHART 2



RELATIONSHIP AND SOURCES OF PETROLEUM-TYPE HYDROCARBONS

NATURAL GAS

Hydrocarbons
Methane
Ethane
Propane
Butanes
Heavier hydrocarbons separated as natural gasoline (CHART 1)
Other constituents
Nitrogen - Helium
Carbon dioxide - Sulfur compounds

CRUDE PETROLEUM

Dissolved gaseous hydrocarbons
Natural gas hydrocarbons (Methane, ethane, propane, butanes)
Liquid hydrocarbons
Higher molecular weight homologues (pentanes and heavier) of natural gas hydrocarbons, and cyclic compounds
Solid hydrocarbons
Paraffin waxes, petrolatum, and cyclic compounds
Other constituents
Asphaltic compounds
Sulfur compounds

Natural gas may occur separately or coexistent with heavier petroleum hydrocarbons (natural gasoline, condensate, crude petroleum). Crude petroleum frequently contains natural gas hydrocarbons but consists primarily of heavier hydrocarbons.

REFINERY PROCESSED PETROLEUM

Gaseous hydrocarbons
Saturated:
Methane
Ethane
Propane
Butanes
Unsaturated:
Ethylene
Propylene
Butylenes
Butadienes
Acetylene
Methylacetylene
Liquid hydrocarbons
(Gasolines, kerosene, diesel fuels, lubricating oils).
Pentanes and higher molecular weight paraffins, naphthenes, unsaturated hydrocarbons, and cyclic compounds.
Solid hydrocarbons
Paraffin waxes, petrolatum, and cyclic compounds.

Refinery gas contains hydrocarbons identical with those in natural gas and in addition contains unsaturated hydrocarbon gases (ordinarily olefins; acetylene hydrocarbons are formed under some conditions). These gases are produced in refinery operations during manufacture of petroleum products, by decomposition and conversion of natural gas, natural gasoline or crude petroleum hydrocarbons. Heavier hydrocarbons contained in refinery products, such as fuels and lubricants, are either natural petroleum hydrocarbons, or are products of decomposition or conversion processes applied to petroleum or its fractions (including natural gas), or are mixtures of natural and synthetic products.

NON PETROLEUM MATERIALS USED FOR SYNTHESIS OF HYDROCARBONS

Coal or coke } Calcium carbide
Limestone }
Coal, coke, or other carbonaceous material } Carbon monoxide and hydrogen
Steam or oxygen }
Coal
Lignite
Oil shale
Vegetative materials subject to fermentation or natural decomposition.

Hydrocarbons identical to natural and refinery processed petroleum hydrocarbons may be made synthetically from non-petroleum materials by chemical methods (Fischer-Tropsch synthesis, hydrogenation of coal, reaction of calcium carbide and water), or obtained from vegetative materials subject to fermentation, or from other carbonaceous materials or materials containing organic matter, such as oil shale.

METHODS FOR CONVERSION OF PETROLEUM HYDROCARBONS DIRECTLY OR INDIRECTLY APPLICABLE TO NATURAL GAS

These definitions of methods of converting hydrocarbons conform to the apparent general usage of the terms in the literature of the petroleum industry.

1. DECOMPOSITION (Thermal, catalytic, electro): The splitting of the hydrocarbon molecule into smaller molecules or into carbon or by electric discharge (pyrolysis), with the aid of catalysts, in pyrolysis, by recombination of some of the products, especially into new compounds.
 Ethane $\xrightarrow{\text{heat, catalyst}}$ Hydrogen + Ethylene
 $C_2H_6 \xrightarrow{\text{heat, catalyst}} H_2 + C_2H_4$
 Ethane $\xrightarrow{\text{heat, catalyst}}$ Hydrogen + Acetylene
 $C_2H_6 \xrightarrow{\text{heat, catalyst}} H_2 + C_2H_2$
 Ethane $\xrightarrow{\text{catalyst}}$ Hydrogen + Carbon
 $C_2H_6 \xrightarrow{\text{catalyst}} H_2 + 2C$

2. OXIDATION (Thermal, catalytic): Reaction of the hydrocarbon molecule with oxygen or catalyst whereby oxygen compounds, activated by heat or catalyst, whereby oxygen is changed into the hydrocarbon molecule, or the molecule is changed to carbon monoxide and hydrogen, carbon dioxide and hydrogen, or finally to carbon dioxide and water.
 Ethane + Oxygen $\xrightarrow{\text{heat, catalyst}}$ Ethyl alcohol
 $C_2H_6 + O_2 \xrightarrow{\text{heat, catalyst}} C_2H_5OH$
 Ethane + Water (Steam) $\xrightarrow{\text{heat, catalyst}}$ Hydrogen + Carbon dioxide
 $C_2H_6 + H_2O \xrightarrow{\text{heat, catalyst}} H_2 + CO_2$
 Ethane $\xrightarrow{\text{catalyst}}$ Water + Carbon dioxide
 $C_2H_6 \xrightarrow{\text{catalyst}} H_2O + CO_2$

3. HALOGENATION (Thermal, catalytic, photo): Reaction of the hydrocarbon molecule with a halogen (fluorine, chlorine, bromine, iodine), activated by heat, light, or catalyst, whereby one or more halogen atoms replace an equivalent number of hydrogen atoms in the hydrocarbon molecule.
 Ethane + Chlorine $\xrightarrow{\text{heat, light}}$ Ethyl chloride + Hydrogen chloride
 $C_2H_6 + Cl_2 \xrightarrow{\text{heat, light}} C_2H_5Cl + HCl$

4. NITRATION (Thermal, vapor phase): Reaction of the hydrocarbon molecule with nitric acid, accelerated by heat and pressure, whereby a nitro group, NO₂, is introduced into the hydrocarbon by replacing a hydrogen atom.
 Ethane + Nitric acid $\xrightarrow{\text{heat, catalyst}}$ Nitroethane + Water
 $C_2H_6 + HNO_3 \xrightarrow{\text{heat, catalyst}} C_2H_5NO_2 + H_2O$

5. SULFURATION (Thermal, catalytic): Reaction of the hydrocarbon molecule with sulfur or hydrogen sulfide to form sulfur-containing compounds such as organic sulfides, mercaptans, disulfides, thiophenes.
 Ethane + Sulfur $\xrightarrow{\text{catalyst}}$ Ethyl mercaptan
 $C_2H_6 + S \xrightarrow{\text{catalyst}} C_2H_5SH$

6. DESULFURATION (Catalytic): Removal of the sulfur atom from a sulfur-containing hydrocarbon molecule to form a sulfur-free molecule. Activated by catalyst.
 Ethyl mercaptan + Hydrogen $\xrightarrow{\text{catalyst}}$ Ethane + Hydrogen sulfide
 $C_2H_5SH + H_2 \xrightarrow{\text{catalyst}} C_2H_6 + H_2S$
 Ethyl mercaptan $\xrightarrow{\text{catalyst}}$ Ethane + Hydrogen sulfide
 $C_2H_5SH \xrightarrow{\text{catalyst}} C_2H_6 + H_2S$

7. HYDROGENATION (Catalytic, thermal, catalytic): Addition of hydrogen atoms to an unsaturated molecule. A molecule to produce one or more saturated molecules. Activated by catalyst or heat and catalyst. Known as destructive hydrogenation when original unsaturated molecule is "cracked" to form more than one subsequently hydrogenated smaller molecule, or non-destructive when no cracking occurs.
 a. Destructive:
 Pentene + Hydrogen $\xrightarrow{\text{heat, catalyst}}$ Propane + Ethane
 $C_5H_{10} + H_2 \xrightarrow{\text{heat, catalyst}} C_3H_8 + C_2H_6$
 b. Non-destructive:
 Ethylene + Hydrogen $\xrightarrow{\text{catalyst}}$ Ethane
 $C_2H_4 + H_2 \xrightarrow{\text{catalyst}} C_2H_6$

8. DEHYDROGENATION (Catalytic, thermal): A form of controlled decomposition where the hydrocarbon molecule is removed from hydrocarbon molecules to form less highly saturated molecules. Known as destructive dehydrogenation when original molecule is "cracked" to form more than one smaller molecule, or non-destructive when no breaking of carbon-carbon bonds occur.
 a. Destructive:
 Propane $\xrightarrow{\text{heat, catalyst}}$ Propylene + Ethylene + Hydrogen
 $C_3H_8 \xrightarrow{\text{heat, catalyst}} C_3H_6 + C_2H_4 + H_2$
 b. Non-destructive:
 Ethane $\xrightarrow{\text{heat, catalyst}}$ Ethylene + Hydrogen
 $C_2H_6 \xrightarrow{\text{heat, catalyst}} C_2H_4 + H_2$

9. ALKYLATION (Thermal, catalytic): Chemical union of an ethyl radical to a hydrocarbon molecule. Used particularly to designate combination of olefin and isoparaffin or aromatic under conditions of high temperature or in presence of a catalyst.
 Ethylene + Isobutane $\xrightarrow{\text{catalyst}}$ Methylcyclohexane (2,2-dimethyl butane)
 $C_2H_4 + C_4H_{10} \xrightarrow{\text{catalyst}} C_6H_{14}$
 Butylene + Isobutane $\xrightarrow{\text{catalyst}}$ Isomeric octenes (alkylate)
 $C_4H_8 + C_4H_{10} \xrightarrow{\text{catalyst}} C_8H_{18}$
 Benzene + Propylene $\xrightarrow{\text{catalyst}}$ Isopropyl benzene (cumene)
 $C_6H_6 + C_3H_6 \xrightarrow{\text{catalyst}} C_9H_{12}(CH_3)$

10. POLYMERIZATION (Thermal, catalytic): Combination of hydrocarbon molecules (olefines) or unlike molecules (non-selective) into chain molecules of higher molecular weight.
 a. Selective:
 Ethylene $\xrightarrow{\text{catalyst}}$ Polyethylene
 $C_2H_4 \xrightarrow{\text{catalyst}} (C_2H_4)_n$
 b. Non-selective:
 Propylene + Anylene $\xrightarrow{\text{catalyst}}$ Mixed octylenes
 $C_3H_6 + C_5H_8 \xrightarrow{\text{catalyst}} C_8H_{16}$

11. ISOMERIZATION (Thermal, catalytic): Transformation of the molecular structure of a hydrocarbon molecule without changing the empirical composition or molecular weight.
 Butane $\xrightarrow{\text{catalyst}}$ Isobutane
 $C_4H_{10}(CH_3)CH_3 \xrightarrow{\text{catalyst}} C_4H_{10}(CH_3)_2$

12. CYCLIZATION AND AROMATIZATION (Thermal, catalytic): Conversion of paraffinic or naphthenic hydrocarbon molecules to cyclic and aromatic molecules. Accompanied by dehydrogenation and by prior polymerization, is used as a process where gaseous hydrocarbons are used as raw material.
 Hexane $\xrightarrow{\text{catalyst}}$ Cyclohexane + Hydrogen
 $C_6H_{14} \xrightarrow{\text{catalyst}} C_6H_{12} + H_2$
 Cyclohexane $\xrightarrow{\text{catalyst}}$ Benzene + Hydrogen
 $C_6H_{12} \xrightarrow{\text{catalyst}} C_6H_6 + H_2$

13. HYDROCARBON SYNTHESIS: Hydrocarbons identical with those from petroleum may be formed from organic or inorganic materials by synthetic processes such as Fischer-Tropsch synthesis or action of water on calcium carbide.
 Synthesis Gas $\xrightarrow{\text{catalyst}}$ Straight chain paraffin
 $nCO + mH_2 \xrightarrow{\text{catalyst}} C_nH_{2m+2}$
 Calcium carbide + Water $\xrightarrow{\text{catalyst}}$ Hydrocarbons + H₂
 $CaC_2 + H_2O \xrightarrow{\text{catalyst}} C_2H_2 + H_2$
 Calcium carbide + Acetylene $\xrightarrow{\text{catalyst}}$ Hydrocarbons + H₂
 $CaC_2 + C_2H_2 \xrightarrow{\text{catalyst}} C_4H_6 + H_2$