Chart 8

Oxidation of the hydrocarbons in natural gas in the form of combustion furnishes the basis for its use as a heat and energy source. The ultimate products of combustion of hydrocarbons are carbon dioxide and water. Controlled and limited oxidation of hydrocarbons produces a number of products highly useful in the production of textiles and plastics and in other industries. Among the oxidation products obtainable from natural gas and other petroleum hydrocarbons are alcohols, acids, fatty acids, and aldehydes. Those of most importance produced commercially from natural gas include methyl, ethyl, isopropyl, propyl, and butyl alcohols, formaldehyde and acetaldehyde, acetone, methylacetone, acetic acid, acetic anhydride, propionic acid, and many derivatives. Both saturated and unsaturated aliphatic hydrocarbons are utilized, ordinarily in the presence of a catalyst, in the production of oxidation products.

The reaction of natural-gas hydrocarbons with steam, oxygen, and carbon dioxide to form a "synthesis gas" for the Fischer-Tropsch synthesis of higher hydrocarbons has reveived much recent attention as a possible method for utilization of methane in the manufacture of motor fuels. In addition, organic chemicals such as alcohols, aldehydes, acids, and esters can be produced concurrently with the motor fuel.

The reaction of methane and steam when carried to completion gives carbon dioxide and hydrogen. This reaction has been the basis for production of hydrogen for many of the plants that produced ammonia and nitric acid for wartime use. Natural gas or hydrogen from natural gas also is used in the manufacture of pure nitrogen from air for use in ammonia manufacture. By means of controlled combustion, the oxygen content of air is removed, leaving nitrogen, carbon dioxide, and water, which are easily separated. Possible byproducts and derivatives besides ammonium nitrate in the manufacture of ammonia and nitric acid include methyl alcohol from hydrogen and carbon monoxide, formaldehyde from methyl alcohol, dry ice from waste carbon dioxide, urea from liquid ammonia and carbon dioxide, and perhaps ammonium sulfate, sodium carbonate, sodium nitrate, dicalcium phosphate, hydrogen cyanide, formamide, and others.

Chart 9

Chart 9 shows products of chlorination as representatives of products obtainable by halogenation of natural gas. Chlorinated hydrocarbons form an important class of chemicals, which are used directly as solvents, refrigerants, degreasing compounds, and for many other purposes; also as intermediates in organic chemical synthesis. Fluoro and fluorochloro compounds, which are used principally as refrigerants, usually are obtained by replacement of chlorine with fluorine in a chloro compound. A few brominated hydrocarbons are in commercial production. Methyl bromide is used as a fumigant and insecticide. Ethylene dibromide is used in tetraethyllead fluids, as a solvent, and as an intermediate in the production of a number of chemicals.

Chart 10

Active research into the nitration of natural-gas hydrocarbons began around 1930 and has produced a variety of products. Commercial production of nitroparaffins by use of the vapor-phase nitration reaction of nitric acid and hydrocarbons from petroleum and natural gas, occurred within the present decade. Uses for these nitroparaffins and their derivatives in many fields already have been developed, and other extensive uses have been prophesied.

Chart 11

Chart 11 shows products obtainable from natural gas and other petroleum hydrocarbons by sulfurization. Production of these products is small, but recent announcements indicate future commercial-scale manufacture of carbon disulfide, thiophene, mercaptans, thioethers, and other sulfur compounds, using natural gas and sulfur or hydrogen sulfide as starting materials. Butyl mercaptan and butyl disulfide are said to be available already in tank-car lots, and other sulfur compounds are being produced in experimental or pilot-plant quantities. One company states that a plant was erected and operated successfully for the manufacture of tertiary dodecyl mercaptan (C_{12}), using as raw materials hydrogen sulfide derived from natural gas, with copolymers from propylene and isobutylene resulting from thermal decomposition of isobutane. The plant was built in anticipation of a demand for the product in the synthetic-rubber program but was shut down when the demand did not materialize. Another company has announced the pilot plant and contemplated commercial production of thiophene. Still another company has announced the pilot-plant development of a process for the manufacture of carbon disulfide by the catalytic reaction of sulfur and hydrocarbons from natural gas.

Many of the uses for sulfurization products shown in chart 11 are those suggested by manufacturers as possible uses and have not yet been proven commercially.

Chart 12

Nonhydrocarbon constituents of natural gas usually are present in relatively small amounts. Some of these materials, such as helium, are of enough value to warrant their recovery even when present in quantities of only a few percent. Others, such as hydrogen sulfide, usually are objectionable and ordinarily must be removed before the hydrocarbon content of the gas can be utilized. Hydrogen sulfide and other objectionable gases may become valuable when separated and used in the production of other products. The use of hydrogen sulfide in the production of sulfur compounds from hydrocarbons already has been mentioned. In at least one natural-gas field it is recovered and used for the production of elemental sulfur.

Some natural gases are composed almost entirely of carbon dioxide. Carbon dioxide from this source may be of value if the wells from which it is produced are geographically situated where the gas may be utilized economically. So far, no economic use for nitrogen in natural gas has been developed.

CHART 10

PRODUCTS OBTAINABLE FROM NATURAL GAS HYDROCARBONS BY NITRATION
THERMAL

NITROMETHANE	NITROETHANE	NITROPROPANES	NITROBUTANES
CH_3NO_2	$C_2H_5NO_2$	$C_3H_7NO_2$	$C_4H_9NO_2$
Methane, Propane, Butane	Ethane	Propane, Isobutane	Butane, Isobutane

SOLVENTS - PAINT and VARNISH REMOVERS
HEAT SENSITIZERS for rubber latex

ALDEHYDES and KETONES
ALDOXIMES
ALKYLHYDROXYLAMINES
AMINES and DIAMINES, synthetic drugs, organic intermediates
AMINOHYDROXYL COMPOUNDS: AMINOALCOHOLS, AMINOGLYCOLS, AMINOALKENETRIOLS and AMINOACETALS, soaps of preceding compounds [emulsifying agents, cosmetics]
CARBOXYLIC ACIDS
CHLORONITRO PARAFFINS and CHLORONITRO ALCOHOLS, 1,1-dichloronitroethane [insecticide (Ethide)], chloropicrin [lachrymator, fumigant, and soil-sterilizing agent]
DINITROPARAFFINS
HYDROXAMIC ACIDS
HYDROXYLAMINE [organic reducing agent] and HYDROXYLAMINE SALTS, hydroxylamine acid sulfate, oximes, hydroxylamine sulfate [intermediates for dyestuffs, pharmaceuticals, resins, flotation agents]
KETOXIMES
NITROAMINES, diamines
NITROHYDROXYL COMPOUNDS: NITROALCOHOLS, NITROGLYCOLS, NITROALKANETRIOLS, organic and inorganic esters of preceding compounds [explosives intermediates], aminohydroxyl compounds
NITROKETONES
NITROOLEFINS

CHART II

PRODUCTS OBTAINABLE FROM NATURAL GAS AND OTHER PETROLEUM HYDROCARBONS BY SULFURIZATION

HYDROGEN SULFIDE

H_2S

Methane and Heavier

SEE CHART 12

CARBON DISULFIDE

CS_2

Methane

SOLVENT - INSECTICIDE
RUBBER VULCANIZATION

CARBON TETRACHLORIDE
XANTHATES, flotation agents
XANTHATES, viscose rayons

MERCAPTANS
(thioalcohols)

RSH

GUM INHIBITORS - FUMIGANTS
INSECTICIDES and FUNGICIDES
ODORANTS for natural gas
FLOTATION AGENTS - ADHESIVES
VULCANIZING ACCELERATORS
CORROSION INHIBITORS
POLYMERIZATION MODIFIERS
ADDITIVES in rubber, plastics, alcohol denaturants, pickling inhibitors, lubricating oils

DETERGENTS and EMULSIFIERS
DISULFIDES
DYESTUFFS
MEDICINAL INTERMEDIATES
MERCAPTALS
MERCAPTOLS
SULFONIC ACIDS
THIOCARBONATES
THIOESTERS
THIOETHERS

ALKYL DISULFIDES

RSSR

FLOTATION AGENTS - INSECTICIDES
STABILIZERS - OIL ADDITIVES

MERCAPTANS
POLYSULFIDES
SYNTHETIC RUBBERS and PLASTICS

ALKYL SULFIDES
(thioethers)

R_2S

FUMIGANTS - INSECTICIDES
RUBBER SOLVENTS - PLASTICIZERS
CORROSION INHIBITORS
FLOTATION AGENTS
OIL ADDITIVES - STABILIZERS

MUSTARD GAS [military poison gas]
POLYSULFIDES
SULFONES
SULFOXIDES
THIOSULFATES

POLYSULFIDES

R_2S_x

RUBBER SOLVENTS
FUMIGANTS
DIESEL FUEL ADDITIVES

POLYSULFIDE POLYMERS
[rubber substitutes (Thiokols)]

THIOPHENES

$C_4H_{4-x}R_xS$

Butane and Heavier

SOLVENTS

DYESTUFF INTERMEDIATES
INSECTICIDES
MEDICINAL INTERMEDIATES
OIL ADDITIVES
PHARMACEUTICAL INTERMEDIATES
PLASTICS and SYNTHETIC RUBBERS
SOLVENTS

SULFONIC ACIDS

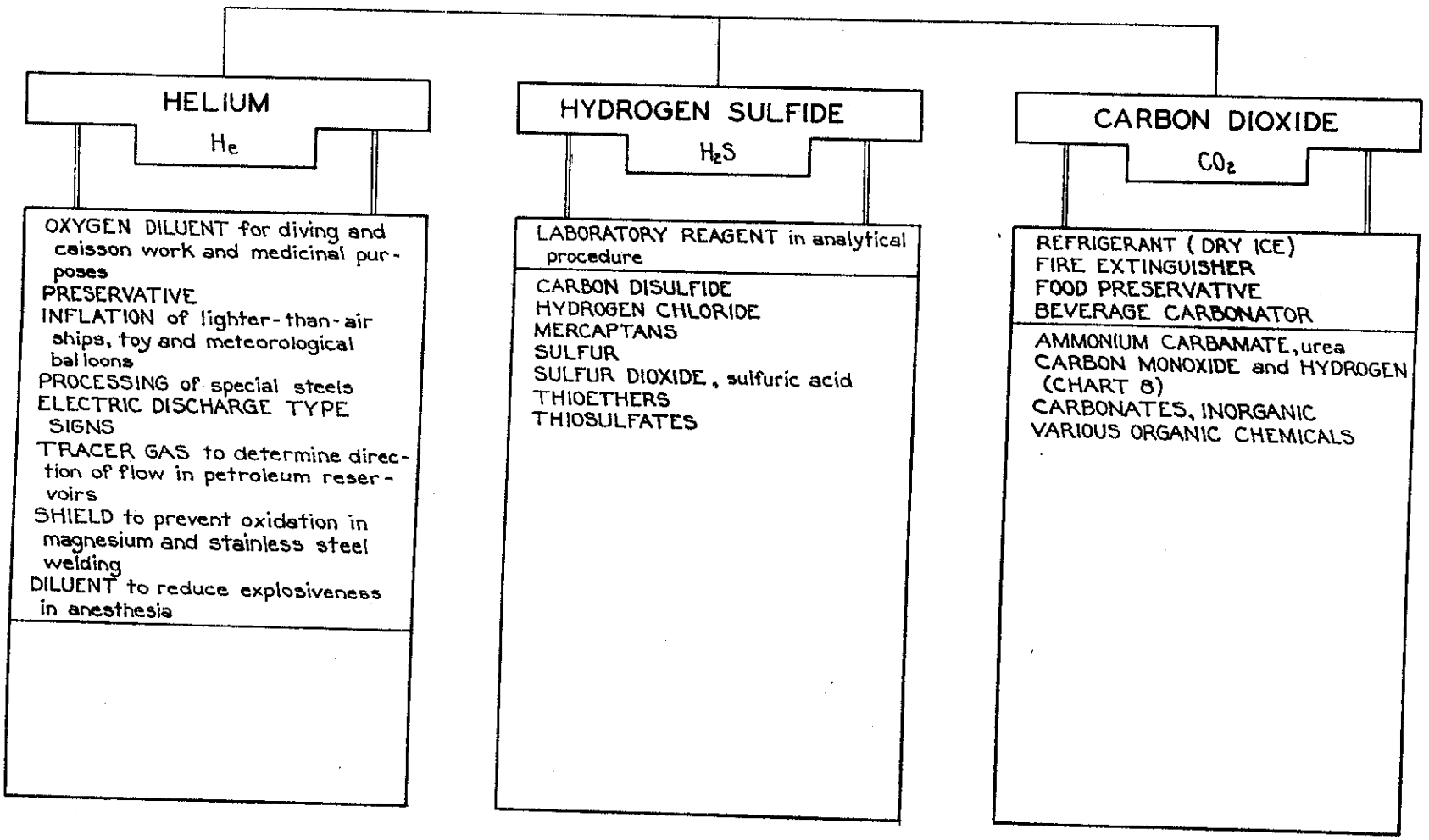
$R\,SO_3H$

EMULSIFIERS - DETERGENTS
INSECTICIDES
WETTING AGENTS
LUBRICANT ADDITIVES

RESINS

CHART 12

USES OF NON-HYDROCARBON NATURAL GAS CONSTITUENTS



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